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## Stabilization and optical activity of polychloral.

Larry Steven Corley  
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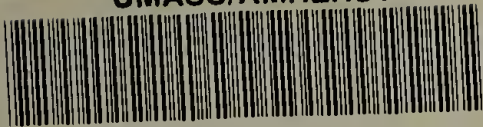
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STABILIZATION AND OPTICAL ACTIVITY OF POLYCHLORAL

A Dissertation Presented

By

L. STEVEN CORLEY

Submitted to the Graduate School of the  
University of Massachusetts in partial fulfillment  
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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Polymer Science and Engineering

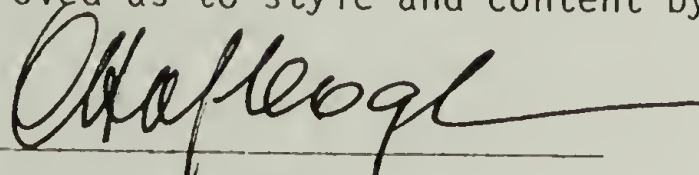
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A Dissertation Presented

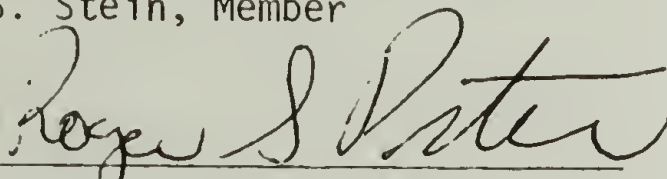
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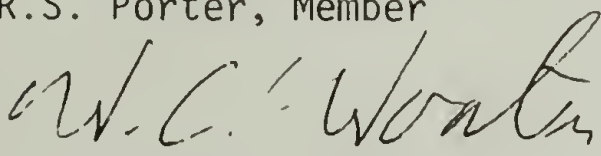
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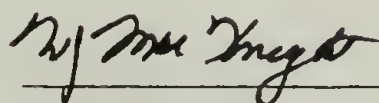
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## DEDICATION

This dissertation is dedicated, with thanks, to my parents, Mr. and Mrs. Grady V. Corley, who, by kind and concerned upbringing, have inspired me through my life to strive for accomplishment, and without whose guidance many years ago I would not be writing this dissertation today.

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## ABSTRACT

### Stabilization and Optical Activity of Polychloral

(February 1979)

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Directed by: Professor Otto Vogl

The polymer of chloral (trichloroacetaldehyde) has a polyacetal structure with bulky trichloromethyl side groups; only the isotactic form, crystallizing in a helix with four monomer units per turn, has been described in the literature. Because of the bulkiness of the side groups, it was thought (from models) that the helices might contain few or no helix reversals and that it might therefore be possible to obtain polychloral which is optically active solely by helicity through use of optically active initiators. However, to measure this optical activity, transparent (and preferably stable) polychloral systems free of birefringence and with a known content of initiator residues were needed.

Initiation mechanisms for chloral polymerization were investigated to determine the fate of initiator residues. It was found by infrared and  $^1\text{H}$  NMR spectroscopy that the tertiary butoxide ion would add quantitatively to chloral above the chloral threshold polymerization temperature and that the alkoxide addition product would cause immediate polymerization of chloral upon cooling, apparently becoming

chemically bound to the polymer. Tertiary amines such as pyridine or 2,4,6-trimethylpyridine and initiators containing chloride ions, which polymerize chloral at much slower rates than does lithium tertiary butoxide, did not add to chloral above its threshold polymerization temperature to form addition products in quantities detectable by  $^1\text{H}$  NMR.

Blends of insoluble, infusible polychloral with other polymers such as polystyrene, poly(methyl methacrylate) and poly(methyl acrylate) could be prepared from mixtures of chloral with other monomers by anionic polymerization of chloral followed by radical polymerization of the other monomer within the polychloral matrix. No grafting onto the polychloral occurred, but radical chain transfer with chloral monomer was extensive in some polymerizations. Some polychloral-polystyrene blends were nearly transparent, in contrast to opaque chloral homopolymer. Blends were characterized by SEM, TEM and tensile measurements.

Hydroxyl endgroups, previously undetectable in polychloral prepared by cryotachensic techniques, could be detected in the infrared spectra of polychloral initiated with high levels of alkoxide initiators and then treated with acid; treatment with  $\text{PCl}_5$  greatly increased the thermal stability of the polychloral and decreased the content of hydroxyl groups as observed by IR, apparently by chlorination.

It was attempted to endcap the alkoxide (or hydroxyl) endgroups of polychloral by a number of techniques. Of posttreatments for preformed cryotachensically prepared polymer, only  $\text{PCl}_5/\text{CCl}_4$  (at reflux) was effective, producing acceptable thermal stability; acetyl chloride

and orthoester or ketal/Lewis acid mixtures left substantial amounts of polymer degrading below 200°C. Among acylating or alkylating additives incorporated directly into the chloral polymerization mixture, dimethyl sulfate could produce complete stabilization, but sometimes irreproducibly inhibited chloral polymerization. Acyl halides and acid anhydrides stabilized only a portion of the polychloral. When halide salts of sulfonium cations or other potentially alkylating cations were used as anionic initiators for chloral polymerization, some stabilization (probably by alkylation) of the polychloral occurred, but even in the most favorable cases not over 70% of stabilized fraction could be obtained in the resultant polychloral. Addition of secondary and tertiary aliphatic isocyanates to chloral polymerization mixtures produced completely stabilized polychloral; infrared data showed the presence of one isocyanate unit for each 200 to 500 chloral units in the polymers.

When polychloral films were prepared with a number of optically active and inactive initiators and their optical rotation was measured in a film cell after annealing, laminates of the films prepared with the optically inactive initiators and some of the optically active initiators were birefringent and showed low rotations. However, laminates of films prepared with two optically active initiators showed very high optical rotation values at a number of cell positions, although the results remain somewhat uncertain because of birefringence. Further confirmatory work is planned in this area.



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## CHAPTER I

### INTRODUCTION

#### A. Structures Leading to Optical Activity

Optical activity, defined as the rotation of the plane of plane-polarized light passing through a material, is a property found in molecules and supramolecular structures which lack a plane of symmetry. Classical and quantum theories of the phenomenon of optical activity have been reviewed in a recently published book (1). Basically, optical activity is a phenomenon found only in molecules or other structures which have no rotation-reflection ( $S_p$ ) axis of symmetry; i.e., a structure whose mirror image is not superimposable on the structure itself (2). Dissymmetric compounds, which generally show optical activity, may have only one or more  $C_p$  (rotational) axes of symmetry; if they have only a  $C_1$  axis, they are referred to as asymmetric.

The type of optical activity of most frequent concern to chemists derives from a carbon atom or other atom, such as nitrogen, phosphorous or silicon, with four (or in some cases three) different substituents. A compound containing such an atom is generally asymmetric, since rotation about  $360^\circ$  on any axis is required to give an equivalent orientation in space, and the structure therefore has only a  $C_1$  axis of symmetry.

Optical activity of compounds containing asymmetric carbon atoms is generally measured in solution and expressed as degrees of rotation



per unit concentration per unit length. However, many types of crystals also exhibit optical activity in the solid state. These crystals are of two major types. The first type includes crystals of small molecules which are themselves molecularly dissymmetric and show optical activity in solution, such as camphor and sucrose. The second and more interesting type is comprised of crystals, not containing optically active small molecules or ions, whose optical activity is produced only by the dissymmetry of the crystal structure itself and which disappears upon destruction of the crystal structure. These crystals include those of sodium chlorate and bromate, quartz (which is polymeric), and a large number of other mostly inorganic substances. Much of the early work on optical activity of crystals is reviewed in chapter 28 of the classic work by Lowry (3).

Some optically active crystals, such as those of quartz, sodium chlorate, and sodium ammonium tartrate, exhibit a phenomenon known as hemihedrism, in which the physical form of the dextrorotatory crystal is the nonsuperimposable mirror image of that of the levorotatory crystal. This phenomenon was used by Pasteur in the first resolution of a racemic compound (sodium ammonium tartrate), in which the two enantiomers crystallized in mirror-image crystals which could be separated under a microscope. However, many optically active crystals are symmetric in morphology and do not show hemihedral faces, with dissymmetry being purely internal. Some optically active crystals, such as those of sodium chlorate and bromate, are isotropic, with rotation per millimeter the same when measured through the crystal in any direction. Most optically active crystals, however, have one or two optic axes. In

uniaxial crystals, such as quartz, optical rotation must be measured in a light path along the optic axis in order to avoid interference from birefringence. In biaxial crystals, such as those of sucrose or tartaric acid, the optic axes often change in direction with wavelength, making measurement of optical activity somewhat more difficult.

### B. Optical Activity in Quartz

The phenomenon of optical rotation in crystals was first discovered by J.B. Biot in 1812 for quartz (4). This account, in fact, represented the first mention in the literature of optical rotation and optical rotatory dispersion, and quartz has remained the most intensively studied of optically active crystals. A relatively recent review of the optical activity of quartz can be found in Gmelin (5).

Optical activity in quartz is based on the helical arrangement of the atoms in the macromolecular network of a quartz single crystal. The alpha-form (low temperature) and the beta-form (high temperature) of quartz are each composed of hexagonal unit cells, with  $a = 4.9\text{\AA}$  and  $c = 5.4\text{\AA}$  for alpha-quartz and  $a = 7.02\text{\AA}$  and  $c = 6.92\text{\AA}$  for beta-quartz. In both forms of quartz, the silicon atoms are arranged in regular tetrahedra, equidistant each from four oxygen atoms. Each oxygen atom forms the common vertex of two tetrahedra centered on adjacent silicon atoms. The atoms are arranged in threefold helical axes whose sense of rotation is different in the d- and l- forms of quartz. These helices are found in both alpha- and beta-quartz, with the difference between the two forms found in a slight shift in the position of the silicon atoms.

The helices of beta-quartz are shown on p. 316 of Gmelin (5); each unit cell contains two interconnected helices, each with 10 silicon and 9 oxygen atoms per turn. This dense packing of helices, which are dissymmetric, results in very high optical activity along the optic axes of single crystals of d- or l-alpha-quartz, with the optical rotation at standard temperature and pressure ranging from  $18.5^\circ/\text{mm.}$  at  $6364 \text{ \AA}$  to  $371^\circ/\text{mm.}$  at  $1854 \text{ \AA}$ . Optical activity is found in quartz because left- and right-handed helices are dissymmetric, whereas carbon atoms with four different substituents, the usual causes of optical activity in organic compounds, are asymmetric. Both are chiral, possessing "left-" or "right-handedness."

### C. Synthesis and Resolution over Optically Active Quartz

The relation of the optical rotatory power of quartz to that of organic molecules has suggested the use of optically active quartz surfaces in asymmetric synthesis or resolution of racemic compounds in the past. In 1935, Tsuchida (6) reported partial resolution of certain racemic cobalt complexes by asymmetric adsorption onto d- or l- quartz powder. Karagunis and Coumoulos (7) subsequently extended this method to elution of  $\text{Cr(en)}_3\text{Cl}_3$  from columns packed with quartz and claimed resolution of the complexes, although eluates had rotations of  $0.1^\circ$  or less for a compound with  $[\alpha]_D > 3000^\circ$ . Similar results were noted by Schwab and collaborators (8,9) in the "enantioselective" dehydrogenation of racemic 2-butanol over d- or l-quartz coated with nickel; recovered unreacted alcohol had specific rotations of less than  $0.1^\circ$ .



Amariglio and Duval (10,11) repeated the previous experiments of these and other investigators which included hydrogenation of methyl ethyl ketone, dehydrogenation and dehydration of 2-butanol, and resolution of 2-butanol, cobalt or chromium complexes and ammonium tartrate. All attempts led to negative results; optical activity in the products was invariably shown to be either within the limits of experimental error or due to minute quartz particles suspended in the observed liquid.

In an attempt to overcome the problems caused by the relatively large experimental errors involved in direct polarimetric measurements in former experiments, the group of Bonner (12-14) determined adsorption of amino acid derivatives on d- and l-quartz by a radiochemical technique. In one experiment (12), tritium-labeled D- and L-alanine hydrochloride in dimethylformamide (DMF) solution were preferentially adsorbed onto d- and l-quartz respectively to the extent of 1 to 1.8% (at the 99% confidence level) as determined by radioactivity counting. However, no adsorption was noted from water or aqueous ethanol solution. Subsequent experiments (13,14) with selectively labeled racemic alanine hydrochlorides in DMF solution showed 10-20% differential adsorption by radiation counting. Gas chromatographic determination of adsorption of racemic alanine isopropyl ester hydrochloride in a variety of non-polar solvents showed up to 12% differential adsorption of the ester enantiomers in fractions eluted with  $\text{CHCl}_3$  and subsequently with  $\text{CH}_3\text{OH}$ . However, in no case was any adsorption of amino acids or their derivatives upon d- or l-quartz found when protic solvents such as water or alcohols were used. Although some authors (15-19) have proposed selective adsorption of amino acids and other molecules now found in



biological systems on naturally occurring deposits of d- or l-quartz as a mechanism for the origin of biological optical activity, the observed inability for such to occur in aqueous systems in the Bonner experiments would seem to militate against this hypothesis.

#### D. Early Work in Optical Activity of Synthetic Polymers

Many investigators, from Pasteur onward, observed the phenomenon of optical activity associated with asymmetric carbon (or other) atoms in small molecules. Others noted the presence of optical activity in such natural polymers as polysaccharides, proteins and nucleic acids, the latter two involving contributions to the optical activity from the helicity of the polymer molecule as well as from the asymmetric carbon atoms. This led to attempts to incorporate optical activity into synthetic polymers through the asymmetric carbon atom. The first recorded work is that of Walden (20), who polymerized the bis ((-)-2-methylbutyl) ester of methylenesuccinic acid to form a polymer no different in optical rotation from the starting monomer.

Many subsequent attempts to synthesize optically active polymers, however, failed because of uncertainty as to the true definition of an asymmetric carbon atom, particularly in polymers, and as to what structures were capable of producing optical activity. Several attempts were made to produce optically active ordinary vinyl polymers through polymerization of optically active monomers and subsequent removal of the asymmetric side chains (21,22) or by initiation of a monomer such as styrene with an optically active initiator (23). However, after the

optically active side chains or initiator residues were removed, the remaining polymer was not optically active.

A paper by Frisch, Schuerch and Szwarc (24) explained the lack of optical activity in these polymers by showing that asymmetric carbons could not be generated from ordinary vinyl monomers  $\text{CH}_2=\text{CXY}$  in high polymers. The CXY carbons in the polymer in the center of a heterotactic triad, between two  $\text{CH}_2=\text{CXY}$  differing in configuration only, were shown to be not asymmetric but pseudoasymmetric and incapable of contributing to the optical activity. The central carbons in an isotactic or syndiotactic triad could be regarded as "asymmetric" only insofar as the two "substituents" forming the polymer chain were of different lengths, which could contribute to optical activity only in the lowest molecular weight oligomers. Remaining methods of synthesis of optically active polymers containing asymmetric carbon atoms, explored in the subsequent literature, included the following:

(1) Polymerization of a nonvinyl monomer (such as a 1-substituted butadiene) which can generate an asymmetric center during polymerization.

(2) Copolymerization of a monomer mixture in which an asymmetric center can be formed by two adjacent comonomer units in the polymer chain.

(3) Polymerization of an optically active monomer such that the asymmetric center is not racemized during the polymerization.

(4) Preferential polymerization of one enantiomer of a racemic monomer by a chiral initiator (stereoelective polymerization).

(5) Polymerization of a racemic mixture by a single initiator into two types of polymers, each formed from a preponderance of one

enantiomer (stereoselective polymerization).

Other methods, such as reaction of a preformed polymer with an optically active reagent, have been relatively unimportant in the literature. The first two methods above will be covered as follows under the heading "Asymmetric Induction" and the latter three as "Asymmetric Selection."

### E. Asymmetric Induction

Probably the first successful attempts at creating asymmetric centers during a polymerization were those of Beredjick and Schuerch (25,26) who copolymerized (-)-1-phenylethyl methacrylate with maleic anhydride with radical initiators to give a copolymer with  $[\alpha]_D^{25} = -50.2^\circ$  before and  $+23^\circ$  after removal of the optically active 1-phenylethyl groups. This result showed that the chirality in the side group had caused the incoming maleic anhydride unit to add asymmetrically to the methacrylate radical, generating a new chiral center. The poly(methacrylic acid) obtained by dealkylation of the optically active methacrylate homopolymer was, of course, optically inactive.

Schmitt and Schuerch (27) similarly obtained an optically active copolymer of maleic anhydride with (-)-1-phenylethyl vinyl ether which retained weak optical activity after dealkylation. Matsuzaki and Sugimoto (28), however, upon copolymerizing (-)-methyl methacrylate with maleic anhydride or N-(p-tolyl) maleimide, obtained copolymers whose optical rotation varied directly with methacrylate content and which retained no optical activity after hydrolysis.

Asymmetric induction in homopolymerizations was probably first



obtained by Natta and coworkers (29), who polymerized the methyl and butyl esters of 2,4-hexadienoic and 5-phenyl-2,4-pentadienoic acids, using as initiators (R)-2-methylbutyllithium or n-butyllithium complexed with an optically active ether. Specific rotations of up to  $+8^\circ$  in the polymers were obtained.

This work was extended to hydrocarbons in a subsequent paper (30) in which 1,3-pentadiene was polymerized with triethylaluminum and titanium tetramenthoxide to give polymers with specific rotations up to  $-21^\circ$  yielding optically active methylsuccinic acid on ozonolysis. The rotatory power was greatest in the fractions having the highest cis-1,4 content; polymers prepared using optically active alkylaluminum compounds with optically inactive titanium alkoxides were inactive. It was later found (31) that an optically active polymer could also be obtained from trans-1,3-pentadiene in a matrix of (-)-(R)-perhydrotriphenylene by  $^{60}\text{Co}$ -gamma ray initiation.

Optically active polymers have similarly been prepared by an asymmetric-induction mechanism from benzofurans using alkylaluminum halides with amino acids, terpene acids, or alkaloids (32,33) or using triethyltin menthoxide (34). The last initiator gave polymers with specific rotations as high as  $+73.8^\circ$ . Naphthofurans were also polymerized (35) to highly optically active polymers with these systems, but initiator systems based on  $\text{BF}_3$  and optically active alcohols or amino acids produced optically inactive polymers with indene and similar olefins (36). Implications of this work for the definition of an asymmetric carbon atom were discussed by Natta and Farina in (37).



F. Asymmetric Selection and Preparation of Optically Active Polymers from Optically Active Monomers

Probably the earliest work in the preparation of optically active polymers from chiral monomers was that involving the polymerization (with loss of  $\text{CO}_2$ ) of anhydrides of N-carboxy- $\alpha$ -amino acids (NCA's) to polypeptides, beginning with the work of Leuchs (38) in 1906. There has been strong interest in these polymerizations of optically active anhydrides since that time because the poly- $\alpha$ -amino acids (polypeptides) which result form simple models for the behavior of many proteins in solution (39). In solvents of low hydrogen-bonding capability, such as 1,2-dichloroethane, the intramolecular hydrogen bonding of the polypeptide forces the chain into a helical conformation in solution. Strongly hydrogen-bonding solvents such as dichloroacetic acid or other carboxylic acids, however, often disrupt the helical arrangement and cause the polypeptides to behave as random coils. For the polymers of natural  $\alpha$ -amino acids of the L-series, the configuration at the asymmetric carbon makes a right-handed helix much more energetically favorable than a left-handed helix. The resultant helical asymmetry in non-hydrogen bonding solvents often contributes strongly to the optical rotation of the polypeptide as observed in solution.

Polymerization of DL-anhydrides ordinarily, of course, yields optically inactive polymers. However, Tsuruta and coworkers (40) apparently obtained slight stereoelectivity in polymerization of DL-alanine NCA when borneol or menthol (alone or modified with  $\text{AlEt}_3$ ) were used as initiators. The resultant polymers had specific rotations of about one degree, but inclusion of initiator residues was not excluded.

A number of other polyamides and polyesters have also been prepared in optically active form. Overberger and coworkers prepared polymers from optically active 3-, 4-, and 6-methylcaprolactam (41) and from 3-, 4-, 5-, and 6-methylheptanolactam (42). However, no helicity could be detected by optical rotatory dispersion (ORD) measurements in solvents in which the polyamides were soluble. Similar results were also obtained by the same group for the corresponding optically active polyesters and polythioesters (43-45), although optically active polyamides containing rigid groups such as piperaziny1 did show significant increases in ORD over the corresponding model compounds (46). Adipamide polymers from L-lysine also showed no behavior indicating solution helicity (47). A polyamide containing chiral binaphthyl groups in the main chain showed an inversion and significant decrease in optical rotation as compared to the model compound (48).

Possibly the most intensely studied polyesters have been the C-substituted poly(hydroxyacetic acids). The optically active methyl derivative poly(S-lactate) was prepared by polymerization of the optically active cyclic dimer with a nonracemizing initiator such as ZnO. It was found by two groups (49,50) to have no ORD anomaly (indicating no helicity) in a number of solvents; the ORD behavior was similar to that of low-molecular-weight model compounds. The corresponding polymer in which the methyl group was replaced by a much bulkier isopropyl group, however, did show optical rotation twenty times that of its model compound (51). The polymer from (-)- $\alpha$ -phenyl- $\alpha$ -ethyl- $\beta$ -propiolactone, with an additional carbon atom adding flexibility to the chain, showed no evidence of a helical structure in solution by ORD or CD measurements

(52).

A substantial number of investigators have homopolymerized acrylates or methacrylates containing optically active side groups and have determined the optical activity of the resultant polymers. Their results have led to some insight into the factors by which the degree of optical activity of a polymer is determined. Acrylic monomers in which the asymmetric carbon in the side chain is not adjacent to the ester oxygen, such as 2-methylbutyl acrylate (53) tended to give polymers whose optical rotation was very close to that of the corresponding model compounds and varied little with tacticity. Those in which the carbon atom adjacent to the ester oxygen atom was asymmetric but part of a relatively rigid cyclic or polycyclic structure, such as (-)-bornyl methacrylate and acrylate (55) and (-)-menthyl methacrylate (56) showed similar behavior. However, those in which the first carbon atom in the side chain was asymmetric and not part of a rigid structure, such as (+)-4-methyl-2-pentyl methacrylate (54,57) and 1-phenylethyl methacrylate (58) formed polymers which showed quite different optical rotation characteristics from those of the monomers or the model compounds, particularly in the case of predominantly isotactic polymers where helicity may play an important role (58).

One of the systems in which stereoselectivity and stereoselectivity have been most intensively studied is that of propylene oxide polymerization. The first significant work in this area was done by Price and Osgan (59,60) in 1956, who prepared (-)-propylene oxide and polymerized it to a low-molecular-weight crystalline polymer with a



specific rotation of  $+25^\circ$  in  $\text{CHCl}_3$  using KOH initiator and to a higher-melting crystalline polymer with the same specific rotation using an initiator system prepared with  $\text{FeCl}_3$  and propylene oxide (61). The optically inactive polymer prepared with racemic propylene oxide and the latter initiator system had the same melting point as the optically active polymer and was thought to be a mixture of d- and l- homopolymers. A partial resolution of this polymer by chromatography over optically active zinc alkoxide and carbohydrate adsorbents was subsequently claimed by Furukawa and coworkers (62), although the observed rotations of the resultant polymers were  $0.1^\circ$  or less. Tsuruta and coworkers (63, 64) showed propylene oxide polymerization with diethylzinc/methanol to be stereoselective by partially resolving the resulting polymer with poly((-)-menthyl glycidyl ether), obtaining fractions with specific rotations of  $\pm 6.4^\circ \pm 1.1^\circ$  ( $\text{CHCl}_3$ ). It was shown (65) that attack occurred on the less hindered carbon atom to an extent of 94-97%. Polymerization with magnesium alkyls was also claimed as stereoselective (66).

Stereoelective polymerization of propylene oxide has been accomplished with diethylzinc/d-borneol ( $[\alpha]_D = 2.5^\circ$  to  $7.4^\circ$ ) (67-70), a modification of the diethylzinc/alcohol system made stereoelective by use of the optically active alkoxide group; the l-monomer was preferentially polymerized, leaving an excess of the d-monomer unreacted. Optically active copolymers with a racemic anhydride were also prepared with this system (71). Diethylzinc/glutamate ester complexes were stereoelective to some degree, giving specific rotations up to  $2.0^\circ$  in the polymers, in spite of some opening of the oxirane ring at the more



hindered carbon (72). Triethylaluminum/L-alanine NCA systems produced polymers with specific rotations up to  $10^\circ$ , but the corresponding diethylzinc complexes were nonstereoelective (73), as were  $\text{FeCl}_3$ /propylene oxide/bornyl ether complexes (74) and diethylzinc/L-propylene oxide/ $\text{H}_2\text{O}$  systems (75,76). However, the most strongly stereoelective initiator reported in the literature was solid magnesium tartrate (77) which gave a polymer with a specific rotation of  $-27.4^\circ$  ( $\text{CHCl}_3$ ) at 1% conversion, with stereospecificity dropping with conversion.

Similar studies to those with propylene oxide have more recently been carried out with the corresponding sulfur and nitrogen compounds (77-84). Optically active propylene sulfide ( $[\alpha]_D^{25} = -32.6^\circ$  (neat)) was polymerized by Spassky and Sigwalt (78) with a number of initiators to a polymer with a maximum specific rotation of  $-129.1^\circ$ ;  $+268^\circ$  was the maximum obtained for the polymer of optically active tert-butylthiirane (79). Stereoelective polymerization of racemic propylene sulfide could be accomplished with reaction products of diethylzinc with d-borneol, l-menthol, or l-leucine, with the last being most effective (80,81). Better results were obtained by substituting for the alcohols optically active glycols, particularly (R)-3,3-dimethyl-1,2-butanediol (82,83) with optical yields of 40 to 60% obtainable with the last system in the polymerization of propylene sulfide and tert-butylthiirane. Optically active polymers of 2-methylaziridine (84) and 2-ethylaziridine (84) were also prepared by ordinary cationic polymerization of the optically active monomers.

Optically active poly( $\alpha$ -olefins) have been prepared from the corresponding optically active monomers and studied quite extensively by

the groups of Pino (86-90), Bailey (91), Nozakura (92), and Goodman (93). Pino and his collaborators prepared isotactic polymers with Ziegler-Natta initiators from a number of chiral  $\alpha$ -olefins, such as (+)-(S)-3-methyl-1-pentene, 4-methyl-1-hexene, and 5-methyl-1-heptene. In most cases, optical rotation per monomer unit for the polymer was found to be considerably higher than molar optical rotation for low-molecular-weight saturated model compounds. The amount of excess rotation for the polymer was found to vary with distance of the asymmetric carbon atom from the chain backbone, reaching a maximum for poly(4-methyl-1-hexene) and becoming quite low as the asymmetric atom was moved several carbons from the chain. The observed excess optical rotation in a given polymer was found to increase with decreasing solubility and presumably increasing isotacticity of the polymer (86-90). Potential energy calculations were performed to determine the number of conformations possible in left- and right-handed helices (in solution) for these polymers and the optical rotation per monomer unit which should be observed in each conformation was calculated by the method of Brewster (94,95). The results of these calculations showed that the calculated optical activities corresponding to the average values over the allowed conformations of the preferred helical forms agreed quite well with the experimental optical rotations in hydrocarbon solvents of the most stereoregular forms of some of the above polymers.

Optically active poly(vinyl ethers), investigated by Pino and coworkers (96-98), Liquori et al. (99) and Schmitt and Schuerch (27) showed behavior in solution very similar to that of the poly- $\alpha$ -olefins, particularly for highly isotactic polymers. The ratio of molar rotation

of polymer to model compound similarly decreased at greater distances of the asymmetric carbon atom from the main chain, and this ratio increased with increased isotacticity of the polymer chain for polymers with asymmetric carbon atoms adjacent to the ethereal oxygen. Pino and Lorenzi (96) found that the optical rotation of poly((S)-(+)-(2-methylbutyl) vinyl ether) was greatly increased by complexation of the ethereal oxygen with triisobutylaluminum in toluene, which was interpreted by the authors as being due to forcing of the polymer into a much more rigid helical conformation by the increased bulk in the side chains.

Goodman and Abe (100,101) polymerized a number of optically active aldehydes such as both enantiomers of 2-methylbutanal, (R)-(+)-citronellal, and (R)-(+)-6-methoxy-4-methylhexanal. Organic compounds of lithium, magnesium, aluminum, and zinc were used as initiators. The molar optical rotations observed for the polyacetals were  $[M]_D^{22} = -140.3^\circ$  ( $\text{CHCl}_3$ ) for the polymer of citronellal ((R)-(+)-3,7-dimethyl-6-octenal) compared to  $+11.2^\circ$  for the diethyl acetal model compound, and  $[M]_D^{26} = +52.8^\circ$  for the polymer of 6-methoxy-4-methylhexanal, compared to  $+8.24^\circ$  for the diethyl acetal, again indicating the importance of branching of the side chain close to the main chain in increasing the optical activity of the polymers. The polymer of 2-methylbutanal was insoluble and optical rotations were not determined on this polymer. Although different initiators produced polymers widely varying in degree of crystallinity, the optical activity in solution of the polymers showed very little dependence on this. (The tacticity of the various polymers was not determined.) Optical rotatory dispersion of the polymers fit a standard Drude plot (102) and did not display an anomaly. The temperature



dependence of polymer optical activity was considerably greater than that for the model compounds.

As a result of many of the above observations, Pino and coworkers have proposed that these polymers exist in solution primarily in the helical conformation of one screw sense, with the helicity strongly contributing to the optical rotation. Statistical mechanical calculations (90) were used by Pino in order to lend support to the hypothesis of helicity, although Nozakura and coworkers (92) thought the assumption of helicity to be tenuous because of the simple Drude-type ORD curves of the polyolefins (in contrast to the more complicated behavior of polypeptides) and the lack of a sharp helix-coil transition with temperature in the polyolefins.

Goodman and Abe (103,104) and later Pino (105) attempted to reconcile these two views in a number of review articles. They considered helicity of the polymer chain in solution as an important factor in causing the excess optical rotations observed for these polymers. However, in contrast to the long and rigid helices observed for polypeptides, the helical regions in these polyolefins and similar polymers were considered as being short-range and constantly coiling and uncoiling, although the total helical content of a polymer solution would remain constant over time at constant conditions. Furthermore, these helices were thought of as contributing to the excess optical rotation primarily by means of preferred conformations at the asymmetric carbons associated with the helicity and not by the rotation caused by the chirality of the helices themselves. Indeed, Pino and coworkers (105-107) have found the specific rotation of certain highly crystalline



polyolefins to be quite different in solution from that in the crystalline state, in which crystalline helical forms exist exclusively.

G. Prospects for Synthesis of Optically Active Polymers  
Not Containing Asymmetric Carbon Atoms

Isotactic polymers, due to energy considerations, crystallize in helical forms (108). However, if these polymers are prepared with optically active or racemic initiators, equal amounts of left- and right-handed helices will be formed, with or without helix reversals. The overall effect of this in the crystal structure is crystallization of a near 50-50 mixture of the two types of helices in all isotactic polymers (except for certain polymers (107) which contain asymmetric carbons in the side chains); normal isotactic polymers have crystal structures containing equal numbers of left- and right-handed helices in the unit cell. Hence, the crystals do not show optical activity due to helical dissymmetry. Furthermore, even if a helical polymer without asymmetric carbon atoms were initiated asymmetrically to give an excess of one form of helix, the specific rotation in solution could not then be measured, since the optical activity would be destroyed upon dissolution as the dissymmetric helices rearranged to random coils.

Hence, for isotactic polymers in solution, optical activity can be demonstrated only when the equilibrium of left-handed helix: random coil: right-handed helix is shifted by some characteristic of the molecule such that one sense of helix predominates over the other. The standard means of accomplishing this in the past has been by introducing asymmetric groups into the side chains of polymers such that one helical

arrangement became more stable than the other because of better packing of the side chains, as discussed in the previous section.

However, if a polymer could be synthesized having the following criteria, the existence of optical activity due purely to helicity in the polymer would appear quite possible.

(1) The polymer must have a rigid helical structure. It must be totally isotactic with no helix reversals, or else there must be a significant length of helix between the initiation site and the first reversal, so that the amounts of right- and left-handed helix formed will not be identical and optical rotation will be caused by the presence of one form of helix predominantly or exclusively, as is the case in quartz.

(2) The optical activity of the polymer must be measured in the crystalline or amorphous solid state. If measurement in solution is attempted, the optical activity will be destroyed by uncoiling of the helices and reequilibration to equal proportions of the two helical forms. For the same reason, the solid polymer cannot be contacted with a solvent in which it is soluble before optical activity is measured.

The polymers which would seem best to fit these criteria are polymers containing side groups which are very bulky adjacent to the polymer chain, preferably which could be obtained in the completely isotactic form. An example would be the hypothetical polymer formed by bond-opening polymerization of 3,3-dimethyl-1-butene, having a polyolefin structure with tertiary butyl side groups. However, polymers of this type are quite difficult to synthesize and considerable isomerization may occur during polymerization (109-111).

A polymer family with equally bulky side groups which can be prepared much more easily is that of the trihaloacetaldehyde polymers, particularly polychloral (112-114). Only one form of polychloral has been described in the literature; this polymer is insoluble in all solvents which have been tested and is isotactic as shown by X-ray crystal structure determination (115). No soluble or atactic forms of polychloral have been identified. The carbon-13 NMR spectrum of a chloral/p-chlorophenyl isocyanate copolymer obtained by spinning a rotor of the solid polymer at the magic angle (116-118) was consistent with a structure free of helix reversals in the chloral sequence (119). The polymer of tribromoacetaldehyde (bromal), which has recently been prepared in this laboratory (120) has the most bulky side chain of any polymer prepared to date and it is impossible to construct a space-filling model of this polymer chain containing a helix reversal.

Hence the polymerization of a trihaloaldehyde such as chloral or bromal with an optically active anionic or cationic initiator, followed by removal of the initiator by extraction and determination of the optical activity of the polymer in the solid state, would seem a most feasible approach to the synthesis of an optically active polymer not containing asymmetric carbon atoms. However, in order to accomplish this, certain problems would have to be overcome, which will be brought up in the following section.

#### H. Historical Development of Higher Aldehyde Polymerization

1. Nonhalogenated aldehydes. Polymers of higher nonhalogenated aliphatic



aldehydes were first prepared by Bridgeman and Conant (121-123) who polymerized n-butyraldehyde, isobutyraldehyde, and n-heptaldehyde without initiator under high pressure. Polyacetaldehyde was first prepared by Letort and Travers in 1936 by "crystallization polymerization" from the liquid phase with no initiator or with peroxides (which yield acids from acetaldehyde) (124-126); later acids were found to be more effective (127). The different types of cationic and anionic acetaldehyde polymerization were investigated most thoroughly by Vogl beginning in 1957. High molecular weight atactic polyacetaldehyde elastomers could be prepared with cationic initiators (128-130) and a crystalline thermoplastic could be obtained anionically and in small amounts also by cationic initiation (129,131,132). This latter crystalline polyacetal was subsequently found by X-ray determination of crystal structure to be isotactic (133); such was later found to be the case with other crystalline polyacetals prepared by anionic techniques also, with cationic polymerization commonly giving a mixture of amorphous atactic and crystalline isotactic polymer (132).

The polymerization was found to proceed faster and to higher yield in solvents of low dielectric constant, such as aliphatic hydrocarbons, which minimize shielding of the propagating ion or ion pair from monomer. All higher aliphatic aldehydes were found to have low ceiling temperatures, with  $-39^{\circ}$  to  $-31^{\circ}\text{C}$ . reported for acetaldehyde polymerization (134) and  $-16^{\circ}\text{C}$ . for n-butyraldehyde polymerization (130).

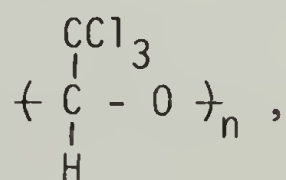
Organoaluminum compounds have been extensively used as initiators for aliphatic aldehydes by Furukawa and other Japanese workers, who have obtained atactic polyacetals by initiation with aluminum alkyls



and quite stereoregular polymers by initiation with aluminum alkoxides (135). Stereoregularity was particularly increased when the alkoxides were derived from bulky alcohols such as borneol. Bulkiness of the alkyl group of the aldehyde was also found to be an important factor in increasing isotacticity. (The aluminum alkoxides derived from borneol were quite similar to those used also in the successful stereoelective polymerizations of racemic propylene oxide.)

2. Halogenated aldehydes. The first observation of polymerization of halogenated aldehydes, as compared to nonhalogenated aliphatic aldehydes, was reported for trichloroacetaldehyde (chloral) by Liebig (136) in 1832. Liebig obtained an intractable white powder upon addition of sulfuric acid to chloral or chloral hydrate. This powder was of the same elemental composition as chloral and was initially referred to as "meta-chloral" by Liebig (136) and Boeseken and Schimmel (137). A similar material was obtained by Gaertner (138) by treatment of chloral with pyridine. Polychloral shares with polystyrene the position of being the first synthetic polymer to be discovered.

Novak and Whalley (139) prepared the polymer from chloral as a powder ("metachloral") by treatment of chloral hydrate with sulfuric acid, or as unstable hard blocks or films by bulk polymerization at room temperature with 4-8 mole percent of pyridine as initiator or at high pressure without initiator. These authors assigned, on the basis of infrared spectral evidence, a linear polyacetal structure,



to the polymer from chloral formerly known as "metachloral"; they renamed it "polychloral." The infrared spectra of the forms of polychloral prepared by these authors were analyzed extensively and most peaks were assigned to specific vibrations of the linear polychloral molecule; peaks due to hydroxyl endgroups could be seen in most samples. The polychloral samples were crystalline to X-ray diffraction, and the authors proposed a helical structure for the polychloral chains within the crystalline regions from the infrared spectral evidence. Although previous investigators had reported "metachloral" as being soluble in pyridine, these authors showed this "solution" to be merely a solution of monomeric chloral in pyridine and were unable to find any solvent in which polychloral would dissolve without degradation.

Busfield and Whalley (140) extended the above work by studying the effect of temperature and pressure on the chloral-polychloral equilibrium in the presence of large amounts of pyridine as an initiator, following the work of Boeseken and Schimmel (137) who had measured equilibrium vapor pressures of chloral over polychloral. Busfield and Whalley found that the concentration of chloral in pyridine-chloral mixtures allowed to stand over polychloral powders would reach an equilibrium value dependent on pressure and temperature. A polymerization threshold temperature of 12.5°C. was determined for chloral polymerization at a mole fraction of 0.1 in pyridine. However, because of the use of hydroquinone as a stabilizer for the chloral monomer in the polymerization mixture, the polychloral in equilibrium with monomer was of low molecular weight.

Furukawa and coworkers (141) polymerized chloral with a number

of organometallic initiators containing lithium, zinc, cadmium and aluminum, obtaining an intractable powder, not degraded by pyridine, in yields of up to 45%. Crystal structure determination by X-ray diffraction (142) showed this polymer to be isotactic with the polymer chains crystallizing in helices with a  $4_1$  spiral. The crystal structure was found to be tetragonal with  $a = 17.38\text{\AA}$ ,  $c = 4.80\text{\AA}$ , a crystalline density of  $2.012\text{ g/cm}^3$ , and inner rotational angles of  $158^\circ$  and  $-84^\circ$ .

Semenido, Ilyina, Shishkina and Krentsel (143,144) polymerized chloral in n-hexane solutions with butyllithium, obtaining a powdered polymer in a yield highly dependent on polymerization time over a period of hours. In view of the subsequently published rates of chloral polymerization determined in our laboratory (145), it seems likely that the butyllithium underwent a side reaction with the chloral and that the actual initiator was chloride ion.

Rosen and coworkers (146) polymerized chloral in bulk and in a number of solvents with cationic and anionic initiators, initiating below the threshold polymerization temperature and obtaining powdery polymers in yields up to 80%. These polymers could be endcapped by post-polymerization treatment with acyl halides or acid anhydrides at temperatures above  $100^\circ\text{C}$ . in the absence of base. The untreated polymers were highly stable to strong mineral acid and very sensitive to attack by base, in sharp contrast to the behavior of polymers of nonhalogenated aliphatic aldehydes. The degree of polymerization could be determined by carbon analysis of polymers endcapped with long-chain ester groups such as laurate. It was invariably found to be less than 600, although the precision of the determination was very low at degrees of polymeri-



zation greater than about 300. The endcapped polymer had considerably higher thermal stability than the raw polymer, as determined by isothermal degradation at 220° or 280°C. in nitrogen or at 130°C. in dimethylformamide. Cationically initiated polychloral prepared with  $H_2SO_4$ , with a degree of polymerization less than 100, showed strong hydroxyl adsorptions in the infrared spectrum prior to endcapping and carbonyl adsorptions after this treatment, while anionically initiated polychloral with a degree of polymerization near 500 showed neither type of endgroup adsorption in the infrared spectrum.

Otsu and coworkers (147,148) similarly used various metal acetylacetonates as initiators in the polymerization of chloral to a powdery polymer. A mechanism of addition of the enol oxygen of the acetylacetonate group to the chloral was proposed, but subsequent work by Uehara and coworkers (149) indicated that chloral most likely added instead to the central carbon atom.

Mita, Imai and Kambe (150) polymerized chloral in tetrahydrofuran with sodium naphthalene initiator under "equilibrium" conditions at various temperatures, noting also the effect of initiator concentration on polymer yield. When the chloral was first polymerized after addition of the initiator, the polymer yield and residual monomer concentration after polymerization (as determined by acetylation and extraction with acetic anhydride) depended highly on the ratio of monomer to initiator, indicating the lack of a true equilibrium. Since immediate polymerization occurs when initiators are added to chloral at low temperatures (p. 28), it is likely that some of the initiator became occluded within polymer and therefore was ineffective. The polychloral could be



depolymerized to liquid initiated chloral monomer by heating to above 80°C. with cooling producing repolymerization; this cycle could be repeated several times. The polymer yield and residual monomer concentration were much more constant after repolymerization than after the initial polymerization, indicating the value of homogeneous dispersion of the initiator in the liquid chloral monomer for reaching an equilibrium during polymerization.

These authors also determined ceiling temperatures (at one molar concentration) for the polymerization of chloral and its derivatives in which chlorine atoms were replaced by methyl groups-- $\alpha,\alpha$ -dichloropropionaldehyde,  $\alpha$ -chloroisobutyraldehyde and trimethylacetaldehyde. The ceiling temperature (1 M) of chloral polymerization in THF was found to be 11°C. from the polymer yield and residual monomer concentration after polymerization. Each substitution of a methyl group for a chlorine atom lowered the ceiling temperature by approximately 30°C., and trimethylacetaldehyde could not be polymerized at all. (A rather anomalous ceiling temperature of 35°C. for chloral polymerization was reported when n-heptane was used as the diluent.)

However, all of the previous experimental work, except that involved with casting polychloral blocks under pressure or preparing films (which degraded readily) from chloral-pyridine mixtures, relied on the polymerization of chloral in solution with the initiator generally added below the threshold polymerization temperature. These techniques all produced powdery polymers with no cohesiveness or mechanical strength and questionable and irreproducible stability; for this reason the flame resistance and other desirable physical properties of

the polychloral could not be exploited.

However, a procedure for preparing strong coherent objects of polychloral, known as cryotachensic polymerization, was discovered by Vogl and collaborators (112,113) at Du Pont in 1962. In this technique, an anionic initiator, such as an alkoxide, carboxylate, tertiary amine, or phosphine, plus in some cases a diluent to aid dispersal of the initiator, is added to chloral monomer above the threshold temperature for bulk polymerization. The monomer remains liquid above this temperature and can be injected into a mold; upon cooling, a tough solid object of polychloral in the shape of the mold is formed within 1 to 60 minutes. A number of different anionic initiators could be used satisfactorily in this technique; cationic initiators (Lewis or Bronsted acids) polymerized the chloral very slowly and usually produced an incoherent polymer (151). The chloral homopolymer produced by this process was opaque; transparent amorphous copolymers could be produced by adding various isocyanates and ketenes to the polymerization mixture (164,165).

The copolymerization of chloral with a number of other monomers has also been investigated. Thuemmler, Lorenz and Thinius (152) prepared polymers from mixtures of chloral and formaldehyde using organometallic compounds of cadmium, zinc, and aluminum as initiators. The initiator was added to a solution of the monomers in toluene or heptane at  $-70^{\circ}\text{C}$ . The product polymers contained from 10 to 40 formaldehyde units per chloral unit; the authors were unable to determine whether copolymers or mixtures of homopolymers were formed.

Holmström and Sörvik (153) copolymerized chloral with trioxane using cationic initiators, particularly  $\text{AlBr}_3$ , to give copolymers

containing from 4 to 17 mole percent of oxymethylene units. The copolymers were amorphous by X-ray diffraction and showed considerably increased stability over chloral homopolymer, with no weight loss observable for the copolymers after heating at 200°C. for one hour. The copolymers, in contrast to polychloral and polyoxymethylene, were also highly resistant to degradation by both strong acids and bases. However, the cationically initiated copolymers could be obtained only as powders with a maximum degree of polymerization of about 40; strong hydroxyl endgroup bands were seen in the infrared spectra.

Rosen and Sturm (154), in an attempt to improve the tractability of polychloral while retaining its desirable properties, copolymerized chloral with dichloroacetaldehyde using a number of organometallic initiators. Initiators were added to the mixture of monomers at -70°C.; polymer precipitated immediately if less than 15 mole percent of dichloroacetaldehyde was in the polymerization mixture, but tough blocks of copolymer could be cast from monomer mixtures containing larger amounts of dichloroacetaldehyde. The resultant polymers, however, were infusible and insoluble in all solvents like chloral homopolymer. The copolymers were less stable than the corresponding chloral homopolymers prepared in (146) after being given the same posttreatments; the mechanical properties of the cast blocks were similar to those of cryotachensically prepared chloral homopolymer (p. 170). Dichloroacetaldehyde was significantly less reactive than chloral in copolymerization.

Extensive work has been performed in the past on the copolymerization of chloral with heterocumulenes such as isocyanates and ketenes.



Takida and Noro (155) copolymerized chloral with phenyl isocyanate at  $-78^{\circ}\text{C}$ . with sodium naphthalene initiator to obtain an insoluble, infusible copolymer containing 8 mole percent of phenyl isocyanate units. A Soviet group (156-160) studied the copolymerization of chloral with aromatic isocyanates in THF or DMF solution with a number of anionic and organometallic initiators. Approximately a 1:1 ratio of chloral to isocyanate was generally used, and the products were soluble, fusible copolymers with a chloral/isocyanate ratio of approximately 2:1. At higher chloral/isocyanate ratios in the monomer feed (4:1), the resultant copolymer was insoluble and contained over 80 mole % of chloral units; both soluble and insoluble (chloral-rich) fractions were found at intermediate monomer feed ratios. The copolymers had much higher thermal stability (as determined by isothermal degradation at  $200^{\circ}\text{C}$ .) than either chloral homopolymer or the homopolymers of the respective aromatic isocyanates. When cobalt (II) bisacetylacetonate was used as the initiator for copolymerization of chloral with phenyl isocyanate, a strictly alternating copolymer was obtained; if n-butyl isocyanate was added to this mixture, it was not incorporated into the resultant copolymer.

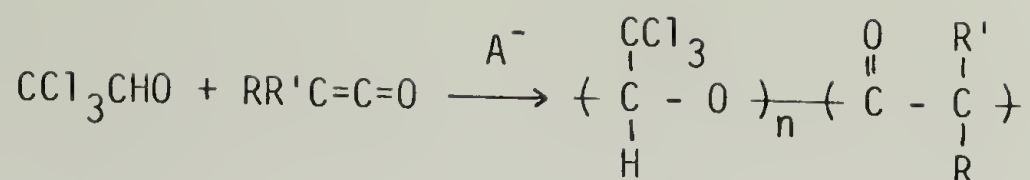
Raes, Karabinos and Dietrich (161) copolymerized chloral with phenyl isocyanate in benzene or toluene at  $25^{\circ}\text{C}$ . using tertiary aliphatic amines as initiators; soluble copolymers with a chloral/isocyanate ratio of approximately 2:1 were obtained from 1:1 or 1:2 chloral/isocyanate ratios in the monomer feed. Odian and Hiraoka (162, 163) copolymerized chloral with phenyl and n-butyl isocyanate in a number of solvents at  $-75^{\circ}\text{C}$ . with n-butyllithium or KCN initiators,



forming copolymers insoluble in hexane, diethyl ether, THF or DMF. When hexane was used as the polymerization solvent, with the volume of hexane greater than that of chloral, only chloral homopolymer was obtained. When the solvent was changed to diethyl ether, copolymerization did occur; reactivity ratios found were  $r_1 = 0.5$  and  $r_2 = 0$  for chloral ( $M_1$ ) and phenyl isocyanate ( $M_2$ ) and  $r_1 = 2-50$  and  $r_2 = 0$  for chloral ( $M_1$ ) and n-butyl isocyanate ( $M_2$ ) in diethyl ether at  $-75^\circ\text{C}$ . with n-butyllithium used as the initiator.

Probably the most extensive study of chloral-heterocumulene copolymerization, however, was performed by Vogl (164,165). In contrast to the above work, which utilized solvents, these polymerizations were conducted cryotachensically in bulk with chloral-isocyanate mixtures initiated with anionic initiators such as lithium tertiary butoxide (LTB) or triphenylphosphine. When less than 70 mole percent of an isocyanate was used in the polymerization mixture, copolymers were obtained which were insoluble in common organic solvents. Most of the work was performed at levels of isocyanate in the polymer mixture below 20 mole percent; these produced copolymers which were generally amorphous and transparent or semitransparent, in contrast to the crystalline, opaque homopolymer of chloral. These copolymers usually contained less than 10 mole percent of isocyanate, with aromatic isocyanates being incorporated into the copolymer to a greater relative extent than aliphatic isocyanates.

Ketenes could be also copolymerized with chloral to give polyacetals containing polyester linkages



similar to the polyacetal-polyurethane structures obtained from chloral-isocyanate mixtures. As in the case of isocyanates, aromatic ketenes such as diphenylketene could be incorporated into the polymer more readily than could aliphatic ketenes such as dimethylketene. Copolymers of chloral with isocyanates and ketenes had considerably greater thermal stability than that of chloral homopolymer.

When chloral-phenyl isocyanate mixtures containing 70 mole % or more of the isocyanate were polymerized in bulk, the resultant copolymers were soluble in benzene and contained about 20 mole % of isocyanate units in the polymer chains. Molecular weights ( $\bar{M}_n$ ) of 50,000 to 150,000 could be obtained.

Several studies (166-169) have been conducted on the polymerization of fluoral (trifluoroacetaldehyde). Fluoral can be polymerized readily to high molecular weight polymers with anionic, cationic, or free-radical initiators. In contrast to the behavior of nonhalogenated aliphatic aldehydes, the crystallinity of polyfluoral seemed to vary more with polymerization temperature than with initiator system, with amorphous elastomers being formed at  $-78^\circ\text{C}$ . or lower and insoluble crystalline polymers at higher temperatures.

It was noticed at this time that fluoral and nonhalogenated acetaldehydes, with nonbulky side groups adjacent to the carbonyl group, could be polymerized to atactic or isotactic polymers, while chloral, containing the bulky trichloromethyl group, could be polymerized only

to an insoluble isotactic polymer. This observation suggested a study of the polymerization of trihaloacetaldehydes containing different combinations of halogen substituents to determine the critical size of the side group required to prevent formation of atactic polymers. Such a study has been undertaken in this laboratory (170-175). It was found that soluble (and presumably atactic) polymer fractions were present in the polymers of trihaloacetaldehydes containing at least two fluorine atoms, but only insoluble and presumably isotactic polymers were formed from the aldehydes either containing only chlorine and/or bromine substituents or containing only one fluorine atom.

#### I. Problems which Must be Solved in the Synthesis of Optically Active Polychloral

It is desired to synthesize a helical isotactic polymer with helices predominantly or exclusively of one screw sense. This polymer should contain no asymmetric carbon atoms and should display optical activity in the solid state due to helicity only. Because of the bulk of the side chain and the ease of polymerization to an insoluble isotactic polymer, chloral was chosen as the monomer.

Initial work in this area was done in 1962 when chloral was polymerized with the lithium salt of cholesterol as an initiator by the cryotachensic method (176). Attempts were made to measure the optical activity of the polymer in the dry state as a pellet. These measurements were unsuccessful because in the dry state the birefringence was extensive and rendered the optical activity unobservable. Hatada and Vogl (177) later tried the same technique with copolymers of chloral with

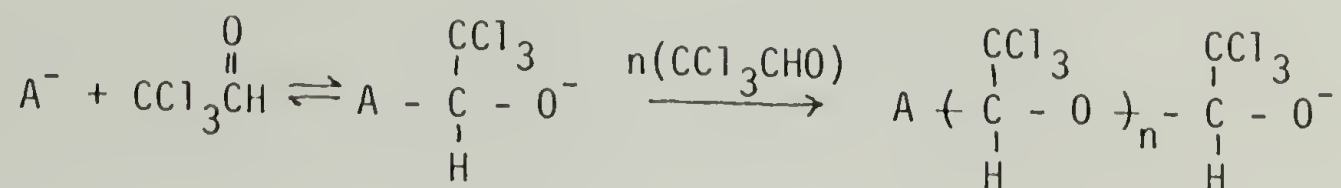


phenyl and p-chlorophenyl isocyanates, which, unlike the opaque, crystalline homopolymer of chloral, are amorphous and transparent. However, even after long extraction and annealing of the samples with acetone, a considerable amount of birefringence remained which rendered the optical activity of the dried sample unobservable, probably due to residual unrelieved stresses in the polymer or to stresses introduced upon drying.

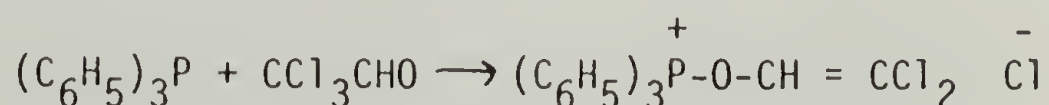
Hence it became apparent that another method would have to be used to prepare samples for optical activity measurements. It was known earlier (178) that chloral homopolymers initiated with alkali alkoxides such as lithium tertiary butoxide were more opaque than polymers prepared with initiators such as ammonium or phosphonium halides or carboxylates. These latter compounds also polymerized chloral more slowly and in a manner more easily controllable. It was felt that one should therefore prepare ammonium and/or phosphonium salts (alkoxides, carboxylates and halides) with optical activity in the cation, the anion, or both. Optical activity of the resultant polychloral should then give indications as to the relative importance of the initiating anion and counteranion in determining the sense of addition of the chloral units to the initiating species to form a left- or right-handed polychloral helix.

However, in determining the optical activity of the resultant polychloral, it is important to know the amount of optical activity coming from the polychloral and the amount coming from initiator residues chemically bound to the polymer. Some anionic initiators such as carboxylates are known to leave residues in the polychloral which cannot be removed by extraction and appear chemically bound to the polymer

(176). These initiators apparently function by adding directly to the chloral to form an alkoxide which can then add more chloral units to cause polymerization:



The fate of the counteranion is unknown but it has been considered as generally being removed (and perhaps replaced by hydrogen) during extraction; in a sample which was initiated with triphenylphosphine and subsequently extracted with acetone, elemental analysis showed only 0.002% P in the polymer, as compared to 0.080% which should have been present if all the phosphorus had remained in the polymer (176). Triphenylphosphine reacts with chloral (179) to form the phosphonium salt triphenyl(dichlorovinyl)phosphonium chloride:

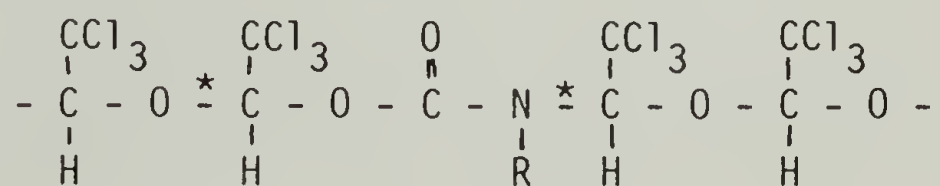


The chloride ion is considered as the actual initiator for chloral polymerization and the phosphonium ion as the counteranion. According to the above extraction result, either the counterions were largely extracted from the polymer and replaced by something else (probably protons) or else the counterions remained in the polymer but only 2.5% of the phosphonium chloride was actually used in initiating the polymer, with the rest remaining as extractable unchanged phosphonium salt.

For these reasons, it is desired to determine the actual

mechanism of initiation by different chloral initiators and to determine which initiator residues will be chemically bonded to the polymer in the case of initiation by such initiators as alkoxides, halides, and amines, and which initiator residues can be removed by extraction. Such will serve as a guide to synthesis and use of optically active initiators not leaving optically active residues in the polymer.

Similarly, in order to facilitate measurement of optical activity, it is desired that the polymer be transparent or semitransparent. Ordinary chloral homopolymer as prepared by the cryotachensic technique is opaque and crystalline. Although one can prepare transparent amorphous polymers by copolymerization of chloral with p-chlorophenyl isocyanate, by so doing one introduces a different monomer unit which may break up the helicity of the polychloral chain and introduce a helix reversal. One also forms undesired asymmetric carbon atoms in the chloral units of the polymer adjacent to the isocyanate unit:



To avoid this problem, it is desired to prepare transparent chloral homopolymer. One possibility concerns the preparation of a blend of polychloral with another polymer with which the polychloral is compatible, such that the other polymer mixes intimately on a molecular level with the polychloral and prevents its crystallization.

Compatible polymer systems are rather rare, although a number of them have been reported in the literature and have been reviewed



recently (180). Compatible polymer systems may arise in some (though few) mixtures of two polymers with very similar polarities and solubility parameters, such as blends of poly(vinyl acetate) with poly(methyl acrylate) (181), poly(methyl methacrylate) with poly(ethyl acrylate) (181,182) and polystyrene with poly(2,6-dimethylphenylene oxide) (183-185). In the aforementioned systems, except for those in which isotactic polystyrene may be used, the components are generally amorphous as homopolymers. However, a stronger thermodynamic driving force for the molecular mixing of polymers and the formation of a compatible system exists when there is a specific interaction between the two polymers. This is the case in the system of poly(vinyl chloride) (PVC) - poly( $\epsilon$ -caprolactone) (PCL) which is compatible over certain composition ranges (186). This system is made still more interesting by the fact that PCL homopolymer is highly crystalline; the crystallinity is destroyed and the polymer goes into an amorphous blend upon admixture with an equal or greater amount of PVC.

Hatada and Vogl (187) found that the PMR absorption peaks of aromatic protons of compounds such as toluene or tetrahydronaphthalene trapped within the rigid polychloral matrix were significantly broadened, much more than were the aliphatic protons of these or purely aliphatic solvents and much more than were the absorptions of aromatic solvent protons in concentrated (>35%) solutions of ordinary polymers such as polyisobutylene or poly(methyl methacrylate) (188,189). This was interpreted as being caused by a specific interaction between the electron-poor trichloromethyl groups of the chloral polymer and the electron-rich aromatic rings of the solvents.

For this reason, we thought that polystyrene, with electron-rich aromatic rings, would be a promising polymer for blending with polychloral in an attempt to inhibit polychloral crystallization. Poly(methyl methacrylate) and poly(methyl acrylate), containing relatively electron-rich ester carbonyl oxygen atoms, were also considered as possibilities for forming compatible blends with polychloral.

However, to determine compatibility or incompatibility of these mixtures by standard techniques, such as observing a single glass transition temperature ( $T_g$ ) for ordinary polyblends (or an elevated glass transition temperature for the non-polychloral component of a compatible blend containing polychloral, since polychloral appears by DSC or torsional pendulum measurements to have no  $T_g$  below the onset of decomposition (146,176)), one would (except, of course, for very low-frequency measurements) have to heat the materials above the  $T_g$ 's of unmodified polystyrene or poly(methyl methacrylate), which are near 100°C., where the decomposition of unstabilized polychloral begins. It was known previously (176) that copolymerization with isocyanates could impart considerably increased stability to polychloral, but such is undesirable in polymers or blends to be used for optical activity measurements, as was discussed previously. Phosphorus pentachloride was also known to be an effective stabilizing agent (176,190), but this method of stabilization required long heating with a solvent such as  $CCl_4$  which could extract linear nonchloral polymers from the blend. After-treatment of the polychloral with acyl halides such as acetyl chloride, found by Rosen (146) to be an effective method of stabilizing powdery non-cryotachensically initiated polychloral by acylation, was found by Kubisa and Vogl

(191) to be ineffective (by IR) in acetylation of cryotachensically prepared polychloral films. When the acyl halides were added directly to the polymerization mixture before gelation, acylation of the polymer chain ends with resultant stabilization did occur but was not quantitative (191).

Hence it is highly desirable to find a rapid method of complete stabilization of chloral homopolymer by a simple procedure which will not affect a nonpolychloral component of a blend. Such could take the form of a post-polymerization treatment, a reagent added to the polymerization mixture before cooling (to start polymerization) which can react with the endgroups after polymerization and thereby stabilize the polymer, or an initiator containing an alkylating cation such as a sulfonium ion, which could alkylate the alkoxide group of the polychloral after polymerization.

Previous experimental work has included no determinations on the actual endgroups in unstabilized cryotachensically initiated polychloral (except determination of carboxylate initiator residues for molecular weight measurements (176)), although the non-initiator-containing endgroups have generally been assumed to be hydroxyl or alkoxide. However, no hydroxyl group absorption can be seen in the infrared spectrum of cryotachensically prepared polychloral films and treatment with  $\text{PCl}_5$ , which stabilizes the films thermally, produces no change in the infrared spectrum (178). Hence it would seem highly desirable to determine experimentally the actual endgroups in polychloral prepared by cryotachensic anionic initiation, particularly insofar as this would be expected to help markedly in finding suitable stabilization



agents.

Finally, it is necessary to determine a satisfactory system for measurement of the optical activity of polychloral, such as the isorefractive suspension or unoriented film systems used by the group of Pino in characterizing the optical activity of polyolefins in the solid state (106). Initial experiments could most likely be performed with optically inactive polychloral, followed by synthesis of appropriate optically active initiators (such as quaternary ammonium and phosphonium salts containing anions which the chiral center very close to the carboxyl or other group in the anion bearing the negative charge, and/or counterions chiral at or near the heteroatom). Chloral polymerization experiments (to give polychloral in the shapes found best for polarimetric measurements) with the optically active initiators could then be carried out, followed by general optical activity determinations on the resultant polychloral.

If the polychloral products were found to be optically active, crystal structure and mechanical property determinations on such would then seem strongly indicated because of the difference in crystal structure which would be caused by incorporation of only one screw sense of helix into the crystals.

# CHAPTER II

## EXPERIMENTAL SECTION

### A. Materials

The following chemicals and reagents were obtained from the indicated sources.

#### 1. Reagents.

Acetic Anhydride	E	n-Butyl Isocyanate	A
Acetyl Chloride	E	tert-Butyl Isocyanate	A
1-Acetylimidazole	A	Calcium Hydride	F
Ammonium Chloride	F	D-Camphor-10-sulfonic Acid	PB
Azobisisobutyronitrile	A	Chloral	MON
Benzyl Alcohol	A	Chloroacetone	E
Benzyl Bromide	E	p-Chlorophenyl Isocyanate	A
Benzyl Chloride	E	1,3,5-Cycloheptatriene	B
Benzyl dimethylsulfonium Bromide	D	Cyclohexanol	E
Benzyl di(n-propyl)sulfonium Bromide	D	Di(n-butyl) Sulfide	P
		Di(tert-butyl) Sulfide	P
Boron Trifluoride Diethyl Etherate	A	Diethanolamine	B
Bromoacetyl Bromide	A	2,2-Dimethoxypropane	A
Bromine	F	3,5-Dimethylpyrazole	A
Brucine	A	Dimethyl Sulfate	E
tert-Butyl Alcohol	MCB	Dimethyl Sulfide	P

Ethyl Bromoacetate	E	Potassium Permanganate	B
Ethyl Chloroacetate	E	Pyridine	A
Hydrochloric Acid, Conc. Aq.	F	Silver Nitrate	F
Iodine	F	Sodium Carbonate	F
Isopropyl Isocyanate	A	Sodium Metal	F
Lithium tert-Butoxide	V	Sodium Chloride	F
Lithium Chloride	F	Sodium Hydroxide	F
Magnesium Sulfate	F	Styrene	A
Methyl Acrylate	A	Sulfuric Acid, Concentrated	F
Methyl Iodide	PB	Sulfuric Acid, 30% Fuming	F
Methyl Methacrylate	A	Tetrabutylammonium Chloride	E
2-Methyl-1,3-oxazoline	A	Tetrabutylammonium Hydroxide (CH <sub>3</sub> OH solution)	E
Molecular sieves	MCB	Tetramethylammonium Hydroxide (CH <sub>3</sub> OH solution)	A
Nitric Acid, Concentrated	F	p-Toluenesulfonic Acid Monohydrate	E
Nitric Acid, Fuming	F	Tributylamine	E
Nitrobenzene	E	Triethylamine	E
p-Nitrobenzyl Bromide	A	Trimethyl Orthoformate	A
Phenacyl Bromide	E	2,4,6-Trimethylpyridine	A
Phenyl Isocyanate	A	1-(Trimethylsilyl)imidazole	A
Phosphorus Pentachloride	V	Trimethylsulfonium Iodide	D
Phosphorus Pentoxide	F	Triphenylphosphine	A
Potassium Bromide	H		
Potassium Carbonate	F		
Potassium Carbonate Sesquihydrate	F		
Potassium Iodate	F		



2. Solvents.

Acetone	F	N,N-Dimethylacetamide	A
Acetonitrile	E	N,N-Dimethylformamide	A
Benzene	E	Dimethyl Sulfoxide	A
Benzene-d <sub>6</sub>	A	Ethanol	F
1-Bromonaphthalene	E	Methanol	F
Carbon Tetrachloride	F	Perfluoro-2-(n-butyl) tetrahydrofuran	PCR
Chloroform	F	2-Propanol	F
Chloroform-d	A	"Skelly B" (mostly n-hexane)	S
1-Chloronaphthalene	E	Sulfolane	A
Cyclohexane	E	Toluene	F,M
Dichloromethane	F	Trifluoroacetic Acid	E
Diethyl Ether	F		
Diphenyl Ether	E		

3. Suppliers.

A	Aldrich Chemical Company
B	J.T. Baker Chemical Company
D	E.I. DuPont de Nemours and Company
E	Eastman Kodak Company
F	Fisher Scientific Company
H	Harshaw Chemical Company
M	Mallinckrodt Chemical Company
MCB	Matheson, Coleman and Bell, Inc.
MON	Montrose Chemical Company
P	Phillips Petroleum Company

PCR	PCR, Inc.
PB	Pfaltz and Bauer, Inc.
S	Skelly Oil Company
V	Ventron Alfa Products

### B. Purification of Solvents and Reagents

Chloral was refluxed overnight over phosphorus pentoxide (about 20g. per liter of chloral) and distilled from the  $P_2O_5$  into another flask. This flask was transferred to a still containing a column packed with glass helices and the chloral was refluxed in this still for one week. Chloral monomer was then removed at a reflux ratio of 10:1. After desired monomer purity was reached, the desired amount of chloral was distilled and used immediately thereafter (114). The impurity level by gas chromatography was below 0.3% in all experiments and below 0.03% in most.

Azobisisobutyronitrile (AIBN) was recrystallized from diethyl ether/acetone, dried for 30 minutes in a stream of dry nitrogen, and stored at  $-10^{\circ}C$ . It was used as a 0.3M solution in benzene.

Benzyl alcohol was dried overnight over  $4\text{\AA}$  molecular sieves before use.

Benzyldimethylsulfonium bromide, benzyldi(n-propyl)sulfonium bromide, and trimethylsulfonium iodide were dried overnight over  $P_2O_5$  at room temperature and 0.1 mm. pressure before use to prepare chloral initiator solutions.

Boron trifluoride diethyl etherate was dried for 4 days over  $CaH_2$  (with 1% of excess diethyl ether added) with magnetic stirring. It

was then distilled and the middle third of the distillate was taken; b.p. 56°C./20 mm. (192).

Bromoacetyl bromide was stirred overnight over dry 4Å molecular sieves to adsorb HBr, a possible impurity. It was then distilled; the middle fraction was distilled directly into a Schlenk tube for storage; b.p. 56-7°C./20mm.

Brucine, purchased as the dihydrate, was dried for one day over P<sub>2</sub>O<sub>5</sub> at 100°C./0.5mm., to render it anhydrous; m.p. 173-178°C., lit. (193) 177-178°C.

n-Butyl isocyanate was distilled under nitrogen at atmospheric pressure; a final fraction of the distillate was found by gas chromatography to contain less than 0.05% impurities and was used.

tert-Butyl isocyanate was distilled under nitrogen at atmospheric pressure; b.p. ~99°C. The final 5 ml. cut from a 50 ml. charge was shown to contain less than 0.05% impurity by gas chromatography and was used.

p-Chlorophenyl isocyanate was distilled at reduced pressure under nitrogen; b.p. 95°C./20mm. Gas chromatography showed less than 0.05% impurity.

1,3,5-Cycloheptatriene was distilled under nitrogen at atmospheric pressure; b.p. 114°C. Gas chromatography revealed two low-boiling impurities in concentrations of 1% and 2% respectively.

Cyclohexanol was dried overnight over 4Å molecular sieves before use.

Diethanolamine was dried one week over 4Å molecular sieves before use.



2,2-Dimethoxypropane was dried for 2 days over liquid NaK alloy with stirring. It was then distilled under nitrogen at atmospheric pressure and the last 15 ml. of a 70 ml. charge was taken; b.p. 80°C. Gas chromatography showed the distillate to contain 2% of a single impurity.

Dimethyl sulfate was dried over anhydrous  $K_2CO_3$  for four days, decanted and distilled under nitrogen at reduced pressure; b.p. 84-85°C./20mm. A center fraction equal to about half the charge was taken.

Dimethyl sulfide, for the reaction with bromoacetyl bromide and for attempted chloral initiation, was dried for 5 hours over  $K_2CO_3$  and then for 4 days over  $CaH_2$ . It was then distilled at atmospheric pressure under nitrogen; b.p. 37-38°C. Gas chromatography (25°C., Carbowax 20M) showed less than 0.05% impurity.

For other sulfonium salt syntheses, the dimethyl sulfide was used as received.

Isopropyl isocyanate was distilled under nitrogen at atmospheric pressure; b.p. 76°C. A middle fraction was taken. Gas chromatography showed less than 0.05% impurity.

Lithium tertiary butoxide (LTB) was sublimed at 135-145°C./0.1mm. and subsequently transferred within a dry-nitrogen-filled glove bag.

Methyl acrylate was dried over  $CaH_2$  for six days and distilled under nitrogen at atmospheric pressure; b.p. 81-82°C. The middle fraction showed the presence of 0.2% of a low-boiling impurity by gas chromatography; this fraction was used.

Methyl iodide for use as a polymerization additive was dried overnight over  $\text{CaH}_2$  and distilled under nitrogen at atmospheric pressure; b.p.  $42-43^\circ\text{C}$ . Methyl iodide for sulfonium and oxosulfonium salt syntheses was used as received.

Methyl methacrylate was dried for 36 hours over  $\text{CaH}_2$  and distilled under nitrogen; b.p.  $101-102^\circ\text{C}$ . The middle two-thirds of the distillate was used; gas chromatography showed less than 0.05% impurity.

2-Methyl-1,3-oxazoline was used as received, gas chromatography showed less than 0.05% impurity.

Molecular sieves were washed with water several times and then kept overnight at  $300^\circ\text{C}/0.05\text{mm}$ . pressure.

Phenacyl bromide, as the commercial material from Eastman, was a dark brown mass. It was distilled at  $150^\circ\text{C}/20\text{mm}$ . in a short-path apparatus, followed by recrystallization from ethanol/water to give colorless crystals; m.p.  $49-50^\circ\text{C}$ ., lit. (194)  $50^\circ\text{C}$ .

Phenyl isocyanate was distilled at atmospheric pressure under nitrogen; b.p.  $162^\circ\text{C}$ . A middle fraction of the distillate was used; gas chromatography showed less than 0.05% impurity.

Pyridine was dried over  $\text{CaH}_2$  for four days and distilled at atmospheric pressure under nitrogen; b.p.  $114^\circ\text{C}$ . The final two-thirds of the distillate, which showed less than 0.05% impurity by gas chromatography, was used.

Styrene was washed once with 10% aqueous  $\text{NaHSO}_3$  solution, twice with 2%  $\text{NaOH}$  solution, and three times with water. It was then dried for 2 hours over  $\text{K}_2\text{CO}_3$  and for five days over  $\text{CaH}_2$  and distilled under nitrogen at reduced pressure; b.p.  $62^\circ\text{C}/20\text{mm}$ . A forecut (about 10%)

was discarded. Gas chromatography revealed less than 0.05% impurity in the main cut.

Tributylamine was distilled at reduced pressure; b.p. 101°C./17mm. A forecut (b.p. 97-101°C./17mm.), comprising about 25% of the material, was discarded.

Trimethyl orthoformate was dried for four days, with stirring, over liquid NaK alloy. It was then distilled under nitrogen at atmospheric pressure; b.p. 98°C. Gas chromatography showed the presence of 0.2% of a low boiling impurity.

2,4,6-Trimethylpyridine was used as received; gas chromatography showed less than 0.05% impurity.

Triphenylphosphine ( $\text{Ph}_3\text{P}$ ) was recrystallized from methanol or from acetone/Skelly B. For kinetic work, it was then also sublimed at 100°C./0.3mm. pressure.

Acetonitrile, for use as a solvent for initiators, was dried overnight over  $\text{CaH}_2$  and then distilled under nitrogen at atmospheric pressure. When used as a solvent for recrystallizations, it was simply dried overnight over  $4\text{\AA}$  molecular sieves.

Benzene and cyclohexane were dried for one day over  $\text{CaH}_2$ , distilled under nitrogen at atmospheric pressure, and stored over liquid NaK alloy. Gas chromatography revealed less than 0.05% impurity.

Carbon tetrachloride was used after standing overnight over  $4\text{\AA}$  molecular sieves.

Chloroform was allowed to stand over  $\text{P}_2\text{O}_5$  for several days to remove ethanol; it was then filtered through a medium-porosity glass filter and stored over  $4\text{\AA}$  molecular sieves. Gas chromatography revealed



less than 0.05% impurity.

Dichloromethane was dried over  $P_2O_5$  for several days, distilled at atmospheric pressure, and stored over  $4\text{\AA}$  molecular sieves.

Diethyl ether was Fisher Electronic Grade and was used as received.

N,N-Dimethylacetamide (DMAc) was dried for two days over  $P_2O_5$  with stirring and was then distilled from the  $P_2O_5$  at reduced pressure under nitrogen; b.p.  $67^\circ\text{C.}/20\text{mm}$ . A middle fraction was taken and stored over  $4\text{\AA}$  molecular sieves. Gas chromatography revealed less than 0.05% impurity.

Dimethyl sulfoxide (DMSO) was dried and refluxed over  $\text{CaH}_2$  for 2 hours and then distilled at reduced pressure; b.p.  $70^\circ\text{C.}/10\text{mm}$ . Gas chromatography revealed less than 0.05% impurity.

Perfluoro-2-(n-butyl)tetrahydrofuran was stored over  $\text{CaH}_2$  for 2 days and then distilled at atmospheric pressure under nitrogen; b.p.  $103\text{--}104^\circ\text{C}$ . Gas chromatography showed the presence of 0.7% of a low-boiling impurity.

Sulfolane was dried over  $\text{NaOH}/\text{CaCl}_2$  for 2 hours and then distilled; b.p.  $110^\circ\text{C.}/0.7\text{mm}$ . The distillate was stored over  $3\text{\AA}$  molecular sieves; a gas chromatogram taken shortly before use showed water content to be less than 0.03%.

Toluene was refluxed over molten sodium for several days, distilled from the sodium at atmospheric pressure under nitrogen, and stored over fresh sodium wire.

Reagents and solvents not listed in one of the above procedures were used as received.

Distillations, except as noted above, were carried out in a distillation head equipped with a 30cm. Vigreux column, with magnetic stirring. In distillations at atmospheric pressure, a serum stopper was placed on one neck of the receiving flask in order that cuts could be withdrawn from the flask with a syringe and distillate composition could be periodically monitored by gas chromatography during the distillation. The distillation apparatus was generally evacuated and refilled with dry nitrogen several times before the start of the distillation. In reduced pressure distillations, an adapter holding several receiving flasks was used so that several fractions could be distilled without breaking the vacuum.

Solvents or other liquids for use as eventual components of chloral polymerization mixtures were stored in Schlenk tubes (topped with stopcocks) which had been dried overnight at at least 120°C. and purged with dry nitrogen. Transfer of solvents to and from these tubes was via syringes under continuous nitrogen blanketing.

Because of the sensitivity of the anionic chloral polymerization to water and other compounds containing acidic hydrogen, a special procedure was used for the preparation of all initiator solutions. All solid initiators, before use in solution preparation, were dried over granular  $P_2O_5$  at 0.05mm. pressure and room temperature for at least one day. Bottles containing the solid initiators were then placed in a polyethylene glove bag, together with flasks (dried overnight at 120°C.), serum stoppers, transfer spatulas, and a small torsion balance. A dish containing anhydrous  $CaSO_4$  was then placed in the bag, which was sealed; the gas in the bag was pumped out and the bag was refilled with dry

nitrogen several times in succession. The initiator bottles were then opened and the initiators were weighed into the flasks, which were closed with serum stoppers. The initiator bottles were then closed and the bag was opened; the flasks containing weighed amounts of initiators were removed and solvents were added with syringes under a nitrogen blanket. If the initiator solutions were not used immediately, they were transferred with dry syringes under nitrogen flow to Schlenk tubes prepared as above, in which they were stored. (These Schlenk tubes were torpedo-shaped flasks with male ground-glass joints, topped with female ground-glass joints attached to 3-way stopcocks such that a syringe needle could be inserted into the tubes to introduce or withdraw liquid under continuous blanketing by dry nitrogen flow.)

### C. Reactions of Chloral with Initiators Above Threshold Polymerization Temperature

#### 1. Reaction with lithium tertiary butoxide.

a. Determination by  $^1\text{H}$  NMR spectroscopy. An NMR tube was washed with dilute  $\text{HNO}_3$  and then with distilled water several times. It was then heated overnight at  $130^\circ\text{C}$ . A solution of LTB, 0.3M in benzene (0.30ml., 0.09 mmol LTB) was added to the NMR tube with a dried syringe. The tube was then evacuated at 30mm. pressure for 15 minutes to evaporate the benzene.

Benzene- $\text{d}_6$  (containing 1% tetramethylsilane (TMS)), 0.15ml., was then injected into the tube with a syringe. The tube was heated in an oil bath at  $70^\circ\text{C}$ . for 5 minutes to dissolve the LTB. A  $^1\text{H}$  NMR spectrum of the resultant solution (60 MHz) (Figure 1B, p. 115) showed that the



singlet of the tert-butyl group of LTB was found 1.3ppm downfield from TMS. The benzene proton peak was at  $\delta$  7.2, and there was a small peak (not a spinning sideband) which was apparently an impurity in the LTB, found at  $\delta$  0.3. (This same peak was also found in the  $^1\text{H}$  NMR spectrum of the original solution of LTB in undeuterated benzene and in the absence of TMS.) The NMR tube was returned to the 70°C. oil bath for 5 minutes.

A 0.1 ml. syringe was filled with 0.02 ml. of benzene- $\text{d}_6$ ; 0.009 ml. (0.013g., 0.09 mmole) of chloral was then taken up into the syringe as a layer under the benzene- $\text{d}_6$ . The contents of the syringe were then injected rapidly directly to the bottom of the NMR tube. The tube was rolled to complete the mixing of the reactants and allowed to remain in the heating bath for 5 minutes. The tube was then cooled to 35°C. and a  $^1\text{H}$  NMR spectrum was taken (Figure 1C, p. 115). The tertiary butyl peak remained at  $\delta$  1.3, and a new singlet at  $\delta$  5.4 had appeared. The integral ratio of the  $\delta$  5.4 and  $\delta$  1.3 peaks was approximately 1:9.

A few small impurity peaks, possibly representing the products of side reactions, were located between  $\delta$  0.8 and 1.3; the strongest of these was at  $\delta$  1.0. No peak could be seen in the chloral proton range downfield from  $\delta$  8.

The tube was then returned to the 70°C. oil bath and heated for an additional 5 minutes. The 0.1 ml. syringe was then again filled with 0.02 ml. of benzene- $\text{d}_6$  followed by 0.009 ml. (0.013g., 0.09 mmole) of chloral. The contents of the syringe were then again rapidly injected directly to the bottom of the NMR tube, to give a mixture containing two molecules of chloral for every original molecule of LTB in the

reaction mixture. The tube was then shaken and allowed to remain in the oil bath for an additional 5 minutes. The tube was cooled to 35°C. and a third NMR spectrum was taken (Figure 1D, p. 115); it was the same as the spectrum after the initial equimolar addition of chloral except that a new peak (that of chloral monomer) had appeared at  $\delta$  8.2. The integral of this peak was slightly greater than that of the acetalic peak at  $\delta$  5.4, indicating addition of a slight excess of chloral. The ratio of the integral of the peak at  $\delta$  5.4 to that of the peak at  $\delta$  1.3, however, did not increase.

The sample was then allowed to stand at room temperature for 2 days and another NMR spectrum was taken. This spectrum showed, in addition to all the peaks in the previous spectrum, three small peaks at  $\delta$  4.3, 4.5, and 5.8. The mixture was then taken from the tube with a dry syringe and injected into a dry, septum-stoppered test tube containing 3ml. (4.6g., 31 mmole) of chloral at 70°C. The tube was shaken to mix the reactants and then placed in an ice-water bath. Gelation occurred within 5 minutes. The tube was left in the ice bath for 24 hours and then kept at room temperature for 3 days. The solid plug of polymer was removed from the tube and extracted for 3 days in a Soxhlet extractor with acetone. It was then dried at 30 mm. pressure for 3 days. Yield of solid polymer: 2.36g. (52% based on original monomer weight). The sample was hard and tough.

The previous experiment was repeated with a 90 MHz Perkin-Elmer R-32 NMR spectrometer with the field locked on benzene in order to determine whether any shift occurred in the tertiary butyl peak position after addition of chloral. The quantity of LTB solution used was 0.60ml.

(0.18 mmole) and 0.30ml. of benzene- $d_6$  was added; after the initial spectral determination (300 Hz sweep width), an excess of chloral (0.029ml., 0.044g., 0.30 mmole) was added all at once with mixing as before.  $^1H$  NMR spectra were determined before and after chloral addition with 4 scans of each spectrum taken.

The tert-butyl peak fell at  $\delta$  1.27 before chloral addition and at  $\delta$  1.30 after chloral addition. The reproducibility of these values confirmed the 0.03 ppm. downward shift of the tert-butyl protons upon chloral addition.

The absorbance of the tert-butyl protons of tertiary butyl alcohol, whose position was determined as a check on the above data, fell between  $\delta$  1.16 and 1.22 in benzene, toluene, cyclohexane, and  $CCl_4$ . The hydroxyl peak position varied between  $\delta$  2.7 and 3.9 (10% concentration).

If the chloral monomer was not added in a rapid stream to the NMR tube with the syringe but was instead allowed to flow down the sides of the tube, a side reaction occurred which produced a peak at  $\delta$  6.2 immediately after chloral addition (in addition to the acetalic peak at  $\delta$  5.4). If the sides of the tube were not kept warm during chloral addition, some of the chloral was polymerized and reaction of the chloral with the LTB was not complete.

b. Determination by infrared spectroscopy. An 0.3M solution of LTB in cyclohexane (2ml., 0.6 mmole) was injected by syringe under nitrogen into a dry, nitrogen-purged, serum-stoppered flask. The serum stopper was punctured then with a needle connected to a vacuum line at 20mm. pressure and the cyclohexane was allowed to evaporate, aided



finally by gentle heating with a heat gun until only dry crystals were left in the flask. The flask was then filled with dry nitrogen and 1 ml. of  $\text{CCl}_4$  (dried 1 day over  $4\text{\AA}$  molecular sieves) was injected into the flask, dissolving the LTB. An infrared spectrum of the LTB solution (0.1mm. NaCl cell with  $\text{CCl}_4$  solvent reference) was taken. The spectrum (Figure 2A, p. 118) showed absorptions at  $2960\text{ cm}^{-1}$  (s),  $2865\text{ cm}^{-1}$  (m, C-H stretching),  $1473\text{ cm}^{-1}$  (m),  $1383\text{ cm}^{-1}$  (m),  $1357\text{ cm}^{-1}$  (s),  $1040\text{ cm}^{-1}$  (w),  $960\text{ cm}^{-1}$  (s),  $750\text{ cm}^{-1}$  (w,b),  $585\text{ cm}^{-1}$  (s,b), and  $510\text{ cm}^{-1}$  (m).

Subsequently, 0.0175 ml. (0.026g., 0.18 mmole) of chloral was dissolved in 0.25 ml. of  $\text{CCl}_4$  to make a solution of approximately 0.7M. An infrared spectrum of this solution was taken under the same conditions as above. The spectrum (Figure 2B, p. 118) showed absorptions at  $3520\text{ cm}^{-1}$  (w) (C-H stretching),  $2860\text{ cm}^{-1}$  (m),  $1770\text{ cm}^{-1}$  (vs, C=O stretching),  $1358\text{ cm}^{-1}$  (m),  $1030\text{ cm}^{-1}$  (m),  $988\text{ cm}^{-1}$  (s),  $855\text{ cm}^{-1}$  (s),  $730\text{ cm}^{-1}$  (s), and  $620\text{ cm}^{-1}$  (s).

To prepare the LTB-chloral addition compound, 0.25 ml. (0.15 mmole) of the LTB solution in  $\text{CCl}_4$  was injected into a dry serum-stoppered flask and 0.0175 ml. (0.026g., 0.18 mmole) of chloral was added with a syringe. The mixture was added by syringe to an infrared cell as above and a spectrum was determined. The spectrum showed absorptions at  $3460\text{ cm}^{-1}$  (w),  $2990\text{ cm}^{-1}$  (s),  $2940\text{ cm}^{-1}$  (m),  $2860\text{ cm}^{-1}$  (m),  $1770\text{ cm}^{-1}$  (s, excess chloral),  $1690\text{ cm}^{-1}$  (m),  $1615\text{ cm}^{-1}$  (m),  $1475\text{ cm}^{-1}$  (m),  $1395\text{ cm}^{-1}$  (m),  $1375\text{ cm}^{-1}$  (s),  $1330\text{ cm}^{-1}$  (m),  $1240\text{ cm}^{-1}$  (s),  $1205\text{ cm}^{-1}$  (s),  $1170\text{ cm}^{-1}$  (s),  $1105\text{ cm}^{-1}$  (w),  $1050\text{ cm}^{-1}$  (m),  $1030\text{ cm}^{-1}$  (m),  $1000$  and  $990\text{ cm}^{-1}$  (s),  $965\text{ cm}^{-1}$  (m),  $917$  and  $910\text{ cm}^{-1}$  (m),  $840\text{ cm}^{-1}$  (s),

$655\text{ cm}^{-1}$  (s),  $622\text{ cm}^{-1}$  (m), and  $505\text{ cm}^{-1}$  (m). See p. 316.

In order to prepare a solution of LTB-chloral addition compound with a slight deficiency of chloral to test for equilibrium, 4 ml. of 0.3M LTB in cyclohexane was injected into a dry serum-stoppered flask and the solvent was removed as before; 2 ml. of  $\text{CCl}_4$  was added and the flask was shaken, but the solid did not dissolve completely. An infrared spectrum of the solution proved to be identical to the spectrum of the LTB- $\text{CCl}_4$  solution determined earlier.

An 0.25 ml. quantity of this LTB solution of unknown concentration (but less than 0.6M) was injected into a dry serum-stoppered flask and 0.01 ml. (0.015g., 0.10 mmole) of chloral was added. The mixture was injected into an infrared cell; the infrared spectrum (Figure 2C, p. 118) showed absorptions at  $3460\text{ cm}^{-1}$  (w),  $2990\text{ cm}^{-1}$  (s),  $2940\text{ cm}^{-1}$  (m),  $2860\text{ cm}^{-1}$  (m),  $1730\text{ cm}^{-1}$  (vw),  $1695\text{ cm}^{-1}$  (w),  $1620\text{ cm}^{-1}$  (m),  $1475\text{ cm}^{-1}$  (m),  $1445\text{ cm}^{-1}$  (w),  $1398\text{ cm}^{-1}$  (m),  $1375\text{ cm}^{-1}$  (s),  $1330\text{ cm}^{-1}$  (m),  $1240\text{ cm}^{-1}$  (s),  $1205\text{ cm}^{-1}$  (s),  $1130\text{ cm}^{-1}$  (vw),  $1045\text{ cm}^{-1}$  (s),  $1000\text{ cm}^{-1}$  (s),  $970\text{ cm}^{-1}$  (s),  $910\text{ cm}^{-1}$  (s),  $835\text{ cm}^{-1}$  (s),  $660\text{ cm}^{-1}$  (s), and  $510\text{ cm}^{-1}$  (m,b). The absence of any chloral carbonyl stretching in this infrared spectrum suggests that the equilibrium (if any) of LTB addition to chloral is shifted far to the side of the addition product.

2. Reaction with triphenylphosphine: determination by  $^1\text{H}$  NMR spectroscopy. A 0.3M solution of triphenylphosphine ( $\text{Ph}_3\text{P}$ ) in cyclohexane, which had been stored under nitrogen in a Schlenk tube, was injected (1 ml., 0.3 mmole) into a 5 mm. NMR tube which had been dried under nitrogen with a heat gun. The solution was held at 30 mm. pressure for

15 minutes to evaporate the cyclohexane. Benzene- $d_6$  (0.3 ml.) was then added to the tube, which was heated in a 70°C. oil bath for about 3 minutes to dissolve the solid completely. A drop of cyclohexane was then added to the solution for a spectral lock. A  $^1H$  NMR spectrum of the solution (90 MHz) was then taken. This spectrum showed  $Ph_3P$  as a doublet with both peaks split several times. The upper peak was centered at  $\delta$  7.11 and the lower peak at  $\delta$  7.41. There were two small subsidiary peaks at  $\delta$  6.40 and 6.80. See p. 291.

The solution was then heated for 5 minutes in the oil bath and 0.029 ml. (0.044g., 0.30 mole) of chloral was added by syringe, propelled (as in the LTB experiments) by 0.02 ml. of benzene- $d_6$ . An oily white precipitate formed, which quickly became a red oil which settled to the bottom of the tube. The tube was allowed to remain in the oil bath for 5 minutes to complete the reaction. The benzene- $d_6$  was then evaporated at 30 mm. pressure during which time the red oil solidified. Chloroform- $d$  (0.30 ml.) was then added with a syringe to dissolve the solid; a drop of cyclohexane was added as a locking standard. A  $^1H$  NMR spectrum of the solution showed a large singlet at  $\delta$  7.93 fused to a doublet with peaks at  $\delta$  8.00 and 8.05. There was a small associated peak at  $\delta$  7.58, possibly associated with the olefinic hydrogen peak of the triphenyldichlorovinylphosphonium chloride product (179). This peak was too close to the others for the respective integrals to be determined unequivocally.

The sample then stood at room temperature for approximately six hours; it was then heated in the 70°C. oil bath for five minutes and 0.029 ml. (0.044g., 0.30 mmole) of chloral was injected, propelled by



0.02 ml. of  $\text{CDCl}_3$ . The tube was shaken and left in the oil bath for 10 minutes; a  $^1\text{H}$  NMR spectrum was then taken (Figure 3C, p. 123). The spectrum showed the peaks of the phosphonium salt plus a new chloral peak at  $\delta$  9.05. No peaks in the  $\delta$ 3-6 region typical of acetalic protons could be seen. (A  $^1\text{H}$  NMR spectrum of  $\text{Ph}_3\text{P}$  in  $\text{CDCl}_3$  for comparison is shown in Figure 3B, p. 123.)

In another similar experiment in which the 60 MHz NMR spectrometer was used, no peaks in addition to those above could be found up to 24 hours after mixing of the phosphonium salt with the chloral. A spectrum determined 48 hours after mixing showed small peaks at  $\delta$  0.9, 1.3, 4.2 (doublet), 6.2 (doublet), and 6.5. A spectrum determined 5 days after mixing showed broad peaks at  $\delta$  0.8 and 1.25, the doublet at  $\delta$  4.2 and small peaks at  $\delta$  6.2 and 6.5. Some of these peaks, particularly the broad peaks at  $\delta$  0.8 and 1.25 and the doublet at  $\delta$  4.2, had increased considerably in area upon standing for three days.

The solution from the NMR tube was injected into a flamed-out, serum-stoppered test tube containing 9.8 ml. (14.8g., 101 mmole) of chloral at  $70^\circ\text{C}$ . This tube was shaken and placed into an ice bath where polymerization to a gel occurred within 3 minutes. The tube was allowed to remain in the ice bath for 24 hours. The polychloral sample was then removed from the tube, extracted in a Soxhlet with acetone for 3 days, dried at 30 mm. pressure for 3 days, and weighed. Yield = 8.16 g. (55% based on original monomer). Similar yields were obtained when the mixture in the NMR tube was allowed to stand for several days before being added to the chloral.

3. Reaction with tetrabutylammonium chloride: determination by  $^1\text{H}$  NMR spectroscopy. An NMR tube was dried overnight at  $120^\circ\text{C}$ . An 0.3M solution of tetrabutylammonium chloride ( $\text{Bu}_4\text{NCl}$ ) in  $\text{CHCl}_3$  (0.5 ml., 0.15 mmoles) was injected into the tube and held at 30 mm. pressure for 15 minutes to evaporate the  $\text{CHCl}_3$ . Then was added with a syringe 0.15 ml. of  $\text{CDCl}_3$  to dissolve the  $\text{Bu}_4\text{NCl}$  crystals. A  $^1\text{H}$  NMR spectrum of the resulting solution (60 MHz) showed three broad peaks at  $\delta$  1.0, 1.6, and 3.4. The tube was then placed in a  $70^\circ\text{C}$ . oil bath for 5 minutes. Chloral (0.015 ml., 0.022g., 0.15 mmoles) was added to the tube, propelled by 0.03 ml. of  $\text{CDCl}_3$ . The tube was shaken to mix the reactants and kept in the oil bath for 5 minutes; an NMR spectrum was taken (Figure 3A, p. 123). The spectrum showed the  $\text{Bu}_4\text{NCl}$  absorbances plus a chloral peak at  $\delta$  9.1. There was no evidence for reaction; however, very small peaks, not eliminated when spinning was discontinued, did appear at  $\delta$  5.0 and 5.3. There was no change in the spectrum after 10 hours of standing at room temperature. After 36 hours, small peaks at  $\delta$  2.15, 5.6, and 8.1 could also be seen; there was no additional change after four days.

The sample was injected into a flamed-out, serum-stoppered test tube containing 3 ml. (4.5g., 31 mmole) of chloral at  $70^\circ\text{C}$ . The tube was then shaken to mix the components and placed in an ice bath. Gelation occurred within 5 minutes. The tube was allowed to remain at  $0^\circ\text{C}$ . for 24 hours and at room temperature for 3 days. The polymer plugs were then removed from the tube, extracted for 3 days in a Soxhlet extractor with acetone, and dried at 30 mm. pressure for 3 days. Yield: 2.76 g. (61%, based on original monomer weight). The sample was hard and tough.

4. Reaction with pyridine and 2,4,6-trimethylpyridine: determination by  $^1\text{H}$  NMR spectroscopy. An NMR tube was placed in an oil bath at  $70^\circ\text{C}$ . and the following reactants were added in the order stated: 0.012 ml. (0.012g., 0.15 mmole) of pyridine, 0.15 ml. of benzene- $\text{d}_6$ , and 0.015 ml. (0.022g., 0.15 mmole) of chloral. The tube was rolled thoroughly to mix the reactants. A  $^1\text{H}$  NMR spectrum was taken of the mixture (Figure 4A, p. 125); this showed the protons of pyridine as a multiplet near  $\delta$  7 and as a doublet near  $\delta$  8.5, together with the chloral singlet at  $\delta$  8.3. No peaks not characteristic of the components were found. The mixture was then returned to the oil bath for 5 minutes. Then another 0.015 ml. (0.15 mmole) of chloral was injected into the tube with mixing. A second  $^1\text{H}$  NMR spectrum showed no difference from the first except for the larger chloral peak. The sample was allowed to stand for two days at room temperature; a subsequent  $^1\text{H}$  NMR spectrum was identical to the previous one except for the appearance of a small peak at  $\delta$  1.6. No peak in the acetalic region of  $\delta$  3-6 indicative of addition of chloral to pyridine could be detected.

The sample was then removed from the NMR tube and injected into a flamed-out, serum-stoppered test tube containing 0.5 ml. (5.13 mmoles) of chloral at  $70^\circ\text{C}$ . When this tube was placed in an ice bath, gelation occurred within 5 minutes. The tube was kept in the ice bath for 24 hours and then at room temperature for 3 days. The polymer plug was removed from the tube with the aid of a heat gun and then worked up as for the sample initiated with  $\text{Ph}_3\text{P}$ . Yield: 0.22g. (30% based on original monomer).

A similar experiment with equivalent amounts of reactants was



performed using 2,4,6-trimethylpyridine (TMP) instead of pyridine. Spectral results were the same, showing no reaction (Figure 4B, p. 125); no new peaks appeared even after standing for 2 days at room temperature. Initiation of polymerization with the mixture was successful and gave polychloral in a yield of 20% after extraction and drying as above.

#### D. Preparation and Properties of Blends of Chloral Polymers with Other Polymers

1. Preparation of blends of polychloral with polystyrene. Twelve 15 x 125 mm. test tubes were flamed out, capped with serum stoppers, dried for 15 minutes at 120°C., and wired. Six pairs of glass plates, 10" x 10" x 1/8", were dried overnight at 120°C. and were then clamped together around the edges, with each pair separated by a 420 denier Lycra fiber, in order to make six molds for the casting of polychloral films (114). The molds were then returned to a 70°C. oven for 2 hours.

Six mixtures of chloral, styrene,  $\text{Ph}_3\text{P}$  (1M solution in benzene), and AIBN (0.3M solution in benzene) were prepared in the twelve test tubes as follows according to Table 5, p. 149. (Two tubes containing each mixture were prepared, one for the preparation of a film and the other for the preparation of a polymer plug.) Chloral, styrene, and AIBN solution were added to each test tube with syringes under nitrogen. The tubes were then placed into a 75°C. oil bath for approximately 10 minutes. The  $\text{Ph}_3\text{P}$  solution was then added with a syringe and each tube was shaken to mix the materials inside. If the mixture in a given tube was to be used to make a film, the film mold was removed from the 70°C. oven and the mixture from the tube was injected into the mold with a

syringe heated to 70°C. The tubes were then removed from the oil bath and the tubes and film molds were then placed into a large ice bath for 16-18 hours. Gelation generally occurred within a few minutes after the tubes were placed into the ice bath. The film molds and tubes were then removed from the ice bath and placed in an air oven at 70°C. for 60 hours (to generate radicals from the AIBN and polymerize the styrene). The molds were kept at room temperature for 24 hours.

The film molds were then taken apart to release the films; the tubes were broken in order to remove the plugs. Each film or plug was divided into three parts. The first part was vacuum dried at 0.025 mm. pressure and room temperature for 24 hours. The second part was extracted with methanol in a test tube for 4 days with daily changes of solvent (about 10 ml. portions). The third part was similarly extracted with acetone. After acetone extraction and drying, the third part was divided into two sections, one of which was extracted with dichloromethane by the same procedure. The solvents from the extraction were allowed to evaporate in tared aluminum pans.

After extraction, the films were allowed to air-dry for 4 hours and the pans from the dichloromethane extraction were allowed to air-dry for 24 hours before being weighed. The extracted plugs and the pans from the methanol and acetone extractions were dried under vacuum at 0.025 mm. pressure for 24 hours before being weighed.

The dichloromethane extracts from the samples, after weighing, were redissolved in  $\text{CH}_2\text{Cl}_2$  and reprecipitated with stirring from a large volume of  $\text{CH}_3\text{OH}$ . The reprecipitated samples were air-dried for 24 hours. The inherent viscosity of each reprecipitated sample was subsequently

determined in toluene at 0.5 g./dl at 30° C. if sufficient sample was available.

A control polystyrene sample plug was prepared in a test tube using 2.96 ml. (25.7 mmole) of styrene and 0.26 ml. (0.077 mole, 0.3 mole%) of AIBN solution in benzene. It was dissolved in 50 ml. of toluene and reprecipitated from 250 ml. of methanol. The reprecipitated material was then dissolved in 50 ml. of dichloromethane, reprecipitated again from 600 ml. of methanol with vigorous stirring, and dried at 30 mm. pressure at room temperature for 36 hours. This sample was subjected to the same measurements as the other samples.

Elemental analyses were performed on a number of the samples to determine blend composition, and thermogravimetric (TGA) analyses were performed on the methanol and acetone extracted plugs. The degradation of the polychloral was nearly complete (as illustrated by the differential thermogravimetric curve in Figure 5, p. 143) before the onset of weight loss in the polystyrene, such that the TGA curve could be calibrated against elemental analysis as a means of analysis of the composition of the blends.

Experimental parameters and results are listed in Table 5 and Table 6, p. 154, in the Results and Discussion section.

## 2. Preparation of blends of polychloral with poly(methyl methacrylate).

a. First experiment. Test tubes and film molds were prepared as in the previous styrene experiment, and mixtures (similar to those before except for the substitution of methyl methacrylate for styrene) were prepared in the test tubes and, in the appropriate cases,



transferred to the film molds as before. The tubes and film molds were then placed in an ice bath for 16 hours and a 70°C. oven for 45 hours.

A control poly(methyl methacrylate) sample plug (sample PMMA) was prepared in a test tube (dried and nitrogen-purged) using 2.7 ml. (26 mmoles) of methyl methacrylate and 0.51 ml. (0.26 mmoles, 1 mole %) of AIBN solution in benzene. This tube was placed in the oven together with the blend tubes and film molds and put through the same heating cycle, although it was not placed in the ice bath. The plug was then dissolved in acetone, reprecipitated from a large volume of methanol, and dried for 36 hours at 30 mm. pressure at room temperature.

The films and plugs were then removed from the molds and tubes respectively. The films were trimmed and divided into three pieces. One portion was vacuum-dried as in the polystyrene experiment. The second piece was vacuum-dried followed by extraction with methanol for 4 days; the third section was extracted with acetone for 4 days without previous vacuum drying. The plugs were divided into two sections, one of which was vacuum dried and the other of which was extracted with acetone as before. Subsequent workup was as in the polystyrene blend experiment.

Inherent viscosity measurements on the extracted polymers and infrared spectra of the films were obtained as before. Experimental parameters and results for this experiment are given in Table 7, p. 157, and Table 8, p. 159.

b. Second experiment. Test tubes and film molds were prepared as in the previous styrene experiment, and mixtures were prepared in the

test tubes and, in the appropriate cases, transferred to the film molds as before. A film of unmodified polychloral was not prepared in this experiment, but an unmodified polychloral plug was prepared. The tubes and film molds were then placed in an ice bath for 16 hours, a 50°C. oven for 48 hours, and a 70°C. oven for 24 hours. The films and plugs were then extracted and the plugs and extracts worked up exactly as in the previous experiment with styrene.

Two control poly(methyl methacrylate) sample plugs (samples C1P and C3P) were prepared in test tubes using 4.35 ml. (41 mmole) of methyl methacrylate for each, with 0.14 ml. (0.041 mmole, 0.1 mole%) of AIBN solution in benzene used for sample C1P and 0.41 ml. (0.12 mmole, 0.3 mole%) for sample C3P. The tubes containing these mixtures were placed through the same oven cycle as the tubes and film molds containing the blends, although they were not placed into the ice bath. The two poly(methyl methacrylate) plugs were then dissolved in 50 ml. each of acetone. Portions of the solutions were reprecipitated from large volumes of methanol with vigorous stirring, washed with methanol, and dried for 36 hours at 30 mm. pressure at room temperature.

Elemental analyses, TGA spectra, and inherent viscosity determinations were obtained in the same manner as for the previous experiment with styrene. Experimental parameters and results are found in Table 7, p. 157, and Table 8, p. 159, of the Results and Discussion section.

### 3. Preparation of blends of polychloral with poly(methyl acrylate).

a. First experiment. The preparative procedure for test tubes,

film molds, and monomer mixtures was the same as in previous experiments. However, two sets of plugs were prepared; the monomer mixtures remaining in the set of test tubes used to prepare the mixtures for the films (after removal by syringe of the portions actually placed into the film molds) formed one set of plugs, and the monomer mixtures prepared in tubes for the express purpose of synthesis of plugs formed the second set of plugs.

The film molds and both sets of tubes were placed in an ice bath for 16 hours. The film molds and the first set of tubes were then placed in a 65-70°C. oven for 48 hours. The plugs in the first set from the compositions containing large amounts of methyl acrylate were found to be quite small and shrunken upon removal from the oven, indicating that a considerable amount of the methyl acrylate might have evaporated before it could polymerize. The films and plugs were then allowed to remain at room temperature for 2 days and were removed from the molds.

The second set of tubes, after removal from the ice bath, was heated in an oil bath at 50°C. for two days and at 70°C. for two days. The plugs were then removed from the tubes.

The trimmed films and the first set of plugs were worked up in a manner identical to those in the first experiment in the poly(methyl methacrylate) series. The plugs from the second set were each divided into three pieces. The first was dried under vacuum for 24 hours at 0.025 mm. pressure. The second was extracted 4 days in a test tube with methanol with daily changes of methanol. The third was extracted 2 weeks in a test tube with acetone with daily changes of acetone, and the



acetone extracts were poured into tared beakers to evaporate. All plugs after extraction were dried for 24 hours at 0.05 mm. pressure, as were the vessels holding the acetone extracts before weighing. After weighing, the extracts were each redissolved in 25 ml. of acetone and reprecipitated from 300 ml. of methanol for purification.

Inherent viscosity measurements on the extracted polymers and infrared spectra of the films were obtained as before. Experimental parameters and results are listed in Table 9, p. 160, and Table 10, p. 164, in the Results and Discussion section.

b. Second experiment. The procedure in this experiment was identical to that in the previous styrene experiment (except for the substitution of methyl acrylate for styrene) in the preparation of the monomer mixtures in tubes and film molds. The tubes and film molds were then transferred to an ice bath for 16 hours, a 50°C. oven for 48 hours, and a 70°C. oven for 24 hours. The films and plugs were removed from the molds and each divided into three parts.

The first part was dried at 0.025 mm. pressure for 24 hours. The second part was extracted with methanol in a test tube for 4 days with daily changes of methanol, and the third part was extracted correspondingly with acetone. The material extracted from the films and plugs was allowed to evaporate in tared aluminum pans. All extracted films and plugs and pans of extracts were dried at room temperature and 0.025 mm. pressure for 24 hours.

After being weighed, the acetone extracts were each redissolved in about 10 ml. of acetone and reprecipitated from about 300 ml. of methanol. The reprecipitated polymers were filtered off, washed with a

stream of methanol, and dried for 24 hours at 15 mm. pressure.

A sample of pure poly(methyl acrylate) for comparison of properties was prepared in a capped tube containing 7.4 ml. (7.1 g., 82 mmole) of methyl acrylate and 0.28 ml. (0.082 mmole, 0.1 mole%) of an 0.3M solution of AIBN in benzene. This tube was placed in an oil bath at 50°C. for 18 hours, at the end of which period a marked increase in viscosity had occurred and autoacceleration had ensued. The tube was then removed from the oil bath and opened. The polymer was dissolved in 30 ml. of acetone, reprecipitated from 600 ml. of stirred methanol, and dried for 36 hours at room temperature and 25 mm. pressure.

Elemental analyses and inherent viscosity and TGA determinations were performed as for the experiment involving polychloral-polystyrene blends.

#### E. Determination of Nature of Stable and Unstable Endgroups in Polychloral

1. Infrared studies of high molecular weight polychloral films. A set of 8" x 8" x 1/4" glass plates were cleaned, rinsed, dipped in 2M HNO<sub>3</sub> for 5 minutes, thoroughly rinsed again with distilled water, and stored in the oven at 70°C. (or 85°C.) overnight before use. The plates were then clamped together in pairs separated by Lycra (or rubber) fibers of appropriate diameters to form molds for films of a 0.1-0.3 mm. thickness. The fibers, when possible, were placed directly under the gripping surfaces of the clamps in order to improve homogeneity of film thickness. The film molds were then returned to the oven.

Test tubes were cleaned and dried overnight as were the plates; the tubes were then cooled under dry nitrogen flow, capped with serum stoppers, and wired. Chloral (5-30 ml.; see also Table 12, p. 176) was then syringed into the test tubes, which were placed in a 70°C. oil bath for 10 minutes and allowed to come to oil bath temperature. Initiator solutions containing  $\text{Ph}_3\text{P}$  (0.3 M in benzene or cyclohexane), pyridine (3 M in cyclohexane) or LTB (0.3 M in cyclohexane) were then injected into the tubes. The tubes were then shaken to mix initiator and monomer and the contents of the tubes were injected into the film molds with syringes at 70°C. fitted with #19 needles. The film molds were then placed into an ice-water bath (0°C.) for 10-24 hours. The molds were then removed from the ice bath and opened. The polychloral films were removed and trimmed, air-dried for approximately 24 hours at room temperature, weighed, extracted for 2 or 3 days in a Soxhlet extractor with acetone, dried at room temperature and 20 mm. pressure for 2 hours, and weighed again. The infrared spectra of the films, regardless of initiator, were the standard spectra of polychloral films with peaks as listed in Table 13, p. 178. However, a small, sharp peak at  $1260\text{ cm}^{-1}$  appeared in many of the samples. No peaks in the hydroxyl region were noted for any of the films.

The films were then held for from 4 to 8 hours in a refluxing 0.85 M solution of  $\text{PCl}_5$  in  $\text{CCl}_4$ , washed three times with  $\text{CCl}_4$ , once with methanol, and once with acetone, dried for 2 hours at room temperature and 20 mm. pressure, and weighed. Infrared spectra of the treated films were always the same as the spectra determined before  $\text{PCl}_5$  treatment except for a disappearance or diminution of the sharp  $1260\text{ cm}^{-1}$  peak.



This spectral change was not always reproducible.

The thermal stability of the polymer films after  $\text{PCl}_5$  treatment was determined by DTG and compared with the stability of untreated films. Stability data for treated and untreated films are listed in Table 12, p. 176.

If film molds were prepared using a stretched natural rubber band as a spacer instead of a Lycra fiber, the stretched rubber band disintegrated upon contact with hot chloral. If large amounts of cyclohexane diluent (equal in volume to the chloral monomer used) were incorporated into the polymerization mixture in an attempt to reduce film thickness at constant spacer thickness, the resultant films were opaque white and had extremely low tear strength, fragmenting upon attempted removal from the molds.

2. Preparation and infrared studies of low molecular weight polychloral films and powders. Six pairs of 10" x 10" x 1/8" glass plates were washed, rinsed with distilled water, and dried overnight at 120°C. Each pair of plates was then clamped together, separated by a 420-denier Lycra fiber, in order to make a film mold. The prepared film molds were then placed in a 70°C. oven for 2 hours until needed.

Six 16 x 150 mm. test tubes were washed with distilled water, flamed out, cooled under dry nitrogen purge, fitted with serum stoppers, and wired. Chloral (8.0 ml., 12.1 g., 82 mmole) was injected into each tube followed by placement of the tube into a 70°C. oil bath. The tubes

were kept in the oil bath for 10 minutes and the appropriate quantity (Table 14, p. 181) of a 0.3 M LTB solution in cyclohexane was injected into the tube. A portion of the initiated monomer mixture in each tube was then injected into a film mold with a 70°C. syringe. The film molds and tubes containing the remaining monomer mixture were then placed into an ice-water bath for 4 hours. Gelation occurred within a few seconds after the plates and tubes were placed into the ice bath. The plates were opened and separated and the films were removed and trimmed.

Each film was cut into 5 portions (A through E) which were respectively treated according to the following procedures:

- (A) Vacuum drying at room temperature and 20 mm. pressure for 2 hours.
- (B) Extraction in a test tube with 3 changes (10 ml. each) of unacidified methanol for 4 days.
- (C) Extraction in a test tube with 10 ml. of a mixture of methanol and 10% (v/v) concentrated aqueous HCl for one day, followed by extraction with 2 changes (10 ml. each) of unacidified methanol for 3 days.
- (D) Treatment with refluxing acetyl chloride for 4 days, followed by washing with methanol, extraction for one day with 10 ml. of unacidified methanol, and subsequent washing with methanol again.
- (E) Treatment with a refluxing 1 M solution of  $\text{PCl}_5$  in  $\text{CCl}_4$  for 4 days, followed by washing with methanol, extraction for one day with 10 ml. of unacidified methanol, and subsequent washing with methanol again.

Each film section was dried for 2 hours at 20 mm. pressure and room temperature after the respective post-polymerization treatment. The weights and percent weight retention for each film section were determined before and after treatment. Infrared and DTG spectra of the films were determined when sufficient film remained after posttreatment for such measurements.

Film #6, made with 2.5 mole percent of LTB initiator, was too brittle to remove from the plates. However, the polymer remaining in tube #6, similarly made with 2.5 mole percent LTB initiator, was powdered by grinding with a spatula and was divided into four unweighed portions which were treated respectively according to procedures (B), (C), (D) and (E). The sample which was placed in methanol according to procedure (B) degraded within a few minutes, leaving no solid residue. Acidified methanol, as in procedure (C), did not degrade the polymer powder, and the powder treated with acidified methanol also did not degrade when subsequently placed in unacidified methanol. Treatment with acetyl chloride according to procedure (D) or with  $\text{PCl}_5$  according to procedure (E) produced polymer powders which did not degrade upon subsequent exposure to methanol. Infrared (KBr pellet) and DTG spectra were taken of all powders available in sufficient quantity.

Data from this experiment are tabulated and discussed in Table 14, p. 181.

3. Preparation and infrared studies of very low molecular weight polychloral powders. Five dried, serum-stoppered test tubes were prepared as in the previous experiment. The empty tubes were injected with the



appropriate quantity of an 0.3 M solution of LTB in cyclohexane (Table 15, p. 187) and placed in a 70°C. oil bath for 10 minutes. Chloral was injected into another test tube and also allowed to come to 70°C. The required quantity of warm chloral was then injected into the LTB solution with a warm syringe. The tubes were shaken to mix the chloral and LTB solution and then placed in an ice bath for 48 hours and allowed to stand at room temperature for 72 hours. The polymers were then removed from the tubes with a spatula. The first two were powders suspended in liquid, the next two were friable solids, and the last tube (lowest initiator concentration) contained a solid with some coherence. Each polymer sample was divided into five parts (A through E), which were respectively treated according to the five procedures A through E of the previous experiment.

The powdered samples, after being given the appropriate post-treatments, were used for determination of DTG and infrared spectra. These latter spectra were determined on  $\text{CCl}_4$  mulls of the powdered polymers (prepared as stated on p. 109). Data from this experiment are tabulated and discussed in Table 15, p. 187.

#### F. Attempted Stabilization of Chloral Homopolymer

1. Preparation of polychloral samples with "standard" initiators and characterization of thermal stability. A number of 15 x 125 mm. test tubes were heated at 150°C. for 2 hours, cooled at 20 mm. pressure and then at atmospheric pressure under dry nitrogen to about 100°C., and then capped with serum stoppers while still hot and under nitrogen. Chloral was placed into the test tubes with syringes, with 8 ml. (12.1 g., 82 mmole) being placed into most of the tubes, 4 ml. (6.04 g., 41 mmole)

being placed into the tubes to be initiated with LTB, LiCl,  $\text{Ph}_3\text{P}$  in  $\text{CH}_3\text{CN}$ , and DMSO alone, and 2 ml. (3.02 g., 20.5 mmole) being placed into the tubes to be initiated with  $\text{Ph}_3\text{P}$  in DMSO. The tubes were placed in an oil bath at  $75^\circ\text{C}$ . and allowed 5 to 10 minutes to come to temperature. Each initiator solution (Table 16, p. 198) was then injected into the tubes with a syringe and the tubes were shaken to disperse the initiators through the chloral. The tubes were then placed into an ice-water bath at  $0^\circ\text{C}$ . for 24 hours to cause polymerization (36 hours, followed by 48 hours at room temperature, for the samples initiated with  $\text{Bu}_4\text{NCl}$ ). The tubes were then opened and the polymer plugs were removed.

The plugs initiated with  $\text{Ph}_3\text{P}$  and  $\text{Bu}_4\text{NCl}$  were each divided into two pieces. In the case of the samples initiated with  $\text{Ph}_3\text{P}$ , one of the pieces was heated one hour in an air oven at  $100^\circ\text{C}$ . and then extracted one day with methanol in a Soxhlet extractor; the other piece was extracted without heating. In the case of the samples initiated with  $\text{Bu}_4\text{NCl}$ , one of the pieces was heated two hours in an air oven at  $100^\circ\text{C}$  and then extracted two days with methanol in a Soxhlet extractor; the other piece was similarly extracted without heating.

The plugs of polymer initiated with other initiators were each divided into three pieces. One piece was heated one hour at  $100^\circ\text{C}$ ., the second piece was treated for one day with 10 ml. of a 90/10 (v/v) mixture of methanol and concentrated aqueous HCl, and no pre-extraction treatment was given to the third piece. All three pieces were then extracted with methanol for 2 days in a Soxhlet extractor. All plugs were then dried at 20 mm. pressure and room temperature for 2 days. The weights of the plugs before and after heating, extraction, and drying were compared. DTG

spectra of appropriate samples initiated by each initiator were then determined. Data from this experiment are listed and discussed in Table 16, p. 198, and Table 17, p. 202.

2. Stabilization of polychloral by use of additives in the polymerization mixture. A number of 15 x 125 mm. test tubes were prepared as in the previous experiment. Chloral (8 ml., 12.1 g., 82 mmole) and the respective additives in the amounts given (Table 19, p. 212) were then injected into each test tube with dry syringes. The tubes were then placed in a 70°C. oil bath for 5 to 10 minutes, injected with initiator solution (LTB or  $\text{Ph}_3\text{P}$ ) and shaken to mix the solution components.

In the case of the tubes in which  $\text{CH}_3\text{I}$  was used as an additive, it was added after the initiator solution. The tubes were then placed into an ice bath for 36 hours to polymerize the chloral and then kept at room temperature for 48 hours, except in the case of the polymerizations in which  $\text{CH}_3\text{I}$  was used as an additive, in which the tubes were kept in the ice bath for 24 hours and then at room temperature for 17 days. The polymer plugs were then removed from the tubes.

The plugs of polymers prepared with bromoacetyl bromide, dimethyl sulfate, and  $\text{CH}_3\text{I}$  as stabilizing additives were extracted for 2 days with methanol in a Soxhlet extractor and then dried for one day at room temperature and 20 mm. pressure. The plugs of polymers prepared with trimethyl orthoformate and 2,2-dimethoxypropane as stabilizing agents were each divided into two parts. One part was extracted and dried as above, while the other was treated with a solution of 0.5 ml. of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  in 50 ml. of trimethyl orthoformate or 2,2-dimethoxypropane respectively at 80°C. for



three days, extracted and dried as above. The weights of plugs before and after extraction and drying were compared, except that the plugs prepared with dimethyl sulfate as a stabilizing additive were not weighed before extraction.

DTG spectra of appropriate samples prepared with each stabilizing additive were then determined. Data from this experiment are tabulated and discussed on pp. 212-220.

### 3. Syntheses of sulfonium and oxosulfonium salt initiators for chloral polymerization.

a. General procedure for synthesis of sulfonium and oxosulfonium salts by nucleophilic displacement. The alkyl halide, dialkyl sulfide and reaction solvent used were combined in a glass-stoppered flask and allowed to stand at room temperature until crystals no longer appeared to be forming at a detectable rate. The crystals were then filtered, washed with solvent and dried overnight over  $P_2O_5$  at room temperature and 0.1 mm. pressure; if the compounds were to be used as chloral initiators, they were recrystallized from appropriate solvents. Trimethyloxosulfonium iodide was prepared by the procedure of Kuhn and Trischmann (199).

Preparative data for these compounds are listed in Table 21, p. 222. Infrared spectral data and  $^1H$  NMR resonances are given in Table 1, p. 76.

b. General procedure for synthesis of sulfonium and oxosulfonium chlorides by metathesis. The molar ratio of sulfonium bromide (or iodide), silver nitrate, and HCl used in these experiments was 1:2:4.

Silver nitrate and concentrated aqueous HCl were each dissolved in 50-100 ml. of water in separate flasks and heated to 80°C. The solutions

TABLE 1

Infrared and  $^1\text{H}$  NMR Spectral Data for Sulfonium and Oxosulfonium Salts

1. Trimethylsulfonium chloride  $(\text{CH}_3)_3\text{SCl}$ .

IR (KBr): Identical to spectrum recorded in reference (195).  
See p. 309.

$^1\text{H}$  NMR ( $\text{CF}_3\text{COOH}/1\%$  TMS, 60 MHz):  $\delta$  3.0 (singlet), see p. 291.

2. Benzyldimethylsulfonium chloride,  $\text{C}_6\text{H}_5\text{CH}_2\text{S}(\text{CH}_3)_2\text{Cl}$

IR(KBr):  $3450\text{ cm}^{-1}$  (w,b, $\text{H}_2\text{O}$ ),  $2990\text{ cm}^{-1}$  (s, C-H stretching),  $2960\text{ cm}^{-1}$  (s),  $2920\text{ cm}^{-1}$  (s),  $1585\text{ cm}^{-1}$  (w),  $1500\text{ cm}^{-1}$  (s),  $1460\text{ cm}^{-1}$  (s),  $1435\text{ cm}^{-1}$  (s),  $1425\text{ cm}^{-1}$  (m),  $1335\text{ cm}^{-1}$  (s),  $1280\text{ cm}^{-1}$  (w),  $1210\text{ cm}^{-1}$  (m),  $1190\text{ cm}^{-1}$  (m),  $1160\text{ cm}^{-1}$  (w),  $1085\text{ cm}^{-1}$  (m),  $1060\text{ cm}^{-1}$  (s),  $1005\text{ cm}^{-1}$  (s),  $945\text{ cm}^{-1}$  (m),  $815\text{ cm}^{-1}$  (w),  $785\text{ cm}^{-1}$  (s),  $775\text{ cm}^{-1}$  (m),  $720\text{ cm}^{-1}$  (s),  $705\text{ cm}^{-1}$  (s),  $655\text{ cm}^{-1}$  (w),  $630\text{ cm}^{-1}$  (s). See p. 309.

$^1\text{H}$  NMR ( $\text{CF}_3\text{COOH}/1\%$  TMS, 60 MHz):  $\delta$  3.25 (singlet, 6H,  $-\text{S}(\text{CH}_3)_2$ ),  $\delta$  5.35 (singlet, 2H,  $\text{PhCH}_2\text{S}-$ ),  $\delta$  7.2-7.8 (multiplet, 5H, aromatic). See p. 292.

3. p-Nitrobenzyldimethylsulfonium chloride,  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{S}(\text{CH}_3)_2\text{Cl}$

IR (KBr):  $3450\text{ cm}^{-1}$  (w,b, $\text{H}_2\text{O}$ ),  $3020\text{ cm}^{-1}$  (m),  $3000\text{ cm}^{-1}$  (m),  $2950\text{ cm}^{-1}$  (s),  $2915\text{ cm}^{-1}$  (m),  $2860\text{ cm}^{-1}$  (w),  $2820\text{ cm}^{-1}$  (w),  $2460\text{ cm}^{-1}$  (w),  $1940\text{ cm}^{-1}$  (vw),  $1820\text{ cm}^{-1}$  (vw),  $1610\text{ cm}^{-1}$  (m),  $1605\text{ cm}^{-1}$  (m),  $1525\text{ cm}^{-1}$  (s),  $1495\text{ cm}^{-1}$  (m),  $1460\text{ cm}^{-1}$  (m),  $1420\text{ cm}^{-1}$  (m),  $1350\text{ cm}^{-1}$  (s),  $1320\text{ cm}^{-1}$  (w),  $1280\text{ cm}^{-1}$  (m),  $1190\text{ cm}^{-1}$  (m),  $1110\text{ cm}^{-1}$  (m),  $1055\text{ cm}^{-1}$  (m),  $1020\text{ cm}^{-1}$  (s),  $995\text{ cm}^{-1}$  (w),  $945\text{ cm}^{-1}$  (w),  $895\text{ cm}^{-1}$  (w),  $865\text{ cm}^{-1}$  (s),  $860\text{ cm}^{-1}$  (s),  $825\text{ cm}^{-1}$  (w),  $810\text{ cm}^{-1}$  (m),  $765\text{ cm}^{-1}$  (w),  $730\text{ cm}^{-1}$  (w),  $710\text{ cm}^{-1}$  (s),  $690\text{ cm}^{-1}$  (m),  $660\text{ cm}^{-1}$  (w),  $635\text{ cm}^{-1}$  (w). See p. 309.

TABLE 1 (continued)

<sup>1</sup>H NMR (CF<sub>3</sub>COOH/1% TMS, 60 MHz): δ 3.1 (singlet, 6H, -S(CH<sub>3</sub>)<sub>2</sub>), δ 4.9 (singlet, 2H, PhCH<sub>2</sub>S-), δ 7.8 (doublet, 2H, aromatic), δ 8.5 (doublet, 2H, aromatic). See p. 292.

4. Phenacyldimethylsulfonium bromide, C<sub>6</sub>H<sub>5</sub>COCH<sub>2</sub>S(CH<sub>3</sub>)<sub>2</sub>Br

IR (KBr): 3025 cm<sup>-1</sup> (m), 3010 cm<sup>-1</sup> (m), 2990 cm<sup>-1</sup> (m), 2960 cm<sup>-1</sup> (w), 2910 cm<sup>-1</sup> (m), 1670 cm<sup>-1</sup> (s, C=O stretching), 1600 cm<sup>-1</sup> (s), 1585 cm<sup>-1</sup> (m), 1455 cm<sup>-1</sup> (m), 1435 cm<sup>-1</sup> (m), 1425 cm<sup>-1</sup> (m), 1350 cm<sup>-1</sup> (s), 1325 cm<sup>-1</sup> (w), 1315 cm<sup>-1</sup> (w), 1310 cm<sup>-1</sup> (w), 1220 cm<sup>-1</sup> (s), 1175 cm<sup>-1</sup> (w), 1055 cm<sup>-1</sup> (m), 1035 cm<sup>-1</sup> (m), 1005 cm<sup>-1</sup> (m), 995 cm<sup>-1</sup> (m), 960 cm<sup>-1</sup> (w), 880 cm<sup>-1</sup> (w), 800 cm<sup>-1</sup> (w), 760 cm<sup>-1</sup> (s), 695 cm<sup>-1</sup> (s), 640 cm<sup>-1</sup> (m). See p. 310.

<sup>1</sup>H NMR (CF<sub>3</sub>COOH/1% TMS, 60 MHz): δ 3.15 (singlet, 6H, -S(CH<sub>3</sub>)<sub>2</sub>), δ 5.4 (singlet, 2H, -COCH<sub>2</sub>S=), δ 7.5-8.2 (multiplet, 5H, aromatic). See p. 293.

Literature (reference (196), DMSO-d<sub>6</sub>): δ 3.05 (singlet, 6H), δ 5.74 (singlet, 2H), δ 7.5-8.2 (multiplet, 5H).

5. Phenacyldimethylsulfonium chloride, C<sub>6</sub>H<sub>5</sub>COCH<sub>2</sub>S(CH<sub>3</sub>)<sub>2</sub>Cl

IR (KBr): 3340 cm<sup>-1</sup> (w), 3010 cm<sup>-1</sup> (s), 2990 cm<sup>-1</sup> (s), 2980 cm<sup>-1</sup> (s), 2950 cm<sup>-1</sup> (m), 2900 cm<sup>-1</sup> (s), 1990 cm<sup>-1</sup> (w), 1960 cm<sup>-1</sup> (w), 1845 cm<sup>-1</sup> (w), 1665 cm<sup>-1</sup> (vs, C=O stretching), 1600 cm<sup>-1</sup> (s), 1580 cm<sup>-1</sup> (s), 1500 cm<sup>-1</sup> (w), 1450 cm<sup>-1</sup> (s), 1435 cm<sup>-1</sup> (m), 1425 cm<sup>-1</sup> (m), 1345 cm<sup>-1</sup> (s), 1320 cm<sup>-1</sup> (m), 1315 cm<sup>-1</sup> (m), 1305 cm<sup>-1</sup> (m), 1220 cm<sup>-1</sup> (s), 1175 cm<sup>-1</sup> (m), 1160 cm<sup>-1</sup> (m), 1055 cm<sup>-1</sup> (s), 1035 cm<sup>-1</sup> (s), 995 cm<sup>-1</sup> (s), 942 cm<sup>-1</sup> (m), 875 cm<sup>-1</sup> (m), 800 cm<sup>-1</sup> (w), 745 cm<sup>-1</sup> (s), 690 cm<sup>-1</sup> (s), 680 cm<sup>-1</sup> (w), 635 cm<sup>-1</sup> (s). See p. 310.



TABLE 1 (continued)

<sup>1</sup>H NMR (CF<sub>3</sub>COOH/1% TMS, 60 MHz): Same as for bromide salt above.  
See p. 293.

6. Phenacyldi(n-butyl)sulfonium bromide, C<sub>6</sub>H<sub>5</sub>COCH<sub>2</sub>S(n-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Br

IR (KBr): 3440 cm<sup>-1</sup> (w,b,H<sub>2</sub>O), 3030 cm<sup>-1</sup> (w), 2960 cm<sup>-1</sup> (s), 2870 cm<sup>-1</sup> (m), 1670 cm<sup>-1</sup> (s, C=O stretching), 1600 cm<sup>-1</sup> (m), 1580 cm<sup>-1</sup> (w), 1450 cm<sup>-1</sup> (m), 1395 cm<sup>-1</sup> (w), 1335 cm<sup>-1</sup> (s), 1320 cm<sup>-1</sup> (m), 1220 cm<sup>-1</sup> (s), 1000 cm<sup>-1</sup> (s), 920 cm<sup>-1</sup> (w), 880 cm<sup>-1</sup> (w), 750 cm<sup>-1</sup> (s), 677 cm<sup>-1</sup> (s).

See p. 310.

<sup>1</sup>H NMR (CF<sub>3</sub>COOH/1% TMS, 60 MHz): δ 1.0 (triplet, 6H, methyl protons), δ 1.3-2.3 (multiplet, 8H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), δ 3.6 (triplet, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), δ 5.4 (singlet, 2H, -COCH<sub>2</sub>S=), δ 7.5-8.2 (multiplet, 5H, aromatic). See p. 294.

7. Carbethoxymethyldimethylsulfonium bromide, C<sub>2</sub>H<sub>5</sub>OCOCH<sub>2</sub>S(CH<sub>3</sub>)<sub>2</sub>Br

IR (KBr): 3440 cm<sup>-1</sup> (w,b,H<sub>2</sub>O), 3010 cm<sup>-1</sup> (s), 3000 cm<sup>-1</sup> (s,sh), 2945 cm<sup>-1</sup> (m), 2890 cm<sup>-1</sup> (m), 1730 cm<sup>-1</sup> (s,b,C=O stretching), 1475 cm<sup>-1</sup> (w), 1450 cm<sup>-1</sup> (w), 1440 cm<sup>-1</sup> (w), 1410 cm<sup>-1</sup> (w), 1400 cm<sup>-1</sup> (m), 1380 cm<sup>-1</sup> (m), 1310 cm<sup>-1</sup> (s), 1295 cm<sup>-1</sup> (w), 1200 cm<sup>-1</sup> (s), 1095 cm<sup>-1</sup> (m), 1055 cm<sup>-1</sup> (m), 1035 cm<sup>-1</sup> (m), 1010 cm<sup>-1</sup> (m), 945 cm<sup>-1</sup> (w), 895 cm<sup>-1</sup> (w), 865 cm<sup>-1</sup> (m), 760 cm<sup>-1</sup> (w). See p. 311.

<sup>1</sup>H NMR (CF<sub>3</sub>COOH/1% TMS, 60 MHz): δ 1.4 (triplet, 3H, CH<sub>3</sub>CH<sub>2</sub>O-), δ 3.2 (singlet, 6H, -S(CH<sub>3</sub>)<sub>2</sub>), δ 4.5 (multiplet, 4H, CH<sub>3</sub>CH<sub>2</sub>OCOCH<sub>2</sub>S=). See p. 295.

Literature (reference (197), solvent not stated): δ 1.40 (triplet, 3H), δ 3.50 (singlet, 6H), δ 4.26 (multiplet, 4H).

TABLE 1 (continued)

Literature (reference (198), solvent not stated):  $\delta$  1.3 (triplet, 3H,  $-\text{CO}_2\text{CH}_2\text{CH}_3$ ),  $\delta$  3.5 (singlet, 6H,  $-\text{S}(\text{CH}_3)_2$ ),  $\delta$  4.3 (quartet, 2H,  $-\text{CO}_2\text{CH}_2-$ ),  $\delta$  5.3 (singlet, 2H,  $-\text{CH}_2\text{S}=$ ).

8. Carbethoxymethyldimethylsulfonium chloride,  $\text{C}_2\text{H}_5\text{OCOCH}_2\text{S}(\text{CH}_3)_2\text{Cl}$

IR (KBr):  $3450\text{ cm}^{-1}$  (w,b, $\text{H}_2\text{O}$ ),  $3000\text{ cm}^{-1}$  (s),  $2930\text{ cm}^{-1}$  (s,b),  $2890\text{ cm}^{-1}$  (s),  $1730\text{ cm}^{-1}$  (vs, C=O stretching),  $1470\text{ cm}^{-1}$  (m),  $1455\text{ cm}^{-1}$  (m),  $1440\text{ cm}^{-1}$  (m),  $1420\text{ cm}^{-1}$  (m),  $1400\text{ cm}^{-1}$  (s),  $1375\text{ cm}^{-1}$  (m),  $1370\text{ cm}^{-1}$  (m),  $1335\text{ cm}^{-1}$  (m),  $1310\text{ cm}^{-1}$  (vs),  $1200\text{ cm}^{-1}$  (vs,b),  $1100\text{ cm}^{-1}$  (m),  $1055\text{ cm}^{-1}$  (s),  $1035\text{ cm}^{-1}$  (s),  $1010\text{ cm}^{-1}$  (s),  $945\text{ cm}^{-1}$  (m),  $905\text{ cm}^{-1}$  (m),  $865\text{ cm}^{-1}$  (s),  $805\text{ cm}^{-1}$  (w),  $765\text{ cm}^{-1}$  (w),  $690\text{ cm}^{-1}$  (w),  $670\text{ cm}^{-1}$  (w). See p. 311.

$^1\text{H}$  NMR ( $\text{CF}_3\text{COOH}/1\%$  TMS, 60 MHz): Same as for bromide salt above. See p. 295.

9. Tert-butyldimethylsulfonium iodide,  $(\text{CH}_3)_3\text{CS}(\text{CH}_3)_2\text{I}$

IR (KBr):  $3440\text{ cm}^{-1}$  (m,b, $\text{H}_2\text{O}$ ),  $2980\text{ cm}^{-1}$  (s),  $2910\text{ cm}^{-1}$  (m),  $1640\text{ cm}^{-1}$  (m,b),  $1470\text{ cm}^{-1}$  (m),  $1425\text{ cm}^{-1}$  (m),  $1380\text{ cm}^{-1}$  (s),  $1340\text{ cm}^{-1}$  (m),  $1170\text{ cm}^{-1}$  (s),  $1050\text{ cm}^{-1}$  (m),  $1000\text{ cm}^{-1}$  (m),  $790\text{ cm}^{-1}$  (m). See p. 311.

$^1\text{H}$  NMR ( $\text{CF}_3\text{COOH}/1\%$  TMS, 60 MHz):  $\delta$  1.7 (singlet, 9H,  $(\text{CH}_3)_3\text{C}-$ ),  $\delta$  2.9 (singlet, 6H,  $-\text{S}(\text{CH}_3)_2$ ). See p. 296.

10. Tert-butyldimethylsulfonium chloride,  $(\text{CH}_3)_3\text{CS}(\text{CH}_3)_2\text{Cl}$

IR (KBr):  $3450\text{ cm}^{-1}$  (m,b, $\text{H}_2\text{O}$ ),  $2990\text{ cm}^{-1}$  (s),  $2920\text{ cm}^{-1}$  (m),  $2650\text{ cm}^{-1}$  (w),  $1480\text{ cm}^{-1}$  (m),  $1435\text{ cm}^{-1}$  (m),  $1380\text{ cm}^{-1}$  (s),  $1340\text{ cm}^{-1}$  (m),  $1175\text{ cm}^{-1}$  (m),  $1060\text{ cm}^{-1}$  (m),  $1050\text{ cm}^{-1}$  (m),  $1020\text{ cm}^{-1}$  (s),  $980\text{ cm}^{-1}$  (w),  $950\text{ cm}^{-1}$  (w),  $800\text{ cm}^{-1}$  (w). See p. 312.

TABLE 1 (continued)

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<sup>1</sup>H NMR (CF<sub>3</sub>COOH/1% TMS, 60 MHz): Same as for iodide salt above.  
See p. 296.

11. Trimethyloxosulfonium iodide, (CH<sub>3</sub>)<sub>3</sub>SOI

IR (KBr): Identical to spectrum recorded in reference (199). See  
p. 312.

<sup>1</sup>H NMR (CF<sub>3</sub>COOH/1% TMS, 60 MHz): δ 3.9 (singlet). See p. 297.

12. Trimethyloxosulfonium chloride, (CH<sub>3</sub>)<sub>3</sub>SOCl

IR (KBr): 2980 cm<sup>-1</sup> (s), 2890 cm<sup>-1</sup> (s), 2450 cm<sup>-1</sup> (w), 2370 cm<sup>-1</sup>  
(w), 2280 cm<sup>-1</sup> (w), 2210 cm<sup>-1</sup> (w), 2070 cm<sup>-1</sup> (w), 1960  
cm<sup>-1</sup> (w), 1700 cm<sup>-1</sup> (w,b), 1525 cm<sup>-1</sup> (w), 1425 cm<sup>-1</sup> (m,b),  
1345 cm<sup>-1</sup> (m), 1315 cm<sup>-1</sup> (m), 1230 cm<sup>-1</sup> (vs), 1060 cm<sup>-1</sup>  
(s), 960 cm<sup>-1</sup> (m), 765 cm<sup>-1</sup> (m), 645 cm<sup>-1</sup> (vw). See  
p. 312.

<sup>1</sup>H NMR (CF<sub>3</sub>COOH/1% TMS, 60 MHz): Same as for iodide salt above.  
See p. 297.

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were then mixed with stirring. The AgCl precipitate was removed by filtering through a medium porosity glass filtering funnel and washed with water until the eluate was neutral.

The sulfonium bromide or iodide was dissolved in water, with a minimum amount of methanol added to increase solubility if necessary. The precipitated silver chloride was then added to the sulfonium salt solution with a ceramic spatula. The suspension was stirred overnight and filtered. The filtrate was evaporated in a rotary evaporator at 30-40°C./20 mm. and then placed in a vacuum desiccator at room temperature and 0.1 mm. pressure over  $P_2O_5$  until crystallization occurred. The crystals were washed and, in most cases, recrystallized from appropriate solvents.

Preparative data for these compounds are listed in Table 23, p. 227. Infrared spectral data and  $^1H$  NMR resonances are given in Table 1, p. 76.

#### 4. Syntheses of miscellaneous salt and ylide initiators for chloral polymerization.

a. Synthesis of diphenyliodonium chloride. This compound was prepared by the condensation of benzene with potassium iodate in acetic acid-acetic anhydride-sulfuric acid according to the procedure of Beringer and coworkers (200). Yield: 19.4 g. (25%) after two recrystallizations from methanol.

The compound decomposed without melting at 214-220°C. [lit. (200) 228-229°C. (rapid heating)]. The infrared spectrum (KBr) showed absorptions at  $3050\text{ cm}^{-1}$  (m),  $3030\text{ cm}^{-1}$  (m),  $3010\text{ cm}^{-1}$  (w),  $2995\text{ cm}^{-1}$  (m),  $1580\text{ cm}^{-1}$  (s),  $1567\text{ cm}^{-1}$  (s),  $1470\text{ cm}^{-1}$  (s),  $1438\text{ cm}^{-1}$  (s),  $1325\text{ cm}^{-1}$  (w),

1267  $\text{cm}^{-1}$  (w), 1177  $\text{cm}^{-1}$  (w), 1160  $\text{cm}^{-1}$  (w), 1090  $\text{cm}^{-1}$  (w), 1065  $\text{cm}^{-1}$  (w), 1012  $\text{cm}^{-1}$  (s), 995  $\text{cm}^{-1}$  (s), 990  $\text{cm}^{-1}$  (s), 980  $\text{cm}^{-1}$  (w), 920  $\text{cm}^{-1}$  (w), 910  $\text{cm}^{-1}$  (w), 860  $\text{cm}^{-1}$  (w), 835  $\text{cm}^{-1}$  (w), 740  $\text{cm}^{-1}$  (s,b), 670  $\text{cm}^{-1}$  (s), 645  $\text{cm}^{-1}$  (s), and 605  $\text{cm}^{-1}$  (w). See p. 313. The  $^1\text{H}$  NMR spectrum ( $\text{CF}_3\text{COOH}/1\%$  TMS, 60 MHz) showed a complex multiplet at 7.4-8.2  $\delta$ . See p. 298.

b. Synthesis of 3,3'-dinitrodiphenyliodonium chloride. This compound was prepared by the condensation of nitrobenzene with iodyl sulfate (prepared by oxidation of iodine in a mixture of fuming  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ) according to the procedure of Beringer and coworkers (201) and treatment of the resulting 3,3'-dinitrodiphenyliodonium hydrogen sulfate with 1 M aqueous NaCl. The resultant crystals were washed with water and ethanol. Yield: 8.5 g. (5.5%); m.p. 207-208°C. (dec.) [lit. (201) 203-205°C. (dec.), (202) 214°C.]. The infrared spectrum (KBr) showed absorptions at 3090  $\text{cm}^{-1}$  (w), 3040  $\text{cm}^{-1}$  (m), 3010  $\text{cm}^{-1}$  (m), 2870  $\text{cm}^{-1}$  (w), 1600  $\text{cm}^{-1}$  (m), 1530  $\text{cm}^{-1}$  (vs), 1460  $\text{cm}^{-1}$  (w), 1420  $\text{cm}^{-1}$  (w), 1350  $\text{cm}^{-1}$  (vs), 1300  $\text{cm}^{-1}$  (w), 1170  $\text{cm}^{-1}$  (w), 1120  $\text{cm}^{-1}$  (w), 1100  $\text{cm}^{-1}$  (w), 1055  $\text{cm}^{-1}$  (w), 995  $\text{cm}^{-1}$  (w), 955  $\text{cm}^{-1}$  (w), 925  $\text{cm}^{-1}$  (w), 865  $\text{cm}^{-1}$  (s), 825  $\text{cm}^{-1}$  (m), 740  $\text{cm}^{-1}$  (s), 730  $\text{cm}^{-1}$  (m), 713  $\text{cm}^{-1}$  (m), 707  $\text{cm}^{-1}$  (m), and 663  $\text{cm}^{-1}$  (m). The material was too insoluble in trifluoroacetic acid for a  $^1\text{H}$  NMR spectrum to be determined. See p. 313.

c. Synthesis of tropylium bromide. This compound was prepared by bromination of 1,3,5-cycloheptatriene in  $\text{CCl}_4$  followed by dehydrobromination at 60°C. and recrystallization from absolute ethanol according to the procedure of Doering and Knox (203). Crude yield: 69.5 g. (81%); yield after recrystallization: 40.2 g. (47%); m.p. 202-3°C. (dec.) [lit.

(203) 203°C. (dec.)]. The infrared spectrum (KBr) was similar to that previously published in the literature (204). See p. 313. The  $^1\text{H}$  NMR spectrum ( $\text{CF}_3\text{COOH}/1\%$  TMS, 60 MHz) showed a singlet at 9.45  $\delta$ . See p. 299.

d. Synthesis of tropylium chloride. This compound was prepared from tropylium bromide and HCl gas in absolute ethanol according to the procedure of Doering and Knox (204). Yield: 5.4 g. (73%); m.p. of material recrystallized from acetonitrile: 103-104°C. (dec.) [lit. (204) 101°C. (dec.)]. The infrared spectrum (KBr) showed absorptions at 3440  $\text{cm}^{-1}$  (broad, prob.  $\text{H}_2\text{O}$ ), 3040  $\text{cm}^{-1}$  (w), 2990  $\text{cm}^{-1}$  (s), 2860  $\text{cm}^{-1}$  (w), 1480  $\text{cm}^{-1}$  (s), 1330  $\text{cm}^{-1}$  (w), 1050  $\text{cm}^{-1}$  (w), 680  $\text{cm}^{-1}$  (s) and 650  $\text{cm}^{-1}$  (s). See p. 314. The  $^1\text{H}$  NMR spectrum ( $\text{CF}_3\text{COOH}/1\%$  TMS, 60 MHz) was similar to that of tropylium bromide. See p. 299.

e. Synthesis of ethyl (dimethylsulfuranylidene) acetate. This compound was prepared by dehydrohalogenation of carbethoxymethyldimethylsulfonium bromide with NaOH in saturated  $\text{K}_2\text{CO}_3$  solution and isolated as a light yellow oil according to the procedure of Payne (198). Yield: 11.4 g. (51%). The infrared spectrum (neat liquid between NaCl plates) was the same as that given in the literature (198) for a solution in  $\text{CHCl}_3$ , except that the carbonyl stretching frequency fell at 1620  $\text{cm}^{-1}$  in the neat liquid and 1602  $\text{cm}^{-1}$  in chloroform solution. The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3/1\%$  TMS, 60 MHz) was also identical to that given in reference (198). See pp. 300 and 314.

The liquid was taken into a syringe through a glass fiber filter, injected into a nitrogen-purged, stopcock-capped Schlenk tube and stored at -10°C.



f. Synthesis of dimethylsulfonium phenacylide. This compound was prepared by dehydrohalogenation of phenacyldimethylsulfonium bromide with aqueous NaOH by the procedure of Trost (205). Repeated recrystallizations from  $\text{CHCl}_3$  (or  $\text{CH}_2\text{Cl}_2$ )/ $\text{CCl}_4$ /hexane with treatment with decolorizing carbon gave a very small yield of light yellow crystals which could not be freed from adhering black oil. The substance had no sharp melting point; an infrared spectrum was not determined because of its oily character (hindering KBr use) and its poor solubility in  $\text{CCl}_4$ . The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ /1% TMS, 60 MHz) showed a small singlet ( $< 1\text{H}$ ) at  $\delta$  2.1 (impurity), a singlet at  $\delta$  4.1 (2H, =CH-), and two multiplets at  $\delta$  7.1-8.1 (5H, aromatic). See p. 300. The  $^1\text{H}$  NMR spectrum given in the literature (205) listed a singlet at  $\delta$  2.89 (6H, =S(CH<sub>3</sub>)<sub>2</sub>), a broad singlet at  $\delta$  4.30 (1H, =CH-), a multiplet at  $\delta$  7.36 (3H, aromatic) and a multiplet at  $\delta$  7.86 (2H, aromatic).

A subsequent experiment, in which all solutions of reactants and all solvents placed in contact with the reaction mixture were deoxygenated by sparging with dry nitrogen, similarly gave only a black amorphous mass in negligible yield.

## 5. Syntheses of amide acetal initiators for chloral polymerization.

a. Synthesis of 1,1-dimethoxytrimethylamine (dimethylformamide dimethyl acetal). This compound was prepared by O-methylation of dimethylformamide with dimethyl sulfate and reaction of the resultant salt with  $\text{NaOCH}_3$  in  $\text{CH}_3\text{OH}$  according to the procedure of Arnold and Kornilov (206). Yield: 143.5 g. (30%); b.p. 104-105°C. [lit. (206) 103°C.]. The infrared and  $^1\text{H}$  NMR spectra are shown in Table 3, p. 86.

b. General procedure for synthesis of higher 1,1-dialkoxytrimethylamines (dimethylformamide acetals). These compounds were prepared by alcohol exchange of the 1,1-dimethoxytrimethylamine with an excess of the alcohol containing the desired alkoxy group according to the procedures of Arnold and Kornilov (206). The reactions were conducted in the pot of a spinning band column with the methanol (or methanol-dimethylamine mixture) distilled out as it was formed. In some cases, 1,1-dimethoxytrimethylamine which contained 60% of trimethyl orthoformate was used as a reactant. The trimethyl orthoformate was distilled from the system after the methanol and did not take part in the reaction.

Preparative data for these compounds are listed in Table 2 below. Infrared spectral data and  $^1\text{H}$  NMR resonances are given in Table 3, p. 86 .

TABLE 2

Preparative Data for 1,1-dialkoxytrimethylamines,  
 $(\text{CH}_3)_2\text{NCH}(\text{OR})_2$

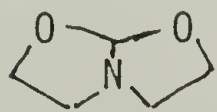
R	Yield, in %	B.p. (lit. (206))
$-\text{CH}(\text{CH}_3)_2$	30	$80^\circ \text{ C.}/50 \text{ mm.}$ ( $150.2\text{--}151.2^\circ \text{ C.}/760 \text{ mm.}$ )
$-\text{CH}_2\text{C}_6\text{H}_5$	33	$135^\circ \text{ C.}/0.02 \text{ mm.}$ ( $118\text{--}120^\circ \text{ C.}/0.2 \text{ mm.}$ )
$-\text{cyclo-C}_6\text{H}_{11}$	65	$100^\circ \text{ C.}/0.02 \text{ mm.}$ ( $76\text{--}77^\circ \text{ C.}/0.25 \text{ mm.}$ )
	74	$55^\circ \text{ C.}/2 \text{ mm.}$ ( $65\text{--}66^\circ \text{ C.}/5 \text{ mm.}$ )

TABLE 3

Infrared and  $^1\text{H}$  NMR Spectral Data for Amide Acetals (a)1. 1,1-Dimethoxytrimethylamine,  $(\text{CH}_3)_2\text{NCH}(\text{OCH}_3)_2$ 

IR: 2990  $\text{cm}^{-1}$  (m), 2950  $\text{cm}^{-1}$  (s), 2880  $\text{cm}^{-1}$  (m), 2835  $\text{cm}^{-1}$  (s), 2785  $\text{cm}^{-1}$  (s), 2650  $\text{cm}^{-1}$  (w), 1475  $\text{cm}^{-1}$  (s), 1380  $\text{cm}^{-1}$  (m), 1350  $\text{cm}^{-1}$  (m), 1300  $\text{cm}^{-1}$  (m), 1225  $\text{cm}^{-1}$  (s), 1195  $\text{cm}^{-1}$  (s), 1160  $\text{cm}^{-1}$  (m), 1120-1050  $\text{cm}^{-1}$  (s,b), 1000  $\text{cm}^{-1}$  (m), 990  $\text{cm}^{-1}$  (m), 925  $\text{cm}^{-1}$  (m), 925  $\text{cm}^{-1}$  (w), 910  $\text{cm}^{-1}$  (w), 875  $\text{cm}^{-1}$  (m). See p. 314.

$^1\text{H}$  NMR: Identical to spectrum recorded in reference (206). See p. 301.

2. 1,1-Diisopropoxytrimethylamine,  $(\text{CH}_3)_2\text{NCH}(\text{OCH}(\text{CH}_3)_2)_2$ 

IR: 2970  $\text{cm}^{-1}$  (s), 2940  $\text{cm}^{-1}$  (m), 2870  $\text{cm}^{-1}$  (m), 2840  $\text{cm}^{-1}$  (w), 2870  $\text{cm}^{-1}$  (w), 1480  $\text{cm}^{-1}$  (w), 1470  $\text{cm}^{-1}$  (m), 1460  $\text{cm}^{-1}$  (m), 1440  $\text{cm}^{-1}$  (w), 1380  $\text{cm}^{-1}$ , 1370  $\text{cm}^{-1}$  (m) (isopropyl "split"), 1325  $\text{cm}^{-1}$  (m), 1295  $\text{cm}^{-1}$  (m), 1220  $\text{cm}^{-1}$  (m), 1180  $\text{cm}^{-1}$  (m), 1135  $\text{cm}^{-1}$  (m), 1080  $\text{cm}^{-1}$  (s), 1050  $\text{cm}^{-1}$  (s), 1030  $\text{cm}^{-1}$  (s), 960  $\text{cm}^{-1}$  (w), 940  $\text{cm}^{-1}$  (w), 880  $\text{cm}^{-1}$  (w), 830  $\text{cm}^{-1}$  (w). See p. 315.

$^1\text{H}$  NMR:  $\delta$  1.1 (doublet, 12H,  $\{\text{OCH}(\text{CH}_3)_2\}_2$ ),  $\delta$  2.2 (singlet, 6H,  $(\text{CH}_3)_2\text{N}-$ ),  $\delta$  3.3 (septet, 2H,  $\{\text{OCH}(\text{CH}_3)_2\}_2$ ),  $\delta$  4.6 (singlet, 1H,  $-\text{CH}(\text{O}i\text{-Pr})_2$ ). See p. 301.

3. 1,1-Dibenzyloxytrimethylamine,  $(\text{CH}_3)_2\text{NCH}(\text{OCH}_2\text{C}_6\text{H}_5)_2$ 

IR: 3440  $\text{cm}^{-1}$  (w,b), 3090  $\text{cm}^{-1}$  (w), 3050  $\text{cm}^{-1}$  (m), 3030  $\text{cm}^{-1}$  (m), 2960  $\text{cm}^{-1}$  (s), 2870  $\text{cm}^{-1}$  (s), 2790  $\text{cm}^{-1}$  (m), 1950  $\text{cm}^{-1}$  (w), 1870  $\text{cm}^{-1}$  (w), 1810  $\text{cm}^{-1}$  (w,b), 1705  $\text{cm}^{-1}$  (w), 1685  $\text{cm}^{-1}$  (s, probably amide impurity), 1610  $\text{cm}^{-1}$  (w), 1590  $\text{cm}^{-1}$  (w), 1500  $\text{cm}^{-1}$  (s), 1480  $\text{cm}^{-1}$  (m), 1455  $\text{cm}^{-1}$  (s), 1440  $\text{cm}^{-1}$  (m), 1380  $\text{cm}^{-1}$  (m), 1365  $\text{cm}^{-1}$  (m), 1340  $\text{cm}^{-1}$  (m), 1300  $\text{cm}^{-1}$  (m), 1260  $\text{cm}^{-1}$  (w), 1215  $\text{cm}^{-1}$  (s), 1175  $\text{cm}^{-1}$  (w), 1050  $\text{cm}^{-1}$  (vs,b), 1030  $\text{cm}^{-1}$  (s), 910  $\text{cm}^{-1}$  (w), 875  $\text{cm}^{-1}$  (w), 830  $\text{cm}^{-1}$  (w), 740  $\text{cm}^{-1}$  (s), 700  $\text{cm}^{-1}$  (s). See p. 315.

$^1\text{H}$  NMR: Identical to spectrum recorded in reference (206) except for a small extraneous peak at  $\delta$  2.7-3.0. See p. 302.



TABLE 3 (continued)

4. 1,1-Dicyclohexyloxytrimethylamine,  $(\text{CH}_3)_2\text{NCH}(\text{OC}_6\text{H}_{11})_2$ 

IR: 2940  $\text{cm}^{-1}$  (s), 2860  $\text{cm}^{-1}$  (s), 2790  $\text{cm}^{-1}$  (w), 1480  $\text{cm}^{-1}$  (w),  
 1450  $\text{cm}^{-1}$  (m), 1365  $\text{cm}^{-1}$  (w), 1340  $\text{cm}^{-1}$  (w), 1320  $\text{cm}^{-1}$  (w),  
 1290  $\text{cm}^{-1}$  (m), 1215  $\text{cm}^{-1}$  (m), 1140  $\text{cm}^{-1}$  (m), 1105  $\text{cm}^{-1}$  (m),  
 1090  $\text{cm}^{-1}$  (s), 1050  $\text{cm}^{-1}$  (s), 1025  $\text{cm}^{-1}$  (s), 975  $\text{cm}^{-1}$  (m),  
 890  $\text{cm}^{-1}$  (m), 870  $\text{cm}^{-1}$  (m). See p. 315.

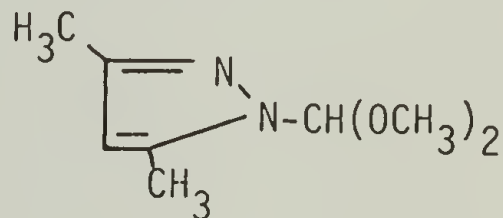
$^1\text{H}$  NMR:  $\delta$  1.0-2.0 (broad multipeaked hump, 20H, methylene hydrogens of cyclohexyl groups),  $\delta$  2.2 (singlet, 6H,  $(\text{CH}_3)_2\text{N}-$ ),  $\delta$  3.5 (broad hump, 2H,  $-\text{CH}(\text{OCH}_2\text{C}_5\text{H}_{10})_2$ ),  $\delta$  4.65 (singlet, 1H,  $-\text{CH}(\text{OC}_6\text{H}_{11})_2$ ). See p. 302.

5. 1-Aza-4,6-dioxabicyclo (0.33) octane,  $\text{CH}_2\text{CH}_2\text{OCHNCH}_2\text{CH}_2\text{O}$ 

IR: 2960  $\text{cm}^{-1}$  (s), 2890  $\text{cm}^{-1}$  (s), 1475  $\text{cm}^{-1}$  (m), 1380  $\text{cm}^{-1}$  (m),  
 1355  $\text{cm}^{-1}$  (m), 1320  $\text{cm}^{-1}$  (w), 1285  $\text{cm}^{-1}$  (w), 1260  $\text{cm}^{-1}$  (s),  
 1215  $\text{cm}^{-1}$  (s), 1155  $\text{cm}^{-1}$  (s), 1140  $\text{cm}^{-1}$  (s), 1070  $\text{cm}^{-1}$  (vs,b),  
 1040  $\text{cm}^{-1}$  (vs,b), 920  $\text{cm}^{-1}$  (s), 840  $\text{cm}^{-1}$  (m), 735  $\text{cm}^{-1}$  (m).  
 See p. 316.

$^1\text{H}$  NMR: Identical to spectrum recorded in reference (206). See p. 303.

## 6. 1-(Dimethoxymethyl)-3,5-dimethylpyrazole,



IR: 3000  $\text{cm}^{-1}$  (w), 2940  $\text{cm}^{-1}$  (m), 2840  $\text{cm}^{-1}$  (m), 1565  $\text{cm}^{-1}$  (m),  
 1450  $\text{cm}^{-1}$  (m), 1425  $\text{cm}^{-1}$  (w), 1395  $\text{cm}^{-1}$  (w), 1380  $\text{cm}^{-1}$  (w),  
 1345  $\text{cm}^{-1}$  (s), 1230  $\text{cm}^{-1}$  (m), 1195  $\text{cm}^{-1}$  (m), 1175  $\text{cm}^{-1}$  (m),  
 1110  $\text{cm}^{-1}$  (s), 1080  $\text{cm}^{-1}$  (s), 1000  $\text{cm}^{-1}$  (m), 990  $\text{cm}^{-1}$  (m),  
 845  $\text{cm}^{-1}$  (m), 810  $\text{cm}^{-1}$  (w), 785  $\text{cm}^{-1}$  (w), 760  $\text{cm}^{-1}$  (w). See p. 316.

$^1\text{H}$  NMR: Identical to spectrum recorded in reference (207). See p. 303.

(a): Infrared spectra determined as neat liquids between NaCl plates;  $^1\text{H}$  NMR spectra determined as 10-15% solutions in  $\text{CCl}_4$ /1% TMS.

c. Synthesis of 1-(dimethoxymethyl)-3,5-dimethylpyrazole. This compound was prepared from trimethyl orthoformate and 3,5-dimethylpyrazole containing p-toluenesulfonic acid as catalyst according to the procedure of Trofimenko (207). Yield: 53 g. (62%); b.p. 34-35°C./0.05 mm. [lit. (207,241) 54-60°C./1.1 mm.]. The infrared and <sup>1</sup>H NMR spectra are shown in Table 3, p. 86.

## 6. Chloral polymerizations with initiators which cause potential stabilization of the polymer.

a. Preparation of polychloral films and plugs with previously prepared potentially stabilizing initiators. This section describes the general procedure used for chloral polymerization with a number of potentially stabilizing initiators of different types and is a composite of the work in several actual experiments. Deviations from the general procedure in specific cases are mentioned either in the text of this section or in the data tables.

A number of pairs of 10" x 10" x 1/8" Pyrex glass plates were dried overnight at 120°C., fitted with clamps and spacers of 1/8" rubber tubing, and returned to a 70°C. oven for about 2 hours until needed for preparation of polychloral films. For chloral polymerization in cylindrical or plug form, a number of 15 x 125 mm. or 25 x 200 mm, test tubes were flamed out or heated overnight at 120°C., cooled under dry nitrogen, fitted with rubber serum stoppers and wired.

Initiator solutions of 0.1, 0.3, or 1 M concentration were prepared in DMSO, DMAc, CHCl<sub>3</sub>, or CH<sub>3</sub>CN by the procedure described on p. 49. In a number of the cases, the initiators could not be completely dissolved in the solvents used at the attempted concentrations. The initiators were

then used as saturated solutions as indicated in Table 24, p. 230.

Chloral (5 or 8 ml. for plug preparation; 30 or 50 ml. for film preparation) was then injected into the test tubes with a syringe. The tubes were placed into a 70°C. oil bath and allowed approximately 10 minutes to come to oil bath temperature. The appropriate amount of initiator solution to obtain the specified initiator concentration (Table 24, p. 230, or Table 25, p. 241) was then injected into each tube and the tubes were shaken to obtain homogeneous mixtures. In some cases (Table 24, p. 230), addition of the initiator solutions to the chloral caused precipitation of some of the initiator, with the precipitates remaining in suspension in the chloral. If this occurred, subsequent polymerization was carried out on the suspension of initiator crystals in chloral.

If films were to be prepared, part of each solution (or suspension) was withdrawn from the tube with a 70°C. syringe and placed in one of the polychloral film molds. Plates and tubes were then placed into an ice-water bath at 0°C. and kept there for from 16 to 24 hours. (Chloral polymerization proceeded rapidly with most initiators, with gelation occurring within from 5 to 10 minutes after cooling.) The film molds were then removed from the ice bath, allowed to air dry, and opened; the polychloral plugs were similarly removed from the test tubes with the test tubes being broken if necessary. The films and plugs of polychloral were each divided into two or more parts which were each weighed and given one of a variety of treatments listed in Table 24, p. 230, and Table 25, p. 241. These treatments included heating for one or two hours at 100° or 120°C. in an air oven, soaking for one day in a 9:1 (v:v) mixture of methanol and concentrated aqueous HCl, and extraction with methanol for



2 days in a Soxhlet extractor.

The treated films and plugs were then dried for one to three days at 20 mm. pressure and weighed again. Percentage weight retention after workup and drying was calculated for each sample and is given in Table 24, p. 230, or Table 25, p. 241. DTG spectra were determined for a number of the samples treated in various ways; important parameters from these spectra are listed in Table 26, p. 241.

In the case of use of 2-methyl-1,3-oxazoline (MOZ) as a chloral initiator, hard solids (almost completely unstable to methanol extraction in a Soxhlet extractor) were obtained when 0.1 to 25% of MOZ with respect to chloral was used, but mixtures containing half and equimolar amounts of MOZ with respect to chloral formed viscous liquids upon standing in the ice bath for 24 hours. The liquid in the tube containing equimolar amounts of MOZ and chloral formed a mass of hard solid particles when kept at 100°C. for one hour. This solid dissolved completely in a mixture of  $\text{CH}_2\text{Cl}_2$  and methanol; hexane was added to cause initial clouding and precipitation. Vacuum evaporation of the mixture gave two crops of crystals in a crude yield of 10.7 g. (89%), an off-white first crop of 7.4 g. (m.p. 116°C.) and a brown second crop of 3.3 g. The first crop of off-white crystals was recrystallized from chloroform-hexane (with use of decolorizing carbon) to give large white crystals, m.p. 118-119°C.

b. Preparation of reaction product of dimethyl sulfide and bromoacetyl bromide and its attempted use for chloral polymerization.

A Schlenk tube (p. 50 ) was dried overnight at 120°C. and purged with dry nitrogen. Dimethyl sulfide (2 ml., 1.7 g., 27 mmoles) was then introduced into the tube (under nitrogen flow) with a dried, nitrogen-purged

syringe. The Schlenk tube was then placed into a dry ice/2-propanol bath and allowed to cool for 10 minutes. Bromoacetyl bromide (1 ml., 2.3 g., 11.5 mmol) was then introduced into the tube (under nitrogen flow) with a dried, nitrogen-purged syringe. The tube was removed from the dry ice bath and allowed to come to room temperature. Fine white crystals soon started to separate from the mixture. The mixture was allowed to stand at room temperature for 10 hours, after which it had changed to a mass of crystals. The Schlenk tube was evacuated to 0.1 mm. pressure at room temperature to remove volatiles and then weighed. Yield of white crystalline compound: 2.44 g. (80%), with the compound assumed to be bromocarbonylmethyldimethylsulfonium bromide.

Tetramethylene sulfone (sulfolane) (9.2 ml.) was then introduced into the tube containing the salt. The salt slowly dissolved over a period of about 4 hours; then, however, a precipitate began to form. The light yellow supernatant liquid (whose  $^1\text{H}$  NMR spectrum is shown on p. 298) was used as an initiator for two tubes each containing 8 ml. (12.1 g., 82 mmol) of chloral; 0.5 ml. of the liquid was introduced into one tube and 1 ml. was introduced into the other tube (at 70°C.). The tubes were then placed in an ice bath at 0°C. and left for 24 hours. No polymerization was observed.

In order to determine the effect of the acid bromide group and also of the sulfolane solvent on the polymerization, a series of tubes were prepared with bromoacetyl bromide as chain transfer agent with LTB and  $\text{Ph}_3\text{P}$  as initiators and another series with  $\text{Ph}_3\text{P}$  as initiator and sulfolane as diluent. The tubes were charged with 8 ml. (12.1 g., 82 mmol) of chloral, heated to 70°C. in an oil bath, injected with initiator, shaken,

injected with additive, shaken, and placed in an ice bath at 0°C.; the tubes were removed from the ice bath after 24 hours. The polymer plugs were then removed from the tubes, extracted 2 days in a Soxhlet extractor with methanol, dried overnight at room temperature and 20 mm. pressure, and weighed. Results are tabulated in Table 19, p. 212.

Bromoacetyl bromide prevented the polymerization of chloral with LTB as initiator, and strongly reduced the yields obtainable in  $\text{Ph}_3\text{P}$ -initiated chloral polymerization. The use of sulfolane as a diluent did not decrease yields in  $\text{Ph}_3\text{P}$ -initiated polymerizations, with 70-80% yields obtained for all samples.

G. Kinetics of Chloral Copolymerization with Aliphatic and Aromatic Isocyanates by  $^1\text{H}$  NMR and Stability Determinations on Resultant Copolymers

A 15 x 125 mm. test tube was washed with soap solution, rinsed with distilled water, soaked for about 10 minutes in 1N  $\text{HNO}_3$ , rinsed again with distilled water, flamed out, allowed to cool under dry nitrogen flow, capped with a serum stopper, and wired. A 4 mm. NMR tube was cleaned according to the above procedure, dried overnight in an oven at 120°C., heated for 5 minutes with a heat gun, allowed to cool under dry nitrogen flow, and quickly capped. The test tube and NMR tube were then placed into an oil bath at 70°C.

Chloral (2 ml., 3.0 g., 21 mmole) was then placed into the test tube with a dried syringe and allowed to stand in the oil bath for about 10 minutes. The initiator solution (0.1 mole % of LTB or 0.2 mole % of  $\text{Ph}_3\text{P}$  as a solution in cyclohexane or benzene) was then added to the chloral with a dried syringe and the tube was shaken. Isocyanate (5 or 10 mole %,



as neat liquid) was then similarly added to the chloral; the tube was again shaken to mix the solution.

Approximately 0.3-0.5 ml. of the initiated monomer mixture was then withdrawn from the test tube with a dried syringe and injected into the NMR tube (its cap being removed only long enough to permit sample transfer) and the cap of the NMR tube was then wrapped with Parafilm. Both the test tube and the NMR tube were then removed from the oil bath and placed into an ice-water bath at 0°C. The NMR tube was then periodically removed from the ice bath and warmed rapidly to 35°C.; an NMR spectrum was then taken. In a separate experiment it was determined (145) that no significant and measurable polymerization or depolymerization of the sample occurred while the sample was at 35°C. After the measurement of each NMR spectrum, the NMR tube was returned to the ice bath in order that polymerization of the sample could continue.

The peak integrals of the chloral and isocyanate protons were determined and compared with the peak integral of the standard, benzene or cyclohexane. Periodic measurements of peak integral were made until the polymerization appeared essentially to have stopped; a final measurement was generally made after a period somewhat greater than one day.

The test tube and NMR tube were then removed from the ice bath; the polymer samples were removed from the two tubes, weighed, extracted with acetone in a Soxhlet extractor for 3 days, dried at room temperature and 20 mm. pressure for 3 days, allowed to stand in the open air for approximately one week, and weighed again. Elemental analyses and DTG spectra were obtained for some samples. Data and results for the chloral-isocyanate copolymerization rate determinations are shown in Table 28,

p. 258, Table 29, p. 260, and Figure 11, p. 249.

In a similar experiment, polymer films were prepared from mixtures of chloral and 10 mole percent of isopropyl or tertiary butyl isocyanate by the following procedure. Four 15 x 125 mm. test tubes were flamed out, cooled under dry nitrogen flow, capped with dried serum stoppers, wired, and placed in an oil bath at 70°C. Four pairs of 10" x 10" x 1/8" glass plates were dried overnight at 120°C.; a 420 denier Lycra fiber was inserted between them as a spacer and they were clamped together and returned to a 70°C. oven for 2 hours until needed. Chloral (6 ml., 9.1 g., 62 mmole) was injected into each test tube and the tubes were allowed to remain in the heating bath for 5 minutes. The initiator solution, followed by the isocyanate, was then similarly injected into each tube (a), (b), (c), and (d) as follows: (a) LTB (0.3 M in benzene), 0.205 ml. (0.062 mmole, 0.1 mole %), isopropyl isocyanate (0.63 ml., 0.53 g., 6.2 mmole, 10 mole %); (b)  $\text{Ph}_3\text{P}$  (0.3 M in benzene), 0.41 ml. (0.123 mmole, 0.2 mole %), isopropyl isocyanate as above; (c) LTB as above, tert-butyl isocyanate (0.70 ml., 0.61 g., 6.2 mmole, 10 mole %); (d)  $\text{Ph}_3\text{P}$  and tert-butyl isocyanate as above.

The tubes were shaken to mix the reactants and the initiated monomer mixture (in about a 5 ml. quantity) was removed from each tube with a 70°C. syringe and injected into the appropriate glass plate assembly. Immediately after transfer of monomer, the plates and corresponding tubes were placed into an ice bath at 0°C. and left there for 24 hours. The film molds were then separated; the films were trimmed around the edges and weighed. The polymer plugs were removed from the tubes and weighed. The films and plugs were extracted for 3 1/2 days with acetone in a

Soxhlet extractor, allowed to air-dry for 3 days, and then reweighed. Infrared spectra were taken of each film; no peaks in the carbonyl region could be seen in these films, which were approximately 0.02-0.03 mm. thick.

When a second experiment was performed in which a mixture of chloral with 5 mole % of isopropyl isocyanate initiated with 0.4 mole % of  $\text{Ph}_3\text{P}$  was polymerized in thicker film molds such that films 0.1 mm. thick resulted after extraction, a carbonyl peak did appear in the infrared spectra of the films. The isocyanate content of the films was calculated from this peak and is discussed on p. 256.

DTG spectra were also obtained for the films in this experiment. Results and data for this experiment are shown in Table 28, p. 258, Table 29, p. 260, and Figure 11, p. 249.

#### H. Miscellaneous Experiments Involving Formation of Optically Inactive Polychloral

1. Initiation of chloral with  $\text{Ph}_3\text{P}$ : effect of amount of initiator used on polymer yield. Nine 15 x 125 mm. test tubes were flamed out, cooled under dry nitrogen flow, and capped with dry serum stoppers. Chloral (8 ml., 12 g., 82 mmole) was injected into each tube with a dried syringe, and the tubes were placed in an oil bath at 75°C. for 5 to 10 minutes. An amount of a 1 M  $\text{Ph}_3\text{P}$  solution in benzene equivalent to from 0.0125 to 3.2 mole percent of  $\text{Ph}_3\text{P}$  with respect to chloral was then injected into each chloral tube with a syringe. The tubes were shaken and placed in an ice-water bath at 0°C. After 24 hours the tubes were taken out and the polymer plugs were isolated, weighed, heated at 100°C. in air for one hour,



weighed again, extracted with methanol in a Soxhlet extractor for one day, dried at 20 mm. pressure and room temperature for 3 days, and weighed again. Yield for each plug was calculated based on initial plug weight and on monomer weight.

Results and data for this experiment are shown in Figure 6, p. 136.

2. Preparation of samples of chloral homopolymer and chloral/5% p-chlorophenyl isocyanate copolymer for magic-angle  $^{13}\text{C}$  NMR spectroscopy.

A 100 ml. flask and three 16 x 150 mm. test tubes were flamed out, cooled under  $\text{N}_2$  flow, and fitted with dried, wired serum stoppers. A board with three holes drilled to accomodate three test tubes was clamped to a ring stand at a height such that an ice bath could be slowly raised around the tubes with a jack.

Chloral (60 ml., 90.7 g., 0.615 mole) was then injected into the flask (monomer reservoir); flask and tubes were placed into an oil bath at  $70^\circ\text{C}$ . for 10 minutes. A 1 M solution of  $\text{Ph}_3\text{P}$  in benzene (1.23 ml., 1.23 mmoles, 0.2 mole %) was then added to the chloral and the flask was shaken to disperse the initiator. The initiated chloral was then injected into the three tubes (20 ml. each) with a  $70^\circ\text{C}$ . syringe.

The tubes were then placed into the above tube holder; the ice bath water surface was then raised onto the tubes at a rate of 5 mm./min. until, after 20 minutes, the ice bath surface was 100 mm. above the bottom of the tubes. (The entire contents of each tube had gelled after 6 minutes, but the polymer at any point did not shrink from the glass until the water level had reached that point.) The tubes were then removed from

the holder and placed completely in another ice bath for 24 hours.

The tubes were then removed from the ice bath, and the polymer samples, which had shrunk from the glass walls of the tubes, were removed. They were sawed with a hacksaw down to the point at which they no longer contained a central cavity; in two of the cases, this left a plug at least 5 cm. long. These two plugs, the actual samples desired, were weighed, refluxed for 7 days in 150 ml. of an 0.64 M solution of  $\text{PCl}_5$  in  $\text{CCl}_4$ , and then extracted for 8 days with acetone in a Soxhlet extractor. The samples were then allowed to air-dry for 6 weeks in the dark and then dried at room temperature and 0.025 mm. pressure for 30 hours. The samples were then weighed again (72% weight retention, calculated on the basis of polymer weight before  $\text{PCl}_5$  treatment) and DTG spectra were obtained. The samples were then sent to Dr. Jacob Schaefer of Monsanto Company in St. Louis for magic-angle  $^{13}\text{C}$  NMR determinations.

A second similar experiment was conducted in which the polymerization mixture consisted of chloral (50 ml., 75.6 g., 0.513 mole), p-chlorophenyl isocyanate (3.22 ml., 3.94 g., 25.7 mmole, 5 mole %) and  $\text{Ph}_3\text{P}$  (1.03 ml., 1.03 mmole, 0.2 mole %) added as a 1 M solution in benzene. The samples were prepared as before; in each tube, the polymerization mixture first turned cloudy and then became transparent again after the entire tube had been in the ice bath for about 20 minutes. A large amount of cracking was seen between the polymer and the tube.

After 1 day in the ice bath, the tubes were broken in order to remove the polymer samples. The samples contained no visible internal cavities and were transparent. They were weighed, sawed down to a length of 10 cm., extracted for 8 days with acetone in a Soxhlet extractor,

allowed to air-dry in the dark for 7 weeks, and then dried at room temperature and 0.025 mm. pressure for 30 hours. The samples were weighed again (63% weight retention, calculated on the basis of polymer weight before extraction) and DTG spectra were obtained. These samples were also then sent to Dr. Schaefer of Monsanto.

3. Preparation of insoluble, apparently polymeric gels from chloral and  $P_2O_5$ . Approximately 4 liters of chloral was allowed to reflux under nitrogen purge for 2 days over 200 g. of  $P_2O_5$  in a 5-liter flask. The chloral was then allowed to stand over the  $P_2O_5$  for 4 days at room temperature. At the end of this period a voluminous gel, covered by a thin layer of chloral, was found in the flask. The monomer was heated to reflux again in an attempt to destroy the gel; overnight reflux, however, apparently increased the volume of the gel still further.

Hence the liquid monomer at the top was poured into another 5-liter flask over approximately 100 g. of  $P_2O_5$ , together with 2 liters of unpurified chloral. The chloral was then refluxed over the  $P_2O_5$  for two days; it was then poured from the  $P_2O_5$  into a 5-liter flask (the pot of a chloral still) and refluxed for one day. The power to the pot was then turned off and left off overnight; it was found the following morning that a gel filled the pot. The gel could not be broken up by heating.

Both gels were extracted individually with acetone in Soxhlet extractors for 5 days and then dried at room temperature and 20 mm. pressure for 2 days. The first gel (after extraction and drying) weighed 3.86 g.; the second gel weighed 32.3 g. and contained 4.3% phosphorus by elemental analysis. A DTG spectrum of the first gel showed an onset



of decomposition near 180°C. and a decomposition rate peak near 300°C.; a corresponding spectrum of the second gel showed peaks at 74°C. (15% of total area) and 285°C. (85%), with the onset of decomposition of the second peak occurring at 180°C.

### I. Attempts at Preparation and Characterization of Optically Active Polychloral

#### 1. Attempts to determine satisfactory system for measurement of optical activity in polychloral.

a. Preparation of reference polychloral and chloral copolymers for optical activity measurements. A number of chloral homopolymers, copolymers and blends were prepared in 16 x 150 mm. test tubes by the standard procedure for preparing polychloral samples (p. 72 ). Polymers were prepared from the following polymerization mixtures:

Chloral initiated with 0.05, 0.1, and 0.2 mole %  $\text{Ph}_3\text{P}$

Chloral with 1,2,3,4, and 5 mole % of p-chlorophenyl isocyanate as comonomer, initiated with 0.2 mole %  $\text{Ph}_3\text{P}$

Chloral initiated with 1.8 mole % 1-(dimethoxymethyl)-3,5-dimethylpyrazole

Chloral with 20 mole % of styrene, with  $\text{Ph}_3\text{P}$  (0.2 mole %) as the initiator for the chloral and AIBN (0.3 mole % with respect to styrene) as the initiator for the styrene.

The  $\text{Ph}_3\text{P}$  and AIBN were used respectively as 1 M and 0.3 M solutions in toluene; all other components were added neat.

The tubes were kept in an ice bath for three days; the tubes containing styrene were then placed in an oven at 70°C. for 60 hours. The polymer plugs were then removed from the tubes. The chloral copolymer samples and the polychloral-polystyrene blends were extracted three days

with acetone in a Soxhlet extractor and dried at room temperature and 20 mm. pressure for 2 days. They were then ground to granules 0.5-1 mm. in diameter with a Thomas ED-5 Wiley mill and then ground to pass a 40-mesh screen with a smaller Wiley mill. The resultant powders were each extracted with methanol at room temperature for 4 days with two changes of methanol and dried as above.

The chloral homopolymer samples were removed from the tubes and ground (without extraction) in the small Wiley mill to pass a 40-mesh screen. The chloral homopolymer samples initiated with  $\text{Ph}_3\text{P}$  were then treated for 3 days with a boiling 0.5 M solution of  $\text{PCl}_5$  in  $\text{CCl}_4$ . All chloral homopolymers were then extracted with methanol at room temperature for 4 days with three changes of methanol and dried as above.

Most of the product polymers appeared transparent or semitransparent in bulk. When each of the above polymers was agitated with diphenyl ether (nearly equivalent in refractive index to polychloral), the resultant suspensions were translucent and iridescent. Addition of 1-bromonaphthalene (to raise the refractive index) or of 1,2-dichlorobenzene (to lower the refractive index) did not make the mixtures visually transparent.

Turbidimetric titrations of the copolymers prepared from mixtures of chloral with 3% and 5% of p-chlorophenyl isocyanate were performed with a Fisher Electrophotometer II turbidimeter. The cell was filled with 10 ml. of diphenyl ether and an unmeasured quantity of the polymer powder was added with stirring; the system was allowed to equilibrate with stirring for 15 minutes to reach a constant transmittance value (at 650 nm.). 1-Bromonaphthalene (or 1,2-dichlorobenzene) was added with a syringe in

portions; the transmittance value was allowed to equilibrate after each addition and then recorded. Titration data are as follows:

1) Polymer from chloral/3% p-chlorophenyl isocyanate mixture;

titrant = 1-bromonaphthalene

Titrant added, ml.	0	0.9	1.9	2.9	3.9	4.9
Transmittance, %	85	90	90	93	93	93

2) Polymer from chloral/3% p-chlorophenyl isocyanate mixture;

titrant = 1,2-dichlorobenzene

Titrant added, ml.	0-5
Transmittance, %	87 uniformly

3) Polymer from chloral/5% p-chlorophenyl isocyanate mixture;

titrant = 1,2-dichlorobenzene

Titrant added, ml.	0	0.2	0.4	0.6	0.8	1.0	1.4	2.0	3.0	4.0
Transmittance, %	68	69	71	72	73	74	75	77	78	78

In each of the above cases, although a progressive increase (or decrease) in the refractive index of the solvent mixture occurred during the titration, the light transmittance reached a plateau and never became 100%.

b. Attempted suspension copolymerization of chloral and p-chlorophenyl isocyanate in perfluoro-2-(n-butyl)-tetrahydrofuran. A 150-ml. resin kettle with an all-glass stirrer was dried overnight at 150°C., assembled, fitted with a rubber serum stopper, wired, and flushed with dry nitrogen. Into the kettle were injected 10 ml. (15.1 g., 103 mmole) of chloral and 0.65 ml. (0.79 g., 5.15 mmole, 5 mole %) of p-chlorophenyl isocyanate; the monomers were immiscible with the fluorinated solvent. The kettle was then placed into a 75°C. oil bath for 25 minutes. An



0.49 M solution of LTB in cyclohexane (0.10 ml., 0.049 mmole, 0.048 mole %) was then injected into the kettle. The stirrer was started (1725 rpm speed), forming a turbid suspension of monomer mixture in fluorocarbon, and the kettle was placed into a dry ice/isopropyl alcohol bath.

The chloral/isocyanate mixture began to polymerize rapidly on cooling. However, the polymerizing droplets of monomer mixture coalesced during the polymerization with stirring, causing the formation of films on the stirrer and the inner surface of the kettle. Even the droplets not encountering the stirrer or the inner surface of the kettle also coalesced, causing the formation of a suspended material resembling a mat of pressed pellets. No fine chloral copolymer powder was formed by this method.

After about 30 minutes at low temperature, the kettle was opened; the polymer was removed, extracted for 2 days with methanol in a Soxhlet extractor, and dried for 2 days at room temperature and 20 mm. pressure. Yield: 0.72 g. (5%).

## 2. Syntheses of optically active initiators for chloral polymerization.

a. Synthesis of benzyltriphenylphosphonium bromide. This salt was prepared from triphenylphosphine and benzyl bromide in chloroform by the procedure of Kroehnke (208); addition of diethyl ether to the reaction mixture caused precipitation of the salt in quantitative yield. Recrystallization from absolute ethanol yielded crystals which sintered at 290-292°C. (lit. m.p. 280-285°C.). The infrared spectrum (KBr) showed absorptions at  $3440\text{ cm}^{-1}$  (w,  $\text{H}_2\text{O}$ ),  $3050\text{ cm}^{-1}$  (m),  $3000\text{ cm}^{-1}$  (w),  $2980\text{ cm}^{-1}$  (w),  $2845\text{ cm}^{-1}$  (m),  $2770\text{ cm}^{-1}$  (m),  $1600\text{ cm}^{-1}$  (w),  $1585\text{ cm}^{-1}$  (m),  $1492\text{ cm}^{-1}$  (m),

1482  $\text{cm}^{-1}$  (m), 1435  $\text{cm}^{-1}$  (s), 1335  $\text{cm}^{-1}$  (w), 1182  $\text{cm}^{-1}$  (w), 1162  $\text{cm}^{-1}$  (w), 1110  $\text{cm}^{-1}$  (s), 1080  $\text{cm}^{-1}$  (w), 1030  $\text{cm}^{-1}$  (w), 990  $\text{cm}^{-1}$  (m), 920  $\text{cm}^{-1}$  (w), 872  $\text{cm}^{-1}$  (m), 822  $\text{cm}^{-1}$  (w), 785  $\text{cm}^{-1}$  (s), 752  $\text{cm}^{-1}$  (s), 744  $\text{cm}^{-1}$  (s), 715  $\text{cm}^{-1}$  (s), 692  $\text{cm}^{-1}$  (s,sh), 685  $\text{cm}^{-1}$  (s), 575  $\text{cm}^{-1}$  (m), 505  $\text{cm}^{-1}$  (s), 490  $\text{cm}^{-1}$  (s). See p. 317. The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ /1% TMS, 60 MHz) showed resonances at  $\delta$  5.2, 5.4 (doublet, 2H,  $-\text{CH}_2-$ ),  $\delta$  7.05 (singlet, 5H,  $\text{C}_6\text{H}_5\text{CH}_2-$ ), and  $\delta$  7.6, 7.75 (doublet, 15H,  $(\text{C}_6\text{H}_5)_3\text{P}-$ ). See p. 304.

b. Synthesis of (+)-ketopinic acid. This compound was prepared by alkaline aqueous permanganate oxidation of crude (+)-camphorsulfonyl chloride by the procedure of Bartlett and Knox (209). Recrystallization from water with treatment with decolorizing carbon produced white crystals in 12% yield, m.p. 238-241°C. (lit. m.p. 232-234°C. (submitters), 240-242°C. (checkers) (209)).  $[\alpha]_{\text{D}}^{23} = +32.9^\circ$  ( $c=4.11$ , acetone);  $+26.5^\circ$  ( $c=4.945$ , methanol)  $[\text{M}]_{\text{D}}^{23} = +59.9^\circ$  ( $c=4.11$ , acetone);  $+48.2^\circ$  ( $c=4.945$ , methanol) Literature:  $[\alpha]_{\text{D}}^{24} = +31.2^\circ$  ( $c=4$ , acetone) (210).

The infrared spectrum (KBr) showed absorptions at 2960  $\text{cm}^{-1}$  (s, vb), 2600  $\text{cm}^{-1}$  (m), 1700  $\text{cm}^{-1}$  (s), 1690  $\text{cm}^{-1}$  (s), 1685  $\text{cm}^{-1}$  (s), 1555  $\text{cm}^{-1}$  (w), 1415  $\text{cm}^{-1}$  (m), 1390  $\text{cm}^{-1}$  (w), 1373  $\text{cm}^{-1}$  (w), 1330  $\text{cm}^{-1}$  (s), 1280  $\text{cm}^{-1}$  (m), 1240  $\text{cm}^{-1}$  (m), 1220  $\text{cm}^{-1}$  (w), 1195  $\text{cm}^{-1}$  (w), 1170  $\text{cm}^{-1}$  (w), 1130  $\text{cm}^{-1}$  (w), 1100  $\text{cm}^{-1}$  (w), 1065  $\text{cm}^{-1}$  (w), 1040  $\text{cm}^{-1}$  (w), 1015  $\text{cm}^{-1}$  (m), 940  $\text{cm}^{-1}$  (m,b), 850  $\text{cm}^{-1}$  (w), 750  $\text{cm}^{-1}$  (s), 625  $\text{cm}^{-1}$  (w), 580  $\text{cm}^{-1}$  (w), 530  $\text{cm}^{-1}$  (w), 415  $\text{cm}^{-1}$  (m). See p. 317. The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ /1% TMS, 60 MHz) showed resonances at  $\delta$  1.15 (singlet, 6H,  $-\text{C}(\text{CH}_3)_2-$ ), and  $\delta$  1.4-2.8 (complex multiplet, 8H, other protons). See p. 304.

c. Synthesis of tetramethylammonium (+)-ketopinate. (+)-

Ketopinic acid (3.68 g., 0.02 mole) was placed into a 25-ml. Erlenmeyer flask with a magnetic stirring bar and titrated to a phenolphthalein endpoint with a 20% solution of tetramethylammonium hydroxide in methanol (5.58 ml.). The resultant viscous solution was evaporated with a rotary evaporator at 20 mm. and then at 0.5 mm. pressure. The crystalline residue was dissolved in 10 ml. of methanol; the solution was heated and 60 ml. of dioxane was added. Further heating evaporated most of the methanol and caused separation of small white crystals of the desired salt. Yield: 3.02 g. (58%); the compound decomposed above 220°C. without melting, giving off an amine odor.  $[\alpha]_D^{23} = +20.1^\circ$  (c=5.1, methanol);  $[M]_D^{23} = +51.4^\circ$ . The infrared spectrum (KBr) showed absorptions at 3450  $\text{cm}^{-1}$  (w,  $\text{H}_2\text{O}$ ), 3010  $\text{cm}^{-1}$  (w), 2950  $\text{cm}^{-1}$  (m), 1730  $\text{cm}^{-1}$  (s, ketonic C=O stretch), 1590  $\text{cm}^{-1}$  (sh), 1575  $\text{cm}^{-1}$  (s, carboxylate C=O stretch), 1490  $\text{cm}^{-1}$  (s), 1390  $\text{cm}^{-1}$  (m), 955  $\text{cm}^{-1}$  (m), 945  $\text{cm}^{-1}$  (s), 790  $\text{cm}^{-1}$  (s). See p. 318. The  $^1\text{H}$  NMR spectrum ( $\text{CF}_3\text{COOH/TMS}$  std., 60 MHz) showed resonances at  $\delta$  1.3 (doublet, 6H,  $-\text{C}(\text{CH}_3)_2-$ ),  $\delta$  1.5-2.9 (complex multiplet, 7H, other peaks of ketopinate ion) and  $\delta$  3.3 (singlet, 12H,  $(\text{CH}_3)_4\text{N}$ ). See p. 305.

ANAL. Calcd. for  $\text{C}_{14}\text{H}_{25}\text{NO}_3$ : C, 65.85%; H, 9.87%; N, 5.49%.

Found: C, 64.51%; H, 10.35%; N, 6.01%.

d. Synthesis of tetrabutylammonium (+)-ketopinate. (+)-Ketopinic

acid (3.57 g., 0.02 mole) was placed into a 125-ml. Erlenmeyer flask with a magnetic stirring bar and titrated with a 10% solution of tetrabutylammonium hydroxide in methanol until blue to litmus (the phenolphthalein endpoint did not show). The resultant solution was evaporated at 20 mm.



pressure in a rotary evaporator and then overnight at 0.5 mm. pressure; it did not crystallize, and also was soluble in diethyl ether upon addition of this solvent. The material was used for chloral initiation as an oil. Yield: 10.3 g. (100%)  $[\alpha]_D^{23} = (+)11.5^\circ$  ( $c=11.11$ , methanol);  $[M]_D^{23} = (+)48.8^\circ$ . The infrared spectrum (KBr) showed absorptions at  $3200\text{ cm}^{-1}$  (s,b),  $2960\text{ cm}^{-1}$  (s),  $2870\text{ cm}^{-1}$  (s),  $2800\text{ cm}^{-1}$  (w),  $1740\text{ cm}^{-1}$  (s, ketonic C=O stretching),  $1590\text{ cm}^{-1}$  (s, carboxylate C=O stretching),  $1480\text{ cm}^{-1}$  (sh),  $1460\text{ cm}^{-1}$  (m),  $1415\text{ cm}^{-1}$  (w),  $1365\text{ cm}^{-1}$  (s),  $1290\text{ cm}^{-1}$  (w),  $1045\text{ cm}^{-1}$  (m),  $960\text{ cm}^{-1}$  (w),  $925\text{ cm}^{-1}$  (w),  $880\text{ cm}^{-1}$  (m),  $850\text{ cm}^{-1}$  (w),  $775\text{ cm}^{-1}$  (m),  $735\text{ cm}^{-1}$  (w). See p. 318. The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ /1% TMS, 60 MHz) showed resonances at  $\delta$  0.6-2.9 (complex multiplet, 41H, ketopinate protons plus  $(n\text{-C}_3\text{H}_7\text{CH}_2)_4\text{N}$ ) and  $\delta$  3.4 (multiplet, 8H,  $(n\text{-C}_3\text{H}_7\text{CH}_2)_4\text{N}$ ). See p. 305.

e. Synthesis of silver (+)-ketopinate. (+)-Ketopinic acid (3.64 g., 0.02 mole) was placed in a 125-ml. Erlenmeyer flask (without solvent) and titrated with aqueous NaOH (approx. 1 M) to the phenolphthalein endpoint. Silver nitrate (3.40 g., 0.02 mole) was dissolved in 15 ml. of water. The silver nitrate solution was poured into the sodium ketopinate solution, producing a copious gray precipitate. The suspension was diluted to approximately 100 ml. with water. The precipitate was broken up, filtered, washed with water, and dried at 0.5 mm. pressure in a bottle wrapped with black tape, first without drying agent and then for 8 hours over  $\text{P}_2\text{O}_5$ . Yield: 3.95 g. (68%).

f. Synthesis of benzyltriphenylphosphonium (+)-ketopinate. Silver (+)-ketopinate (3.11 g., 0.0108 mole) was suspended in 75 ml. of methanol in a 250-ml. Erlenmeyer flask with magnetic stirring. Benzyltriphenyl-

phosphonium bromide (4.37 g., 0.0101 mole) was dissolved in 50 ml. of methanol; this solution was added slowly to the suspension of silver (+)-ketopinate with stirring. The mixture was stirred overnight and then filtered to remove precipitated AgBr, which was washed with methanol. The filtrate was evaporated, first at 20 mm. pressure (rotary evaporator) and then at 0.5 mm. pressure to give a glassy residue which could be crystallized by addition of 20 ml. of warm acetone. The crystals were filtered and dissolved in 10 ml. of  $\text{CHCl}_3$ ; the solution was evaporated to a glassy residue which crystallized again upon addition of acetone. This was the only form of recrystallization found possible for the compound. Yield: 1.66 g. (29%); m.p. 170-175°C. (dec.)  $[\alpha]_{\text{D}}^{23} = +10.1^\circ$  (C=4, methanol);  $[M]_{\text{D}}^{23} = +54.2^\circ$ .

The infrared spectrum (KBr) showed absorptions at 3450  $\text{cm}^{-1}$  (w,b,  $\text{H}_2\text{O}$ ), 3050  $\text{cm}^{-1}$  (w), 2980  $\text{cm}^{-1}$  (m), 2950  $\text{cm}^{-1}$  (m), 2935  $\text{cm}^{-1}$  (m), 2880  $\text{cm}^{-1}$  (m), 2850  $\text{cm}^{-1}$  (m), 2780  $\text{cm}^{-1}$  (m), 1730  $\text{cm}^{-1}$  (s,sh), 1725  $\text{cm}^{-1}$  (s, ketone C=O stretching), 1600  $\text{cm}^{-1}$  (sh), 1575  $\text{cm}^{-1}$  (vs, carboxylate C=O stretching), 1560  $\text{cm}^{-1}$  (sh), 1490  $\text{cm}^{-1}$  (w), 1480  $\text{cm}^{-1}$  (w), 1455  $\text{cm}^{-1}$  (w), 1435  $\text{cm}^{-1}$  (s), 1395  $\text{cm}^{-1}$  (s), 1380  $\text{cm}^{-1}$  (s), 1160  $\text{cm}^{-1}$  (w), 1105  $\text{cm}^{-1}$  (s), 1030  $\text{cm}^{-1}$  (w), 990  $\text{cm}^{-1}$  (m), 920  $\text{cm}^{-1}$  (w), 870  $\text{cm}^{-1}$  (m), 850  $\text{cm}^{-1}$  (w), 790  $\text{cm}^{-1}$  (s), 753  $\text{cm}^{-1}$  (s), 745  $\text{cm}^{-1}$  (sh), 720  $\text{cm}^{-1}$  (s), 695  $\text{cm}^{-1}$  (s), 685  $\text{cm}^{-1}$  (s), 625  $\text{cm}^{-1}$  (w), 580  $\text{cm}^{-1}$  (m), 540  $\text{cm}^{-1}$  (w), 505  $\text{cm}^{-1}$  (s), 490  $\text{cm}^{-1}$  (s), 415  $\text{cm}^{-1}$  (w), 392  $\text{cm}^{-1}$  (w), 345  $\text{cm}^{-1}$  (w), 270  $\text{cm}^{-1}$  (m). See p. 319. The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ /1% TMS, 60 MHz) showed resonances at  $\delta$  1.1 (doublet, 6H,  $-\text{C}(\text{CH}_3)_2-$ ),  $\delta$  5.3, 5.5 (doublet,  $\sim 2\text{H}$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{P}\equiv$ ),  $\delta$  7.1 (singlet, 5H,  $\text{C}_6\text{H}_5\text{CH}_2-$ ),  $\delta$  7.65 (multiplet, 15H,  $(\text{C}_6\text{H}_5)_3\text{P}$ ), plus small peaks at  $\delta$  2.2, 4.2, and 7.35 apparently caused by impurities,

See p. 306.

ANAL. Calcd. for  $C_{35}H_{35}O_3P$ : C, 78.63%; H, 6.60%. Found: C, 77.01%, 77.13%; H, 6.80%, 6.84%.

g. Synthesis of (+)-methyl(n-propyl)phenylbenzylphosphonium

(+)-ketopinate. (+)Methyl(n-propyl)phenylbenzylphosphonium chloride ( $[\alpha]_D^{23} = 37.2^\circ$  (C=1.655, methanol); see p. iv) (0.402 g., 0.0014 mole) was dissolved in 10 ml. of methanol. Silver (+)-ketopinate (0.47 g., 0.0016 mole) was suspended in 20 ml. of methanol in a 50 ml. Erlenmeyer flask with magnetic stirring. The phosphonium salt solution was then poured into the silver ketopinate suspension; the character of the solid rapidly changed to the clumped appearance of precipitated silver chloride. The mixture was stirred overnight and filtered. The filtrate was evaporated at 20 mm. pressure on a rotary evaporator and then at 0.5 mm. pressure with a vacuum pump to give a yellow oil. The oil could not be recrystallized from acetone, methanol/acetone, chloroform/acetone or chloroform/hexane; it was used as an oil for chloral initiation.

$$[\alpha]_D^{23} = +20.95^\circ \text{ (C=1.81, methanol); } [M]_D^{23} = +88.95^\circ$$

The infrared spectrum (KBr) showed absorptions at  $3400\text{ cm}^{-1}$  (w,b,  $H_2O$ ),  $2930\text{ cm}^{-1}$  (s,b),  $2310\text{ cm}^{-1}$  (w),  $1720\text{ cm}^{-1}$  (s),  $1695\text{ cm}^{-1}$  (sh),  $1570\text{ cm}^{-1}$  (s),  $1450\text{ cm}^{-1}$  (w),  $1380\text{ cm}^{-1}$  (s),  $1300\text{ cm}^{-1}$  (w),  $1230\text{ cm}^{-1}$  (w),  $1140\text{ cm}^{-1}$  (w),  $1110\text{ cm}^{-1}$  (m),  $920\text{ cm}^{-1}$  (w),  $790\text{ cm}^{-1}$  (w),  $745\text{ cm}^{-1}$  (w).

See p. 319. The  $^1H$  NMR spectrum ( $CDCl_3$ /1% TMS, 60 MHz) showed resonances at  $\delta$  1.2 (doublet,  $-C(\underline{CH}_3)_2-$ ),  $\delta$  1.0-2.8 (multiple peaks, 23H, protons of ketopinate ion and methyl and n-propyl groups of phosphonium ion),  $\delta$  4.3, 4.6 (doublet, 2H,  $C_6H_5\underline{CH}_2P\equiv$ ),  $\delta$  7.1 (singlet, 5H,  $C_6H_5CH_2P\equiv$ ), and  $\delta$  7.6 (doublet, 5H,  $C_6H_5P\equiv$ ). See p. 306.



3. Polymerization of chloral with optically active initiators and attempted measurement of optical activity of resultant polychloral. A number of molds for preparation of polychloral films were prepared from pairs of glass plates separated by 420-denier Lycra fiber spacers as on p. 60 ; a number of 25 x 200 mm. test tubes were dried for six hours at 120°C., cooled under dry nitrogen flow, fitted with rubber serum stoppers, and wired. The tubes were then injected with chloral (usually 50 ml.) and placed in a 70°C. oil bath for 10 minutes. The initiator solutions (Table 31, p. 270 ) were then added and the tubes were shaken to obtain homogeneous mixtures. About 7 ml. of each solution was then withdrawn from the tube with a 70°C. syringe and injected into one of the film molds. The tubes and film molds were then placed in an ice-water bath at 0°C. for 1 1/2 (or 12) hours, removed, and allowed to air dry.

The polychloral films and plugs were removed from the molds and test tubes. They were weighed, soaked for one or two days in a mixture of methanol and 10% (v/v) concentrated aqueous HCl, and extracted for two days with methanol in a Soxhlet extractor. The polymer films were dried for one or two days in the open air at room temperature and weighed; the polymer plugs were dried overnight at room temperature and 0.5 mm. pressure and weighed. Yields are listed in Table 31, p. 270.

Discs were cut from the polymer film samples with a cork borer; the discs were soaked for from two to six days in diphenyl ether at 50°C. The discs from each film were then laminated with diphenyl ether and placed in the polarimetric film cell (p. 110); optical rotation measurements on the films in the cell were performed as described on pp. 269-273. Optical rotation data are given in Table 32, p. 271.

### J. Measurements

Infrared spectra were obtained on a Perkin-Elmer 283 Infrared Spectrometer ( $4000\text{-}200\text{ cm}^{-1}$ ) with a scan time of 12 minutes or on a Perkin-Elmer 727 Infrared Spectrometer ( $4000\text{-}600\text{ cm}^{-1}$ ) at a "normal" scan rate. Polymer films were used as such. Solid low molecular weight compounds were generally incorporated into KBr pellets, while the infrared spectra of liquids were usually measured on neat samples between NaCl plates. Polymer powders were sometimes used as KBr pellets, but better results were generally obtained when polymer powder spectra were measured on mulls of the polymer in  $\text{CCl}_4$  between NaCl plates. The polystyrene band at  $1601\text{ cm}^{-1}$  was used as the calibration standard.

Proton nuclear magnetic resonance spectra ( $^1\text{H}$  NMR) were generally obtained on a 60 MHz Hitachi Perkin-Elmer R-24 NMR Spectrometer; when greater precision was necessary, some spectra were obtained on a 90 MHz Perkin-Elmer R-32 NMR Spectrometer. Kinetic measurements were performed on polymer gels; spectra of soluble samples were generally obtained on solutions of 5-10% concentration in carbon tetrachloride, chloroform- $d$ , benzene- $d_6$  or trifluoroacetic acid, with TMS as the internal standard.

Melting points of compounds were measured on a MEL-TEMP capillary melting point apparatus and are uncorrected.

Thermogravimetric (TGA) and differential thermogravimetric (DTG) spectra were recorded on a Perkin-Elmer TGS-1 Thermobalance under nitrogen at a heating rate of  $10^\circ\text{C./minute}$  for TGA and  $20^\circ\text{C./minute}$  for DTG spectra. The heating rate was regulated by a Perkin-Elmer UU-1 Temperature Program Control.

Inherent viscosities of the polymers were determined at 30°C. in toluene solution with a Ubbelohde capillary viscometer. Solution and solvent efflux times were greater than 70 seconds; the average value of from five to ten determinations was used in the calculation of the inherent viscosity.

Gas chromatograms were obtained with a Varian Associates Model 920 gas chromatograph, generally with a 2 meter column packed with Chromosorb W (100/120 mesh) coated with 36% by weight of diisodecyl phthalate.

Polarimetric measurements were obtained using a Perkin-Elmer 141MC or 241MC Polarimeter (electronic) or a Carl Zeiss 369415 visual polarimeter. Optical rotations of soluble materials were measured on solutions in appropriate solvents; rotations of insoluble polymers were measured on swollen films between glass plates. For the latter measurements, a cell was constructed of two circular pieces, 27 mm. in diameter, of 1/8" aluminum sheet. A center hole 10 mm. in diameter was drilled in each sheet; over this hole was attached, using epoxy resin, on the interior side, a piece of optically inactive glass 1/8" thick and 14 mm. in diameter. Around the perimeter of the glass, six holes were drilled in a hexagonal pattern. Bolts were placed in three holes alternately so that the cell could be bolted together to hold liquid-soaked films in the polarimeter beam. Through the remaining holes, the cell could be screwed to the mounting platform in the Perkin-Elmer 141MC polarimeter so that optical rotation could be measured at angles of orientation of the cell differing by 120°. The empty cell (with a drop of liquid between the plates) had zero optical rotation.



## CHAPTER III

### RESULTS AND DISCUSSION

#### A. Objectives

The objectives of this work were the preparation of polychloral optically active due to helicity only and the determination of a satisfactory technique for measurement of the optical activity of solid polychloral. Subsidiary to these objectives were determination of initiation mechanisms for chloral with various types of initiators (alkoxide, amine, phosphine, halide), determination of a satisfactory method for complete thermal stabilization of chloral homopolymer, determination of the nature of the endgroups in stable and unstable forms of polychloral, and synthesis and physical characterization of blends of polychloral with various addition polymers, with particular emphasis on obtaining transparent blends.

Optically active polychloral, if its formation could be unequivocally proven, would be the first known optically active polymer containing no individual asymmetric atoms but possessing optical activity solely because of a dissymmetric helical structure. Because of having only one, instead of two, mirror-image forms of helix, it should crystallize in a structure different from the normal polychloral structure, which could be determined by wide-angle X-ray scattering techniques.

Because of this likely difference in crystal structure, optically

active polychloral should also have different mechanical properties from those of normal polychloral.

Determination of initiation mechanisms for chloral polymerization with different types of initiators is essential for knowing which types of initiators may be effective in introducing optical activity into the polymer. The synthesis and characterization of chloral homopolymer blends is also indicated since the use of transparent blends could provide one way to measure the optical activity of the normally opaque chloral homopolymer.

The blends would also be of theoretical interest as compatible or incompatible polymer systems. If a compatible blend containing polychloral could be prepared, the resultant increase in the observed glass transition temperature of the non-polychloral component of the blend would provide a means for determining the glass transition temperature of polychloral, which has not been previously determined.

The determination of a method for complete thermal stabilization of chloral homopolymer to 200°C. would be highly desirable for any practical uses of chloral homopolymer and these blends.

#### B. Anionic Initiation Mechanisms for Chloral Polymerization

The anionic initiation of chloral polymerization was found by <sup>1</sup>H NMR and IR spectroscopy to proceed by two quite different types of processes dependent on the basicity and nucleophilicity of the initiators used. LTB, a strongly basic initiator, was found to add essentially quantitatively to chloral above the ceiling temperature of chloral poly-

merization to form a 1:1 adduct which could then initiate polymerization when cooled. Initiators containing less basic tertiary amine groups or halide ions were found not to form adducts with chloral above its threshold polymerization temperature, but rather to initiate chloral polymerization by processes occurring to a detectable extent only below the threshold polymerization temperature of chloral.

The reaction of LTB with chloral was followed by  $^1\text{H}$  NMR spectroscopy in Figure 1, p. 115. When chloral was added to an equimolar amount of LTB in benzene- $\text{d}_6$  at  $70^\circ\text{C}$ . and the  $^1\text{H}$  NMR spectrum of the reaction mixture was measured, it was evident that an essentially quantitative reaction between LTB and chloral had occurred. The aldehydic proton of chloral showed a singlet in the  $^1\text{H}$  NMR spectrum with a chemical shift of  $\delta$  8.3 (Figure 1A) but the exact value of the chemical shift depended somewhat on the concentration of chloral and the type of solvent; in  $\text{CDCl}_3$  or  $\text{CCl}_4$  solution or without solvent, the chemical shift of the aldehydic proton of chloral was  $\delta$  9.2. The tertiary butyl protons of LTB showed a singlet (when observed at 90 MHz) at  $\delta$  1.27 (Figure 1B). When LTB and chloral were mixed in equimolar quantities (Figure 1C), a new signal at  $\delta$  5.4 appeared. This has been assigned to the acetal proton of the new alkoxide anion formed by addition of chloral to the tertiary butoxide anion. In addition, the tertiary butyl protons of the new alkoxide absorbed at  $\delta$  1.30, shifted downfield by 0.03 ppm. from the tertiary butoxide absorption. If chloral was in excess, the aldehyde proton absorption could be observed in the presence of the alkoxide addition compound (Figure 1D). However; under normal conditions, no equilibrium between the LTB-chloral mixture and the new alkoxide (I) could be detected at the



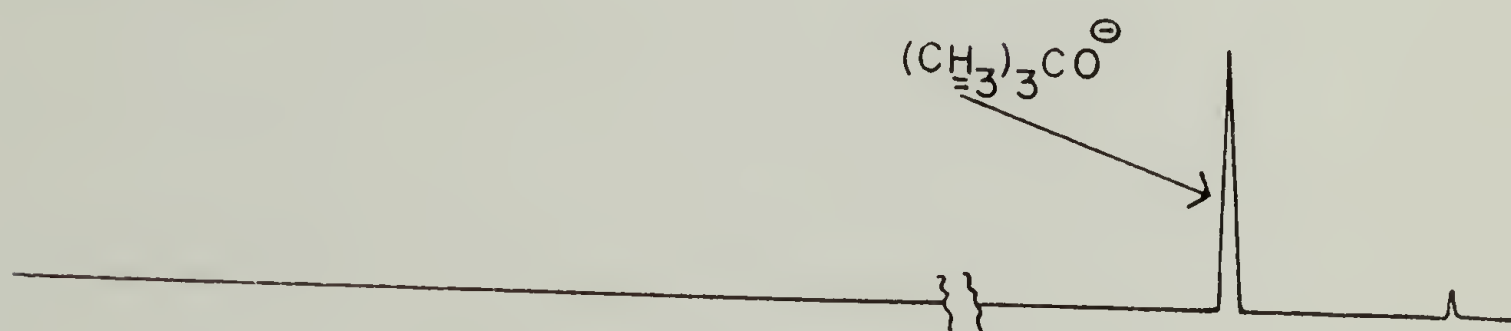
Figure 1.  $^1\text{H}$  NMR Study of Reaction of LTB with Chloral at 35°C.  
(All components 0.6M in  $\text{C}_6\text{D}_6$ )

- a. Chloral
- b. LTB
- c. Chloral/LTB (1/1)
- d. Chloral/LTB (2/1)

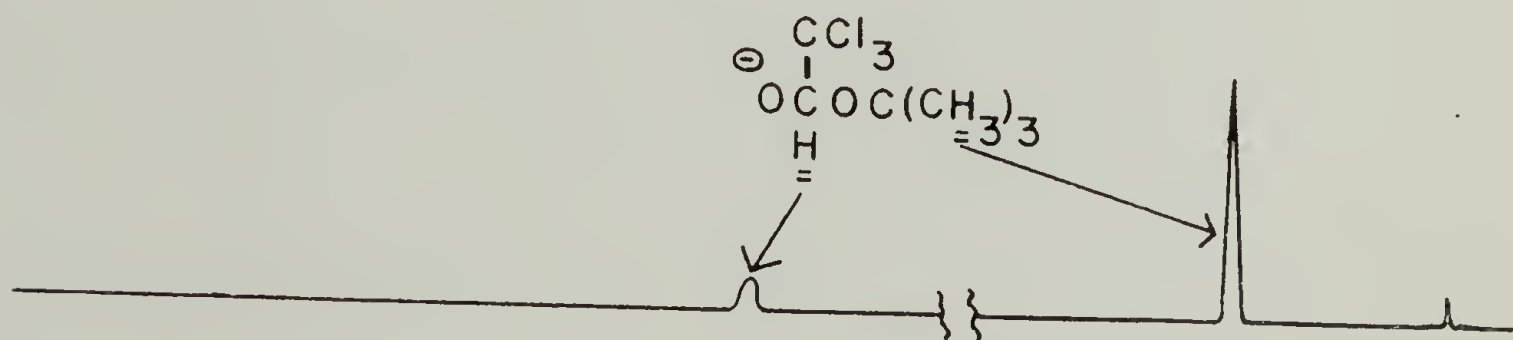
(a) Chloral



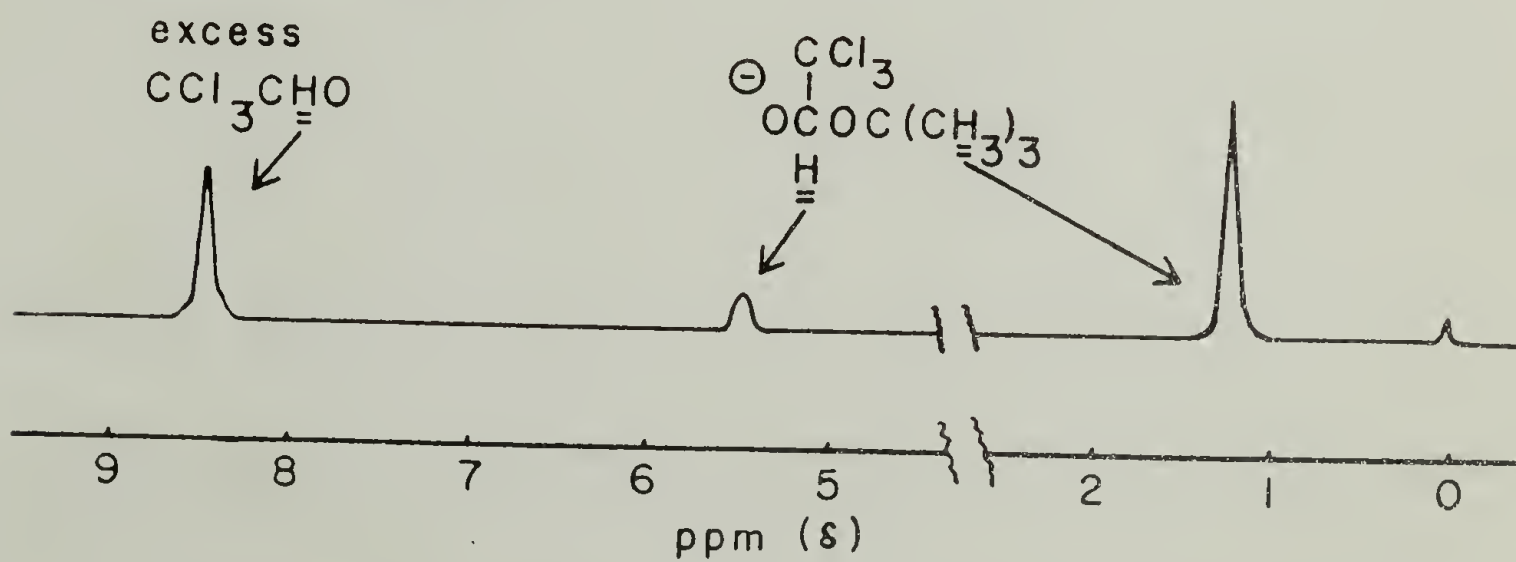
(b) LTB

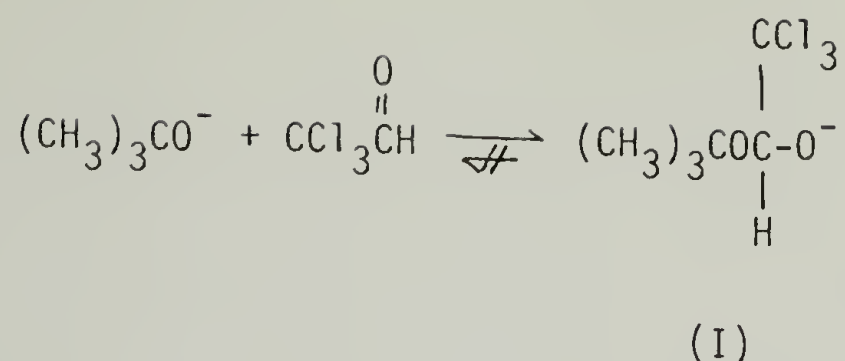


(c) Chloral / LTB (1/1)



(d) Chloral / LTB (2/1)





accuracy of the  $^1\text{H}$  NMR measurements. These results indicated that the reaction between LTB and chloral was fast, almost instantaneous, and that the equilibrium of this reaction was more than 95% on the right side.

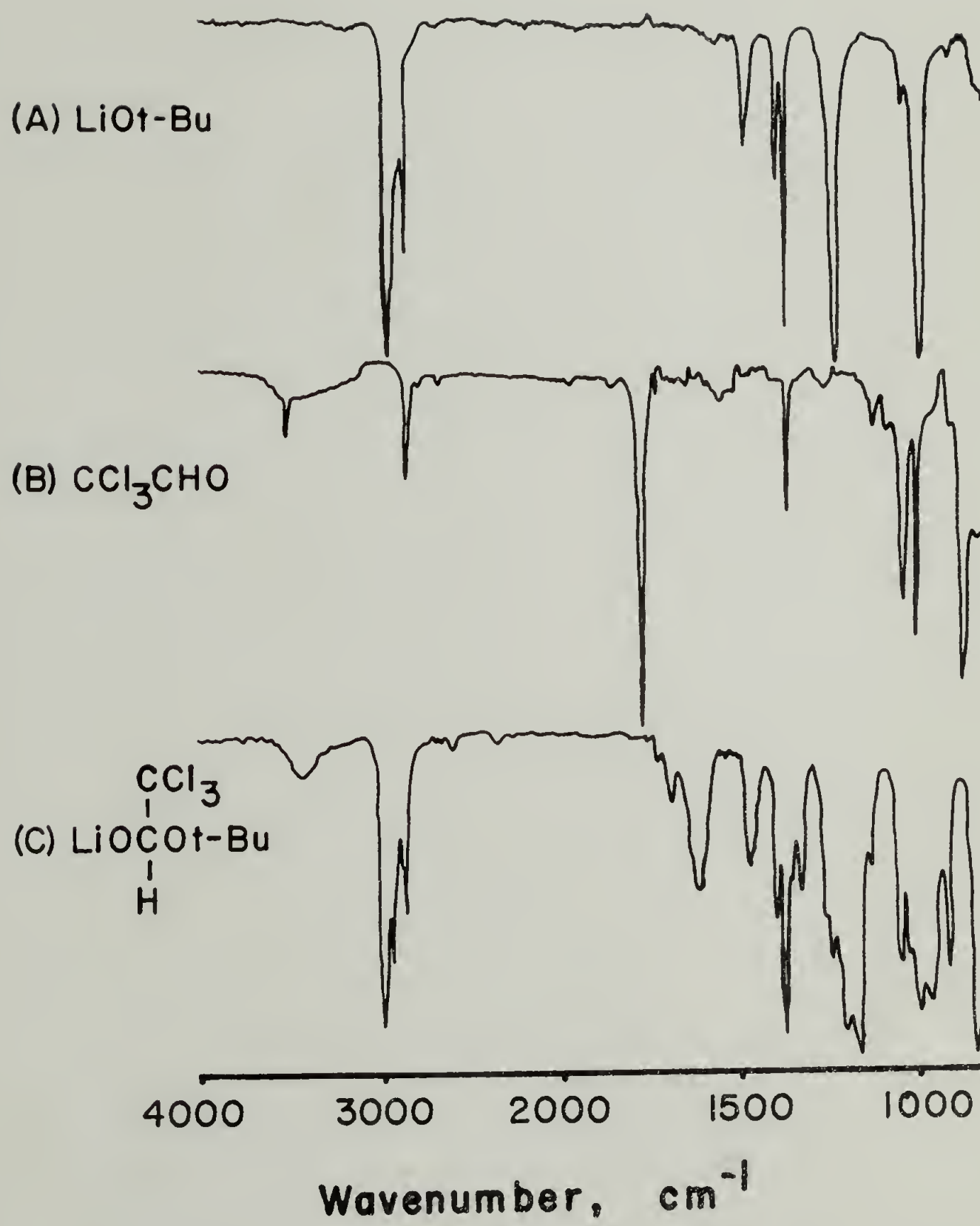
Even stronger support for lack of a measurable equilibrium between tertiary butoxide, chloral, and the addition product is provided by infrared spectroscopy. When a slightly less than equimolar amount of chloral was added to a 0.6 M solution of LTB in  $\text{CCl}_4$ , the infrared spectrum of the resultant product had no carbonyl peak (Figure 2C, p. 118). This infrared spectrum resembled neither the spectrum of LTB nor that of chloral nor the sum of these spectra, with a number of new peaks appearing in the spectrum of the product. The lack of a carbonyl peak in the spectrum of the combined solution shows that the level of chloral monomer is below the limit of detection by infrared spectroscopy, well below 1% of the amount of chloral monomer originally introduced. When apparently equimolar quantities of LTB and chloral were mixed in  $\text{CCl}_4$  solution, a carbonyl peak at  $1760\text{ cm}^{-1}$  did appear, thought to be due to small amounts of excess chloral.

Small proton signals were observed in the  $^1\text{H}$  NMR spectrum of a 1:1 mixture of LTB and chloral, especially when the mixture was allowed to stand at  $70^\circ\text{C}$ . for more than a few minutes. Alkoxide (I) was not stable and underwent further reactions which caused the formation of some spurious



Figure 2. IR Study of Reaction of LTB with Chloral at Room Temperature (all components 0.6M in  $\text{CCl}_4$ ).

- a. LTB
- b. Chloral
- c. Chloral/LTB (slightly lower than 1/1 ratio)



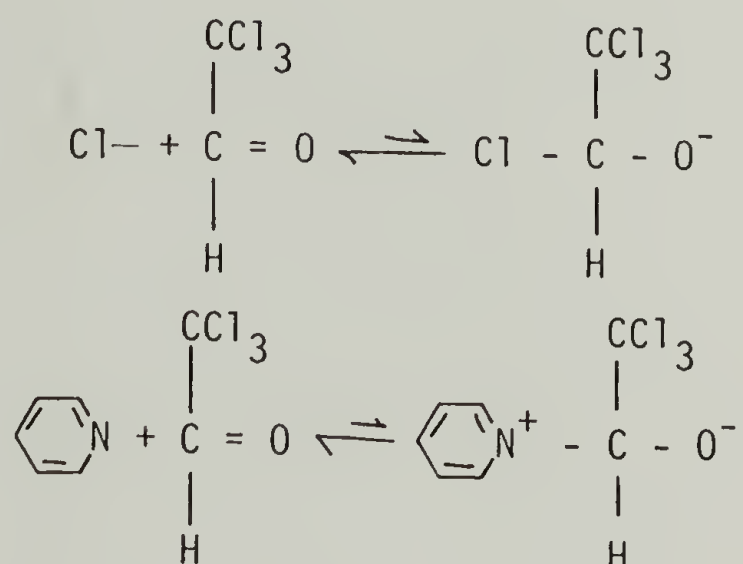
signals in the PMR spectrum of the alkoxide (I). Similarly, if the chloral monomer was not added rapidly to the NMR tube containing the LTB solution but was instead allowed to flow slowly down the sides of the tube, a side reaction occurred which produced a peak at  $\delta$  6.2 immediately after chloral addition (in addition to the acetal proton peak at  $\delta$  5.4). In other work (145), it was found that alkoxide (I) could not be isolated but could be acetylated with acetic anhydride or methylated with dimethyl sulfate in very high yields. When alkoxide (I) was heated under reflux in cyclohexane for several hours, tertiary butyl 1,2,2,2-tetrachloroethyl ether was obtained as the main reaction product.

When the solution of (I) from the NMR tube was added to a test tube of chloral above its threshold polymerization temperature and the test tube was then placed in an ice bath, immediate polymerization to a hard, tough block of polychloral occurred.

Since it has been established that alkoxide (I) had a proton resonance of 5.4 ppm., the appearance of a proton signal in this region was considered indicative for the formation of an alkoxide which would have been produced by the addition of any anion to the carbonyl double bond of chloral. As a consequence, additional studies of 1:1 mixtures of chloral with other compounds that were known to initiate the chloral polymerization at levels that could be detectable by PMR spectroscopy were undertaken in order to detect individual initiation equilibria for various initiators. Mixtures of  $\text{Bu}_4\text{NCl}$ /chloral, pyridine/chloral and 2,4,6-trimethylpyridine/chloral (Figures 3A, 4) did not show any signals in the  $\delta$  5 to 5.5 region (except for two very small signals in the  $\text{Bu}_4\text{NCl}$ /chloral mixture) which would be indicative of an initiation equilibrium where the



equilibrium concentration of the alkoxide was sufficient to be detectable by PMR spectroscopy (signals of 0.5 mole percent concentration could be detected). This observation suggested that the initiation equilibrium was essentially but not completely on the left-hand side of the equations below because in all cases polymerization of chloral in the presence of



the above mentioned initiators occurred even though the initiators were added in large or even equimolar quantities. Polychloral samples obtained were tough and of reasonable molecular weight. Good mechanical properties also indicated a high molecular weight of the polychloral samples which demonstrated that the amount of actual initiator produced from the added compound was relatively small; the initiation reaction was not detectable by PMR spectroscopy but the initiation still effected chloral polymerization. It is evident that the initiating species in  $\text{Bu}_4\text{NCl}$  initiation was the chloride ion.

The initiation of chloral with  $\text{Ph}_3\text{P}$  proceeded in two steps. When  $\text{Ph}_3\text{P}$  was added to excess chloral, it reacted instantaneously with one mole of chloral to form triphenyldichlorovinylphosphonium chloride (165,179).



The structure of this compound (II) has been well established by infrared (165) and, more recently, X-ray spectroscopy. The progress of this reaction could also be followed by  $^{31}\text{P}$  NMR spectroscopy (145). The chemical shift of  $^{31}\text{P}$  in  $\text{Ph}_3\text{P}$  (+ 5.5 ppm.) changed to -68 ppm. in the phosphonium salt from triphenylphosphine and chloral (II).

The formation of II could also be followed by  $^1\text{H}$  NMR spectroscopy. When equimolar amounts of  $\text{Ph}_3\text{P}$  and chloral were allowed to react at 70°C. in benzene- $\text{d}_6$ , an oily product separated which was brought into solution by evaporation of the  $\text{C}_6\text{D}_6$  and addition of  $\text{CDCl}_3$ . The  $^1\text{H}$  NMR spectrum of a solution of (II) (shown in Figure 3C after addition of an extra mole of chloral) showed that the phenyl protons had shifted 0.7 ppm. downfield and a new proton signal at 7.5 ppm. had appeared apparently in agreement with a 1 to 15 proton ratio, although integration was difficult because of peak overlap. This solution initiated the chloral polymerization the same way as a solution of  $\text{Ph}_3\text{P}$ .

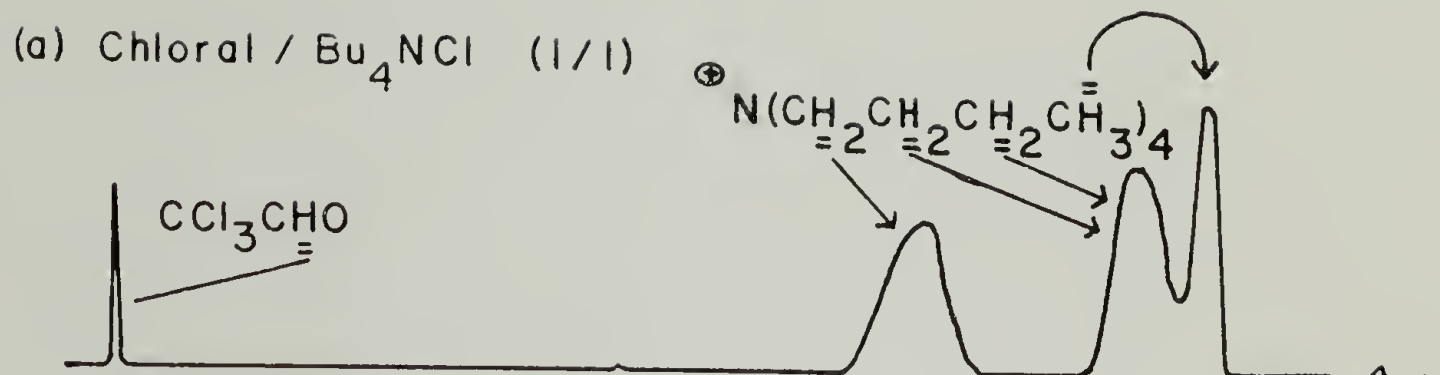
Based on the identification of (II) as the actual reaction product of  $\text{Ph}_3\text{P}$  with 1 mole of chloral, it became clear that (II) was the actual initiator for chloral polymerization and, in fact, polymerized chloral at the same rate as if  $\text{Ph}_3\text{P}$  was added directly (instead of purified (II)) to the chloral as the initiator for its polymerization. Initiation with prepurified (II) or by direct addition of  $\text{Ph}_3\text{P}$  gave polychloral of identical mechanical properties.

When (II) was added to excess of chloral at 70°C., no reaction was observed by  $^1\text{H}$  NMR spectroscopy, but when the reaction mixture was

Figure 3.  $^1\text{H}$  NMR Study of Reaction of Chloral with  $\text{Bu}_4\text{NCl}$  and  $\text{Ph}_3\text{P}$  at  $35^\circ\text{C}$ . (all components 1M in  $\text{CDCl}_3$ ).

- a. Chloral/ $\text{Bu}_4\text{NCl}$  (1/1)
- b.  $\text{Ph}_3\text{P}$
- c. Chloral/ $\text{Ph}_3\text{P}$  (2/1)





(b)  $\text{Ph}_3\text{P}$



(c) Chloral /  $\text{Ph}_3\text{P}$  (2/1)

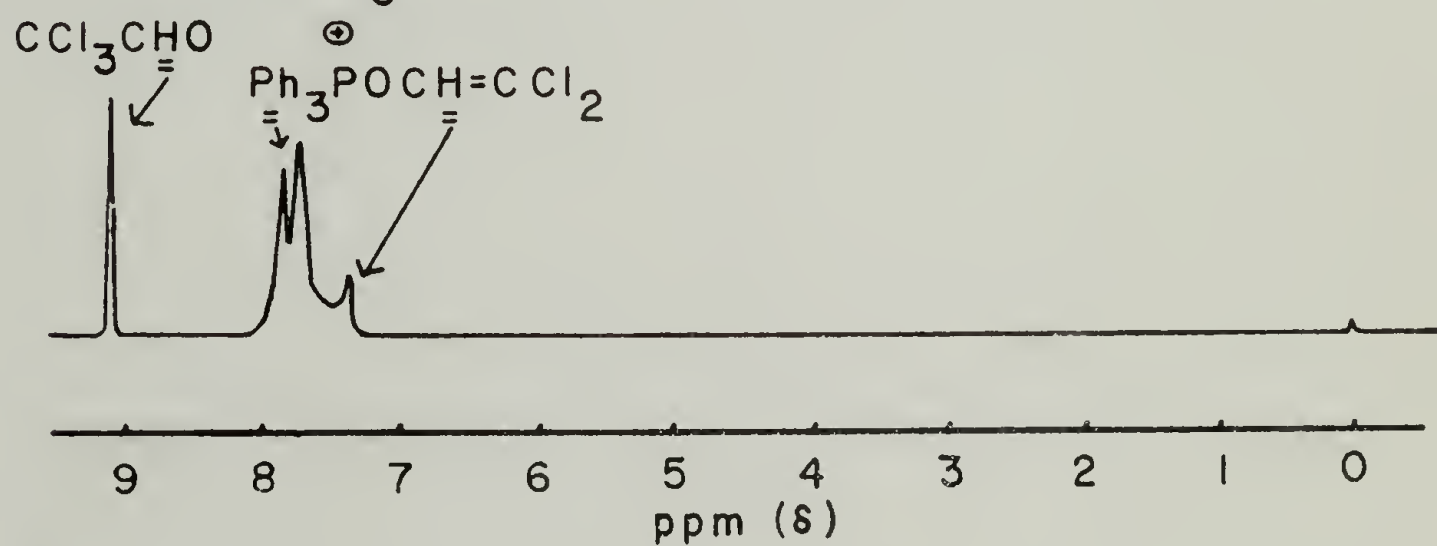
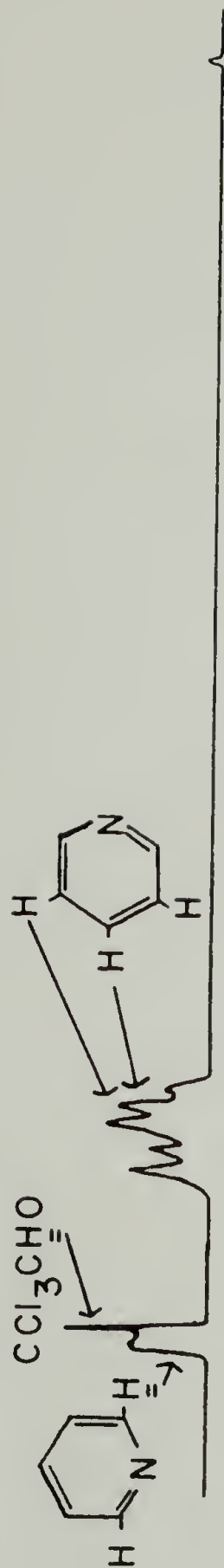
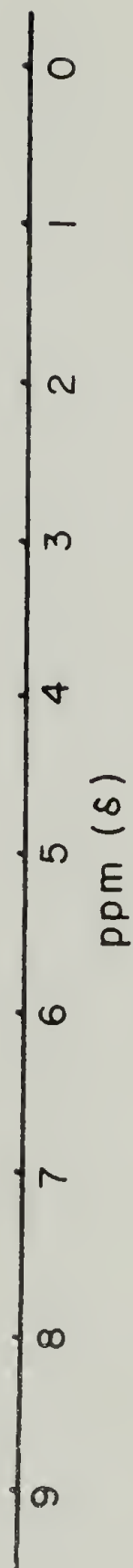
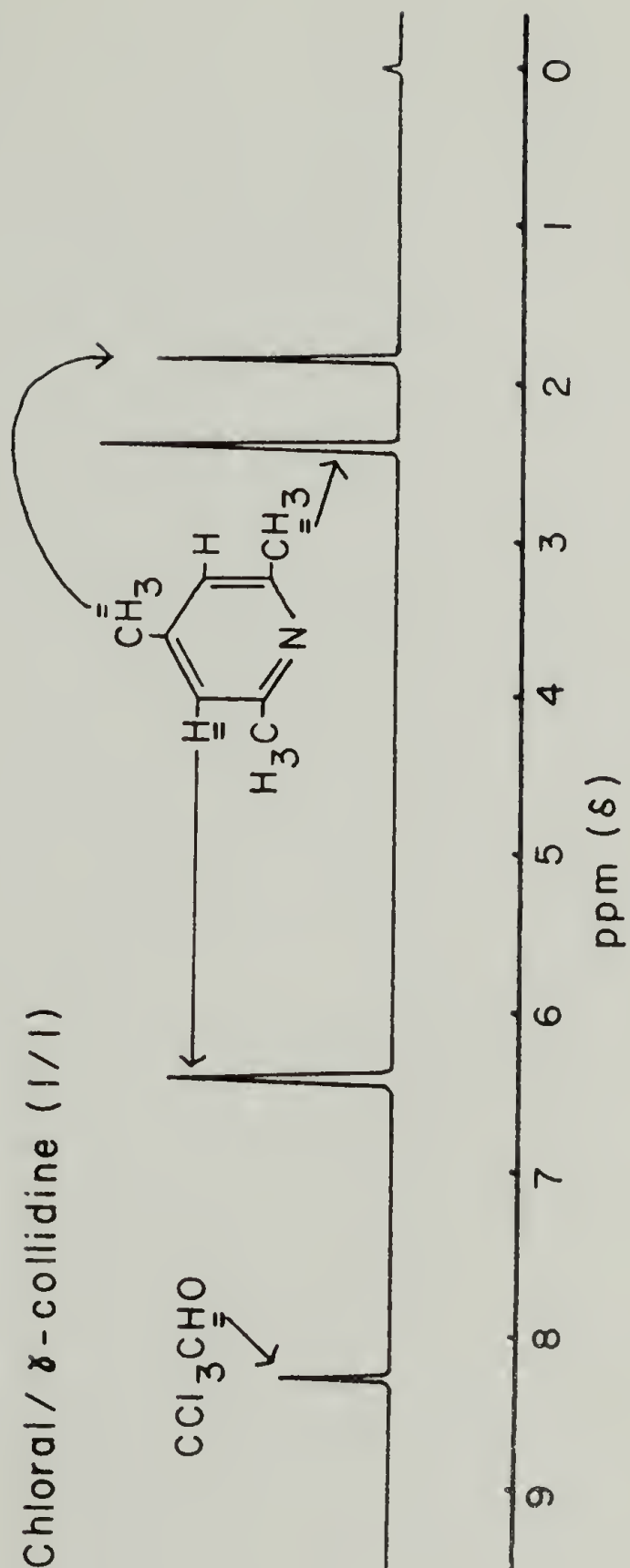


Figure 4.  $^1\text{H}$  NMR Study of Reaction of Chloral with Pyridine and 2,4,6-Trimethylpyridine at 35°C. (all components 1M in  $\text{C}_6\text{D}_6$ ).

a. Chloral/pyridine (1/1)

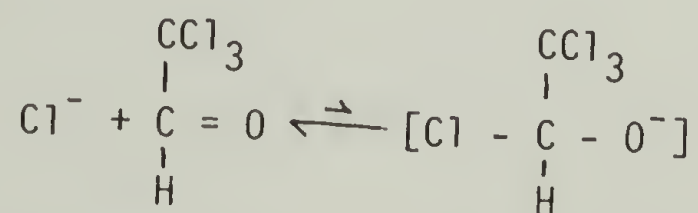
b. Chloral/2,4,6-trimethylpyridine (1/1)

(a) Chloral / pyridine (1/1)

(b) Chloral /  $\delta$ -collidine (1/1)

allowed to stand at 60°C., two new single peaks of equal intensity appeared at 5.5 ppm. and 6.3 ppm. Although it was initially believed that this was an indication for the establishment of an initiation equilibrium in chloride ion initiation of chloral, it was later shown that these were the two peaks of 1,2,2,2-tetrachloroethyl 2,2-dichlorovinyl ether, the main product of the reaction of (II) with 1 mole of chloral at elevated temperatures, which could be isolated by gas chromatography and identified (145).

It was therefore concluded that the so-called initiation of chloral polymerization with  $\text{Ph}_3\text{P}$  was actually the initiation with the chloride ion of (II), similar to the initiation of chloral with  $\text{Bu}_4\text{NCl}$  or triphenylmethylphosphonium chloride, all of which gave similar rates of chloral polymerization.

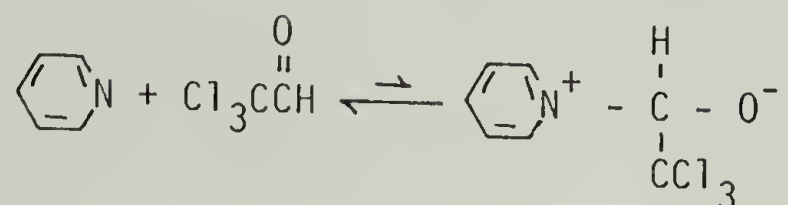


The initiating species in chloral initiation with pyridine and 2,4,6-trimethylpyridine is still unknown. One possibility is that the amines react with chloral in a manner similar to that of triphenylphosphine to give quaternary ammonium salts containing chloride ions which function as the actual initiating species. However, such reactions would be expected to proceed more rapidly at higher temperatures, and in the PMR experiments no new peaks could be detected in amine/chloral mixtures even after standing for two days, while these amines cause polymerization of chloral to 30-70% conversions within 10 minutes of cooling to 0°C. (145).

Hence it would seem more likely that the actual initiating species



in amine initiation of chloral is a zwitterionic species caused by reaction of one molecule of chloral with one molecule of amine:



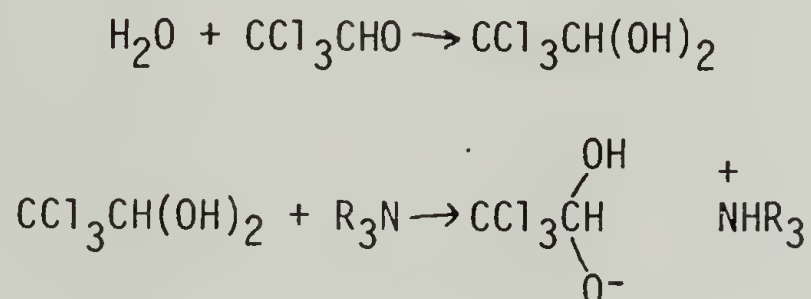
In the formation of this zwitterion, charge separation would occur, which would perhaps make this initiation pathway seem less likely. However, similar well-characterized zwitterionic species are formed by the reaction of  $\text{Ph}_3\text{P}$  with  $\beta$ -propiolactone (211) in anionic polymerization of  $\beta$ -propiolactone and also in the reactions of pyridine and other amines with  $\beta$ -propiolactone, propane sultone, or acrylic acid (212).

This author proposes that the zwitterion in the above equation may be present in amine-chloral mixtures in concentrations too small to be detected by  $^1\text{H}$  NMR. As long as the mixture remains above the threshold polymerization temperature of chloral polymerization, the position of the equilibrium remains far to the left. When the mixture is cooled below the chloral threshold temperature, however, the zwitterion is removed from the equilibrium by rapid propagation with formation of polychloral as a gel phase. In the liquid phase entrapped within the gel, remaining amine and chloral can then react to form further zwitterion which itself will be removed from the equilibrium as fast as it is formed. By this process, tertiary amines can act as initiators for chloral to cause polymerization to conversions comparable to those obtainable in initiation with alkoxide or chloride ions.

Further support for the "unstable zwitterion" hypothesis for initiation of chloral polymerization by tertiary amines is found in the

polymerization of bromal (tribromoacetaldehyde) (120), dibromochloroacetaldehyde (175), and bromodichloroacetaldehyde (174). Pyridine and other tertiary amines effectively polymerize these aldehydes, whereas compounds such as alkali bromides or triphenylphosphine (which reacts with these aldehydes to yield salts with bromide anions) do not cause polymerization. (The preformed triphenylphosphine-chloral reaction product, which is a chloride salt, does polymerize these brominated aldehydes.) If pyridine and other tertiary amines were to initiate trihaloacetaldehyde polymerization by reacting first with the aldehyde to give a quaternary halide, as does triphenylphosphine, the halide salts from the brominated aldehydes would be expected to be bromides. But bromide ion is not an effective initiator for polymerization of these aldehydes. Hence initiation by tertiary amines must be by another mechanism, with the zwitterionic mechanism seeming most likely.

It must also be mentioned that McCain and Sanders (213) proposed that initiation of chloral with tertiary amines required water or another protic coinitiator and proceeded as follows:



The latter anionic species could then add chloral units, initiating a polymer chain. This mechanism cannot be excluded because of the tendency of very small amounts of protic impurities to form upon standing of chloral pure to gas chromatography. Thin films of pyridine-initiated polychloral

do not show evidence of pyridine residues in the infrared spectrum after extraction with acetone or methanol, but such does not exclude the zwitterionic initiation pathway because of possible solvolysis of the cationic endgroup during extraction and also because of high molecular weight in the polychloral films.

With regard to the above mechanism, it must be mentioned that polychloral initiated with amines tends to adhere very tenaciously to glass; it is often very difficult to separate the two glass plates of a mold containing an amine-initiated polychloral film. Such suggests that the polychloral may be chemically bonded to the glass; the amine may deprotonate surface hydroxyl groups of the glass to form  $\text{Si-O}^-$  anionic sites which could initiate polychloral chains bound to the glass surface.

From our work, both the zwitterionic mechanism for chloral initiation by tertiary amines and the mechanism dependent on protic impurities must be considered possible; sufficient evidence is not available to differentiate between the two.

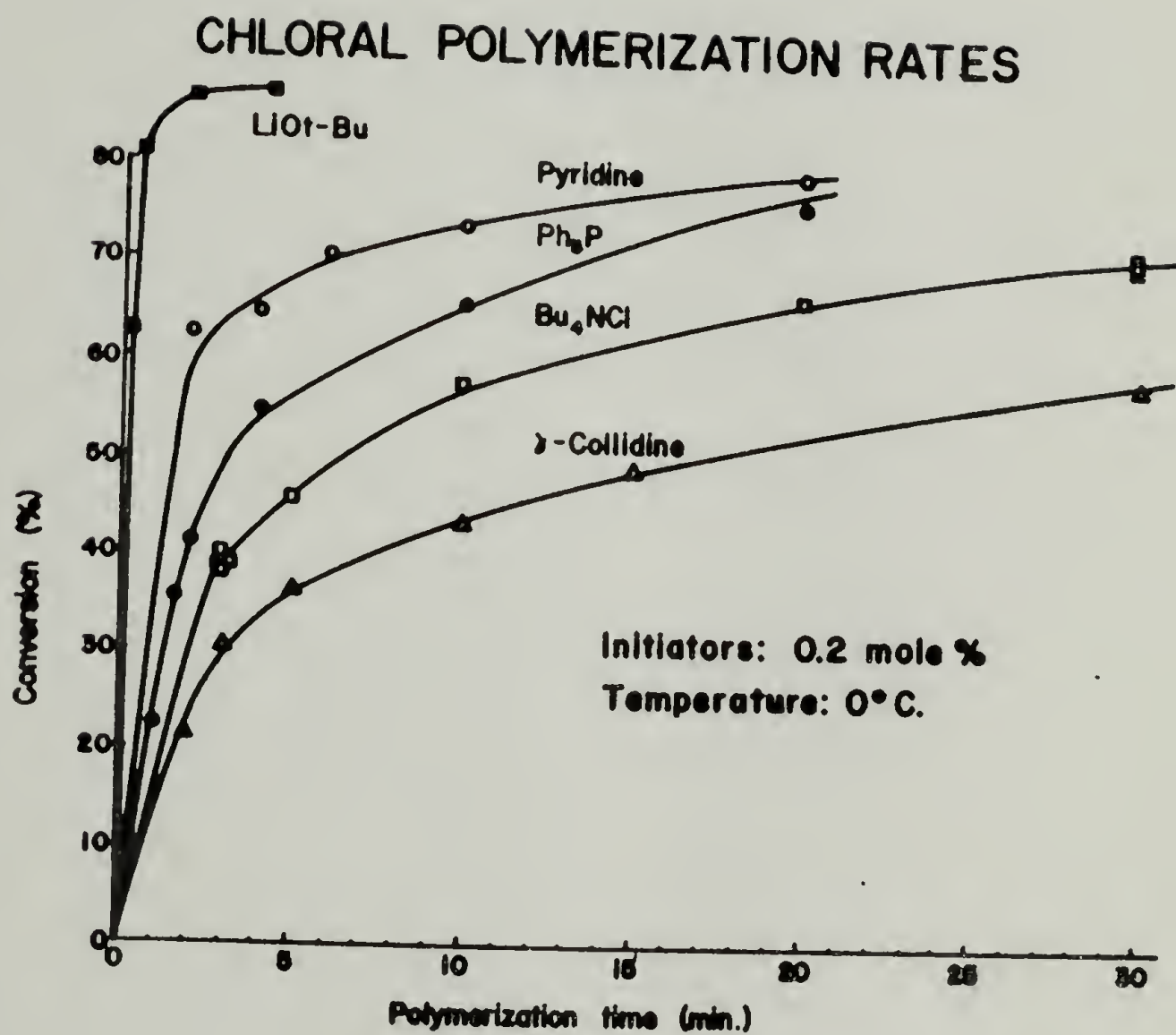
The rates of chloral polymerization observed with LTB by  $^1\text{H}$  NMR were much higher than those found for the other four initiators tested (145) (Figure 5). This result is consistent with the above proposed initiation pathways for the respective initiators. The initiating species in chloral polymerization by LTB is the 1:1 adduct of tertiary butoxide ion with chloral (I) which is formed quantitatively above the threshold temperature of chloral polymerization and is therefore present in the system upon cooling in a concentration equal to the original concentration of LTB in the system, with each adduct alkoxide anion immediately capable of propagation to a polychloral chain upon cooling. Hence the polymerization

Figure 5.  $^1\text{H}$  NMR Study of Rates of Bulk Polymerization of Chloral with Different Anionic Initiators (0.2 mole % of each initiator with respect to chloral; polymerization temperature  $0^\circ\text{C}.$ ).

Initiators:

- a. LTB
- b. Pyridine
- c.  $\text{Ph}_3\text{P}$
- d.  $\text{Bu}_4\text{NCl}$
- e. 2,4,6-Trimethylpyridine





rate of chloral with LTB initiation is controlled in very small systems by the actual rate of propagation of the polychloral chain (and by monomer diffusion in later stages of the polymerization) and in larger systems by the rate of diffusion out of the system of the heat liberated by polymerization of the chloral, which must be removed in order to keep the system below the threshold polymerization temperature so that chloral polymerization can continue.

In initiation by chloride ions or tertiary amines, on the other hand, the initial combination with chloral of chloride ion (to form the tetrachloroethoxide anion) or amine (to form the zwitterion or reaction product with a protic species) is the slow step in the polymerization sequence; as soon as these initiating species are formed, they should be able to add chloral and undergo propagation at the same rate as the adduct of chloral and tert-butoxide anion. Hence the difference in polymerization rates is explained in that for "rapid" initiators such as alkoxides, propagation (including thermal and monomer diffusion) is the rate-controlling factor, while for "slow" initiators such as chloride ion or tertiary amines, initiation--the addition of these species to one molecule of chloral to form the actual species which can propagate--is the step which controls the rate of the polymerization.

Because of the low concentration of these initiating species (tetrachloroethoxide anion or amine-generated species) above the threshold temperature for chloral polymerization, and their immediate removal from the equilibrium when formed below the threshold temperature, it has not been possible to trace the existence, concentration and rate of formation of these species by spectroscopic or other means.

We realize that the above explanation of observed polymerization rates ignores counterion effects and that a more valid comparison of polymerization rates of chloral by different anionic initiators would involve a series of initiators with the same counteranion, such as lithium. However, if the lithium counterion were chosen, for example, lithium chloride would be soluble in, and dispersible in chloral by, only highly polar solvents such as dimethylformamide or dimethyl sulfoxide. Phosphonium counterions could not be used uniformly because phosphonium alkoxides are unstable, and in cases of initiation by tertiary amines the structure of the tertiary amine itself would determine the "counteranion" formed. Hence, although it is recognized that the lithium ion might coordinate more strongly with the polychloral anionic endgroup than quaternary ammonium or phosphonium ions and thereby influence propagation rates to some extent, it was not possible to make a thorough study of this effect. In any case, stronger coordination of the lithium ion with the polychloral anion would generally be expected to decrease the propagation rate in systems with lithium counterions as opposed to larger, more loosely bound counterions, whereas the chloral polymerization rate actually observed was much higher for LTB than for any other initiator used. Hence the above conclusions as to initiation mechanisms with different initiators are not changed by consideration of respective counterion effects. The problem of polychloral anion-counteranion binding is treated in more detail in the discussion of thermal stabilization on pp. 220-245.

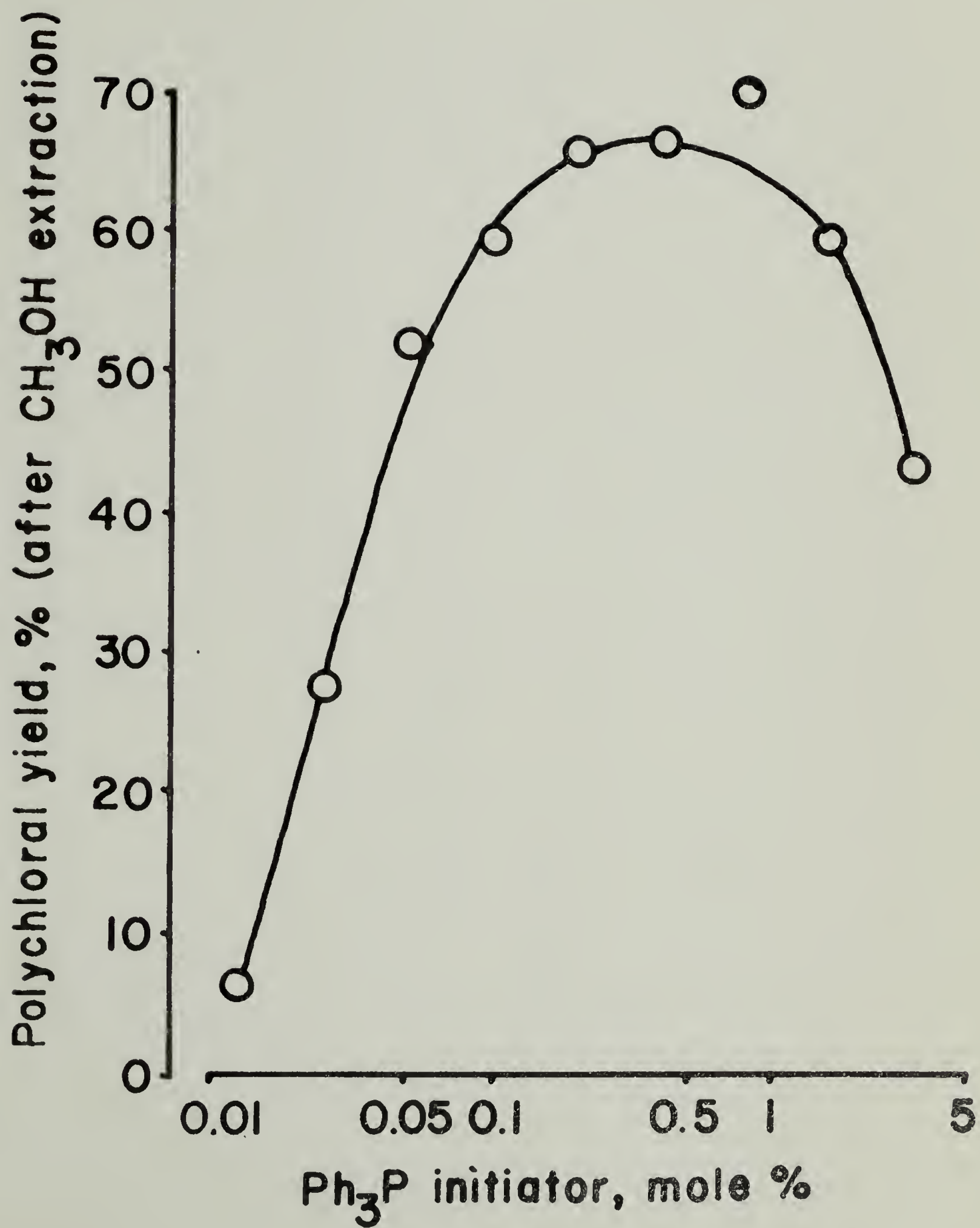
### Polychloral Yields

Yields of polychloral (after workup and extraction) for a series of chloral homopolymer blocks prepared in test tubes were determined for initiation by various concentrations of a "slow" initiator,  $\text{Ph}_3\text{P}$ . The yield data are shown in Figure 6. For chloral homopolymerization by  $\text{Ph}_3\text{P}$ , the polymer yield (after polymerization for 24 hours, heating at  $100^\circ\text{C}$ . for one hour, and Soxhlet extraction with methanol for 1 day) was very low for low initiator concentrations (below 0.05 mole % initiator with respect to chloral). From 0.2 to 0.8 mole % initiator, polymer yield reached a plateau near 70%; yields in the 70-75% range were almost always reported in a large number of chloral polymerizations (with initiation by  $\text{Ph}_3\text{P}$  in these intermediate concentrations) when polymer samples were sufficiently large ( $> 10$  g.), although yields after extraction (which causes some degradation) were often lower for films or other small samples. For  $\text{Ph}_3\text{P}$  initiator concentrations greater than 1 mole percent, polymer yield began to fall again.

The low polychloral yields at low initiator concentrations may be caused by consumption of some initiator by side reactions (as noted in the  $^1\text{H}$  NMR investigations on pp. 112-133 ) or by inability of an initiated polychloral chain to propagate beyond a certain length because of burial of the living anionic endgroup in the polychloral matrix (including its own chain) with no further diffusion of monomer to the living end possible. If a low concentration of initiator were used completely to initiate polymerization in this manner, polymerization would stop after consumption of the initiator. Also, perhaps a certain critical number of growing



Figure 6. Chloral Homopolymerization by  $\text{Ph}_3\text{P}$ : Polychloral  
Yields at Different Initiator Levels.



chains must be clustered together in order for chloral polymerization to be thermodynamically favored. The problem of poor polymerization at low initiator concentrations is discussed at greater length on pp. 147-148 with reference to the preparation of polychloral blends.

At very high  $\text{Ph}_3\text{P}$  concentrations (over 1 mole percent) in chloral homopolymerization by  $\text{Ph}_3\text{P}$ , polymer yield (on the basis of monomer) after extraction began to drop again from its levels at intermediate initiator concentrations. This phenomenon may be related to the large amounts of unreacted initiator which remain in the polymer after polymerization and are extracted by methanol or acetone, giving a polychloral sample with a more porous and open structure more susceptible to degradation by the warm methanol or acetone during Soxhlet extraction.

Although some low molecular weight polychloral might have been formed at high  $\text{Ph}_3\text{P}$  initiator concentrations, the polychloral plug obtained even with 3.2 mole percent of this initiator was hard and tough, indicating no substantial loss of molecular weight as compared with plugs prepared with lower  $\text{Ph}_3\text{P}$  concentrations. This result is in sharp contrast to the initiation behavior of LTB, which when used in concentrations greater than 1 mole percent produced polychloral with no mechanical strength, which crumbled easily to a powder. (See p. 184.)

This respective behavior observed for the two initiators is exactly that which would be predicted from the initiation mechanisms proposed previously on pp. 116 and 126. Since the initiating species formed from the tertiary butoxide ion is present quantitatively above the chloral threshold temperature and each ion is capable of immediate propagation upon cooling, the number average molecular weight of LTB-

initiated polychloral would be expected to vary inversely with molar ratio of initiator to monomer. On the other hand, in initiation with halide ions or halide ion precursors such as triphenylphosphine, the actual initiating species, tetrachloroethoxide ion, is formed slowly by reaction between chloride ion and chloral monomer. This species is thought to propagate to high molecular weight polychloral rapidly below the chloral polymerization threshold temperature. Hence increasing the halide ion concentration would increase the initiation rate proportionately but still leave it far below the initiation rate with LTB; the propagation rate would continue to be far higher and the final polymer product would be a high molecular weight solid block enclosing a substantial amount of unreacted initiator.

For a number of the chloral homopolymers produced with low concentrations of  $\text{Ph}_3\text{P}$ , hypothetical number-average degree of polymerization values were calculated from the weights of the extracted and dried polymer samples with the assumptions that all initiator molecules were effective in initiating polymer chains and that no kinetic chain transfer occurred during polymerization. These values are given as follows for five polymer plugs, each prepared from 12.1 grams of chloral:



TABLE 4

Calculated Degree of Polymerization for Polychloral Initiated with  $\text{Ph}_3\text{P}$ 

Mole %, $\text{Ph}_3\text{P}$ used	0.0125	0.025	0.05	0.1	0.2
Weight after extraction, gms.	0.727	3.440	6.313	7.247	8.059
Millimoles monomer unit	4.93	23.34	42.83	49.17	54.68
Millimoles initiator	0.0103	0.0205	0.041	0.080	0.160
Minimum $\overline{\text{DP}}_n$	480	1140	1050	615	342

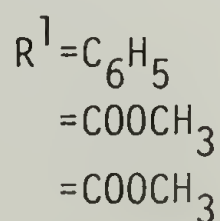
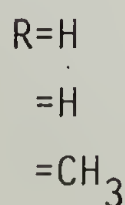
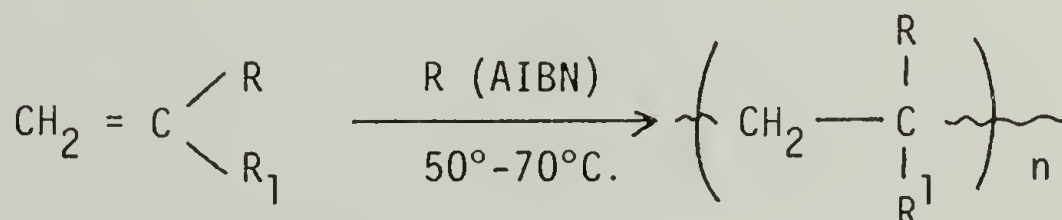
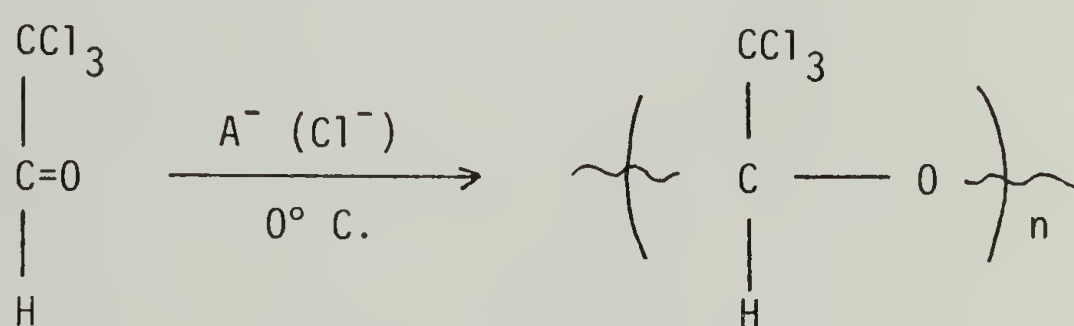
The above values should be regarded as minimum degrees of polymerization, especially at the higher initiator concentrations, since it is likely that much of the initiator does not react. It is felt that the degree of polymerization does not decrease with increasing initiator concentration since mechanical properties are unchanged and also for the theoretical reasons discussed before. Hence the number average  $\overline{\text{DP}}$  for most standard samples of polychloral initiated with  $\text{Ph}_3\text{P}$  is probably around 1000.

### C. Polychloral Blends

Because polychloral is infusible and insoluble in all solvents, blends of it with other polymers cannot be prepared by standard melt or solution blending techniques. In a preliminary investigation (214), it was found that other polymers could be incorporated into polychloral as blends by three different methods: polymerizing chloral containing a dissolved polymer, imbibing a monomer into a piece of preformed polychloral

and polymerizing the monomer in situ, or sequentially polymerizing a mixture of chloral with another monomer. The third method, which is applicable over broader monomer composition ranges than the first two, was chosen for further investigation in this work.

Polymer blends of chloral homopolymer with various olefinic addition polymers have been prepared by a sequence of two polymerizations. Initially the mixture of chloral, the olefinic addition monomer and its initiator was heated above the threshold temperature of chloral polymerization. The initiator for chloral polymerization was then added and the chloral was polymerized by cryotachensic polymerization. After the chloral polymerization the mixture was warmed to the decomposition temperature of the radical initiator for the polymerization of the olefinic addition monomer and this polymerization was then carried out within the polychloral matrix.



In order to evaluate the successful preparation of the blends the samples were usually divided into three pieces. One portion was held overnight at room temperature and 0.025 mm. pressure to remove volatile monomers and solvent. The second part was extracted with methanol. The third portion was extracted with acetone or methylene chloride. The individual samples were then analyzed for their composition by elemental analysis, TGA, and IR; the results are recorded in Tables 5-10, pp. 149, 154, 157, 159, 160, 164.

The differential thermogravimetric spectra of these polychloral blends were bimodal (Figure 7, p. 143). For each set of blends, it was found that the polychloral degraded essentially completely before the addition polymer began to degrade. The percentage of total weight loss above a specified temperature (327°C. for polystyrene, 302°C. for poly(methyl acrylate), and 277°C. for poly(methyl methacrylate)) could be plotted linearly as a function of olefinic addition polymer content of the blends as determined by carbon-hydrogen analysis (Figure 8, p. 145). Hence TGA could be used as a technique to analyze the composition of the blends.

It has been established that blends of polychloral with polystyrene, poly(methyl methacrylate) (PMMA), and poly(methyl acrylate) (PMA) could be prepared in compositions near the initial feed compositions by this sequential polymerization technique. Polymer blends of polychloral with polystyrene, PMMA and PMA were formed as translucent plugs or cylinders when the polymerization was carried out directly in the test tube or as transparent films when the polymerization was carried out in the assembly for polymer film preparation (114). Plugs and films could be extracted

Figure 7. Thermogravimetric Behavior of a 54% Polychloral-46% Polystyrene (w/w) Blend.

- a. Differential Thermogravimetric Spectrum (DTG)
- b. Thermogravimetric Spectrum (TGA)



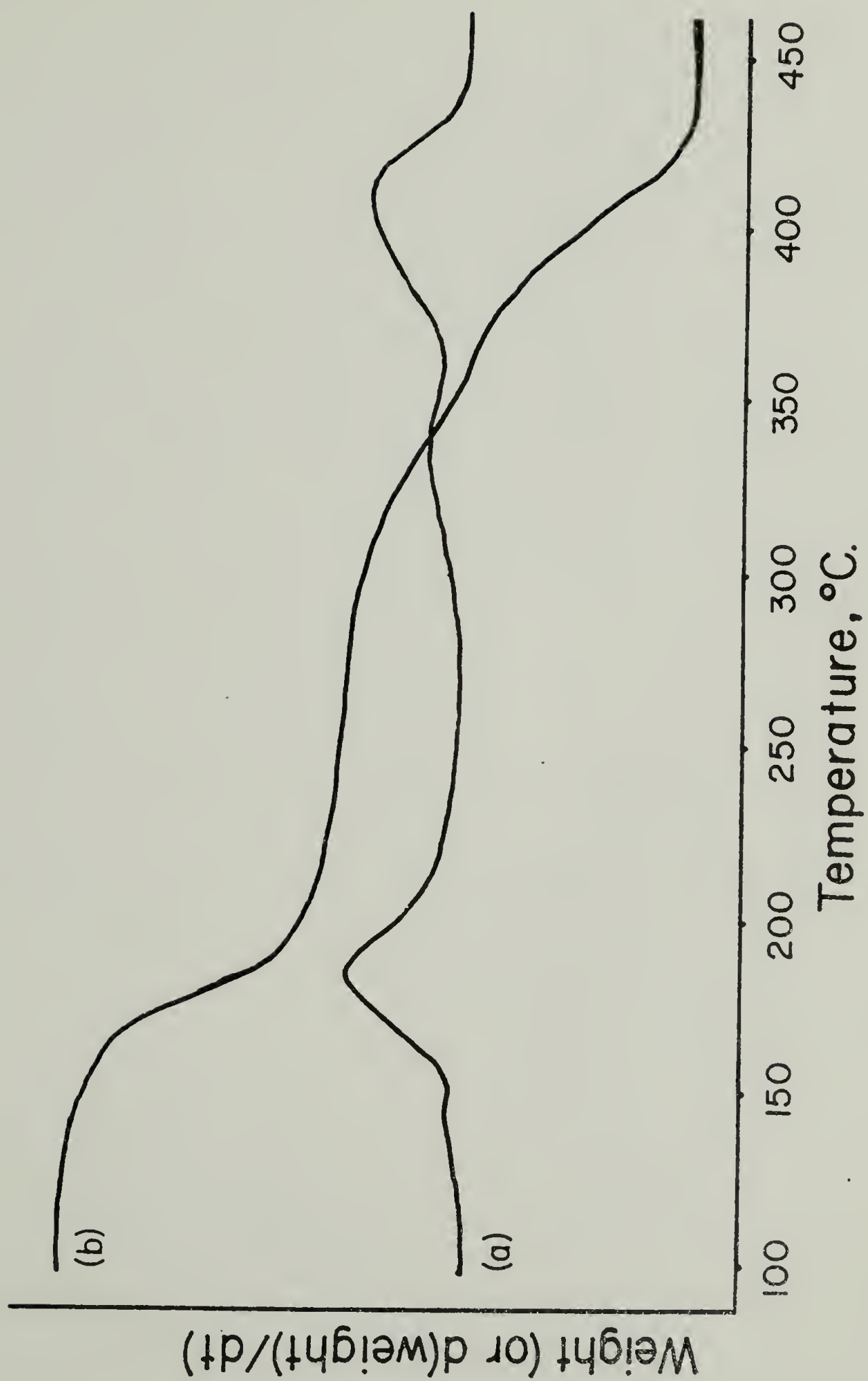
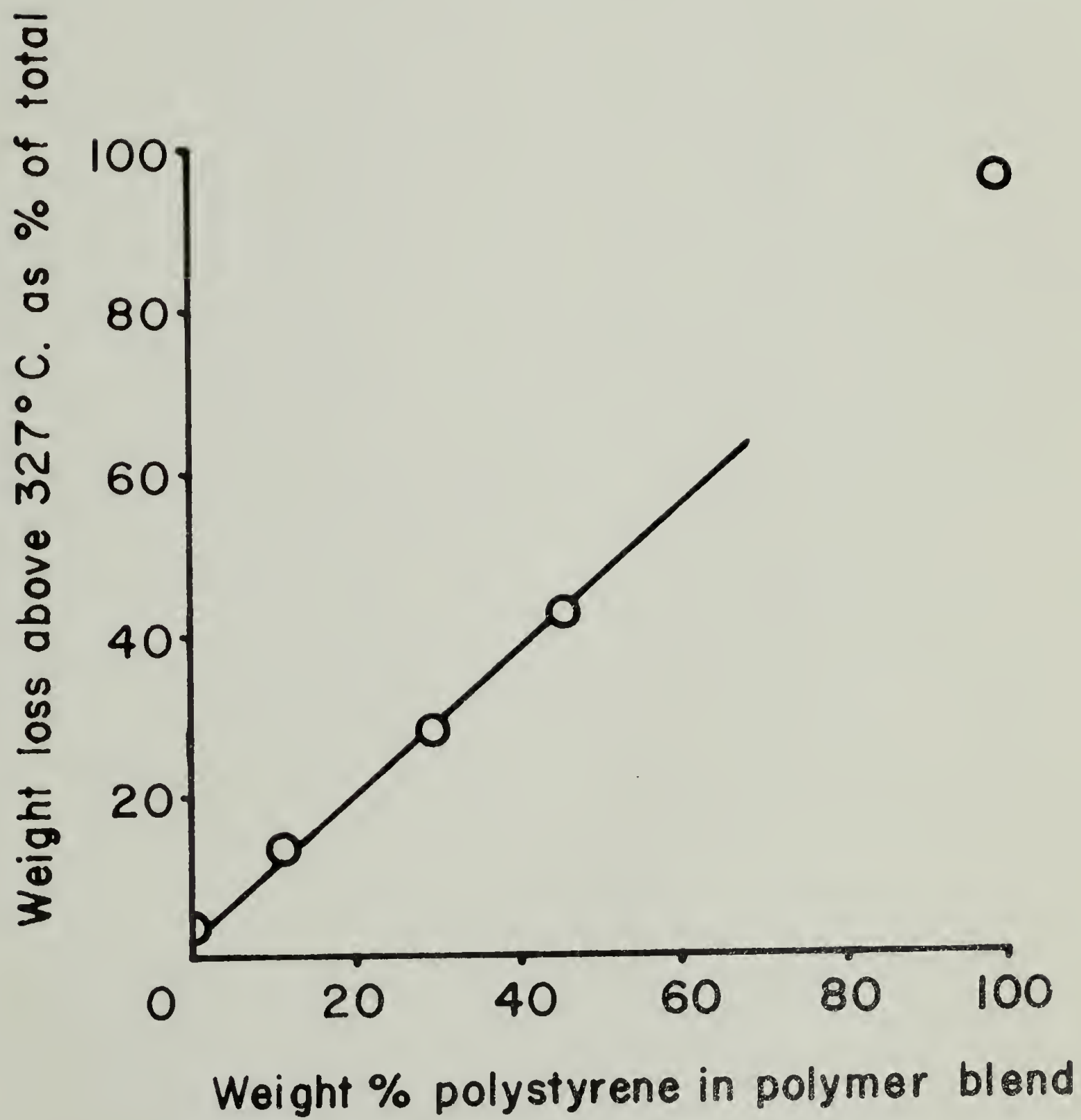


Figure 8. Thermal Degradation of Polychloral Blends with Polystyrene (heating rate: 10°C./min.; sample size: 2 mg.).



with solvents for the olefinic addition polymers or with nonsolvents for these polymers. If nonsolvents were used, for example methanol, only monomers and very low molecular weight polymers were extracted. When good solvents, such as acetone, benzene, or methylene chloride, were used, the addition polymer was either completely extracted or extracted to an extent of more than 95% which indicated that no grafting of the addition polymer on the polychloral was obtained. It has, however, been shown that unreacted chloral acts as a chain transfer agent in the polymerization of the olefinic addition polymer, even though the initiator used for these polymerizations, AIBN, produces radicals which are not sufficiently reactive to abstract chlorine from the polychloral matrix, thus causing no grafting. Furthermore, the growing polymeric radicals produced by the addition monomers used in this investigation are also apparently not reactive enough to abstract the chlorine from the polychloral matrix.

As in other anionic cryotachensic polymerizations, polychloral is deposited as a gel from the polymerization mixture which appears homogeneous but whose detailed structure and morphology have not been investigated thoroughly. However, it has chloral monomer, solvent, and, in the case of sequential polymerization, the addition monomer imbibed within its structure. The polychloral gel, however, is insoluble and most probably this insolubility is a contributing factor in its unreactivity in the subsequent radical polymerization of the addition monomer.

All our evidence has indicated that chloral polymerizes to a polymer which consists of a stable polychloral fraction, an unstable polychloral fraction and unreacted chloral monomer which is tightly



associated with the polychloral sample. Evaporation at 0.025 mm. Hg at room temperature overnight removed a substantial part of the unreacted monomer. The remainder is apparently largely used up during the polymerization of the addition monomer as a chain transfer agent. A substantial portion of the chloral polymer prepared with  $\text{Ph}_3\text{P}$  was unstable and was degraded to chloral monomer which was leached out by the solvent when the polymer sample was extracted with methanol, acetone, or methylene chloride. In the case of methanol extraction the chloral is extracted as the hemiacetal.

The polymerization of the olefinic addition monomers styrene, MMA and MA apparently goes to completion with AIBN, the initiator which was exclusively used for this polymerization. Other radical initiators such as benzoyl peroxide or other acyl peroxides or hydroperoxides were not considered because it was expected that they would interfere with the chloral polymerization. Other peroxides such as tertiary butyl peroxide could not be used because their decomposition temperature was too high, within the range where thermal depolymerization of polychloral which had been formed in the first part of the sequential polymerization occurred at a significant rate.

## 1. Synthesis and chemical characterization.

a. Polychloral-polystyrene blends. Blends of polychloral with polystyrene were prepared primarily in the form of 12 x 50 mm. plugs in test tubes with  $\text{Ph}_3\text{P}$  as initiator for the chloral and AIBN for the styrene polymerization. Blends were prepared with 0 to 50 mole % styrene in the monomer feed. It was found in initial experiments that an increase in

$\text{Ph}_3\text{P}$  initiator concentration was required to produce satisfactory chloral polymerization with decreasing chloral concentration in the mixture. As a consequence, as the concentration of styrene monomer in the mixture was increased from 0 to 50 mole % the amount of  $\text{Ph}_3\text{P}$  used to initiate the chloral polymerization was also increased from 0.2 to 2.0 mole %. The initiator concentration for the styrene polymerization was 0.3 mole % AIBN in all cases. This particular balance, which was described specifically in Table 5, p. 149, was found appropriate to prepare good blends of polychloral and polystyrene. After the polymerization was completed, the polymer blends were freed of volatiles by overnight drying at 0.025 mm. at room temperature, after which treatment 87-93% of polymer was left. Other portions of the polymer sample were also extracted with methanol, which is a nonsolvent for high molecular weight polystyrene and of course also a nonsolvent for polychloral. After 4 days of soaking with daily changes of solvent, 65-74% of the polymer blend remained depending on the individual blend composition.

As indicated earlier, this treatment removed unreacted chloral if there was any left and degraded unstable, most probably living but dormant, polychloral terminated with alkoxide end groups. The chloral conversion was 58-73% as determined by carbon-hydrogen analysis or, more simply and equally effectively, by determination of the fraction of the blend degrading above 327°C. under TGA at a heating rate of 10°C./min., which was linearly related to the fraction of polystyrene in the blend (Figure 8, p. 145). Below this temperature polychloral degrades essentially quantitatively to chloral monomer which evaporates and polystyrene does not degrade at all; the result is a bimodal DTG spectrum as shown in

TABLE 5

Composition of Polychloral-Polystyrene Blends<sup>(1)</sup>

Mole % (2) styrene (weight %)	Mole % Ph <sub>3</sub> P (3)	Total conversion after vacuum drying, in weight %	After Methanol (Acetone) Extraction			Percent chloral conversion <sup>(4)</sup> after CH <sub>2</sub> Cl <sub>2</sub> <sup>(6)</sup> extraction
			Total con- version in % (4)	Chloral conversion in %	Styrene conversion in %	Polychloral- polystyrene ratio by weight
0	0.2	87	68 (72)	68 (72)	--	100:0 (100:0)
17 (12.7)	0.4	88	65 (54)	66 (56)	60 (35)	89:1 (92:8)
28.5 (22.0)	0.8	95	74 (63)	73 <sup>5</sup> (65)	79 <sup>5</sup> (54)	77:25 (81:19)
37.5 (29.8)	1.2	94	66 (48)	66 (53)	67 (37)	70:30 (77:23)
44.5 (36.2)	1.6	95	67 (43)	62 <sup>5</sup> (50)	75 <sup>5</sup> (31)	59:41 (74:26)
50 (41.5)	2.0	93	63 (40)	58 (48)	70 (29)	54:46 (70:30)

(1) Monomer cast in cylinders (plugs), 0.3 mole % AIBN with respect to olefinic addition monomer used as initiator.

(2) Total number of moles of both monomers in mixture is 100.

(3) Chloral in initiator monomer mixture is 100.

(4) Conversion to polymer after extraction.

(5) Determined by TGA: other compositions determined by elemental analysis (C,H).

(6) Quantitative extraction of polystyrene.



Figure 7A, p. 143. This temperature and these conditions have been carefully worked out in test experiments, the results of which are summarized in Figure 8.

The methanol treatment left about 60-80% of the polystyrene in the polymer blend, as determined by elemental analysis and/or by the TGA degradation of the polymer composite. Polystyrene of very low molecular weight and some small amount of styrene monomer were extracted by the methanol. The methanol solution left a gummy residue upon evaporation.

The final compositions of the polychloral-polystyrene blends after methanol extraction showed that a polymer blend which was prepared from a chloral-styrene mixture with a weight fraction of 12.7% of styrene had 11% of polystyrene in the blend. A polychloral-polystyrene blend which contained 23% of polystyrene after methanol extraction was obtained from a monomer mixture with 22% of styrene in the feed. A polychloral-polystyrene blend with 30% of polystyrene was produced with an almost similar feed ratio. As the ratio of styrene to chloral in the monomer feed increased, the polychloral-polystyrene blends became slightly richer in polystyrene. This seems to indicate that the polymerization of chloral is somewhat decreased at high styrene concentration or that the proportion of unstable polychloral in the total increases as the polychloral-polystyrene blend increases in polystyrene composition. This is also borne out by the observation that although total conversion after vacuum drying remains relatively constant with increasing styrene/chloral ratio, the total percentage of chloral conversion to polychloral after methanol extraction decreases slightly.

If one compares the observed apparent conversion of chloral after



methylene chloride extraction with the styrene content of the monomer feed, one finds that the percentage of stable polychloral decreased as the styrene content increased in the original monomer mixture from 72% for no styrene to 47% for 41.5 wt. % styrene.

Polystyrene was isolated from the polychloral-polystyrene blends by an initial acetone extraction, which was followed by a methylene chloride extraction. Polystyrene obtained from these blends by methylene chloride extraction of samples previously extracted by acetone had an inherent viscosity of 0.10 dl/g, indicating very low molecular weight. If the same sample of styrene was polymerized with the same amount of AIBN initiator in bulk, polystyrene was obtained with an inherent viscosity of 0.94 dl/g. This indicated that the growing polystyrene radicals most likely had undergone extensive chain transfer with chloral. This is particularly important since it would have been expected that the polymerization of styrene in a rigid matrix might have been subject to the Trommsdorff effect which would have caused an increase in molecular weight. The molecular weight of polystyrene extracted from the polychloral-polystyrene blends was significantly less than that of the polystyrene obtained under bulk polymerization conditions which indicates extensive chain transfer which is expected from the polystyrene radical with chloral. Polystyrene extracted from the polychloral-polystyrene blends was also investigated by PMR spectroscopy and compared with bulk-polymerized polystyrene. The PMR spectra of the two samples were found to be superimposable.

Elemental analysis of polystyrene prepared in the presence of chloral by sequential polymerization showed 0.78% of chlorine, indicating

a number-average molecular weight of 13,000 or a  $\overline{DP}$  of about 100 if one assumes 3 Cl atoms per polymer molecule, a result which is in agreement with the chain-transfer activity of the chloral in styrene polymerization. The polystyrene samples on which the viscosity measurements and chlorine analyses were performed had been obtained by methylene chloride extraction from blends which had previously been extracted with acetone which had removed about 65% of the polystyrene. Hence the average molecular weight of the total polystyrene produced in this system was undoubtedly lower.

The low molecular weight of polystyrene produced in the sequential polymerization of polychloral and polystyrene is probably the major reason for the difference in observed styrene conversions as determined after methanol and acetone extraction. Much of the polystyrene produced is of sufficiently low molecular weight to be even soluble in, and consequently extracted by, methanol.

Polystyrene was quantitatively extracted by methylene chloride from the blends, as shown by the absence of any of the characteristic polystyrene bands in the infrared spectra of polychloral-polystyrene blends extracted with methylene chloride.

Several of the blend cylinders after extraction with acetone were almost transparent, similar to copolymers of chloral with isocyanates and in sharp contrast to unmodified chloral homopolymer which is nearly opaque. This effect was particularly pronounced with the plugs which contained 10 to 20 wt. % of polystyrene after acetone extraction. Methanol extracted blends did not show this transparency.

Polychloral-polystyrene blends were also prepared as films of

about 0.03 mm. thickness by monomer casting between glass plates separated by a Lycra fiber. The plates were placed through the same temperature cycle as the tubes for preparing the cylindrical samples. The films were extracted as were the plugs; the weight retention data are given in Table 6, p. 154. The films, as a rule, tended to contain less polystyrene with respect to polychloral than did the polymer plugs, perhaps because of (1) evaporation of some of the styrene monomer from the film assemblies during polymerization at 60°C, and (2) increased accessibility of the polystyrene in the films to the extracting solvents because of the much greater surface/volume ratio of the films as compared with the plugs. The stability of polychloral to extraction was also somewhat lower in the high-polystyrene films than in the corresponding plugs, probably because of reason (2) above.

The film data are only roughly comparable to the data for the polymer plugs, however, because the plug data represent true conversions of monomer to polymer and the film data represent simple weight retentions after a variety of treatments on the films. Determination of exact conversion data for the films would have been difficult because the exact amount of monomers used in actual film formation was not known and because the films had to be trimmed before treatment.

All films extracted with dichloromethane showed infrared spectra which were superimposable on the infrared spectrum of polychloral, with no polystyrene peaks. This was true also of the acetone-extracted films prepared from monomer mixtures containing less than 25% styrene and of the methanol-extracted films prepared from monomer mixtures containing less than 15% styrene.



TABLE 6

Weight Retention in Polychloral-Polystyrene Films<sup>(1)</sup>

Mole % (2) styrene (weight %)	Mole % Ph <sub>3</sub> P (3)	Weight Retention, %, After			
		Vacuum drying	Methanol extraction	Acetone extraction	CH <sub>2</sub> Cl <sub>2</sub> extraction (after acetone extraction)
0	0.2	85	71	79	78
17 (12.7)	0.4	95	76	57	55
28.5 (22.0)	0.8	90	66 (a)	41	39
37.5 (29.8)	1.2	92	62	48	45
44.5 (36.2)	1.6	84	43	51	49
50 (41.5)	2.0	95 (b)	70 (c)	20	17

(1) Monomer cast in films, 0.3 mole % AIBN with respect to styrene used as initiator.

(2) With respect to total number of moles of both monomers in mixture.

(3) With respect to chloral.

(a) 10% polystyrene in film by carbon analysis.

(b) 13% polystyrene in film by carbon analysis.

(c) 26% polystyrene in film by carbon analysis.



b. Polychloral-poly(methyl methacrylate) blends. Blends of polychloral and PMMA were made which contained 0 to 40 wt. % (up to 50 mole %) of MMA in the original monomer mixture. The chloral was initially polymerized by cryotachensic polymerization with 0.2-2.0 mole %  $\text{Ph}_3\text{P}$  as the initiator. As with the chloral-styrene mixtures, the amount of initiator had to be increased as the percentage of MMA in the monomer mixture was increased.

After the sequential polymerization to prepare the blends was completed, the 12 x 50 mm. cylindrical pieces were divided into three parts. The first portion was evacuated overnight at 0.025 mm. pressure and it was found that no weight loss occurred, indicating that the polymerization had gone to completion or that the small amount of chloral which may have been left over after the polymerization remained absorbed in the polymer sample. The second portion of the polymer was extracted with methanol to remove monomers and low molecular weight materials and at the same time to degrade unstable polychloral portions. The third portion was extracted with acetone for this same purpose and then divided into two sections, one of which was then extracted with methylene chloride to remove high molecular weight PMMA. Acetone was found to be ineffective in extracting the high molecular weight polymer.

The total conversion after exhaustive methanol extraction was between 85% and nearly 100%. This is substantially higher than the 60-70% which was observed for the polychloral-polystyrene blends. The fact that the conversion of MMA to PMMA is almost uniformly 100% seems to indicate that all the weight loss that is observed during the extraction comes from the degradation of an unstable fraction of polychloral which is, however,

much less in amount than in the case of blends prepared from chloral and styrene. These results indicate that the MMA and/or PMMA play an additional beneficial role for the stabilization of the polymer of the chloral portion of the blend.

The ratio of polychloral to PMMA in the final polymer is very similar to the initial feed ratio of chloral and MMA. However, at high percentages of MMA the polychloral fraction in the blend is less because of the formation of a higher percentage of an unstable fraction of polychloral which is degraded during the extraction.

PMMA, when extracted from the blends by methylene chloride, showed an inherent viscosity of 0.48 dl/g which is comparable to the inherent viscosity (0.31 dl/g) of PMMA obtained with the same monomer, initiator concentration, and polymerization temperature in bulk. The extracted sample of PMMA was compared with the bulk-polymerized sample by PMR. The spectra of the two samples were found to be superimposable.

PMMA was nearly quantitatively extracted from the blends by methylene chloride, as seen in Table 7, p. 157. Approximately 5% of the original PMMA remained in the blends after dichloromethane extraction, as shown by the carbon/hydrogen analysis of a sample containing 49 wt. % PMMA before extraction. Likewise, films of polychloral-PMMA blends continued to show definite, though not strong, PMMA carbonyl bands after methylene chloride extraction. It is believed that the lack of total extractability of PMMA is due simply to impaired diffusion of high molecular weight PMMA through the polychloral matrix. It is not believed that grafting occurred, in part because extracted PMMA gave a negative Beilstein test for chlorine and no chlorine was detected by

TABLE 7

Composition of Polychloral-Poly(Methyl Methacrylate) Blends<sup>(1)</sup>

Mole % MMA (2) (weight %)	Mole % $\text{Ph}_3\text{P}$ (3)	Total conversion after vacuum drying, in weight %	After Methanol Extraction			Percent chloral conversion <sup>(4)</sup> after $\text{CH}_2\text{Cl}_2$ extraction
			Total conversion in % <sup>(4)</sup>	Chloral conversion in %	MMA conversion in %	Polychloral-PMMA ratio in final polymer
0	0.2	87	68	68	--	100
17 (12)	0.4	100	98	93	100	83:17
28.5 (21)	0.8	100	88	82 <sup>5</sup>	100 <sup>5</sup>	67:33
37.5 (29)	1.2	100	88	77	100	63:37
44.5 (35)	1.6	100	94	91 <sup>5</sup>	98 <sup>5</sup>	63:37
50 (40)	2.0	100	84	70	100	51:49

(1) Monomer cast in cylinders (plugs), 0.3 mole % AIBN used as initiator (with respect to olefinic addition monomer).

(2) Total numbers of both monomers in mixture is 100.

(3) Chloral in initial monomer mixture is 100.

(4) Conversion of polymer after extraction.

(5) Determined by TGA: other compositions determined by elemental analysis ( $\text{C}, \text{H}$ ).



elemental analysis.

Films of blends of polychloral with poly(methyl methacrylate) were prepared between plates (following the same temperature program as the samples in test tubes) in two separate experiments, the first using 1 mole % AIBN with respect to MMA and the second 0.3%. The films were extracted and dried as were the corresponding plugs; the weight retention data are given in Table 8, p. 159. The films tended to be deficient in PMMA with respect to chloral as compared with the polymer plugs, and to be more susceptible to degradation during extraction, probably for the same reasons as the polychloral/polystyrene blend films. Dichloromethane extraction appeared to remove most, but not all, of the poly(methyl methacrylate) from the films as determined by infrared spectroscopy.

The films prepared with 0.3 mole % AIBN as initiator for the poly(methyl methacrylate) appeared to be much more stable to acetone extraction than those prepared with 1 mole % AIBN, probably because of higher molecular weight of the poly(methyl methacrylate). The stabilities of the two classes of films to methanol extraction were not significantly different. No attempt was made to determine the intrinsic viscosity of the poly(methyl methacrylate) extracted from the films because of the small quantities available.

c. Polychloral-poly(methyl acrylate) blends. Blends of polychloral and PMA were also prepared under conditions similar to those developed for the preparation of polychloral-PMMA blends (Table 9, p. 160). The combined monomer conversion to polymer blend after vacuum drying was always greater than 85%, indicating high conversions of both



TABLE 8

Weight Retention in Polychloral-Poly(Methyl Methacrylate) Films<sup>(1)</sup>

Mole % MMA (2) (weight %)	Mole % Ph <sub>3</sub> P (3)	Weight Retention, %, in First (Second) Experiment, After			
		Vacuum drying	Methanol extraction	Acetone extraction	CH <sub>2</sub> Cl <sub>2</sub> extraction (after acetone extraction)
0	0.2	86	64	69	
17 (12)	0.4	94 (93)	69 (74)	64 (77)	(62)
28.5 (21)	0.8	94(a) (89)	58 (63)	48 (66)	(61)
37.5 (29)	1.2	92 (89)	53 (54)	26 (55)	(36)
44.5 (35)	1.6	95 (91)	58 (61)	20 (57)	(49)
50 (40)	2.0	94 (90)	44 (56)	11 (42)	(29)

(1) Monomer cast in films, 1 mole% AIBN with respect to MMA used as initiator in first experiment, 0.3 mole% in second experiment.

(2) With respect to total number of moles of both monomers in mixture.

(3) With respect to chloral.

(a) 7% poly(methyl methacrylate) in film by carbon analysis.

TABLE 9

Composition of Polychloral-Poly(Methyl Acrylate) Blends<sup>(1)</sup>

Mole % MA (2) (weight %)	Mole % Ph <sub>3</sub> P (3)	Total conver- sion after vacuum drying, in weight %	After Methanol Extraction				Percent chloral conversion <sup>(4)</sup> after acetone extraction
			Total conversion in % <sup>(4)</sup>	Chloral conversion in %	MA conversion in %	Polychloral- PMA ratio in final product	
0	0.2	88	68	68	---	100	72
17 (10.6)	0.4	100	83	79	100	86:14	84
28.5 (18.9)	0.8	95	64	58 <sup>5</sup>	92 <sup>5</sup>	73:27	47
37.5 (26.0)	1.2	96	57	45	90	59:41	39
44.5 (32.1)	1.6	89	50	26 <sup>5</sup>	99 <sup>5</sup>	36:64	46
50 (36.9)	2.0	86	44	24	78	35:65	32

(1) Monomer cast in cylinders (plugs), 0.3 mole% AIBN with respect to olefin addition monomer used as initiator.

(2) Total number of moles of both monomers in mixture is 100.

(3) Chloral in initial monomer mixture is 100.

(4) Conversion to polymer after extraction.

(5) Determined by TGA: other compositions determined by elemental analysis (C,H).

monomers to polymer. The total conversion to polymer blend after methanol extraction decreased as the mole percent MA in the monomer feed mixture increased. The percent conversion of MA to methanol-insoluble PMA dropped from nearly quantitative in the 17 mole % MA mixture to 78% in the mixture containing 50 mole % MA. The chloral conversion to methanol-stable polychloral decreased from 79% at 17 mole % to 24% at 50 mole % MA in the initial monomer mixture.

These values are also reflected in the drop of the total conversion after methanol extraction from 83% to 44% with increasing MA fraction in the monomer feed. The relatively high value of MA conversion to PMA combined with a low chloral conversion value gave a final blend mixture consisting of 2 parts of PMA to 1 part of polychloral at 50 mole % MA in the feed.

In polychloral-PMA blends the extracted stable blends are enriched in PMA over the initial monomer feed ratios and indicate that an unusually large proportion of the polychloral portion of the blend is degraded during the methanol extraction. We have no plausible explanation at this time why a much larger fraction of the chloral polymer portion is unstable (76% vs. 32% in the standard) when the chloral polymerization with  $\text{Ph}_3\text{P}$  is carried out in the presence of large amounts of MA, although the impurity present to the extent of 0.2% in the methyl acrylate may have been one factor (p. 45 ). A larger amount of  $\text{Ph}_3\text{P}$  initiator had always been used for the chloral polymerization at the higher concentrations of olefinic monomers used for the blends but no such pronounced decrease of the stable fraction had been detected in blends of polychloral-polystyrene and polychloral-PMMA at higher concentrations of

$\text{Ph}_3\text{P}$  and olefinic addition monomer.

The acetone extracted samples of high PMA-polychloral ratio also show substantially decreased conversion of chloral to polychloral which can only mean that this is an inherent property of the sample, not of the extraction method.

PMA extracted from the blends of polychloral and PMA had an inherent viscosity of 0.31 dl/g in comparison with an inherent viscosity of 0.89 dl/g for PMA prepared in bulk with the same monomer, initiator concentration, and polymerization temperature as for the blend polymerization. It could be that in the bulk polymerization branching occurred with a subsequently higher viscosity-average molecular weight in the resultant polymer which is not possible in the case of the MMA polymerization, but we have not attempted to establish this fact.

Some chain transfer with chloral monomer does occur in the radical polymerization of MA in the polychloral matrix, because acetone-extracted PMA showed a chlorine content of 0.69% by elemental analysis. With the assumption of 3 Cl atoms per polymer molecule, this result indicates a number-average molecular weight of 15,000 corresponding to a  $\overline{\text{DP}}$  of about 180. This chain transfer in MA polymerization is not as effective as in styrene polymerization but more effective than in MMA polymerization, which showed no incorporation of chlorine into PMMA and whose average molecular weight was also not decreased when the polymerization was carried out in sequence after chloral polymerization.

Films of blends of polychloral with poly(methyl acrylate) were prepared between plates (following the same temperature program as the samples in test tubes) in two separate experiments, the first using



0.6 mole % AIBN with respect to MA and the second 0.3%. The films were extracted and dried as were the corresponding plugs; the weight retention data are given in Table 10, p. 164.

The stability of the films to vacuum drying and methanol extraction differed little from that of the corresponding plugs. However, the films, in the few cases in which elemental analyses were determined, contained less than 15% of poly(methyl acrylate). Considerable evaporation of methyl acrylate most likely occurred during polymerization.

The reason for the considerably different stability to acetone extraction of the films prepared in the two separate experiments is not known. It is not caused by different amounts of poly(methyl acrylate) being left in the films, because the acetone-extracted films almost always showed no carbonyl peak characteristic of poly(methyl acrylate).

d. Interpenetrating networks. Interpenetrating networks, or perhaps more properly pseudointerpenetrating networks (215) of polychloral with polystyrene and poly(methyl methacrylate) have been prepared from chloral/styrene/divinylbenzene and chloral/methyl methacrylate/ethylene dimethacrylate mixtures respectively (216). In 0.03-0.05 mm. films of these compositions, substantial fractions of the polystyrene and almost all of the poly(methyl methacrylate) produced (at high methyl methacrylate concentrations) were crosslinked and not extractable with benzene. However, to obtain this degree of crosslinking, relatively high concentrations of difunctional monomer (5.4% of divinylbenzene and 7.6% of ethylene dimethacrylate) had to be used, and the resultant films were very brittle. This work is covered in more detail in reference (216).

TABLE 10

Weight Retention in Polychloral-Poly(Methyl Acrylate) Films<sup>(1)</sup>

Mole % MA <sup>(2)</sup> (weight %)	Mole % Ph <sub>3</sub> P <sup>(3)</sup>	Weight Retention, %, in First (Second) Experiment, After		
		Vacuum drying	Methanol extraction	Acetone extraction
0	0.2	88 (83)	79 (78)	80 (69)
17 (10.6)	0.4	90 (93)	75 (78(b))	69 (67)
28.5 (18.9)	0.8	88 (95)	75 (80(c))	63 (43)
37.5 (26.0)	1.2	90 (90)	71 (72)	52 (49)
44.5 (32.1)	1.6	81 (89(d))	64 (63)	54 (37)
50 (36.9)	2.0	89(a) (92)	70 (71)	48 (25)

(1) Monomer cast in films, 0.6 mole% AIBN with respect to MA used as initiator in first experiment, 0.3 mole% in second experiment.

(2) With respect to total number of moles of both monomers in mixture.

(3) With respect to chloral.

(a) 7% poly(methyl acrylate) in film by carbon analysis.

(b) 3% poly(methyl acrylate) in film by carbon analysis.

(c) 5% poly(methyl acrylate) in film by carbon analysis.

(d) 14% poly(methyl acrylate) in film by carbon analysis.

## 2. Physical characterization.

a. Electron microscopy. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements have been carried out on a number of chloral homopolymers initiated with LTB and  $\text{Ph}_3\text{P}$  and also on methanol- and acetone-extracted polychloral/polystyrene blends. When surfaces of polychloral samples (prepared with either of the above initiators and extracted with methanol or acetone) were examined by SEM, the morphology appeared to be strongly dependent on the way in which the surface was prepared. Surfaces which had been exposed to the atmosphere during polymerization (the top surfaces of the polymer in the test tubes) were very uneven, with numerous pores of 0.5 to 3  $\mu\text{m}$  in diameter. Fracture surfaces prepared by fracturing a block of polychloral at  $-178^\circ\text{C}$ . with a hammer and razor blade showed a variable morphology. Some fracture surfaces prepared from LTB-initiated polychloral showed a porous morphology similar to that found for surfaces exposed during polymerization; in others, the only evident surface feature was a striated pattern possibly produced by the razor blade itself. Others showed lines in a "river" pattern produced by internal stresses within the polymer sample. Fracture surfaces in  $\text{Ph}_3\text{P}$ -initiated samples were sometimes fibrous or porous and sometimes almost featureless; it was often difficult to determine which fracture surface features actually reflected the internal morphology of the polymer sample and which were the result of experimental artifact.

Polychloral (only unstabilized polychloral was examined) proved highly susceptible to degradation under the electron beam, in a manner similar to poly(methyl methacrylate). When smooth fracture surfaces were coated with Au/Pd and examined at high magnification, decomposition



products tended to collect under the metallic coating, producing a bubble which would finally burst. On uneven surfaces, however, this did not occur; the electron beam burned a clean hole into the surface.

Sections of polychloral and also of methanol and acetone extracted polychloral-polystyrene blends were cut with a microtome and examined by TEM and scanning transmission electron microscopy (STEM). The sections were 600 to 1500 Å thick. Upon examination, the polychloral sections appeared to have a porous structure at 3000-6000 X and a mica-like layered appearance at 50,000 X. An opaque methanol-extracted blend of polychloral with 46 wt. % polystyrene showed at 8000 X a surface similar to that of the unmodified polychloral but somewhat smoother and with less apparent porosity. When the magnification was increased to 50,000 X in an attempt to detect domain structure, satisfactory resolution could not be obtained. A nearly transparent acetone-extracted blend of polychloral with 23 wt. % polystyrene had, at 6000 and 15,000 X, a nearly featureless appearance, not greatly different from that of a solvent-cast poly(methyl methacrylate) film. In attempted examination of polychloral-poly(methyl methacrylate) blends at 40,000-60,000 X, satisfactory resolution for structural determination could not be obtained.

With respect to our previous hypothesis as to the compatibility of polychloral-polystyrene blends, the available evidence from our preliminary electron microscopic work, particularly the electron micrographs for the nearly transparent acetone-extracted blends, appears consistent with this hypothesis but not proof for it. There is no evidence from electron microscopy for a domain structure.



b. Tensile testing. Films of chloral homopolymer (initiated with  $\text{Ph}_3\text{P}$ ) and its blends with polystyrene, poly(methyl methacrylate) and poly(methyl acrylate) were subjected to tensile testing with the TENSILON tensile tester at an elongation rate of 40 mm./min. The film thickness ranged from 0.03 to 0.07 mm., the width from 7 to 11 mm., and the length between grips from 20 to 40 mm. The observed ranges of tensile strength, tensile modulus, and elongation to break observed for unmodified and modified polychloral are listed in Table 11, p. 170, and compared with literature values (217) typical of commercial grades of general purpose polystyrene and poly(methyl methacrylate). A typical stress-strain curve of unmodified polychloral is shown in Figure 9 (p. 169).

As can be seen from Table 11, the incorporation of 13 wt. % of polystyrene or 7 wt. % of poly(methyl methacrylate) into polychloral films produced considerable increases in tensile strength and modulus, but at significant cost in elongation to break. The blends appeared to have tensile properties falling between those of polychloral and polystyrene or poly(methyl methacrylate) in these three categories. Incorporation of poly(methyl acrylate) (6 wt. %) decreased elongation to break but produced no corresponding increase in tensile strength or modulus. (Unfortunately, the tensile modulus and elongation values given here are somewhat uncertain because some of the thin films used had a tendency to slip within the grips of the instrument during measurement. Although some films were mounted between thicker sheets of polychloral with epoxy resin to avoid this problem, the epoxy resin adversely affected the tensile strength of the polychloral.)

Figure 9. Typical Stress-Strain Curve of High Molecular Weight Polychloral Film.

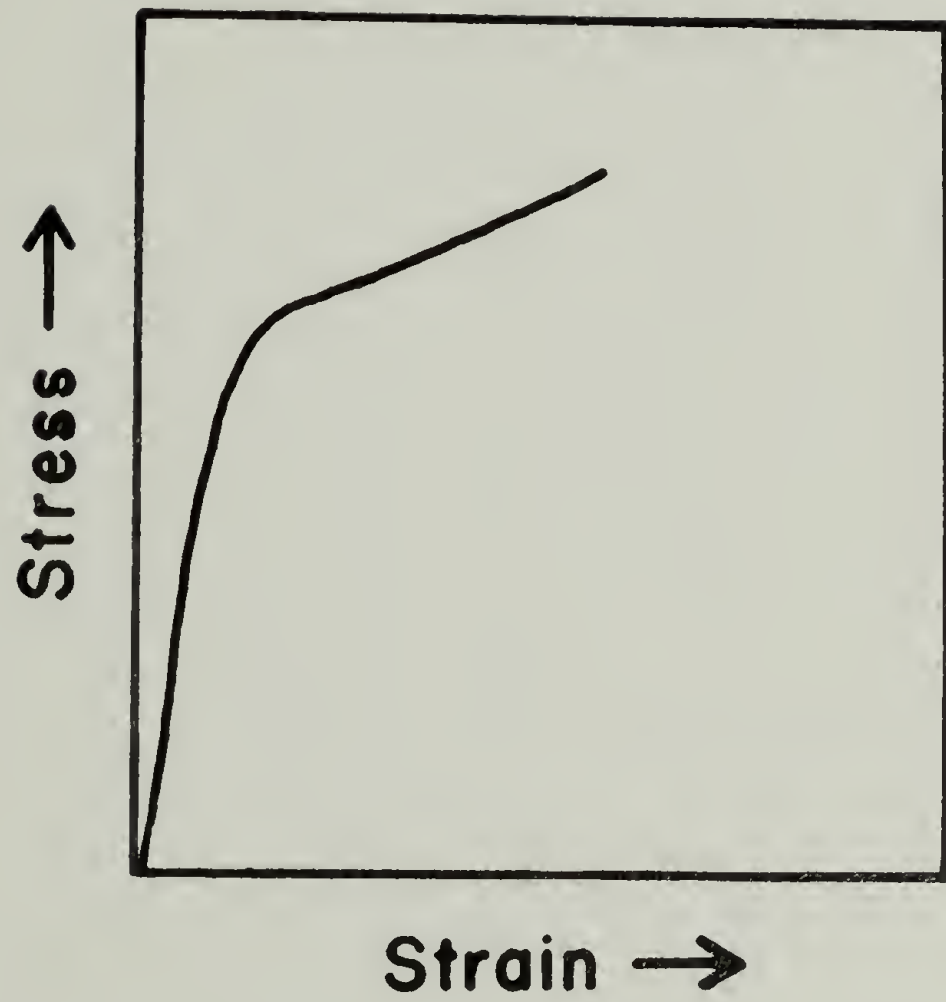


TABLE 11

## Polychloral and Polychloral Blend Tensile Characteristics

Addition polymer in blend (weight %)	Tensile Strength, psi (MPa)	Elongation, % to break	Tensile modulus, psi (MPa)
Polystyrene (13%)	6500-8000 (45-55)	5-8	230-270,000 (1.6-1.85) (a)
Poly(methyl methacrylate) (7%)	6000-7000 (40-50)	4-5	200-230,000 (1.4-1.6) (a)
Poly(methyl acrylate) (6%)	4000-6500 (27-45)	3-8	170-205,000 (1.15-1.42) (a)
None	5000-6000 (27-40)	5-30	185-210,000 (1.25-1.43)
Comparisons: (b)			
Polystyrene, general purpose	5000-12000 (35-80)	1-2.5	400-600,000 (2.7-4.1)
Poly(methyl methacrylate), molding grade	7000-11000 (50-75)	2-10	380-450,000 (2.6-3.1)

(a) Minimum values; somewhat uncertain due to experimental problems.

(b) Data from Modern Plastics Encyclopedia, 1974-75.



The elongation range reported for unmodified polychloral was very large because of differing quality of the polychloral films. If precautions taken to exclude water from the film mold before polymerization were not rigorous enough--if drying temperatures were not high enough, or the glass plates were allowed to remain out of the oven too long during mold assembly--the resultant films would tend to have a tensile strength of 20-30 MPa with an elongation to break of 5%. Comparable values for a "good" chloral homopolymer film were 40 MPa and 25%. This difference was also very pronounced in the stress-strain curve (Figure 9, p. 169). Tough polychloral films had a substantial degree of elongation beyond the yield point. The length of the post-yield curve was greatly reduced in blends of polychloral with other polymers (though yield and break strength were increased), while brittle polychloral films of poor quality showed no yield point at all, with a short straight line from origin to break.

c. Continuing work in physical characterization of polychloral blends. Films of polychloral blends are currently being studied by wide-angle X-ray scattering (WAXS) to determine the effect of incorporation of the nonchloral polymer upon the crystallinity of the polychloral; it is also planned to use small-angle X-ray scattering (SAXS) and small-angle light scattering (SALS) to determine the sizes of possible domains. This work is now being carried out by Dr. Yuzo Sumida of this laboratory. Although DSC and Rheovibron measurements (to determine polymer compatibility) are useless with blends containing unstabilized chloral homopolymer because the onset of decomposition of this polymer falls near 100°C., it is planned to carry out such measurements on blends of poly-

styrene with amorphous chloral-isocyanate copolymers, which are much more stable than chloral homopolymer. These latter blends were synthesized by Dr. Shamil Vezirov in this laboratory.

D. Elucidation of Nature of Endgroups in  
"Stable" and "Unstable" Polychloral

One of the problems in past attempts to stabilize polychloral thermally has been that the nature of the actual endgroups of polychloral, especially of polychloral prepared by anionic initiation, was not known.

Rosen and coworkers (146) prepared polychloral by initiation with Brönsted and Lewis acid initiators such as  $\text{H}_2\text{SO}_4$ ,  $\text{AlCl}_3$ , and  $\text{AlBr}_3$ , anionic initiators such as tributylamine and methyltributylammonium iodide, and organometallic initiators such as diethylzinc. In all cases, the initiators were added to chloral monomer (with or without solvent) below its threshold polymerization temperature; the polymer therefore formed as a powder instead of a coherent block or film. The polymer was then treated with carboxylic acid chlorides or anhydrides at 125-180°C. The stability to treatment with DMF at 130°C. for 30 minutes was vastly increased by this "endcapping" procedure. An attempt was made to determine molecular weight of the polychloral by treating the polymer with lauroyl chloride at 180°C. and analyzing the treated polymer for carbon, with the assumption that each polymer chain had two hydroxyl endgroups which were fully acylated by the treatment. By this procedure, the degree of polymerization of all cationically initiated polychloral samples tested was determined to be below 200,

while the best anionically initiated samples were estimated as having  $\overline{DP}$  values near 600. However, the precision of this method was very low for  $\overline{DP}$  values above 300, and the presence of two hydroxyl endgroups on all polychloral chains could not be verified.

In polychloral determined as being of "low" molecular weight by the above procedure, infrared absorptions which had been attributed by Novak and Whalley (139) to hydroxyl groups were seen, which disappeared after treatment with the acid halides, to be replaced by a peak in the carbonyl region ( $1753\text{ cm}^{-1}$ ) attributed to ester endgroups. In polychloral whose  $\overline{DP}$  was estimated at 550, neither type of peak could be seen.

No change in the infrared spectrum of a polychloral film prepared cryotachensically by anionic initiation was detected after refluxing with acetyl chloride (191). However, the use of acetyl chloride or other acyl halides or acid anhydrides in a cryotachensic polymerization mixture itself did lead to some thermal stabilization of the resultant polychloral and the appearance of carbonyl absorption in the infrared spectrum (191). In this case, the degree of polymerization of the resultant polychloral was estimated at near 200 by infrared carbonyl absorption intensity, and the films were brittle with poor mechanical properties.

However, it was known from previous preliminary work that polychloral prepared with different initiators had different degrees of thermal stability, with polychloral prepared anionically by cryotachensic methods often less stable than cationically prepared polychloral. This suggested a difference in endgroups. The following work was under-



taken in an attempt to determine, by infrared spectroscopy, extraction stability and DTG analysis, the endgroups in polychloral prepared by different initiators and given different posttreatments.

1. Attempted endgroup determinations on high molecular weight polychloral films. A number of polychloral films were prepared with low concentrations of LTB, pyridine and  $\text{Ph}_3\text{P}$  initiators, to determine the stabilizing effect and infrared spectral changes caused by posttreatment with a refluxing 0.85M solution of  $\text{PCl}_5$  in  $\text{CCl}_4$ , a procedure known from past preliminary experiments (176) to increase the thermal stability of chloral homopolymer.

The films were prepared between glass plates by the standard procedure (114). In some of the early experiments, the film molds were assembled from glass plates, rubber tubing, and clamps before the glass plates had been dried in the oven; the mold assemblies were then placed in a 70-85°C. oven for a few hours or overnight to dry before use. However, this proved to be an inadequate drying procedure, yielding often gelatinous films composed predominantly of monomer. Drying of the plates overnight at 120-150°C. followed by removal from the oven, rapid assembly of the film molds, and return to a 70°C. oven not more than two hours before use proved to be an adequate drying procedure for obtaining tough films.

After removal from the molds, the films were extracted with acetone in a Soxhlet extractor and then treated with a refluxing 0.85M solution of  $\text{PCl}_5$  in  $\text{CCl}_4$  for from 4 to 16 hours. DTG spectra were determined after, and in some cases before,  $\text{PCl}_5$  treatment, and infra-



red spectra before and after  $\text{PCl}_5$  treatment were determined for all suitably thin films (Table 12, p. 176).

Extraction stability of films prepared under these conditions was much lower than for massive polychloral plugs prepared in test tubes (cf. p. 153), possibly because of better penetration of the extracting solvent into the films which have high surface area. Although the control polychloral films in the preparation of blends appeared much more stable to extraction than the films prepared in this series of experiments, the extraction conditions were not the same, with the blend controls being extracted at room temperature and the films from this experiment at the boiling point of acetone in a Soxhlet extractor. The films initiated with pyridine were less than 1% stable to extraction and extremely brittle.

The  $\text{PCl}_5$  treatment was most effective generally with thinner films, especially those initiated with LTB. These often could, after a few hours in refluxing  $\text{PCl}_5/\text{CCl}_4$ , be brought to a point at which the onset of weight loss occurred at 170-200°C. and the DTG peak above 280°C., in contrast to the decomposition onset near 100°C. and DTG peak near 200°C., generally observed for unstabilized extracted  $\text{Ph}_3\text{P}$ -initiated polychloral (see p. 202). Stabilization of thicker films (and a few of the thin ones) with  $\text{PCl}_5$  was much less successful, with the onset of weight loss occurring at 110-140°C. and DTG peaks in the 180-220°C. range, characteristic of unstabilized polychloral chains, appearing frequently in the DTG spectra.

Infrared spectra on all thin films (before treatment with  $\text{PCl}_5$ ) were similar and are listed in Table 13, p. 178. (Actual typical spectra

TABLE 12  
Preparation of Polychloral Films at Low Initiator Concentration

Initiator	Film thickness, mm.	% Stable fraction after extraction	PCl <sub>5</sub> treatment time, hr.	DTG decomposition onset (°C.)	DTG peaks (°C.)
Ph <sub>3</sub> P, 0.2 mole%	0.03	14%	8	130	182, 282
Ph <sub>3</sub> P, 0.3 mole%	0.06		4	140	222, 320
"	0.03		8	180	310
"	0.03		3	180	310
"	0.03		8	180	325
"	0.50	54%	16	150	202, 357
"	0.04	40%	10	130	212, 334
Pyridine, 2 mole%	(too brittle to determine)				
"	0.7% 0.9%				
Ph <sub>3</sub> P, 0.3 mole%	0.25	33%	16	130	187, 345
"	0.08	30%	10	130	222, 320
"	0.02	47%	10	110	149, 277
"	0.20	35%	16	130	187, 327
LTB, 0.3 mole%	0.02	38%	7	190	282
"	0.02	35%	7	170	282

are shown on p. 308.) These spectra are compared with the infrared spectrum obtained by Novak and Whalley (139) for polychloral produced by cationic initiation with sulfuric acid. All of the major peaks are the same in the two spectra, but there are differences with respect to some of the weaker absorptions. Most significantly, no film prepared by initiation with pyridine or  $\text{Ph}_3\text{P}$  showed broad absorptions in the region near  $3300\text{--}3500\text{ cm}^{-1}$  characteristic of hydroxyl endgroups. By contrast, polychloral powders initiated with  $\text{H}_2\text{SO}_4$  and  $\text{SbCl}_5$ , when examined as  $\text{CCl}_4$  mulls between NaCl plates, showed a very strong, broad peak at  $3400\text{ cm}^{-1}$ , indicative of hydroxyl endgroups. Hence hydroxyl groups could not be detected in the films of thickness  $0.02\text{--}0.06\text{ mm}$ . used, but the actual endgroups remained unknown. No change in the infrared spectrum in this region was noted upon treatment of the films with  $\text{PCl}_5$ .

One change did occur in the infrared spectra of most of the films in this series upon  $\text{PCl}_5$  treatment. In the polychloral films which had been extracted with boiling acetone but had not been treated with  $\text{PCl}_5$ , a small sharp peak at  $1260\text{ cm}^{-1}$  appeared which disappeared upon  $\text{PCl}_5$  treatment. It was thought initially that this peak might be due to alkoxide endgroups, but, for unknown reasons, the peak did not appear at all in most polychloral films prepared later. The peak generally appeared in films extracted with hot acetone immediately after polymerization; it may represent a chloral-acetone reaction product.

Hydroxyl peaks which disappeared upon stabilization by esterification or etherification had been noted in the past in the infrared

TABLE 13

Comparison of Infrared Absorptions of Anionically Initiated Polychloral Films and Cationically Initiated Polychloral Powder of Novak and Whalley (139)

Wave number, cm <sup>-1</sup> (films)	Wave number, cm <sup>-1</sup> (Novak and Whalley)	Peak assignments (Novak and Whalley)
3980 (vw)		
3810 (vw)		
3640 (vw)		
	3500 (vw) }	OH stretching (end groups)
	3360 (vw) }	
2955 (m)	2945 (m)	CH stretching
	2910 (w)	? CH stretching (non-crystalline)
	2845 (vw)	CH stretching or combination
2705 (vw)		
	2680 (vw)	1360 + 1325
2620 (w)		
2350 (w)		
2190 (w)	2180 (vw)	2 x 1085
2150 (w)	2150 (vw)	1085 + 1070
1385 (w)	1386 (w)	803 + 582
1360 (s)	1360 (m)	CH bending
1325 (s)	1325 (s)	CH bending
1260 (w, irreproducible)		
1230 (vw)	1230 (vw)	
1125 (vs)	1122 (vs) }	C-O stretching
1085 (s)	1085 (vs) }	
1070 (vs)	1070 (vs) }	
1030 (m)	1028 (m)	CH bending (?)
970 (vs)	975 (vs)	C-O stretching



TABLE 13 (continued)

Wave number, cm <sup>-1</sup> (films)	Wave number, cm <sup>-1</sup> (Novak and Whalley)	Peak assignments (Novak and Whalley)
847 (s)	842 (vs)	C-C and C-Cl stretching
830 (s)	840 (vs)	
805 (vs)	803 (vs)	
682 (s)	681 (s)	C-Cl stretching
678 (s)	675 (s)	
	630 (w,sh)	
585 (s)	582 (s)	skeletal, non-crystalline
492 (m)	496 (m)	C-Cl stretching
		C-Cl stretching or skeletal bending
	463 (w)	
	448 (w)	
	422 (vw)	skeletal bending
	402 (vw)	
	388 (vw)	
	376 (sh)	
365 (m)	366 (m)	? C-Cl bending
	345 (vw)	
	330 (vw)	
	306 (w)	
272 (w)		
265 (w)		

spectra of films of polyacetaldehyde and poly(n-butyraldehyde) (218). The failure to observe such absorptions in polychloral films prepared by standard cryotachensic procedures left open the question as to the nature of the actual endgroups of polychloral.

2. Preparation, stabilization and infrared study of low molecular weight polychloral. It was felt that a possible reason for absence of observable hydroxyl absorption in the infrared spectra of the polychloral films described in the previous section was that the molecular weight of the polychloral was too high for endgroup absorptions to be observed reliably. Hence it was decided to prepare polychloral of lower molecular weight. To accomplish this, increased concentrations of a "rapid" initiator, LTB (for which initiation was instantaneous relative to propagation) were used. "Slow" initiators, such as  $\text{Ph}_3\text{P}$ , are ineffective in producing low molecular weight polychloral even when used at high concentration, for reasons discussed on pp. 137-138.

Two experiments were performed in an attempt to prepare (and characterize) low molecular weight polychloral by cryotachensic techniques. In the first experiment, plugs and films of polychloral were prepared from polymerization mixtures containing from 0.1 to 2.5 mole percent LTB with respect to chloral. The resultant polymers were treated by one of five different procedures and the stability of the polymers after these treatments was determined; infrared and sometimes DTG spectra were taken on the samples after treatment. The results are shown in Table 14, p. 181.

Several salient points are obvious from Table 14. First,

TABLE 14

Stability and DTG Determinations for Low Molecular Weight  
Polychloral Films Subjected to Various  
Posttreatments

LTB concentration, in mole%, used for chloral initiation	Treatment				
	A	B	C	D	E
<u>0.1</u>					
Stability, in %	100	4	87	98	98
DTG peaks, °C. (% of total area)	224 (100)		217 (100)	205 (36) 300 (64)	300 (100)
<u>0.2</u>					
Stability, in %	100	11	89	96	96
DTG peaks, °C. (% of total area)		240 (100)			
<u>0.4</u>					
Stability, in %	100	4	86	89	90
DTG peaks, °C. (% of total area)				200 (40) 290 (60)	
<u>0.8</u>					
Stability, in %	100	1	77	86	87
<u>1.6</u>					
Stability, in %	100	0	75	81	86
<u>2.5</u>					
DTG peaks, °C. (% of total area)	225 (100)			165 (78) 274 (22)	290 (100)

Treatments: A - vacuum drying at room temp./20 mm. pressure for 2 hrs.  
 B - methanol extraction for 3-4 days at room temp. followed by (A).  
 C - methanol/10% HCl treatment for one day followed by (B).  
 D - treatment with refluxing acetyl chloride for 4 days, followed by (B).  
 E - treatment with 1 M  $\text{PCl}_5/\text{CCl}_4$  for 4 days at 60°C. followed by (B).

polychloral initiated with LTB is very unstable to extraction with methanol, with stability decreasing generally with increasing amount of LTB initiator used. The sample prepared with 2.5 mole % LTB (for which the film was not coherent and the friable polymer plug was used) depolymerized completely upon treatment with methanol. Preliminary treatment for one day with methanol containing 10% (v/v) of concentrated aqueous HCl produced over 80% stabilization to methanol extraction in the polychloral films prepared with less than 0.4 mole % LTB and over 70% stabilization in the lower molecular weight polymer. Treatment with acetyl chloride or phosphorus pentachloride caused stabilization to methanol extraction approximately 10% in excess of that obtained by pretreatment with acidified methanol alone. Simple vacuum drying at 20 mm. pressure with no prior extraction caused no weight loss; volatile chloral monomer had apparently evaporated before the films were placed into the vacuum chamber.

DTG spectra of samples unextracted, extracted with methanol, or pretreated with acidified methanol followed by extraction with methanol were all similar, with peaks between 215°C. and 240°C. The samples treated with acetyl chloride showed considerably increased stabilization, with the DTG spectra bimodal, showing one peak near or below 200°C. and another in the range of 270-300°C. This bimodality suggests the presence of two different types of polymer fractions based on polymer molecules with two different endgroups. It was thought that the first peak might represent hydroxyl-ended polymer and the second acetylated polymer, but no carbonyl peaks could be seen in the spectra of the polymer treated with acetyl chloride even in a sample in which



the 300°C. peak included 64% of the total area under the DTG curve. The extent of stabilization with acetyl chloride treatment decreased with increasing amount of LTB initiator used to prepare the polymer, with the higher temperature DTG peak accounting for only 22% of the total area for the powdery sample initiated with 2.5 mole % LTB.

Treatment with  $\text{PCl}_5$  in  $\text{CCl}_4$  at 60°C., in contrast to acetyl chloride treatment, eliminated the lower DTG peak both in samples prepared with small (0.1 mole %) and large (2.5 mole %) amounts of LTB initiator. The onset of decomposition in  $\text{PCl}_5$ -treated samples did not occur until near 200°C., indicating the elimination of polymer fractions of low stability which decomposed below this temperature.

No characteristic broad hydroxyl peak in the 3300-3500  $\text{cm}^{-1}$  range could be observed for any of the polymers prepared except for the polymer powder prepared with 2.5 mole % LTB when observed in a pellet of (hygroscopic) KBr and one of the unextracted polymer films containing significant amounts of monomer. It was, however, noticed that a number of the films showed a carbonyl peak at 1770  $\text{cm}^{-1}$  characteristic of chloral monomer. All unextracted samples and samples treated with acidified methanol showed this peak. Of the samples treated with acetyl chloride, the ones prepared with lower concentrations of initiator did not show this peak, while those prepared with higher concentrations of LTB initiator did. Samples extracted with unacidified methanol only and those treated with  $\text{PCl}_5$  before extraction showed no carbonyl peaks (although the films extracted with unacidified methanol were very thin).

If monomer concentration in films similarly extracted and of

the same thickness is considered as related to the concentration of unstable polymer endgroups within the films, it would appear that  $\text{PCl}_5$  (and, for polymers made with low initiator concentrations, acetyl chloride) are relatively effective in reducing the concentration of these endgroups, corroborating the DTG data. Although monomer peaks were also absent in the films extracted with only unacidified methanol, these films were considerably thinner than were the other films, facilitating escape of slowly liberated monomer.

Because it was difficult to detect hydroxyl peaks in the spectra of the films prepared in the two previous experiments, it was decided to use still higher initiator concentrations--from 1.8 to 29 mole % of LTB with respect to chloral. Polychloral films prepared at these initiator concentrations were incoherent; infrared spectra therefore had to be determined on polymer powders ground in a mortar. KBr pellets could not be used, however, if the purpose of determining the infrared spectrum was to detect the hydroxyl peak, because of the hygroscopicity of KBr. Nujol mulls and films pressed from the polymer powder gave poor spectra. The technique which was found to give the best results, and which was used thereafter, was to place the polymer powder between NaCl plates and then to add a drop or two of  $\text{CCl}_4$ , which filled the spaces between the particles and decreased infrared scattering. All infrared spectra were determined on these powders wet with  $\text{CCl}_4$ .

The polymer powders were treated by the same five procedures used in the previous experiment and infrared and DTG spectra were determined. In the infrared spectra, broad hydroxyl absorptions centered

at  $3400\text{ cm}^{-1}$  were seen for most samples, in contrast to the results of previous experiments. Three peaks on each spectrum were measured: the broad hydroxyl absorption centered at  $3400\text{ cm}^{-1}$ , the sharp C-H stretching absorption at  $2955\text{ cm}^{-1}$  (used as a standard), and the residual monomer peak near  $1770\text{ cm}^{-1}$ . For each peak, the ratio  $A$  of transmittance  $T$  at the peak to baseline transmittance  $T_0$  was determined. Since the C-H stretching peak at  $2960\text{ cm}^{-1}$  would be unaffected by posttreatments intended to stabilize the polychloral by endcapping, this absorption was used as a reference standard for estimating changes in the concentrations of other species caused by posttreatments. Since, by Beer's law,

$$A = \epsilon b C$$

where  $A$  is absorbance,  $\epsilon$  is molar absorptivity,  $b$  is path length, and  $C$  is molar concentration, it follows that for two absorptions (1) and (2) within the same sample,

$$\frac{A_2}{A_1} = \frac{\epsilon_2}{\epsilon_1} \frac{C_2}{C_1}$$

Let absorption (1) be that of the C-H stretch. Then, since  $\epsilon_1$  and  $\epsilon_2$  are constant, the equation becomes

$$\frac{A_2}{A_1} = k C_2$$

where  $k$  is a constant. Hence the absorbance ratio  $A_2/A_1$ , where  $A_2$  is the hydroxyl or chloral monomer peak absorbance, should indicate the relative concentration of the given species in each polymer sample.



These ratios are tabulated in Table 15, p. 187, for hydroxyl and carbonyl peaks in each sample, together with DTG data.

As can be seen from Table 15, there is a general increase in the absorbance ratio of OH to CH and CO to CH with increase in initiator concentration for a given posttreatment technique, and, at constant initiator concentration, a general decrease as posttreatment technique changes from  $\text{CH}_3\text{OH}/\text{HCl}$  soaking to  $\text{CH}_3\text{COCl}$  reflux to  $\text{PCl}_5/\text{CCl}_4$  reflux. The stabilization of the polymer samples as shown by the change in the DTG peak temperatures parallels particularly the decrease of the relative absorbance of the OH group. The effect of  $\text{CH}_3\text{COCl}$  and  $\text{PCl}_5$  treatment upon the OH and CH peaks of the polymer sample initiated with 7.3 mole % of LTB is shown in Figure 10, p. 189. The much greater suppression of the hydroxyl peak relative to the CH stretching peak by the effective stabilizing agent  $\text{PCl}_5$  than by the much less effective stabilizing agent acetyl chloride can be readily seen.

The infrared data for polymers prepared with 15 and 29 mole percent LTB were very erratic; the polymers obtained were probably higher molecular weight fractions of mixtures in which the fractions of lower molecular weight (containing five or fewer monomer units) were soluble in, or degraded by, methanol. Unextracted materials and those extracted by unacidified methanol only are omitted from Table 15 because the unextracted samples rapidly degraded to chloral monomer and produced chloral hydrate crystals upon contact with the atmosphere. All samples degraded completely when placed into methanol but were stable when treated with acid first.

No trace of the characteristic absorption frequencies of the



TABLE 15

Polychloral Endgroups: O-H/C-H and C=O/C-H Peak Absorbance Ratios (a) and DTG Maximum Degradation Rate Temperatures (b) for Low Molecular Weight Polychloral After Various Posttreatments

Mole % LTB initiator (with respect to chloral)	1.8	3.7	7.3
<u>Posttreatment</u>			
<u>CH<sub>3</sub>OH/HCl (one day, room temp.)</u>			
OH/CH	0.32	0.65	1.32
CO/CH	0	0.79	0.64
DTG, °C. (initial decomposition)	110	120	
(peaks)	166 (57%) 222 (43%)	154 195 (sh)	
<u>CH<sub>3</sub>COCl (2 days, reflux)</u>			
OH/CH	0.18	0.13	0.82
CO/CH	0	0.09	0.33
DTG, °C. (initial decomposition)	80	50	50
(peaks)	152 260 (sh)	102 (sh) 166	91 (16%) 173 (84%)
<u>PCl<sub>5</sub>/CCl<sub>4</sub> (2 days, 60°C.)</u>			
OH/CH	0	0.02	0.37
CO/CH	0	0	0.10
DTG, °C. (initial decomposition)	190	190	150
(peak)	274	275	265

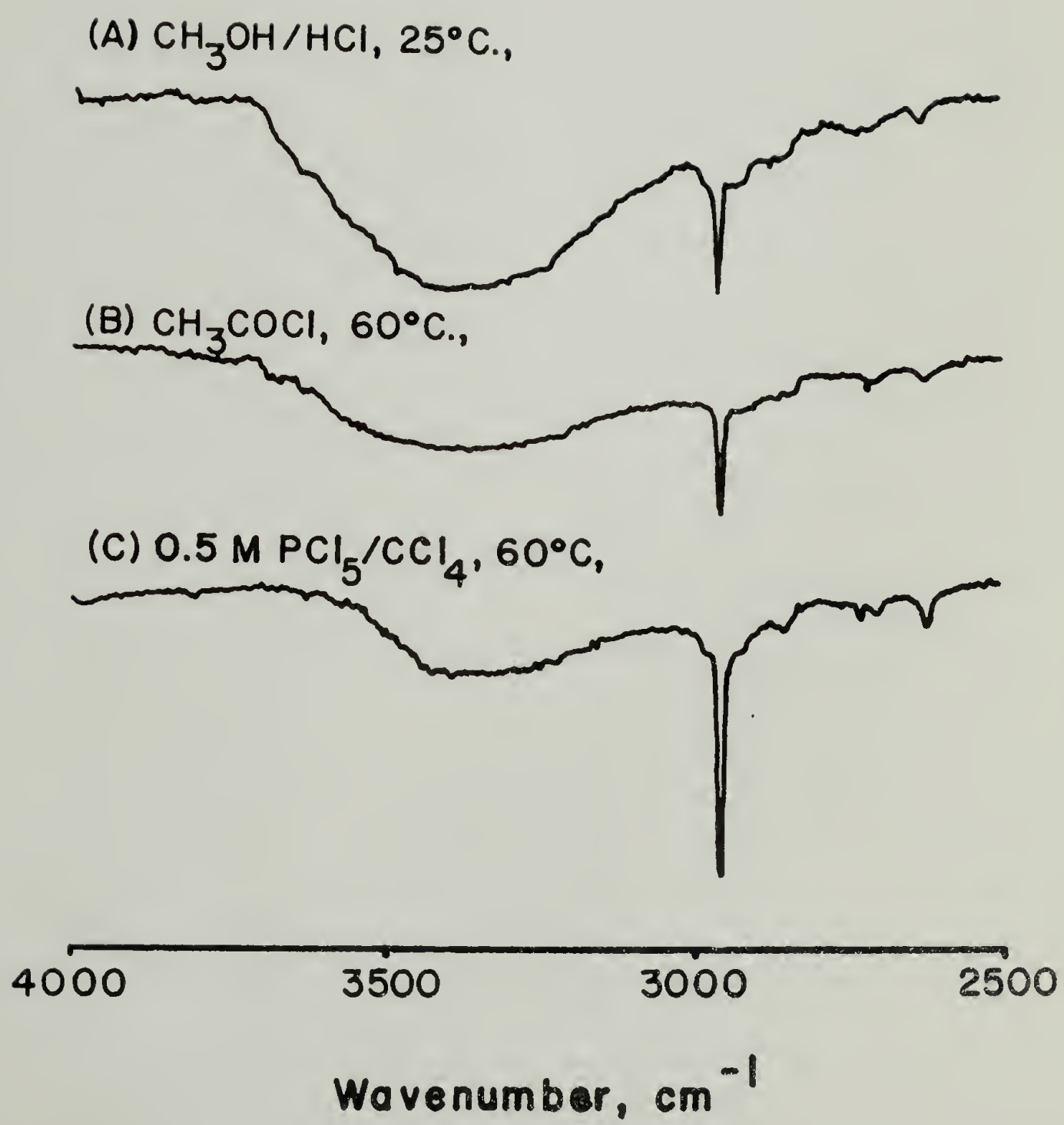
(a) IR spectra determined on powders in CCl<sub>4</sub> mull: OH absorbance at 3300-3500 cm<sup>-1</sup>, CH at 2955 cm<sup>-1</sup>, CO at 1770 cm<sup>-1</sup>.

(b) Heating rate 20°C./min.

Figure 10. Infrared Spectra of Low Molecular Weight Polychloral, Posttreated ( $\text{CCl}_4$  mulls).

Posttreatments:

- a.  $\text{CH}_3\text{OH}/\text{HCl}$ ,  $25^\circ\text{C}$ ., 1 day
- b.  $\text{CH}_3\text{COCl}$ ,  $60^\circ\text{C}$ ., 2 days
- c.  $0.5\text{M } \text{PCl}_5/\text{CCl}_4$ ,  $60^\circ\text{C}$ ., 2 days



tertiary butyl group at  $1355$  and  $1380\text{ cm}^{-1}$  could be seen in the polymers, even those of lowest molecular weight, because these were overlain by polychloral bands. (In the infrared spectrum of the addition compound of LTB with one mole of chloral (Figure 2, p.118) the  $1355$ - $1360\text{ cm}^{-1}$  peak is very weak although the peak at  $1380\text{ cm}^{-1}$  is strong.)

In comparison with the values observed in Table 10 for low-molecular weight anionically initiated polychloral, a sample prepared cationically by initiation with 1.2 mole % of  $\text{H}_2\text{SO}_4$  had OH/CH and CO/CH absorbance ratios of 1.68 and 0.41 respectively and a DTG peak at  $230^\circ\text{C}$ . A sample prepared by initiation with 2.0 mole % of  $\text{SbCl}_5$  had OH/CH and CO/CH absorbance ratios of 1.40 and 0.72 and a similar DTG peak. As one can see from these data, the concentration of hydroxyl endgroups is apparently higher in these cationically polymerized samples than even in the anionically polymerized samples initiated with 7.3 mole % of LTB. Hence the samples produced cationically are apparently very low in molecular weight, which accounts for the difficulty in obtaining coherent polymers by cationic processes.

This author recognizes that Beer's law is only an approximation to the infrared behavior of these systems since the spectra of the polychloral samples were determined on mulls of particles rather than on molecularly homogeneous solutions. Therefore, the above infrared data should be considered as only semiquantitatively significant.

Caution must also be used in the interpretation of the  $3440\text{ cm}^{-1}$  peak as completely due to hydroxyl groups, because a similar peak appears in the infrared spectrum of the LTB-chloral addition compound (Figure 2, p. 118). However, it is felt that the peak is due pre-



dominantly to hydroxyl groups because these spectra were determined on polymers pretreated with acidified methanol. Pretreatment with acidified methanol dramatically improves the stability of LTB-initiated polychloral apparently by transforming the labile alkoxide groups into more stable hydroxyl groups.

From the above endgroup studies, we can draw the following conclusions:

1. Polychloral, at least when initiated with LTB, is terminated with living alkoxide groups which are degraded when the polymer samples are extracted with methanol (Table 14, p. 181). Extraction with methanol degrades lower molecular weight polychloral completely and leaves less than 10% residue when higher molecular weight polychloral is extracted.

There remains, however, a possibility that adventitious (or internally generated) protic impurities may convert a portion of the alkoxide endgroups to hydroxyl endgroups, which, in the presence of methanol, may revert to alkoxide during extraction (because of the alkaline conditions prevalent during the extraction). This process would eventually cause a significant proportion of the hydroxyl-terminated polymer to degrade in the alkoxide form, causing most of the polymer to be lost during extraction. Possible support for this point of view comes from the DTG spectrum of a plug of unextracted polychloral initiated with 0.1% LTB. This spectrum contained a peak at 100°C. possibly due to the alkoxide-terminated polychloral (48%) and a peak at 211°C. falling within the hydroxylic region typical of cationic polychloral and acid-treated polychloral films (52%). How-

ever, only 18% of the polychloral remained after methanol extraction.

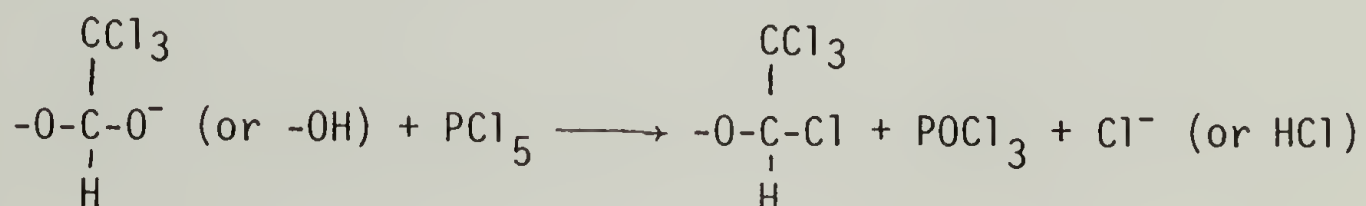
2. Pretreatment of LTB-initiated polychloral with acidified methanol dramatically increases its stability to subsequent extraction with unacidified methanol, as shown in Table 14, p. 181. This stabilization apparently occurs by protonation of alkoxide endgroups, neutralization of alkoxide residues in the polymer by the acid, and possible removal of lithium salts from the polymer. The resultant hydroxyl groups can be detected in the infrared spectra of polychloral prepared with 1.5-2 mole % or more of LTB, but not of higher molecular weight polychloral. Cationically initiated polychloral has very strong hydroxyl absorptions in the infrared. Hydroxyl-terminated polychloral will have a DTG degradation rate peak in the 200-220°C. range if of reasonably high molecular weight, with the peak sometimes lower in very low molecular weight polychloral.

3. Posttreatment with refluxing acetyl chloride will stabilize LTB-initiated polychloral to subsequent methanol extraction. It will also produce a DTG peak near 300°C. with most of the polymer degrading at this point, in high molecular weight polychloral films but not in powdery low molecular weight polychloral. Although acetylation of the alkoxide or hydroxyl endgroups is thought to be the stabilization mechanism, no carbonyl groups have ever been detected in the infrared spectra of polychloral films stabilized with acetyl chloride in either this work or a previous study (191). Either the molecular weight of the acetylated polychloral is too high (no hydroxyl endgroups have ever been detected in sections of the same films treated with acidified methanol) or stabilization by acetyl chloride occurs by another process

such as chlorination, known in the conversion of triphenylmethanol to triphenylchloromethane by acetyl chloride (219).

Cationically initiated polychloral can be easily acetylated by acetyl chloride, the acetate endgroups being detectable in the infrared spectrum (146).

4. Treatment with refluxing  $\text{PCl}_5/\text{CCl}_4$  for several days will quantitatively stabilize polychloral films and powders (except those of extremely low molecular weight), giving a DTG peak at 275-300°C. with no weight loss occurring below 190-200°C. in the DTG spectrum. The hydroxyl peak at  $3400\text{ cm}^{-1}$  in the infrared spectrum either disappears or is greatly reduced upon stabilization with  $\text{PCl}_5$ . No new peaks appear in the spectrum upon  $\text{PCl}_5$  treatment. For this reason, we propose that  $\text{PCl}_5$  stabilization occurs by the following mechanism:



Introduction of a chlorine atom, unlike introduction of other endgroups, would be expected to produce no change in the infrared spectrum of a polymer already so rich in chlorine. The above reaction is analogous to the conversion of carboxylic acids to acid chlorides, or of alcohols to chloroalkanes, by  $\text{PCl}_5$ .

$\text{PCl}_5$  treatment of very low molecular weight polychloral (made with 7 mole % or more of LTB initiator) did not effectively stabilize the polymer. Considerable hydroxyl absorption remained in the infrared spectrum after treatment, and initial weight loss occurred near 140°C. in the DTG spectrum.



### E. Polychloral Stabilization by Endcapping

From the work in the previous section, it was apparent that the endgroups in propagating or "living" anionically initiated polychloral are alkoxide groups and that these groups are predominant in polychloral before workup, although some groups may be converted to hydroxyl by adventitious (or possibly internally generated) protonic impurities. Treatment with methanol tends to degrade living polychloral to monomer, while treatment with acidified methanol transforms the living endgroups to hydroxyl groups which are stable to further methanol treatment. High molecular weight polychloral terminated with hydroxyl groups, when analyzed by DTG at a heating rate of 20°C./min., begins to show weight loss at 100-130°C. and shows a decomposition rate peak at 200-230°C. in the DTG spectrum. This degree of thermal stability is unacceptable for most uses.

Also, the hydroxyl endgroups of polychloral are sufficiently acidic that they can be converted to easily degradable alkoxide groups in basic environments; for example, polychloral initiated with LTB or  $\text{Ph}_3\text{P}$  can be degraded quantitatively to monomer by refluxing with piperidine (220) and low molecular weight hydroxyl-terminated polychloral can be degraded to monomer by pyridine at room temperature (139). Most importantly, however, hydroxyl-terminated polychloral, even after exhaustive extraction with methanol, gives off monomer very slowly at room temperature, apparently by slow depolymerization in the same manner by which paraformaldehyde always has an odor of monomer, and chloral hydrate always exists in equilibrium with a small amount



of chloral and water, largely dissociating to these constituents at its boiling point (221). The slow degradation of hydroxyl-terminated polychloral can be illustrated by the corrosion of pieces of metal held adjacent to a block of  $\text{Ph}_3\text{P}$ -initiated, acetone-extracted polychloral for several weeks (222) and the slow buildup of the carbonyl peak of chloral monomer at  $1770\text{ cm}^{-1}$  in the infrared spectrum of hydroxyl-terminated polychloral films of approximately 0.03 mm. thickness over a period of months to years (178). This slow evolution of chloral monomer, which can form corrosive compounds in a moist oxidative atmosphere, makes hydroxyl-terminated polychloral unsuitable for many applications.

From a more fundamental standpoint, it was of interest to determine the  $T_g$  of polystyrene and other polymers in blends with polychloral (p. 152). Since some of these blends were clear, in contrast to opaque unmodified polychloral, and appeared much less crystalline than unmodified polychloral by X-ray, it seemed likely that polystyrene could be compatible with polychloral in certain composition ranges. Then, however, one would expect a pronounced raising of the polystyrene  $T_g$  by the stiff polychloral chains. However, this could not be determined by methods such as DSC or Rheovibron because hydroxyl-terminated polychloral starts to decompose near  $100^\circ\text{C}.$ , in the region of the polystyrene or poly(methyl methacrylate)  $T_g$ . Raising the polychloral decomposition onset temperature by stabilization could make possible the measurement of glass transition temperatures of such blends.

In the previous section, it was shown that treatment with a refluxing solution of  $\text{PCl}_5$  in  $\text{CCl}_4$  would stabilize polychloral films

or powders so that the onset of weight loss by DTG would occur near 200°C. and the decomposition peak near 300°C. However, this stabilization, which occurred apparently by transformation of hydroxyl to chlorine endgroups, required accessibility of the endgroups to  $\text{PCl}_5$  so that reaction could occur. Hence this technique was much more effective for thin films than for thicker sections, with the latter requiring many days of boiling the samples under reflux in the "capping" solution for diffusion of the  $\text{PCl}_5$  into the inner portions of the polymer. Some thick films (0.5 mm. or thicker) could not be satisfactorily stabilized even after a week of this treatment. Also, if attempts were to be made to stabilize polychloral/polystyrene blends by this method, the solvent,  $\text{CCl}_4$ , would probably extract the polystyrene from the blend.

Hence it was desired to find a method of stabilizing chloral homopolymer which could be quickly and easily performed and which would be as effective on thick sections of polychloral as is  $\text{PCl}_5$  treatment on thin sections. To this end, four avenues of approach were tried as follows:

1. Treatment of preformed polychloral with potential endcapping agents.
2. Use of potential endcapping agents in the chloral polymerization mixture.
3. Use of anionic chloral initiators with countercations which could be used as alkylating or arylating agents for the polychloral after completion of the polymerization.

4. Use in the chloral polymerization mixture of sterically hindered isocyanates, which neither copolymerize readily with chloral nor homopolymerize under the polymerization conditions.

These four methods are discussed in the following four sections; the first covers the stability of polychloral prepared with various "standard" anionic initiators such as LTB,  $\text{Ph}_3\text{P}$ , amines, and quaternary ammonium salts.

1. Stability of polychloral prepared with various "standard" anionic initiators. It was desired to determine the stability to various heating and extraction procedures of polychloral prepared with various "standard" anionic initiators in order to have a base of data by which to judge the success of future stabilization efforts.

Polychloral samples were prepared in test tubes by the standard anionic cryotachensic method with a number of initiators at different concentrations. The polychloral samples, in most cases, were divided each into three pieces. The first was heated for one hour in air at  $100^\circ\text{C}$ . and then extracted for two days with methanol in a Soxhlet extractor. The second was treated for one day with methanol containing 10% (v/v) of concentrated aqueous HCl at room temperature and then extracted as above. The third was extracted for two days with methanol in a Soxhlet extractor without prior treatment. The three pieces were dried and yields were determined; the yields (weight of the polymer sample after treatment as a percentage of raw polymer sample weight) are shown in Table 16, p. 198. Some data from DTG

TABLE 16

Stability to Heating and Extraction of Polychloral Samples Prepared With  
Different "Standard" Anionic Initiators (a)

Initiator, mole % with respect to chloral	Percent Weight Retention After			
	Heating, 1 hr./100°C. in air	Heating in air 1 hr./100°C. followed by CH <sub>3</sub> OH extraction 2 days in Soxhlet (b)	CH <sub>3</sub> OH/10% HCl 1 day at room temp. followed by CH <sub>3</sub> OH extraction 2 days in Soxhlet (b)	CH <sub>3</sub> OH (b) extraction 2 days in Soxhlet
LTB, 0.3M in C <sub>6</sub> H <sub>6</sub>	(4 ml. chloral in each tube)			
0.1	39, 6 (c)	24, 6	54	6, 11, 14, 16, 37, 51
0.2	66	47	64	60
0.4	31	15	53	5
LiCl, 0.3M in DMSO	(4 ml. chloral in each tube)			
0.1	50	25	71	0
0.2	61	28	74	0
0.4	47	13	68	0
Pyridine, 1.78M in CHCl <sub>3</sub>	(8 ml. chloral in each tube)			
0.59	53	6	36	0
1.17	53	2	50	7
2.34	43	1	42	0
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, 1.40M in CHCl <sub>3</sub>	(8 ml. chloral in each tube)			
0.46	60	22	43	0
0.92	21	10	41	0
0.84	14	4	35	0



TABLE 16 (continued)

Initiator, mole % with respect to chloral	Percent Weight Retention After			
	Heating, 1 hr./100°C. in air	Heating in air 1 hr./100°C. followed by CH <sub>3</sub> OH extraction 2 days in Soxhlet (b)	CH <sub>3</sub> OH/10% HCl 1 day at room temp. followed by CH <sub>3</sub> OH extraction 2 days in Soxhlet (b)	CH <sub>3</sub> OH (b) extraction 2 days in Soxhlet
(n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N, 1.59M in CHCl <sub>3</sub>	(8 ml. chloral in each tube)			
0.52	25	14	37	0
1.05	19	9	33	0
2.09	4	1	23	0
(n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NCl, 0.3M in CHCl <sub>3</sub>	(8 ml. chloral in each tube)			
0.1	21 (c)	12 (c)		83
0.2	8 (c)	4 (c)		75
0.4	0 (c)	0 (c)		65
DMSO, neat	(4 ml. chloral in each tube)			
4.5	24	9	13	12
9.3	32	12	18	22
18.6	33	8	31	32
Ph <sub>3</sub> P, 0.3M in cyclohexane	(8 ml. chloral in each tube)			
0.1	92	72		73
0.2	92	70		74
0.4	93	73		79
Ph <sub>3</sub> P, 0.3M in benzene	(8 ml. chloral in each tube)			
0.1	91	68		78
0.2	92	65		68
0.4	94	70		75

TABLE 16 (continued)

Initiator, mole % with respect to chloral	Percent Weight Retention After			
	Heating, 1 hr./100°C. in air	Heating in air 1 hr./100°C. followed by CH <sub>3</sub> OH extraction 2 days in Soxhlet (b)	CH <sub>3</sub> OH/10% HCl 1 day at room temp. followed by CH <sub>3</sub> OH extraction 2 days in Soxhlet (b)	CH <sub>3</sub> OH (b) extraction 2 days in Soxhlet
Ph <sub>3</sub> P, 0.3M in CHCl <sub>3</sub>	(8 ml. chloral in each tube)			
0.1	84	55		62
0.2	89	66		74
0.4	92	74		79
Ph <sub>3</sub> P, 0.3M in CH <sub>3</sub> CN	(4 ml. chloral in each tube)			
0.1	92	62		78
0.2	91	62		79
0.4	90	64		84
Ph <sub>3</sub> P, 0.3M in DMSO	(8 (2) ml. chloral in each tube); first (second) experiment			
0.1	70 (32)	35 (2)		35 (0)
0.2	73 (16)	41 (2)		40 (31)
0.4	76 (41)	31 (8)		51 (0)

(a) Cylindrical samples approx. 12 mm. in diameter and weighing 2 to 5 grams were used.

(b) Solvent temperature 45-65°C. (cyclical).

(c) Heated 1 hr. at 120°C.

spectra determined on the polychloral samples after workup are shown in Table 17, p. 202.

The samples initiated with LTB at 0.1-0.4 mole % concentrations (Table 16) showed highly variable and unpredictable behavior upon heating or extraction with unacidified methanol. The stability of samples to heating in air for one hour at 100°C. ranged from 6 to 66%; when these samples were then extracted, from less than 6 to 47% of the pre-heating weight was retained. Similarly, when the samples were extracted with methanol with no pretreatment, weight retentions for the polychloral plugs ranged from 5 to 60 percent. This result compares with a range of zero to 11 percent observed for the films shown in Table 14, p. 181. Pretreatment of the polychloral plugs with methanol/HCl for one day caused the stability of the plugs to subsequent methanol extraction to be much more constant (53-64%). Although these values are lower than the 75-89% stability range observed for the films in Table 14, the films were extracted with methanol at room temperature while the plugs in this experiment were extracted with refluxing methanol in a Soxhlet extractor in which the temperature cycled periodically from 45° to 65°C.

The reason for the observed increased stability of a few samples in the absence of acid treatment is not known. However, it may be related to the observed transformation of the addition compound of chloral with LTB to tertiary butyl 1,2,2,2-tetrachloroethyl ether upon long refluxing in cyclohexane (145), with the alkoxide group being replaced by chlorine. This self-stabilization does seem to occur often in samples which have been allowed to stand at room temperature for several days or weeks before workup. A sample of polychloral initiated

TABLE 17

DTG Spectra of Polychloral Samples Prepared With  
Different "Standard" Anionic Initiators

Initiator (mole %)	Weight percent remaining in sample used after treat- ment given (a)	DTG Parameters (b)	
		Onset of decomposi- tion, °C.	Degradation rate maxima, °C. (% of total area)
LTB, 0.3M in $C_6H_6$ (0.2)	47	140	231 (100)
LiCl, 0.3M in DMSO (0.1)	25	110	210 (100)
Pyridine, 1.78M in $CHCl_3$ (0.59)	6	90	179(79), 317(21)
$(C_2H_5)_3N$ , 1.40 M in $CHCl_3$ (0.46)	22	90	190 (100)
$(n-C_4H_9)_3N$ , 1.59M in $CHCl_3$ (0.52)	14	110	185(86), 294(14)
$(n-C_4H_9)_4NCl$ , 0.3M in $CHCl_3$ (0.1)	12 83 (c)	160 120	265(100), 350(shoulder) 208 (100)
DMSO, neat (9.3)	12	105	205 (100)
$Ph_3P$ , 0.3M in $C_6H_6$ (0.12)	58 (d)	140	210(60), 310(40)
$Ph_3P$ , 0.3M in DMSO (0.1)	35	150	239 (100)

(a) Heating at 100°C. for 1 hr., then  $CH_3OH$  extraction in Soxhlet for 2 days.

(b) Heating rate: 20°C./min.

(c) Extracted in Soxhlet with  $CH_3OH$  for 2 days without previous heating.

(d) Heated at 120°C. for 1 hr., then extracted in Soxhlet with  $CH_3OH$  for 2 days.



with 0.1 mole % LTB was allowed to stand at room temperature for one week before workup. The raw unextracted sample had DTG peaks at 82°C. (19% of total area) and 254°C. (81%) and 49% of the polymer was stable to Soxhlet extraction. By contrast, a sample prepared identically the same day and allowed to stand for only two days at room temperature before workup showed, before extraction, DTG peaks at 100°C. (48%) and 211°C. (52%), but only 17% of the polymer was stable to extraction. However, the reproducibility of the extent of self-stabilization was poor; a polymer sample initiated with 0.1 mole % of LTB and allowed to stand 17 days before workup was only 37% stable to Soxhlet extraction.

Polychloral produced by lithium chloride initiation showed heating and extraction stability similar to that obtained with LTB, with HCl treatment similarly considerably improving extraction stability. Raw polymer not heat treated or HCl treated degraded almost completely when Soxhlet extracted. Polychloral initiated with pyridine, triethylamine, or tri(n-butyl)amine showed the same characteristics but was even more unstable, with less than 20% of each polymer sample stable to Soxhlet extraction, regardless of whether or not the identical samples were given a preliminary heat treatment. Pretreatment with  $\text{CH}_3\text{OH}/\text{HCl}$  greatly improved the stability of amine-initiated polychloral to Soxhlet extraction with stabilities generally 30-50%. However, even these stability values were not as high as the stability values for the correspondingly acid-treated polymers initiated with LTB or LiCl.

The high susceptibility of amine-initiated polychloral to degradation may illustrate the tendency of amine initiator residues within the polymer to convert hydroxyl endgroups in the polymer to

labile alkoxide groups by deprotonation during heating or methanol extraction. This alkoxide-terminated polychloral could then degrade rapidly. The sensitivity of polychloral to degradation by traces of amines was studied by McCain and Sanders (213), who found both polychloral thought to have hydroxyl endgroups and polychloral believed to be endcapped by ester endgroups to be unstable in the presence of amines; an aminolysis (or tertiary amine-assisted hydrolysis) of the ester endgroup was proposed to explain the instability of "endcapped" polychloral. Novak and Poziomek (223-225) utilized the facile degradation of a chloral-dichloroacetaldehyde copolymer by traces of amines to develop a method for amine detection. Lipp (220) degraded polychloral with piperidine in an attempt to measure the degree of crystallinity of polychloral.

Tetrabutylammonium chloride, when used as an initiator, produced polychloral with an unusual stability pattern. This polymer was very stable (65-85%) to extraction with  $\text{CH}_3\text{OH}$  without any pretreatment, while heating at  $100^\circ\text{C}$ . destroyed most of the polymer. Stability to both extraction and heating decreased with increasing initiator concentration. DMSO, which was found, surprisingly, to initiate chloral polymerization itself (220), gave polymer in low yield after all post-treatments. When 4-19 mole % of initiator was used, 10 to 35% of the resultant polychloral was stable after heating 1 hr. at  $100^\circ\text{C}$ . or Soxhlet extraction with methanol. Polymer stability was higher at higher initiator concentrations, in sharp contrast to the behavior of polychloral initiated by amines. Pretreatment with methanolic  $\text{HCl}$  did not increase the stability of DMSO-initiated polychloral to further

Soxhlet extraction with methanol.

Among the "standard" initiators,  $\text{Ph}_3\text{P}$  gave polychloral with the highest stability under a variety of conditions. Stability to heating in air for one hour at  $100^\circ\text{C}$ . was over 90% for most polychloral samples initiated with 0.1-0.4 mole % of  $\text{Ph}_3\text{P}$  in cyclohexane, benzene, chloroform or acetonitrile. Weight retention of the polymers after Soxhlet extraction with methanol for two days ranged from 60 to 80%, while weight retention after a combination of these treatments ranged from 55 to 75%. When DMSO was used as the solvent for  $\text{Ph}_3\text{P}$ , however, polychloral stability was much lower and irreproducible. (Polychloral of considerably higher stability was produced by initiation with some sulfonium salts dissolved in the same DMSO used to prepare the  $\text{Ph}_3\text{P}$  solution and on the same day: see Table 24, p. 230.)

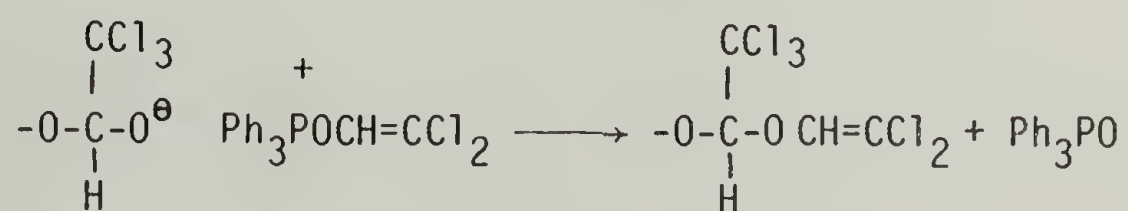
From the listing of DTG parameters in Table 17, p. 202, the polychloral samples initiated with LTB, LiCl and DMSO and the sample initiated with tetrabutylammonium chloride and extracted without prior heat treatment seem to show the DTG behavior typical of hydroxyl-ended polychloral, with an onset of decomposition near  $100^\circ\text{C}$ . and a DTG peak of maximum rate of degradation slightly above  $200^\circ\text{C}$ .

This type of DTG behavior was noted for high molecular weight LTB-initiated polychloral films treated with HCl (p. 181) and many polychloral samples prepared with cationic initiators (226). (In this context, "high molecular weight" polychloral refers to hard, tough polychloral which forms films which are not brittle, and "low molecular weight" refers to the soft, crumbly material obtained by initiation with large mole percentages of LTB, although actual molecular weights have



not been determined for the different samples because of insolubility.) Polychloral samples initiated with amines showed lower DTG degradation rate maxima at 180-190°C., and in some cases small peaks near or above 300°C. The lower peak temperatures may be caused by small amounts of amine residues remaining in the polymer after extraction. The lower peak temperatures may also be caused by polymer fractions of low molecular weight, as in the hydroxyl-terminated polychloral powders in Table 15, p. 187. The peaks falling near or above 300°C., in the region of polychloral stabilized with  $\text{PCl}_5$ , may originate from alkylating or chlorinating species formed by reaction of chloral monomer with amines at high temperatures.

Polychloral initiated with  $\text{Ph}_3\text{P}$  showed the typical DTG peak at 200-240°C. normally associated with hydroxyl endgroups, but some samples also showed a sizeable peak in the 300°C. region characteristic of the endcapped polymer. The mechanism by which endcapping occurs is not definitely known. However, since the actual initiator in these polymerizations is triphenyl(dichlorovinyl)oxyphosphonium chloride, an Arbuzov-type reaction may occur between this salt and the alkoxide endgroups of the polychloral.



This reaction would be analogous to the known formation of trichloroethylene by thermal decomposition of triphenyl(dichlorovinyl)oxyphosphonium chloride (179). It has been established in separate experi-



ments that when chloral is initiated with  $\text{Ph}_3\text{P}$  and the resultant polymer is extracted with acetone, over 95% of the phosphorus from the  $\text{Ph}_3\text{P}$  can be found in the acetone as  $\text{Ph}_3\text{PO}$  (176). Much of this  $\text{Ph}_3\text{PO}$  formation, however, may be due to hydrolysis (179) (which may also liberate  $\text{HCl}$ ), since reagent grade acetone contains 0.5-1% water. Like other endgroups in polychloral initiated with  $\text{Ph}_3\text{P}$ , dichlorovinyl groups, if present, could not be detected by infrared spectroscopy of thin films because of high polymer molecular weight.

The relatively high main decomposition peak temperature of  $265^\circ\text{C}$ . and the shoulder at  $350^\circ\text{C}$ . in the DTG spectrum of the polychloral sample initiated with tetrabutylammonium chloride and heated before extraction may indicate some alkylation of the polychloral alkoxide endgroups by the tetrabutylammonium ion during heating. However, if such occurred, this would liberate tributylamine, which could catalyze the thermal depolymerization of the polychloral, causing the low thermal stability of unextracted polychloral initiated with tetrabutylammonium chloride. On the other hand, because the DTG spectrum is that of a sample retaining only 12% of its pre-heating weight, the DTG spectrum may merely be that of the more stable fraction of the original sample.

In conclusion, polychloral initiated with LTB or lithium halides is, before workup, terminated at least predominantly with "living" alkoxide groups which degrade upon heating and especially upon extraction with unacidified methanol; pretreatment with acidified methanol converts the alkoxide endgroups to hydroxyl groups which are stable to further methanol extraction and have characteristic DTG spectra. Polychloral initiated with amines behaves similarly, generally

degrading completely upon extraction with unacidified methanol; any end-groups converted to hydroxyl are likely eventually to be reconverted to alkoxide by reaction with amine residues. Stabilization of the polychloral samples with acidified methanol is somewhat less effective for amine-initiated polymers than for polychloral initiated by lithium salts, particularly for polychloral initiated with high concentrations of amine. This may be caused by degradation of the polychloral by methanol diffusing into the polymer in the presence of excess amine residues before sufficient HCl has diffused in with the methanol to protonate all the excess amine. (Excess amine residues may also be the reason that the stability of untreated amine-initiated polychloral to heating at 100°C. was found to decrease sharply in some cases with increasing initiator concentration.)

In comparison with polychloral initiated with lithium salts and amines, polymer initiated with "onium" salts--quaternary ammonium or phosphonium (including the phosphonium salt derived from  $\text{Ph}_3\text{P}$  and chloral) or tertiary sulfonium salts (Table 24, p. 230)--generally showed considerably higher stability, especially to extraction of the raw polymer with methanol. The greatly increased stability to unacidified methanol extraction of polychloral initiated with  $\text{Ph}_3\text{P}$  via triphenyl(dichlorovinyl)oxy)phosphonium chloride as compared to that initiated with lithium chloride could be rationalized by proposing a hydrolysis of the phosphonium salt by water in the methanol (179):



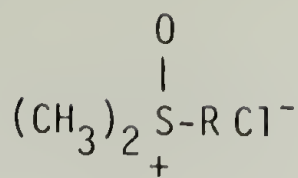
The resulting hydrogen ion would then protonate the alkoxide endgroup

of the polychloral chain, rendering it stable to further extraction with methanol. This mechanism may indeed operate and be responsible in part for the stability of  $\text{Ph}_3\text{P}$ -initiated polychloral to unacidified methanol extraction. However, it is much more difficult to explain the stability to unacidified methanol extraction of unheated polychloral initiated with tetrabutylammonium chloride. Although a Hofmann degradation to produce tributylamine, 1-butene and hydroxyl-terminated polychloral could occur in the "living" polychloral samples before extraction, the tributylamine produced could then destabilize the polymer (compare the low stability of tributylamine-initiated polychloral). Also, no Hofmann degradation is possible in polychloral initiated with trimethylsulfonium or benzyldimethylsulfonium halides, which also shows good stability to methanol extraction without prior heating (Table 24, p. 230). These polymers, after extraction, showed predominantly DTG peaks characteristic of hydroxyl-terminated polychloral, so alkylation of the polymer by the cation is not the reason for the good stability of the polymer to methanol extraction.

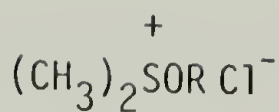
At this point, therefore, the reason for the much greater extraction stability of polychloral initiated with "onium" halides as compared with the polymer initiated with LTB or  $\text{LiCl}$  remains unknown.

The fact that DMSO will initiate chloral polymerization is surprising. DMSO proved to be a very weak initiator, with yields low but increasing with increasing initiator concentration. DMSO may react with chloral to form an (unstable) oxosulfonium chloride of types A or B (in analogy with the known reactions of DMSO with methyl iodide and methyl p-toluenesulfonate (227)) or an oxosulfonium zwitterion of type

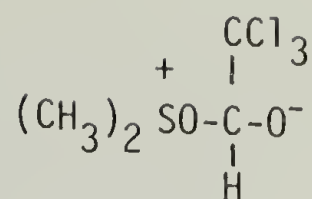




(A)



(B)



(C)

C, any of which might initiate chloral polymerization. Upon contact with methanol, species B or polymeric C would be expected to methanolyze readily (227) to produce polymer-stabilizing hydrogen ions. Polychloral initiated with DMSO, in any case, shows behavior characteristic of polychloral prepared with "onium" initiators, with extraction stability not improved by HCl pretreatment and increasing with increasing initiator concentration, rather than decreasing as in initiation by amines.

Although a degree of "self-stabilization" was found for some LTB-initiated polychloral samples after long standing at room temperature, and some samples initiated with  $\text{Ph}_3\text{P}$  showed DTG decomposition peaks near  $300^\circ\text{C}$ ., none of the "standard" initiators could produce polychloral with a stability comparable to that obtainable by  $\text{PCl}_5$  treatment of thin polychloral films. Hence treatment with specific endcapping agents was investigated in the next section.

2. Stability of polychloral posttreated with endcapping agents or prepared with endcapping additives in the polymerization mixture. Polychloral was posttreated with a number of potential acylating and alkylating agents, or in some cases these were incorporated into the polymerization mixture in an effort to find a simple and rapid stabilization technique for bulk polychloral as effective as is  $\text{PCl}_5$  treatment of thin films. Extraction stability and DTG data for posttreated poly-



TABLE 18

## Stability of Posttreated Polychloral Samples (a)

Posttreatment	Weight percent of polymer remaining after extraction ( $\text{CH}_3\text{OH}$ , room temp., 3 days)	DTG Parameters (heating rate $20^\circ\text{C./min.}$ )	
		Onset of decomposition, $^\circ\text{C.}$	Degradation rate maxima, $^\circ\text{C.}$ (% of total area)
None	4-11	110	240 (100)
$\text{CH}_3\text{OH}/10\%$ conc. $\text{HCl}$ , room temp., 1 day	87	150	217 (100)
$\text{CH}_3\text{COCl}$ , reflux, 3 days	98	140	205 (36), 300 (64)
$\text{HC}(\text{OCH}_3)_3/\text{BF}_3$ (b)	33 (c)	140	230-300 (broad)
$(\text{CH}_3)_2\text{C}(\text{OCH}_3)_2/\text{BF}_3$ (b)	26 (c)	150	253 (100)
0.5M $\text{PCl}_5$ in $\text{CCl}_4$ , reflux, 2 days.	99	200-210	300 (100)

(a) Initiator: LTB, 0.1 mole% with respect to chloral.

(b) 0.5 ml. of  $\text{BF}_3/\text{Et}_2\text{O}$  in 50 ml. of orthoester or ketal; 3 days at  $80^\circ\text{C.}$ (c) Extraction by  $\text{CH}_3\text{OH}$  in Soxhlet for 2 days.

TABLE 19  
Extraction Stability of Polychloral Samples Prepared with Additives  
in the Polymerization Mixture

Initiator (mole %) (b)	Additive (mole %) →	Weight % of Polymer Remaining After Extraction (a)									
		0	0.2	0.4	0.8	1.6	3.2	6.4	12.8	25.2	
Ph <sub>3</sub> P (0.2)	BrCH <sub>2</sub> COBr		4	0	8	15	10	5			
LTB (0.1)	(CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> (c)		37				(48)	33			
Ph <sub>3</sub> P (0.2)	(CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> (c)		2(11)	2(3)	1(3)	1(2)	0(2)	2(1)			
LTB (0.1)	CH <sub>3</sub> I (d)	37	20	10	36	50	33	38	62	50	
LTB (0.1)	Additive (mole %) →							5.6	11.1	22.2	
Ph <sub>3</sub> P (0.2)	HC(OCH <sub>3</sub> ) <sub>3</sub> (e)							25(21)	34(25)	46(33)	
LTB (0.1)	HC(OCH <sub>3</sub> ) <sub>3</sub> (e)							75(25)	31(7)	14(4)	
Ph <sub>3</sub> P (0.2)	(CH <sub>3</sub> ) <sub>2</sub> C(OCH <sub>3</sub> ) <sub>2</sub> (e)							12(22)	64(26)	48(26)	
	(CH <sub>3</sub> ) <sub>2</sub> C(OCH <sub>3</sub> ) <sub>2</sub> (e)							74(55)	0(0)	0(0)	
Ph <sub>3</sub> P (0.2)	Additive (mole %) →							3.4	6.9	13.8	
	Sulfolane							74	79	80	

- (a) Extraction with methanol in Soxhlet extractor for 3 days.
- (b) LTB was 0.3M in benzene or cyclohexane; Ph<sub>3</sub>P was 1M in toluene.
- (c) In examples in parentheses, dimethyl sulfate was added to initiated chloral; otherwise initiator was added to warm chloral-dimethyl sulfate mixture. See text.
- (d) Tubes were kept 17 days at room temperature before opening.
- (e) In examples in parentheses, polymer sample was treated with a solution of 0.5 ml. of BF<sub>3</sub>·Et<sub>2</sub>O in 50 ml. of additive at 80°C. for 3 days before extraction.

TABLE 20

Thermal Stability of Polychloral Samples Prepared with Stabilizing Additives (a)

Additive (mole %)	Weight percent of polymer remaining after extraction (CH <sub>3</sub> OH in Soxhlet, 3 days)	DTG Parameters (Heating Rate 20°C./min.)	
		Onset of decomposition, °C.	Degradation rate maxima, °C. (% of total area under peak)
None	4 (c) 37	110 130	224 (100) 214 (100)
CH <sub>3</sub> COCl (0.55) (b)	81 (d)		230 (30), 290 (70)
(CH <sub>3</sub> CO) <sub>2</sub> O (0.65) (b)	72 (d)		230 (87), 290 (13)
C <sub>6</sub> H <sub>5</sub> COCl (0.85) (b)	78 (d)		230 (65), 290 (35)
BrCH <sub>2</sub> COBr (1.6) (b)	15	160	254 (74), 350 (26)
(CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> (0.2) (3.2) (6.4)	37 48 33	120 120 205	157 (42), 287 (58) 180 (13), 289 (87) 277 (100)
HC(OCH <sub>3</sub> ) <sub>3</sub> (22)	46	140	195 (60), 317 (40)
(CH <sub>3</sub> ) <sub>2</sub> C(OCH <sub>3</sub> ) <sub>2</sub> (20)	48	180	262 (100)
CH <sub>3</sub> I (12.8) (25.2)	62 50	130 150	212 (100) 229 (100)

(a) Initiator: LTB (0.1 mole% with respect to chloral).

(b) Initiator: Ph<sub>3</sub>P, 0.2 mole% (first three values from reference (191)).(c) Extracted with CH<sub>3</sub>OH at room temperature for 3 days.

(d) Extracted with acetone in Soxhlet for 2 days.

chloral films are in Table 18, p. 211; preparative and extraction stability data for polychloral samples prepared with additives in the polymerization mixture are given in Table 19, p. 212; while the corresponding DTG thermal stability data are shown in Table 20, p. 213.

As can be seen from Table 18, polychloral films initiated with 0.1 mole % of LTB were apparently endcapped (either acetylated or chlorinated) to the extent of 64% by refluxing with acetyl chloride for 3 days, although no infrared spectral change could be seen in treated films of 0.02-0.04 mm. thickness, perhaps because of high molecular weight (see also p. 191). (A treatment with boiling acetyl chloride was ineffective in stabilizing low molecular weight LTB-initiated polychloral (p. 191).) Treatment with  $\text{BF}_3$  in trimethyl orthoformate or 2,2-dimethoxypropane, highly effective stabilizing (methylating) agents for polyacetals such as poly(n-butyraldehyde) (218), caused an increase in DTG peak temperature but not the appearance of a new peak near 300°C. These ambiguous results will be further discussed later (p. 218). Of the posttreatments tested, only treatment with refluxing  $\text{PCl}_5/\text{CCl}_4$  stabilized polychloral quantitatively to give a DTG weight loss onset near 200°C. and a decomposition rate peak near 300°C.; even this treatment was not very effective for thick polychloral samples (p. 175).

It was thought that one reason for the poor performance of posttreatments in stabilization of polychloral could be inability of the stabilizing agents to diffuse to all of the reactive alkoxide or hydroxyl endgroups of the polychloral samples. Incorporation of stabilizing agents into the polymerization mixture, so that these agents would be already dispersed within the polymer matrix at the end of the poly-



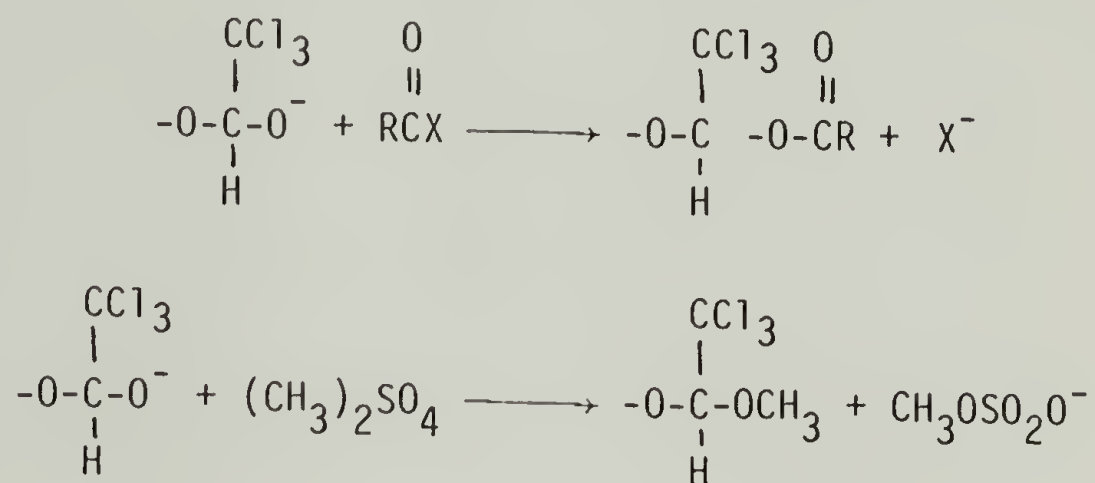
merization, was therefore tried in an attempt to overcome the diffusion problem and make possible rapid stabilization of thick polychloral sections.

In previous work, acid chlorides or anhydrides were added to warm chloral initiated with LTB or  $\text{Ph}_3\text{P}$  prior to cryotachensic polymerization (191). The best stabilization results obtained from this work are summarized in the first part of Table 20, p. 213. Acetyl chloride, when used at a concentration of 0.55 mole % with respect to chloral, produced a polymer with a DTG peak at  $300^\circ\text{C}$ . with 70% of the total area under the DTG spectrum. When the acetyl chloride concentration was increased in an attempt to obtain complete stabilization, however, reduction in polymer yield resulted and the percentage of stable fraction in the polymer was not increased (191). Acetic anhydride and benzoyl chloride were considerably less effective stabilizing agents than acetyl chloride.

In an attempt to extend this work to acylating agents of higher reactivity, bromoacetyl bromide was used in several concentrations in chloral polymerization mixtures initiated with LTB and  $\text{Ph}_3\text{P}$  (Table 19, p. 212). At all concentrations used, bromoacetyl bromide inhibited chloral polymerization with LTB, just as did acetyl chloride (191). Chloral polymerizations initiated with  $\text{Ph}_3\text{P}$  in the presence of bromoacetyl bromide gave only small yields of polymer stable to methanol extraction. Probably much of the tetrachloroethoxide initiating species (see p. 126) was acylated by the highly reactive acid bromide before it could initiate chloral polymerization, although we did not attempt to determine the presence of tetrachloroethyl bromoacetate in

the polymer samples produced. Although yields of polymer were very low, some of the polymer was stabilized, since a peak at 350°C. contained 26% of the area in the DTG spectrum.

Dimethyl sulfate was also added to LTB- and  $\text{Ph}_3\text{P}$ -initiated chloral polymerization mixtures as a potential stabilizing agent. It was thought that dimethyl sulfate could methylate the alkoxide-terminated polychloral chain just as acyl halides could acylate it:



In  $\text{Ph}_3\text{P}$ -initiated chloral polymerizations over a range of dimethyl sulfate concentrations, very low yields of polymer stable to methanol extraction (1-10%) were obtained. This was the case regardless of whether the  $\text{Ph}_3\text{P}$  or the dimethyl sulfate was added first to the warm chloral. Perhaps a mechanism operated here similar to that which lowered polymer yield when bromoacetyl bromide was used as an additive.

In sharp contrast to the situation with  $\text{Ph}_3\text{P}$  initiation, addition of dimethyl sulfate to LTB-initiated chloral polymerization mixtures led to highly irreproducible results. In the experiment shown in Table 19, twelve test tubes were dried and capped under identical conditions on the same day and filled with chloral from the same distillation cut. The tubes were warmed to 70°C. and injected with LTB solution

and the specified concentration of dimethyl sulfate; to six tubes the LTB was added first and to the other six tubes the dimethyl sulfate was added first. When the tubes were held at 0°C. overnight, no polymerization occurred in nine of the tubes; in three tubes, randomly distributed in the tube sequence, hard, tough polymers were formed. These were the tubes containing 0.2 and 6.4 mole % of dimethyl sulfate in which LTB was added to the warm chloral-dimethyl sulfate mixture and the tube containing 3.2 mole % of dimethyl sulfate which was added to the warm initiated chloral. These polymers had much higher weight retention after methanol extraction (30-50%) than did the polychloral samples initiated with  $\text{Ph}_3\text{P}$  in the presence of dimethyl sulfate. The LTB-initiated polymer samples from this experiment all showed sizable DTG peaks in the "stabilized" region near 300°C., and the sample prepared with 6.4 mole % of dimethyl sulfate showed only a DTG peak at 277°C. with weight loss onset at 205°C., indicating essentially complete stabilization.

The reason why the chloral polymerizations succeeded in three randomly placed tubes in the two series and failed in the nine others prepared under apparently identical conditions is not known. Perhaps small differences in residence time of the mixtures in the oil bath were responsible. However, when chloral polymerizations in its presence can be made to succeed, dimethyl sulfate appears to be quite an effective stabilizing agent when used in sufficient amount.

Methyl iodide ( $\text{CH}_3\text{I}$ ), a methylating agent very similar in characteristics to dimethyl sulfate, was also tested as a potential stabilizer for LTB-initiated polychloral over a wide range of concentrations in the polymerization mixture. It did not inhibit chloral polymerization,



but yields of polychloral (after  $\text{CH}_3\text{OH}$  extraction) from the mixtures containing  $\text{CH}_3\text{I}$  ranged from 10 to 60 percent, the very wide range being typical of LTB-initiated polymers not treated with acid before extraction. However,  $\text{CH}_3\text{I}$  did not stabilize polychloral even when used at 25 mole % levels and allowed to stand in the polymer for 17 days before workup; the only peaks found in the DTG spectrum were those in the hydroxyl region near  $220^\circ\text{C}$ .

Trimethyl orthoformate and 2,2-dimethoxypropane were used as additives in LTB-initiated chloral polymerizations and portions of the resultant polymers were then heated with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  dissolved in more of the orthoester or ketal. Both additives, at levels of 10 mole % or higher, strongly reduced post-extraction yields of polychloral initiated with  $\text{Ph}_3\text{P}$ , and 2,2-dimethoxypropane completely inhibited the  $\text{Ph}_3\text{P}$ -initiated polymerization of chloral at these levels. Yields of LTB-initiated polymer were in the same 10-60% range observed in the absence of additives. The treatment at  $80^\circ\text{C}$ . with  $\text{BF}_3$  in the orthoester or ketal often decreased substantially the weight retention of the polychloral after methanol extraction, sometimes by more than half.

Treatment of polyacetals such as poly(n-butyraldehyde) and low molecular weight polychloral with orthoformates or ketals with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  caused a substantial increase in polymer stability by methylating hydroxyl endgroups (218). In this work, although some stabilization, with respect to ordinary polychloral, was noted for the polychloral samples treated with  $\text{BF}_3$  and trimethyl orthoformate or 2,2-dimethoxypropane (Table 18, p. 211), the degree of stabilization by DTG was no higher than for the same samples prepared with the orthoester or ketal



additive in the polymerization mixture but not posttreated with  $\text{BF}_3$ . Hence the  $\text{BF}_3$  etherate-orthoester or ketal treatment is ineffective in stabilizing cryotachensically initiated polychloral, tending rather to degrade it instead. The reason for the apparent stabilization to some degree of polychloral prepared with orthoester or ketal additives in the absence of subsequent  $\text{BF}_3$  treatment is unknown; chloral monomer itself may function as a weak Lewis acid, or small amounts of acidic impurities sufficient to catalyze methylation may be formed during polymerization and workup.

In summary, polychloral containing alkoxide endgroups (initiated for example, with LTB by the standard anionic cryotachensic process) could be stabilized by protonation with acidified methanol to a moderately stable hydroxyl-terminated polychloral. This material had an onset of observable weight loss by DTG (heating rate of  $20^\circ\text{C./min.}$ ) at  $100\text{--}150^\circ\text{C.}$  and a decomposition rate peak at  $200\text{--}250^\circ\text{C.}$  A number of treatments could produce a more stable form of polychloral with an onset of weight loss near  $200^\circ\text{C.}$  and a DTG decomposition rate peak near  $300^\circ\text{C.}$  which is thought to represent endcapped polychloral (p. 196).

Acetyl chloride posttreatment could stabilize polychloral, though not quantitatively;  $\text{PCl}_5$  treatment could do this apparently quantitatively for thin sections. Acyl halides and acid anhydrides could be used in the polymerization mixture to stabilize polychloral; these, however, did not produce quantitative stabilization, and inhibited chloral polymerization altogether at high concentrations. Dimethyl sulfate stabilized polychloral much more effectively when used in the polymerization mixture; at high dimethyl sulfate concentrations,

stabilization was apparently quantitative, but polymerizability was highly irreproducible. Methyl iodide, however, was not an effective endcapping agent. Posttreatment with  $\text{BF}_3$  etherate and triethyl orthoformate or 2,2-dimethoxypropane apparently did not methylate polychloral, although use of these additives (without  $\text{BF}_3$ ) in the polymerization mixture appeared to stabilize polychloral somewhat by an unknown mechanism.

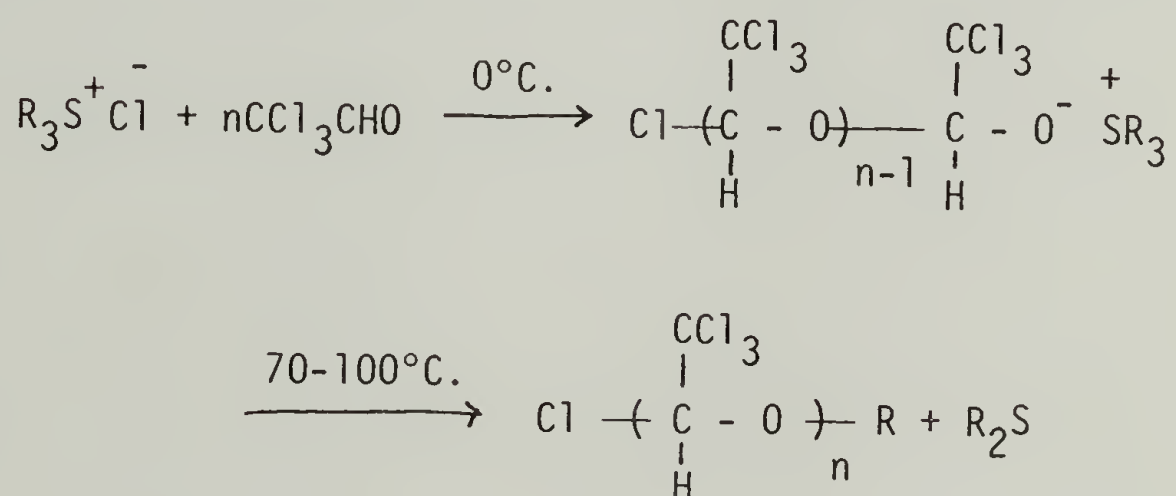
3. Stabilization of polychloral by use of anionic initiators with cations which can act as alkylating, arylating or acylating agents. No simple and rapid posttreatment can quantitatively endcap polychloral, especially in thick sections, and no additive to the chloral polymerization mixture (except for, in some cases, dimethyl sulfate) will give polychloral which is completely stabilized by endcapping. It was thought that one of the problems hindering polychloral stabilization with additives, particularly acylating agents, was difficulty in diffusion of the additive to the reactive polychloral alkoxide endgroups because of occlusion of the endgroups in inaccessible locations.

It was therefore thought that the use of halides of alkylating or arylating cations, such as trialkylsulfonium, trialkyloxosulfonium, or diaryliodonium, as initiators would circumvent this difficulty because of the electrical attraction of the alkylating cation for the anionic polychloral alkoxide group. It was assumed that the counter-cation would remain paired with the anionic endgroup throughout the chloral polymerization and therefore be immediately in a position to endcap the chain end at the end of the polymerization.

Although sulfonium ions may react with nucleophiles in solution

with deprotonation to produce ylides or carbenes (198,205,228), particularly if the sulfonium ion contains a substituent which can delocalize a negative charge such as p-nitrobenzyl or phenacyl, the thermal decomposition of trialkylsulfonium salts, even those containing electronegative groups, generally gives alkyl halides and dialkyl sulfides in high yield (229,230). Hence it was thought that trialkylsulfonium halides, particularly chlorides, could be used as initiators which, on thermal treatment of the polymer, could stabilize polychloral prepared anionically with these initiators.

The initiators were to be added to warm chloral and the polymerization conducted at 0°C. followed by heating at 70-100°C., at which temperature the nucleophilic polymer alkoxide anion would displace an alkyl group from the sulfonium cation and be endcapped in a manner similar to the thermal decomposition of sulfonium salts:



A number of sulfonium and oxosulfonium salts were synthesized and tested as stabilizing initiators for chloral polymerization. Bromide and iodide salts were generally synthesized (Table 21, p. 222) by reaction of the appropriate alkyl halide and dialkyl sulfide in an appropriate solvent at room temperature. Judicious choice of the

TABLE 21  
Preparation of Sulfonium and Oxosulfonium Salts by Nucleophilic Displacement (a)

Compound Prepared	Dialkyl Sulfide or Sulfoxide		Alkyl Halide		Reaction Solvent		Reaction time, days
	ml.	g. moles	ml.	g. moles	ml.	ml.	
$C_6H_5CH_2S(CH_3)_2Cl$ (d)	$(CH_3)_2S$	64 54 0.87	$C_6H_5CH_2Cl$	91 100 0.79	$H_2O$	120	(b)
$p-O_2NC_6H_4CH_2S(CH_3)_2Br$	$(CH_3)_2S$	14.6 12.4 0.2	$p-O_2NC_6H_4CH_2Br$	21.6 0.1	$CH_2Cl_2$	100	4
$C_6H_5COCH_2S(CH_3)_2Br$	$(CH_3)_2S$	21.9 18.6 0.3	$C_6H_5COCH_2Br$	30 0.15	$CH_3COCH_3$	45	12
$C_6H_5COCH_2S(n-C_4H_9)_2Br$	$(n-C_4H_9)_2S$	13 11 0.075	$C_6H_5COCH_2Br$	10 0.05	$(C_2H_5)_2O$	30	28
$C_2H_5OOCCH_2S(CH_3)_2Br$	$(CH_3)_2S$	58.6 49.7 0.8	$C_2H_5OOCCH_2Br$	55.5 83.5 0.5	$CH_3COCH_3$	150	12
$(CH_3)_3CS(CH_3)_2I$	$(t-C_4H_9)_2S$	17.0 13.9 0.095	$CH_3I$	6.2 14.1 0.1	$(C_2H_5)_2O$	50	70
$(CH_3)_3SOI$	$(CH_3)_2SO$	14.5 16.0 0.20	$CH_3I$	30 69 0.48	None		(c)



TABLE 21 (continued)

Compound prepared	Yield		Recrystallization Solvent	M.p., °C. (lit.)
	g.	%		
$C_6H_5CH_2S(CH_3)_2Cl$ (d)	118	79	2-propanol-diethyl ether	105 (dec.)
$p-O_2NC_6H_4CH_2S(CH_3)_2Br$	27.8	87	None	195-210(dec.) (114-116(230), 112-113(231))
$C_6H_5COCH_2S(CH_3)_2Br$	38	97	Methanol-acetone	140-141(dec.) (151-152(196))
$C_6H_5COCH_2S(n-C_4H_9)_2Br$	12.8	74	None	75-76(dec.) (88-89 (232))
$C_2H_5OOCCH_2S(CH_3)_2Br$	100.4	88	None	85-87(dec.) (85-87(197), 78-80(198))
$(CH_3)_3CS(CH_3)_2I$	4.0	33	None(washed with $CH_2Cl_2$ )	150-150(dec.)(160(dec.)(233))
$(CH_3)_3SOI$	15.1	34	Water (100 ml.)	187-190(dec.) (200(199), 220(227))

(a) Reactions performed at room temperature.

(b) Reaction mixture held at reflux for 8 hrs. with stirring and at room temp. for 10 hrs.; then extracted with 75 ml. of hexane and 4 x 75 ml. of diethyl ether and evaporated at room temp. and 0.1 mm. pressure to yield crystals (synthetic procedure in reference (234)).

(c) Reaction mixture held at reflux for 6 days and at room temperature for 3 days.

(d) ANAL. Calcd. for  $C_9H_{13}SOI$ : C, 57.28%, H, 6.94%. Found: C, 57.21%; H, 7.33%.

reaction solvent gave the sulfonium salts as large crystals without the need for recrystallization. Benzyldimethylsulfonium chloride was prepared by heating under reflux a mixture of benzyl chloride, dimethyl sulfide and water until the reaction mixture was homogeneous. Unreacted starting materials were removed by ether extraction and the solution was evaporated to give the crystalline salt (234). Trimethyloxosulfonium iodide was prepared by heating under reflux a mixture of DMSO and methyl iodide and recrystallizing the separated salt from water (199).

Some alkyl halide-dialkyl sulfide mixtures did not react to give sulfonium salts under the conditions used. A number of alkyl halides did not react with di(n-butyl) or di(tert-butyl) sulfides at room temperature to give hexane- or heptane-insoluble products; ethyl chloroacetate and acetyl chloride also failed to react with dimethyl sulfide in diethyl ether (Table 22, p. 225). Chloroacetone gave with dimethyl sulfide a small amount of a crystalline reaction product which reverted to an oil when attempts were made to isolate this material.

The mechanism of chloral initiation by bromide and iodide ions is not known; in previous work (176) no bromide or iodide ions could be detected by elemental analysis (sensitive to 0.003% of Br or I in the polymer) in polychloral initiated with bromide or iodide salts. For this reason, a number of the sulfonium and oxosulfonium bromides and iodides were converted to chlorides by metathesis. The bromide and iodide salts were dissolved in water (with a minimum amount of methanol added if necessary to keep the salts in solution) and a 2 molar excess of freshly precipitated AgCl was added to the sulfonium salt solution. The mixture was stirred overnight and filtered; the sulfonium salt was

TABLE 22  
Unsuccessful Sulfonium Salt Syntheses (a)

Desired Compound	Dialkyl Sulfide		Alkyl Halide		Reaction Solvent		Reaction time, in months				
	ml.	g.	ml.	g.	ml.	moles					
$(n-C_4H_9)_3SBr$	$(n-C_4H_9)_2S$	17.4	14.6	0.1	$n-C_4H_9Br$	10.9	13.7	0.1	$(C_2H_5)_2O$	50	1
$C_2H_5OOCCH_2S(n-C_4H_9)_2Br$	$(n-C_4H_9)_2S$	10.5	8.8	0.06	$C_2H_5OOCCH_2Br$	5.5	8.4	0.05	$(C_2H_5)_2O$	30	1
$p-O_2NC_6H_4CH_2S(n-C_4H_9)_2Br$	$(n-C_4H_9)_2S$	13	11	0.075	$p-O_2NC_6H_4CH_2Br$		10.8	0.05	$(C_2H_5)_2O$	50	7
$C_6H_5CH_2S(t-C_4H_9)_2Br$	$(t-C_4H_9)_2S$	17.0	13.9	0.095	$C_6H_5CH_2Br$	11.9	17.1	0.1	None		1
$C_2H_5OOCCH_2S(CH_3)_2Cl$	$(CH_3)_2S$	7.3	6.2	0.1	$C_2H_5OOCCH_2Cl$	5.3	6.1	0.05	$(C_2H_5)_2O$	30	1
$CH_3COS(CH_3)_2Cl$	$(CH_3)_2S$	14.6	12.4	0.2	$CH_3COCl$	10.7	11.8	0.15	$(C_2H_5)_2O$	25	1
$CH_3COCH_2S(CH_3)_2Cl$	$(CH_3)_2S$	11.0	9.3	0.15	$CH_3COCH_2Cl$	8.0	9.3	0.1	$CH_3COCH_3$	30	1 wk. (b)

(a) Reactions conducted at room temperature; no precipitate was formed upon pouring reaction mixture into large excess of hexane or heptane after indicated reaction time.

(b) Crystals separated from reaction mixture which reverted to oil upon attempted filtration and drying.

isolated by evaporation and recrystallized. Data for the various salts prepared by this method are in Table 23, p. 227. Yields were highly variable; the low yield of the carbethoxymethyldimethylsulfonium chloride was probably caused by hydrolysis of the ester linkage while standing overnight in aqueous solution. Water instead of methanol or ethanol solutions were used for these metathesis reactions, however, because a number of sulfonium salts were found to be more susceptible to solvolysis in alcoholic than in aqueous solutions (233,238).

A number of sulfonium bromides could not be converted to chlorides by the above metathesis procedure. Benzyldimethylsulfonium bromide gave a 28% yield of trimethylsulfonium chloride. Benzyldi(n-propyl)sulfonium bromide gave a viscous oil which would not crystallize. Phenacyldi(n-butyl)sulfonium bromide gave ether-soluble crystals which decomposed when attempts were made to purify them.

Some of the sulfonium salts had melting points which differed markedly from the literature values. However, since all sulfonium salts melt with decomposition, the "melting" point is often quite dependent on heating rate; when more than one melting or decomposition point for a salt is given in the literature, the temperatures listed often vary considerably. Infrared and  $^1\text{H}$  NMR spectra (Table 1, p. 76 ) and where indicated, elemental analyses were determined to verify the identity of the compounds prepared.

The salts were dissolved in appropriate solvents and used as initiators for chloral polymerizations. Unfortunately, the only satisfactory aprotic solvent for many of the salts was DMSO, which tends to undergo side reactions above 80°C. However, DMSO was the only available



TABLE 23

Preparation of Sulfonium and Oxosulfonium Chlorides by Metathesis

Compound prepared	Starting Salt (a)		Reaction Solvent		Recrystallization Solvent	Yield	
		g. moles		ml.		g.	%
$(\text{CH}_3)_3\text{SCl}$	Iodide	10.2 0.05	$\text{H}_2\text{O}$	100	Methanol-acetone	2.7	47
$p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{S}(\text{CH}_3)_2\text{Cl}$	Bromide	13.9 0.05	$\text{H}_2\text{O}$	100	Methanol-acetone	(b)	
$\text{C}_6\text{H}_5\text{COCH}_2\text{S}(\text{CH}_3)_2\text{Cl}$	Bromide	7.8 0.033	$\text{H}_2\text{O} + \text{CH}_3\text{OH}$	75 25	Methanol-acetone	4.3	60
$\text{C}_2\text{H}_5\text{OOCCH}_2\text{S}(\text{CH}_3)_2\text{Cl}$	Bromide	5.0 0.022	$\text{H}_2\text{O}$	50	None	0.3	7
$(\text{CH}_3)_3\text{CS}(\text{CH}_3)_2\text{Cl}$	Iodide	3.0 0.012	$\text{H}_2\text{O}$	50	Methanol-acetone	1.9	56
$(\text{CH}_3)_3\text{SOCl}$	Iodide	11.0 0.05	$\text{H}_2\text{O}(\text{c})$	100	Methanol-acetone	4.1	64

TABLE 23 (continued)

Compound prepared	M.p., °C. (lit.)	Calcd., %			Found, %		
		C	H	Cl	C	H	Cl
$(\text{CH}_3)_3\text{SCl}$	165-175 (dec.) (170-173(dec.)(235))						
$\text{p-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{S}(\text{CH}_3)_2\text{Cl}$	129-132 (dec.) (131-132 (230))						
$\text{C}_6\text{H}_5\text{COCH}_2\text{S}(\text{CH}_3)_2\text{Cl}$	137 (dec.) (145 (236))						
$\text{C}_2\text{H}_5\text{OOCCH}_2\text{S}(\text{CH}_3)_2\text{Cl}$	88-92	39.02	7.10	19.20	39.05	7.31	18.91
$(\text{CH}_3)_3\text{CS}(\text{CH}_3)_2\text{Cl}$	140-144 (dec.)	46.58	9.77		46.29	10.77	
$(\text{CH}_3)_3\text{SOCl}$	187-190 (dec.) (220-222 (237))						

(a) Molar ratio of AgCl to starting salt was 2:1.

(b) Most of compound lost during workup, before recrystallization.

(c) Reaction was started at 100°C. and allowed to cool to room temperature.

aprotic solvent which would dissolve many of the initiators to a concentration of  $>0.1$  M, and therefore, was in most cases used as the carrier solvent for dissolving the initiators in the warm chloral before polymerization.

Polychloral plugs, after polymerization, were generally cut into two pieces. One piece was heated at  $100^{\circ}\text{C}$ . (or  $120^{\circ}\text{C}$ .) for one to two hours in an effort to effect the stabilization reaction between the polychloral alkoxide endgroups and the sulfonium ions. The other piece was extracted with methanol in a Soxhlet extractor without preheating as a control sample. After heating, the sample was divided into two parts, one of which was also Soxhlet extracted with methanol. Heating and extraction stability data for polychloral prepared with the various initiators are shown in Table 24, p. 230, while DTG data are given in Table 26, p. 243.

As can be seen from Table 24, most of the polychloral samples prepared with sulfonium initiators were at least 65% stable to the heat treatment and at least 40% stable to extraction with or without the heat treatment. The heat treatment generally had little effect on subsequent extraction stability (with the pre-workup sample as a base) and in most cases the amount of initiator used (from 0.1 to 0.4 mole %) had little effect on extraction stability. Some of the polychloral samples, particularly those prepared with trimethylsulfonium and benzyldimethylsulfonium halides, had stability to heating and extraction comparable to that found in  $\text{Ph}_3\text{P}$ -initiated polychloral.

With regard to stabilization, although initial work with sulfonium salts (Table 26) led to quite promising results, attempts to

TABLE 24

Stability to Heating and Extraction of Polychloral Samples Prepared with Sulfonium, Oxosulfonium, Iodonium, and Tropylium Salt and Sulfonium Ylide Initiators<sup>(a)</sup>

Initiator mole % with respect to chloral	Percent Weight Retention After		
	Heating, 2 hr./100°C. in air	Heating in air 2 hr./100°C followed by methanol extraction 2 days in Soxhlet	Methanol extraction 2 days in Soxhlet (no prior heating)
(CH <sub>3</sub> ) <sub>3</sub> S I (1M in DMSO) (film) 0.77	42 (b)		26
(CH <sub>3</sub> ) <sub>3</sub> SI (satd. solu. in DMAc) 0.5 ml. solu./5 ml. chloral	66 (b)	15 (b)	
(CH <sub>3</sub> ) <sub>3</sub> SCI (0.3M in DMSO)			
0.1	79	56	69
0.2	75	48	68
0.4	73	31	62
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> Br (0.3M in DMSO) (polymers nearly transparent)			
0.1	79	54	54
0.2	84	54	46
0.4	82	46	59
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> Br (satd. solu. in DMAc) 0.5 ml. solu./5 ml. chloral	64 (b)	8 (b)	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> Cl (0.3M in DMSO) (polymers nearly transparent)			
0.1	89 (c)	60 (c)	62
0.2	85 (c)	44 (c)	45
0.4	86 (c)	44 (c)	56
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> Br (0.5M in DMAc)			
0.2	50 (b)	2 (b)	



TABLE 24 (continued)

Initiator, mole % with respect to chloral	Percent Weight Retention After		
	Heating, 2 hr./100°C. in air	Heating in air 2 hr./100°C. followed by methanol extraction 2 days in Soxhlet	Methanol extraction 2 days in Soxhlet (no prior heating)
$C_6H_5CH_2S(n-C_3H_7)_2Br$ (0.5M in $CH_2Cl_2$ ) 0.5	no polymerization		
$C_6H_5CH_2S(n-C_3H_7)_2Br \cdot LiOC(CH_3)_3$ (0.19M in $CH_2Cl_2$ ) 0.046 0.18	32 (powder) (c) low (c)		
$p-O_2NC_6H_4CH_2S(CH_3)_2Cl$ (0.3M in DMSO) (polymers nearly transparent)			
0.1	84	57	45
0.2	81	50	46
0.4	72	29	44
$C_6H_5COCH_2S(CH_3)_2Br$ (satd. solu. in DMAc) 1.0 ml. solu./8 ml. chloral	35 (b)	1 (b)	
$C_6H_5COCH_2S(CH_3)_2Cl$ (0.3M in DMSO)			
0.1	67	43	33
0.2	72	34	39
0.4	65	22	39
$C_6H_5COCH_2S(n-C_4H_9)_2Br$ (0.5M in $CH_2Cl_2$ ) 0.5	no polymerization		
$C_6H_5COCH_2S(n-C_4H_9)_2Br \cdot LiOC(CH_3)_3$ (0.19M in $CH_2Cl_2$ ) 0.046 0.18	93 (c) 33 (c) 51 (c) 3 (c)		
$CH_3CH_2OCOCH_2S(CH_3)_2Cl$ (0.3M in DMSO)			
0.1	69	34	29
0.2	70	33	40
0.4	44	6	17

TABLE 24 (continued)

Initiator, mole % with respect to chloral	Percent Weight Retention After		
	Heating, 2 hr./100°C. in air	Heating in air 2 hr./100°C. followed by methanol extraction 2 days in Soxhlet	Methanol extraction 2 days in Soxhlet (no prior heating)
$(\text{CH}_3)_3\text{CS}(\text{CH}_3)_2\text{Cl}$ (0.3M in DMSO) (two experiments)			
0.1	57, 24	28, 2	20, 23
0.2	74, 69	39, 23	35, 30
0.4	68, 65	24, 19	55, 62
$(\text{CH}_3)_3\text{SOI}$ (satd. solu. in DMSO) 3 ml. solu./30 ml. chloral	61 (b)		2
$(\text{CH}_3)_3\text{SOI}$ (satd. solu. in DMAc) 0.5 ml. solu./5 ml. chloral	60 (b)	6 (b)	
$(\text{CH}_3)_3\text{SOCl}$ (satd. solu. in DMSO) 3 ml. solu./30 ml. chloral	75 (b)		6
$(\text{CH}_3)_3\text{SOCl}$ (satd. solu. in DMAc) 0.5 ml. solu./5 ml. chloral	60 (b)	12 (b)	
$(\text{CH}_3)_3\text{SOCl}$ (0.3M in DMSO)			
0.1	78	51	51
0.2	75	35	58
0.4	65	15	56
$(\text{C}_6\text{H}_5)_2\text{ICl}$ (satd. solu. in DMSO) 3 ml. solu./30 ml. chloral	31 (b)		33
$(\text{C}_6\text{H}_5)_2\text{ICl}$ (0.3M in DMAc) 0.5 ml. solu./5 ml. chloral	59 (b)	14 (b)	
$(\text{C}_6\text{H}_5)_2\text{ICl}$ (0.3M in DMSO)			
0.1	67	43	50
0.2	77	43	59
0.4	80	38	57

TABLE 24 (continued)

Initiator, mole % with respect to chloral	Percent Weight Retention After		
	Heating, 2 hr./100°C. in air	Heating in air 2 hr./100°C. followed by methanol extraction 2 days in Soxhlet	Methanol extraction 2 days in Soxhlet (no prior heating)
Tropylium bromide (0.3M in DMSO)			
0.1	36	6	0
0.2	20	3	0
0.4	43	9	0
Tropylium bromide, 0.3M in DMSO + LTB, 0.3M in benzene			
0.2	47	7	48
Tropylium chloride, satd. solu. in CH <sub>3</sub> CN (approx. 0.3M)			
	(parenthesized numbers in third column are for samples treated with CH <sub>3</sub> OH/10% HCl for one day before extraction)		
0.1	24 (c)	15 (c)	20 (19)
0.2	59 (c)	35 (c)	43 (35)
0.4	78 (c)	60 (c)	70 (57)
LTB, 0.1, + tropylium chloride, 0.3M in CH <sub>3</sub> CN (same as above)			
(mole%)			
0.1	52 (c)	8 (c)	31 (25)
0.2	35 (c)	8 (c)	25 (27)
0.4	88 (c)	56 (c)	72 (65)
C <sub>6</sub> H <sub>5</sub> COCH=S(CH <sub>3</sub> ) <sub>2</sub> , 0.3M in CHCl <sub>3</sub>			
0.1	30 (c)	0 (c)	0
0.2	70 (c)	5 (c)	2
0.4	88 (c)	6 (c)	5
CH <sub>3</sub> CH <sub>2</sub> OCOCH=S(CH <sub>3</sub> ) <sub>2</sub> , 0.3M in CHCl <sub>3</sub>			
0.1	67 (c)	11 (c)	3
0.2	29 (c)	5 (c)	17

- (a) Samples were cylindrical, about 12 mm. in diameter and weighing 2 to 5 grams, except as noted.  
 (b) Heated at 120°C. for one hour.  
 (c) Heated at 100°C. for one hour.

perfect the stabilization capabilities of the systems did not increase the amount of stable fraction. Trimethylsulfonium iodide and chloride produced polychloral samples sometimes containing over 50% of stable polymer fraction (with a DTG peak near 300°C.) in the heated or extracted polymer. However, the "stabilized" fraction as a percentage of initial polymer weight was low (6-22%) because of extensive degradation of the polymer during heating and extraction.

It was thought that the problem hindering stabilization of the polychloral by the trimethylsulfonium cation could be resistance of the cation to nucleophilic attack by the polychloral alkoxide anion. Hence sulfonium salts were prepared containing substituent groups such as benzyl, p-nitrobenzyl, phenacyl, carbethoxymethyl and tert-butyl; it was felt that these groups would be considerably easier to displace nucleophilically than the methyl group. In the thermal decomposition of benzyldimethylsulfonium (230) or phenacyldimethylsulfonium (229) salts, the benzyl or phenacyl halide and dimethyl sulfide were formed in high yield, showing that attack by the anion occurred preferentially on the benzyl or phenacyl group and not on the methyl group.

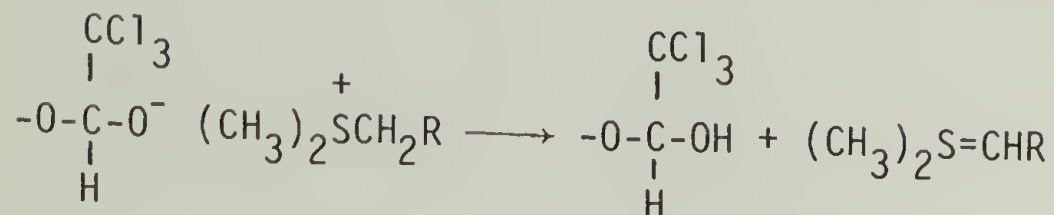
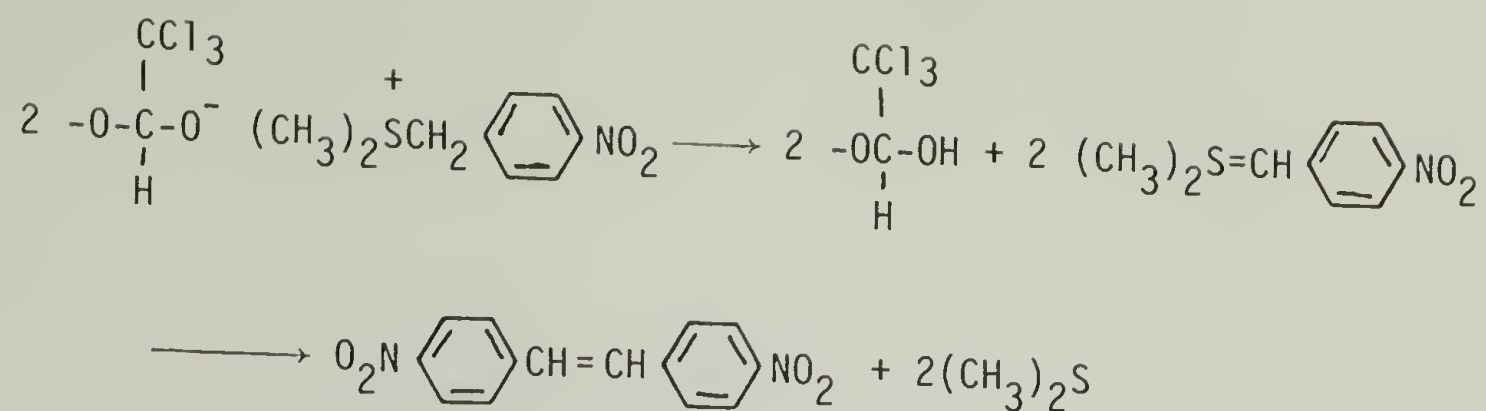
When these salts were used as chloral initiators, the benzyldimethylsulfonium chloride produced some significant stabilization of the polychloral, even when used as a solution in DMSO. A polychloral section which was heated and then extracted with methanol contained 30% of a "stabilized" fraction with a DTG peak temperature above 300°C., but another section from the same sample which was extracted with methanol without prior heating contained 60% of this "stabilized" fraction. (These corresponded respectively to 16% and 37% of the



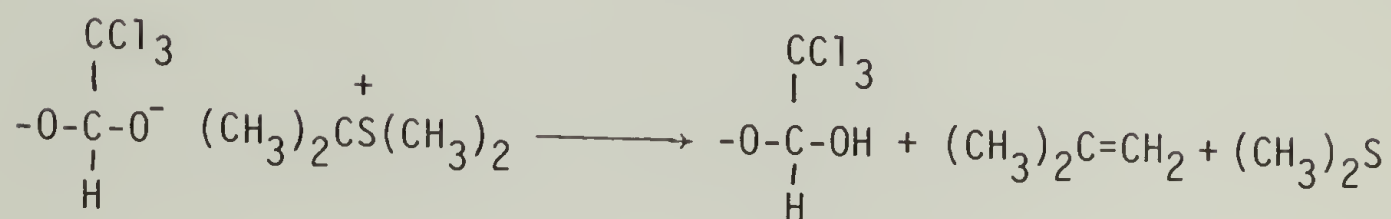
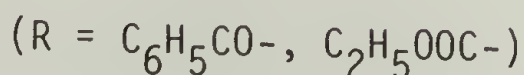
original polymer weight.) The higher percentage of stabilized fraction in the unheated than in the heated sample suggested that the reaction between the polychloral alkoxide group and the benzyldimethylsulfonium ion had taken place extensively in the polymer before heating, or perhaps that methanol application might have promoted the desired reaction, with application of heat instead causing side reactions. Benzyldimethylsulfonium bromide (as a DMSO solution) when used as an initiator did not appear to cause any endcapping, although a small amount of stabilization was noticeable when a DMAc solution was used as an initiator.

Dimethylsulfonium bromides or chlorides containing p-nitrobenzyl, phenacyl, carbethoxymethyl, or tert-butyl substituent groups were effective chloral polymerization initiators, although the yield of polychloral after extraction was lower than for the trimethyl- or benzyldimethylsulfonium salts. However, no endcapping could be detected in the DTG spectra of polychloral initiated with these salts; the DTG spectra of the heated, methanol-extracted polymers resembled that of polychloral containing only hydroxyl endgroups.

Although this result at first appeared very puzzling in light of the observed stabilization of polychloral by trimethyl- and benzyldimethylsulfonium salts, it may be possible that hydroxyl groups (which would not be alkylated by sulfonium ions) are formed from the growing polychloral alkoxide groups by one of the following reactions:



$\longrightarrow$  further products



The first reaction has been observed when p-nitrobenzylsulfonium salts are hydrolyzed with hydroxide ion in aqueous solution (228); tert-butyldimethylsulfonium salts are also known sometimes to lose a proton to give dimethyl sulfide and isobutylene (233). The second reaction of ylide formation is known for a number of sulfonium salts having electronegative substituent groups (such as phenacyl or carbethoxymethyl) in aqueous base (198,205); the resulting sulfonium ylides tend to decompose thermally to disubstituted ethylenes or trisubstituted cyclopropanes. Ylide formation from ions such as trimethyl- or dimethylbenzylsulfonium which lack carbonion-stabilizing groups generally requires much stronger bases in nonaqueous solvent systems (237), although

ylide intermediates may function in some reactions of sulfonium salts without ylide-stabilizing groups in aqueous systems (234).

Although thermal decomposition of sulfonium salts generally gives alkyl halides and dialkyl sulfides by an  $S_N2$  pathway, halide ions are very weak bases but considerably stronger nucleophiles. When the anion in a sulfonium "salt" is the polychloral alkoxide anion, which is a relatively strong base but a relatively weak nucleophile because of steric crowding, proton abstraction reactions might begin to be favored over nucleophilic displacement reactions in the thermal decomposition of the sulfonium "salt." This behavior is known for some sulfonium salts in hydrolysis by aqueous base, containing the strongly basic, but rather weakly nucleophilic hydroxide ion (198,205,233).

The above suggestion gives one possible reason for the lack of any stabilization of polychloral by these four sulfonium salts. However, it may be only one factor in causing such and not the major one, since benzyldimethylsulfonium bromide and diphenyliodonium chloride (see below and Table 26) also failed to give any stable polychloral under certain (but not all) reaction conditions. The reason for this remains unknown. Generation of the protic impurities by thermal decomposition of DMSO, as mentioned above, may have been a problem in some cases, although the best stabilization obtained for any sulfonium salt was noted for polychloral initiated with benzyldimethylsulfonium chloride in DMSO.

(It should be mentioned that, although trialkylsulfonium salts do tend to decompose to alkyl halides and dialkyl sulfides to some degree in warm solvents of low dielectric constant, the initiation of chloral



polymerization by sulfonium salts observed in this work was not caused by the possible decomposition product, dimethyl sulfide. When dimethyl sulfide was added to warm chloral at levels of 4 to 18 mole %, it caused no polymerization upon cooling.)

Benzyl-di(n-propyl)- and phenacyl-di(n-butyl) sulfonium bromides were prepared in hope of increasing the solubility of the initiators in ordinary organic solvents to eliminate the need for DMSO. However, these salts, when used as solutions in DMAc, produced very poor chloral polymers in low yield. When  $\text{CH}_2\text{Cl}_2$  was used as the initiator solvent, these salts would not initiate chloral polymerization at all. When these salts were used as 1:1 initiating mixtures with LTB, low yields of polymer were also generally obtained. In no case could any endcapping of polychloral by these salts be identified by thermal degradation behavior.

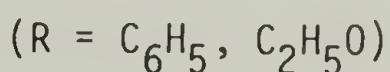
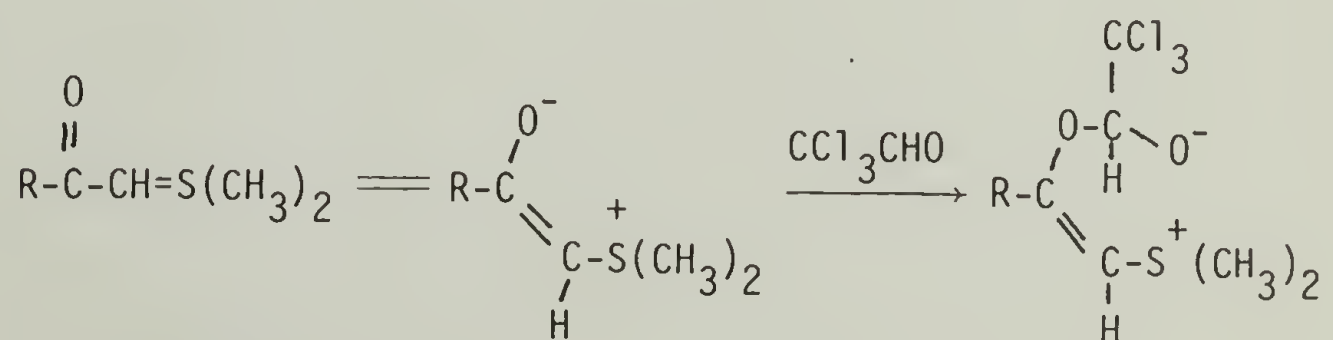
Trimethyloxosulfonium iodide and chloride and diphenyliodonium chloride were also synthesized and used as chloral initiators. The former compounds act as alkylating agents for nucleophiles in a manner similar to sulfonium salts (199), while the last functions as an arylating agent (239,240), decomposing thermally to iodobenzene and chlorobenzene. These salts gave polychloral of a heating and extraction stability comparable to that obtained with trimethylsulfonium or dimethylbenzylsulfonium salts (Table 24). Very small amounts of apparent endcapping were seen in the polymers, as shoulders in the DTG spectra of polychloral initiated with oxosulfonium salts and as small peaks (~20% of total peak area) in the DTG spectra of polychloral initiated with diphenyliodonium chloride. However, in no case was more than 10%



of the initial polymer stabilized. (3,3'-Dinitrodiphenyliodonium chloride was also prepared but was not used as a chloral initiator because no satisfactory dispersing solvent could be found.)

Because of the undesired reactions which possibly contributed to lack of stabilization of polychloral by sulfonium salts which contained electronegative substituent groups (p. 236), it was decided to prepare the ylides from two of these salts and to test the ylides themselves (as  $\text{CHCl}_3$  solutions) as chloral initiators, also avoiding the problems attendant to use of DMSO as solvent. The liquid ylide ethyl(dimethylsulfuranylidene)acetate was prepared from carbethoxymethyldimethylsulfonium bromide by the procedure of Payne (198), and phenacylidene dimethylsulfurane was prepared from phenacyldimethylsulfonium bromide according to Trost (205). However, multiple recrystallizations led invariably to crystals contaminated with an adhering black oil; no such problem was mentioned in the literature. The still impure ylide obtained after several recrystallizations was used for chloral initiation.

It was thought that the ylides could perhaps initiate chloral according to the following reaction sequence:



with the final species then being able to propagate by adding more chloral. The two sulfonium ylides did indeed initiate chloral polymerization, but the resultant polymer had low stability to heating and extraction (Table 24) and the DTG spectra showed no evidence of endcapping with the ethoxycarbonyl ylide and dubious evidence (a broad DTG peak) with the phenacyl ylide. The chloral-ylide reactions were not investigated further.

A number of nitrogen-containing compounds which can act as potential alkylating or acylating agents were also tested as initiators for chloral polymerization (Table 25, p. 241). Amide acetals, particularly the dialkyl acetals of dimethylformamide and 1-formyl-3,5-dimethylpyrazole, were reported in a patent (241) to be effective initiators for chloral polymerization and to give polymers of high thermal stability without extraction, although only chloral-isocyanate copolymers were listed in the patent examples.

In order to test these materials as initiators for chloral homopolymerization, we prepared the dimethyl, diisopropyl, dicyclohexyl, and dibenzyl acetals of DMF, as well as 1-aza-4,6-dioxabicyclo(0.3.3)octane and 1-(dimethoxymethyl)-3,5-dimethylpyrazole. The first four compounds produced chloral homopolymer samples which were weak and crumbly and had very low stability to heating in air (Table 25). The fifth compound did not homopolymerize chloral at all, while the sixth produced a nearly transparent polymer of intermediate stability to heating in air. The DTG spectrum of this polymer (Table 26), however, gave dubious, if any, evidence for endcapping. It seems rather noteworthy that in polychloral initiated with this pyrazole amide acetal

TABLE 25  
Heating and Extraction Stability of Polychloral Prepared with Miscellaneous  
Potentially Stabilizing Initiators (a)

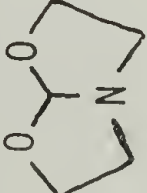

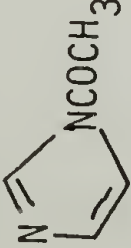
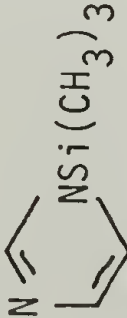
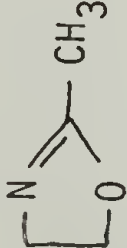
Initiator, mole % with respect to chloral (b)	Percent Weight Retention After			
	Heating, 1 hr./100°C. in air	Heating in air 1 hr./100°C. followed by methanol extraction, 2 days in Soxhlet	Methanol/10% HCl 1 day at room temp. followed by methanol extraction, 2 days in Soxhlet	Methanol extraction 2 days in Soxhlet
$(\text{CH}_3)_2\text{NCH}(\text{OCH}_3)_2$	0.8 1.6	8-29 14		
$(\text{CH}_3)_2\text{NCH}(\text{OCH}(\text{CH}_3)_2)_2$	0.8	3		
$(\text{CH}_3)_2\text{NCH}(\text{O-cyclo-C}_6\text{H}_{11})_2$	0.8	46		
$(\text{CH}_3)_2\text{NCH}(\text{OCH}_2\text{C}_6\text{H}_5)_2$	0.8	31		
	0.8	No polymerization		
	0.1 0.2 0.4 0.8 1.6	42 56 61 67 71, 77		20 24 29 30 23, 27

TABLE 25 (continued)

Initiator, mole % with respect to chloral (b)	Percent Weight Retention After			Methanol extraction 2 days in Soxhlet
	Heating, 1 hr./100°C. in air	Heating in air 1 hr./100°C. followed by methanol extraction, 2 days in Soxhlet	Methanol/10% HCl 1 day at room temp. followed by methanol extraction, 2 days in Soxhlet	
 0.3M in CHCl <sub>3</sub>	67 65 48	13 7 4	65 69 42	6 4 5
 0.3M in CHCl <sub>3</sub>	57 49 6	1 0 0	55 59 31	0 34 0
 0.1-100	<1			

(a) Samples were cylindrical, about 12 mm. in diameter, weighing 3-10 grams.

(b) Initiator used as neat liquid unless otherwise specified.



TABLE 26

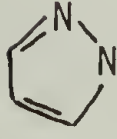
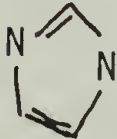
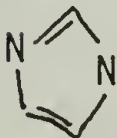
DTG Spectra of Polychloral Samples Prepared with "Onium"  
Salt and Other Potentially Stabilizing Initiators

Initiator (mole %)	Percent of Initial Weight Remaining in Sample Used After Treatment Given	DTG Parameters (d)	
		Onset of Decomposition, °C.	Degradation Rate Maxima, °C. (% of total area)
$(\text{CH}_3)_3\text{SI}$ , 1M in DMSO (0.77)	42 (a)	160	220 (47), 272 (53)
$(\text{CH}_3)_3\text{SI}$ , satd. in DMAc (Table 24)	15 (b)	140	244 (60), 320 (40)
$(\text{CH}_3)_3\text{SCl}$ , 0.3M in DMSO (0.1)	56 (b)	100	237 (87), 283 (13)
$\text{C}_6\text{H}_5\text{CH}_2\text{S}(\text{CH}_3)_2\text{Br}$ , 0.3M in DMSO (0.1)	54 (b)	100	210 (100)
	54 (c)	110	231 (100), 170 (sh)
$\text{C}_6\text{H}_5\text{CH}_2\text{S}(\text{CH}_3)_2\text{Br}$ , satd. in DMAc (Table 24)	8 (b)	135	210 (90), 310 (10)
$\text{C}_6\text{H}_5\text{CH}_2\text{S}(\text{CH}_3)_2\text{Cl}$ , 0.3M in DMSO (0.1)	60 (b)	130	209 (70), 327 (30)
	62 (c)	110	191 (40), 322 (60)
$\text{C}_6\text{H}_5\text{CH}_2\text{S}(\text{n-C}_3\text{H}_7)_2\text{Br}$ , 0.5M in DMAc (Table 24)	2 (b)	130	205 (100)
$p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{S}(\text{CH}_3)_2\text{Cl}$ , 0.3M in DMSO (0.1)	57 (b)	110	224 (100)
	45 (c)	120	250 (100), 180 (sh)
$\text{C}_6\text{H}_5\text{COCH}_2\text{S}(\text{CH}_3)_2\text{Br}$ , satd. soln. in DMAc (Table 24)	1 (b)	120	200 (100)
$\text{C}_6\text{H}_5\text{COCH}_2\text{S}(\text{CH}_3)_2\text{Cl}$ , 0.3M in DMSO (0.1)	43 (b)	100	215 (100)
$\text{C}_6\text{H}_5\text{COCH}_2\text{S}(\text{n-C}_4\text{H}_9)_2\text{Br} \cdot \text{LiOC}(\text{CH}_3)_3$ 0.19M in $\text{CH}_2\text{Cl}_2$ (0.18)	51 (b)	110	175 (100)

TABLE 26 (continued)

Initiator (mole %)		Percent of Initial Weight Remaining in Sample Used After Treatment Given	DTG Parameters (d)	
			Onset of Decomposition, °C.	Degradation Rate Maxima, °C. (% of total area)
$\text{CH}_3\text{CH}_2\text{OCOCH}_2\text{S}(\text{CH}_3)_2\text{Cl}$ , 0.3M in DMSO (0.1)		34 (b)	120	226 (100)
$(\text{CH}_3)_3\text{CS}(\text{CH}_3)_2\text{Cl}$ , 0.3M in DMSO	0.1	28 (b)	130	230 (100)
	0.2	23 (b)	130	210-225 (100)
$(\text{CH}_3)_3\text{SOI}$ , satd. soln. in DMSO (Table 24)		61 (a)	120	194 (94), 250 (6)
$(\text{CH}_3)_3\text{SOI}$ , satd. soln. in DMAc (Table 24)		6 (b)	130	197 (100), 267 (sh)
$(\text{CH}_3)_3\text{SOCl}$ , satd. soln. in DMSO (Table 24)		75 (a)	130	210 (100), 247 (sh)
$(\text{CH}_3)_3\text{SOCl}$ , satd. soln. in DMAc (Table 24)		12 (b)	140	220 (100), 300 (sh)
$(\text{CH}_3)_3\text{SOCl}$ , 0.3M in DMSO (0.1)		51 (b)	110	219 (100)
$(\text{C}_6\text{H}_5)_2\text{ICl}$ , satd. soln. in DMSO (Table 24)		31 (a)	120	180 (100)
$(\text{C}_6\text{H}_5)_2\text{ICl}$ , satd. soln. in DMAc (Table 24)		14 (b)	140	225 (80), 320 (20)
$(\text{C}_6\text{H}_5)_2\text{ICl}$ , 0.1M in DMSO (0.1)		43 (b)	120	205 (83), 283 (17)
Tropylium bromide, 0.3M in DMSO (0.1)		6 (b)	140	215 (100)

TABLE 26 (continued)

Initiator (mole %)	Percent of Initial Weight Remaining in Sample Used After Treatment Given	DTG Parameters (d)	
		Onset of Decomposition, °C.	Degradation Rate Maxima, °C. (% of total area)
Tropylium bromide, 0.3M in DMSO (0.2) + LTB, 0.3M in benzene (0.1)	7 (b)	130	202 (100)
Tropylium chloride, approx. 0.3M in CH <sub>3</sub> CN (0.4)	78 (b)	130	217 (100)
	70 (c)	120	196 (100)
Tropylium chloride ~0.3M in CH <sub>3</sub> CN (0.2) + LTB, 0.3M in benzene (0.1)	8 (b)	120	202 (100), 252 (sh)
C <sub>6</sub> H <sub>5</sub> COCH=S(CH <sub>3</sub> ) <sub>2</sub> , 0.3M in CHCl <sub>3</sub> (0.2)	5 (b)	130	230-310 (broad)
C <sub>2</sub> H <sub>5</sub> OCOCH=S(CH <sub>3</sub> ) <sub>2</sub> , 0.3M in CHCl <sub>3</sub> (0.2)	5 (b)	130	212 (100)
 N-CH(OCH <sub>3</sub> ) <sub>2</sub> , neat (1.6)	77 (a)	50	162 (87), 264 (13)
 N-COCH <sub>3</sub> , 0.3M in CHCl <sub>3</sub> (0.2)	7 (b)	110	212 (100)
 N-Si(CH <sub>3</sub> ) <sub>3</sub> , 0.3M in CHCl <sub>3</sub> (0.1)	1 (b)	110	195 (100), 152 (sh)

(a) Heated without extraction (1 or 2 hours at 100-120°C in air; see Tables 24 and 25 for details).

(b) Heated followed by Soxhlet extraction with methanol.

(c) Soxhlet extracted with methanol without prior heating.

(d) DTG data for sample after heating or extraction (listed in weight percentage column).

initiator, polymer stability to heating and extraction generally increased rather than decreased with increasing initiator concentration. This is in sharp contrast to the behavior of polychloral initiated with pyridine, triethylamine, or tributylamine (Table 16). Even though the pyrazole amide acetal contains a basic nitrogen, excess initiator apparently does not catalyze polymer thermal decomposition or methanolysis as is the case with polychloral initiated with other amines (pp. 203-204).

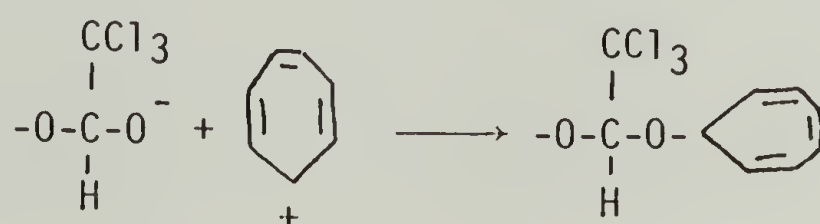
Because of the tendency of acyl- or silylimidazoles to act as acylating or silylating agents for hydroxyl groups (242,243), N-acetyl-imidazole and N-(trimethylsilyl)-imidazole were also tested as chloral initiators, in the hope that the polychloral endgroups would be acetylated or trimethylsilylated by these materials. However, polychloral prepared with these initiators showed the standard behavior of amine-initiated polychloral (Table 25), with stability to heating low and decreasing with increasing initiator concentration and stability to methanol extraction very low but markedly increased by acid treatment. The DTG spectra of polychloral prepared with these initiators showed no evidence of endcapping.

2-Methyl-2-oxazoline, a member of a class of compounds first prepared and polymerized by Litt and coworkers (244) and later found by other groups to serve as initiators for, and comonomers with, many electrophilic monomers such as beta-propiolactone, was tested as an initiator for cryotachensic polymerization of chloral over a concentration range from 0.1 mole % to equimolar. At low initiator concentrations, soft, weak polychloral gels were formed which were less than



1% stable to heating 1 hr. in air at 100°C. followed by methanol extraction. At equimolar initiator concentration, a crystalline compound was formed which melted at 118-119°C. after recrystallization from chloroform/hexane.

To test further the concept of stabilization by initiators and to explore the limits of initiation in the presence of reactive cations, however, we wished to use an initiator containing a countercation which could react with the polychloral alkoxide anion without the necessity of displacement of a group from the cation. Hence tropylium bromide and chloride were prepared and tested as initiators for chloral polymerization. It was thought that the halide ion would initiate a standard anionic polymerization of chloral, but that the tropylium ion would react with any polychloral alkoxide endgroup encountered immediately upon contact to form a cycloheptatrienyl ether endgroup:



This reaction occurs rapidly in methanol with sodium methoxide and tropylium bromide (204).

Tropylium bromide dissolved in DMSO was a poor initiator for chloral polymerization (Table 24, p. 230). The resultant polymers have a low stability to heating and methanol extraction. The polymer produced with a mixture of 0.2 mole % tropylium bromide and 0.1 mole % LTB was somewhat more stable to extraction, but neither form of polymer showed any trace of endcapping by DTG (Table 26, p. 243). It may be

argued that the reason for these results is that much of the tropylium bromide was consumed by a side reaction with DMSO. Tropylium chloride was therefore prepared, dissolved in  $\text{CH}_3\text{CN}$  and used as a chloral initiator. This produced chloral polymers which were much more stable to heating and extraction than those prepared with tropylium bromide in DMSO, but which also showed no peak near  $300^\circ\text{C}$ . in the DTG spectrum. The same results were observed when tropylium chloride was used as an additive to chloral initiated with LTB.

The failure of tropylium salts to endcap polychloral chains is difficult to explain. Such results might be expected if the polymerization occurred by a cationic, rather than an anionic, mechanism. However, the polymer obtained from chloral by tropylium salt initiation is hard and tough, not powdery like typical cationically initiated polychloral. Most likely, tropylium ion may undergo a side reaction with chloral (and/or acetonitrile) converting it into a species which cannot endcap the polychloral chain.

One attempt was made to use as an initiator for chloral polymerization a salt containing an acid bromide group,  $\text{BrCOCH}_2\text{S}(\text{CH}_3)_2\text{Br}$ . However, this salt, or rather the uncharacterized reaction product of bromoacetyl bromide with dimethyl sulfide, as a solution in sulfolane, did not polymerize chloral.  $\text{Ph}_3\text{P}$  in the presence of bromoacetyl bromide (or sulfolane) did cause chloral polymerization.

4. Stabilization by copolymerization with isocyanates and endcapping with hindered isocyanates. Of all of the different stabilization methods previously used for polychloral, only two were found to cause

complete stabilization of the homopolymer under any circumstances. These were posttreatment with a refluxing solution of  $\text{PCl}_5$  in  $\text{CCl}_4$ , which was effective in thin sections, and use of dimethyl sulfate as an additive in the polymerization mixture. The first was not effective in thick sections because of diffusion limitations and required reaction times; polymers such as polystyrene could also be leached from blends with polychloral. None of the compounds tried as stabilizing initiators for chloral polymerization would quantitatively endcap the polychloral, although a number of them produced partial stabilization. Hence it was strongly desired to find another, better method for polychloral stabilization.

Such a method was eventually found through a study of the copolymerization of chloral with isocyanates. The kinetics of the homopolymerization of chloral were followed by  $^1\text{H}$  NMR spectroscopy, with conversion being calculated from the progressive decrease of the chloral monomer peak integral (145). Chloral polymerization rates were followed with a number of initiators of different types (Figure 5, p. 131), and with different hydrocarbons used as diluents for the polymerization. This work was followed by similar determination of the homopolymerization kinetics by  $^1\text{H}$  NMR of bromodichloroacetaldehyde (174), dibromochloroacetaldehyde (175), and bromal (120).

We then decided to extend this work to the copolymerization of chloral with aromatic and aliphatic isocyanates of different structure. The polymerization procedure was similar to that described in (145) except that isocyanate was added to the chloral after initiation and before transfer to the NMR tube. The rate of polymerization of the



chloral and isocyanate was followed by the decrease of the integrals of the chloral and isocyanate  $^1\text{H}$  NMR peaks relative to the peak integral of an unreactive hydrocarbon diluent (cyclohexane for aromatic isocyanates, benzene for aliphatic isocyanates). LTB and  $\text{Ph}_3\text{P}$  were used as initiators.

The rates of copolymerization of phenyl, n-butyl, isopropyl, and tert-butyl isocyanates with chloral with LTB initiation are shown in Figure 11, p. 252. As one can see, phenyl isocyanate tended to copolymerize at a rate somewhat faster than chloral itself, while lowering the rate (and ultimate conversion) of chloral polymerization obtainable somewhat as compared to that in chloral homopolymerization (Figure 5, p. 131). n-Butyl isocyanate did not decrease substantially the rate of chloral polymerization but was incorporated into the copolymer at a much slower rate than chloral, with the polymer initially formed being primarily the homopolymer of chloral and the final polymer (formed after approximately 20 minutes reaction time) containing substantial amounts of isocyanate. Isopropyl isocyanate appeared not to copolymerize with chloral, with no decrease in the isocyanate peak integral detectable by  $^1\text{H}$  NMR spectroscopy even after one day of reaction, although it did not substantially decrease the rate of chloral homopolymerization. Tert-butyl isocyanate showed no evidence of copolymerization by NMR and also, when added to previously LTB-initiated chloral, strongly decreased the ultimate conversion of chloral in the polymerization. (When the tert-butyl isocyanate was added to the chloral before the LTB, a white precipitate formed on addition of the LTB and no polymerization occurred after subsequent cooling (245).)



Figure 11.  $^1\text{H}$  NMR Study of Rates of Chloral-Isocyanate Copolymerization.

Isocyanates: 5 mole % with respect to chloral

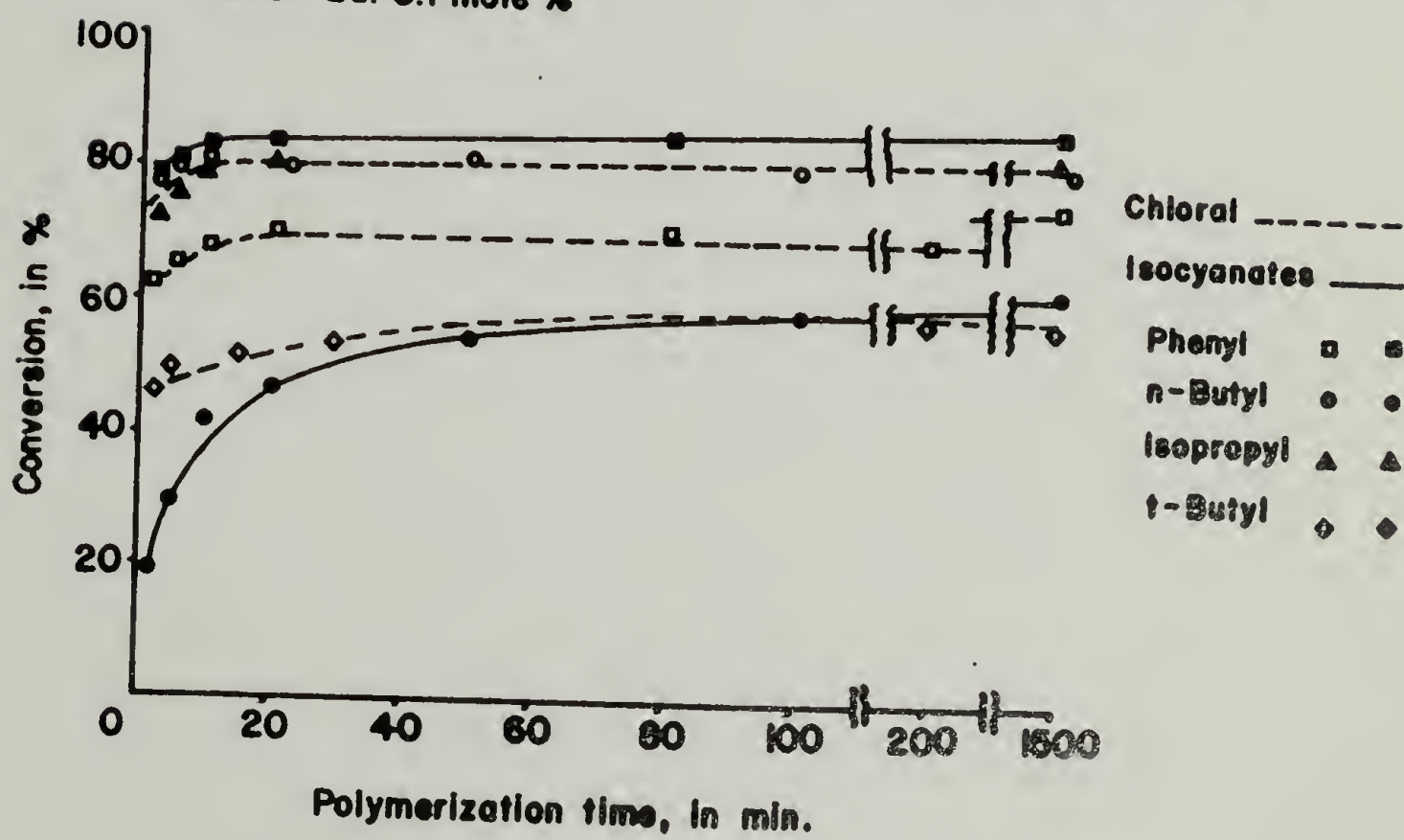
Initiator: LTB, 0.1 mole % with respect to chloral

Polymerization Temperature:  $0^\circ\text{C}$ .

# CHLORAL COPOLYMERIZATION WITH ISOCYANATES

ISOCYANATE: 5 mole %  
LiOt-Bu: 0.1 mole %

BATH TEMPERATURE: 0° C.



The data in Figure 11 represented values from two or more reproducible experiments; it was necessary to perform several experiments in some cases, particularly when polymerization rates were slow, because of considerable deviation in rates among different experiments.  $\text{Ph}_3\text{P}$  was also used as an initiator in the copolymerization of chloral with isocyanates, but reproducible data were obtained only for mixtures of chloral with isopropyl and tert-butyl isocyanates in  $\text{Ph}_3\text{P}$ -initiated polymerizations. The chloral polymerizations with  $\text{Ph}_3\text{P}$  initiation in the presence of these isocyanates proceeded at the same rate as chloral homopolymerization with  $\text{Ph}_3\text{P}$  (Figure 5) with no sign (by  $^1\text{H}$  NMR) of isocyanate incorporation into the polymer.

Chloral polymerization rates (with both LTB and  $\text{Ph}_3\text{P}$  initiators) were also determined for a number of aromatic isocyanates containing various electron-donating and electron-withdrawing groups (246,247). With LTB initiation, the copolymerization rates of the different substituted aromatic isocyanates with chloral were not very different from that of phenyl isocyanate, with copolymerization rates of p-chlorophenyl, o-chlorophenyl, p-methylphenyl, and p-methoxyphenyl isocyanate all quite similar. When  $\text{Ph}_3\text{P}$  was used as the initiator, rates of isocyanate incorporation into the copolymers were low and irreproducible. However, this work with substituted aromatic isocyanates, which was performed primarily by Dr. T. Teshirogi, is not especially pertinent to the following discussion and will not be covered further.

The enhanced thermal stability of copolymers of chloral with isocyanates over that of unstabilized chloral homopolymer has been mentioned a number of times in previous preparations of these copolymers

(155-165). These have also been reported as being much more thermally stable than homopolymers of isocyanates (156-160). Most previous thermal stability determinations on these copolymers have involved relative rates of isothermal weight loss at specific temperatures above 100°C. However, for comparison of the thermal degradation characteristics of the chloral-isocyanate copolymers with our previously prepared stabilized chloral homopolymers, we determined DTG spectra for the copolymers. Pertinent data from these DTG determinations are listed in Table 27, p. 255. Chloral-isocyanate copolymers containing from 4 to 6 mole percent of phenyl isocyanate (or four substituted aromatic isocyanates) or n-butyl isocyanate showed DTG spectra similar to those obtained for completely stabilized chloral homopolymers (for example, thin films treated with  $\text{PCl}_5$ ), with an onset of weight loss near 200°C. and a DTG decomposition peak near 300°C. Surprisingly, however, the polymers which had been prepared from mixtures of chloral and isopropyl or tert-butyl isocyanate, which had shown no isocyanate incorporation into the polymers by  $^1\text{H}$  NMR and which, after extraction and drying, gave carbon-hydrogen analyses within experimental error for chloral homopolymer, showed similar degradation characteristics (by DTG) to the copolymers with aromatic isocyanates.

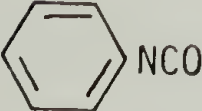
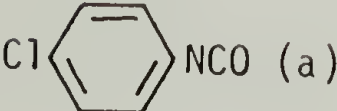
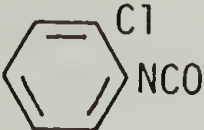


This was the case for polymers prepared from mixtures of chloral with isopropyl and tert-butyl isocyanates initiated with both LTB and  $\text{Ph}_3\text{P}$ . As a further check on the presence of isocyanate in the polymers, films of 0.01-0.03 mm. thickness were prepared from mixtures of chloral with 10 mole % of isopropyl and tert-butyl isocyanates initiated with 0.1 mole % LTB or 0.2 mole %  $\text{Ph}_3\text{P}$ . The films had similar



TABLE 27

DTG Data for Anionically Initiated Chloral-Isocyanate Copolymers

Initiator: LTB (0.1 mole%), 0.3M in cyclohexane or benzene

Isocyanate	Mole % isocyanate in copolymer	DTG degrada- tion rate maximum, in °C.
None	--	224
	5.5	314
 (a)	6.0	317
	4.9	297
	4.0	302
	4.3	305
n-BuNCO	6.0	297
i-PrNCO	<< 1.0	307
t-BuNCO	<< 1.0	317

(a) 0.05 mole% LTB as initiator.

degradation characteristics to the polymers prepared in the  $^1\text{H}$  NMR experiments, with initial weight loss occurring near  $200^\circ\text{C}$ . and decomposition rate peaks near  $300^\circ\text{C}$ . in the DTG spectrum. However, no peaks in the carbonyl region (which would indicate isocyanate incorporation into the polymers) could be seen in the infrared spectra of these films; the infrared spectra resembled those of chloral homopolymer. When films of 0.10-0.12 mm. thickness were prepared from  $\text{Ph}_3\text{P}$ -initiated chloral-5% isopropyl isocyanate mixtures, broad peaks centered at  $1745\text{ cm}^{-1}$  did appear in the infrared spectrum which were absent from spectra of chloral homopolymer films prepared without isocyanates. A thin film of chloral-p-chlorophenyl isocyanate copolymer containing 3.6 mole % of p-chlorophenyl isocyanate had a similarly broad carbonyl peak centered at  $1755\text{ cm}^{-1}$ .

The percentage of isopropyl isocyanate unit in the thick films was, from this information, calculated from the absorbances of the carbonyl peaks (relative to the C-H stretching peak at  $2960\text{ cm}^{-1}$  and the peak at  $2150\text{ cm}^{-1}$  as standards) by the method outlined on p. 185. This method showed that from 250 to 450 chloral units were present for each isopropyl isocyanate unit in the 0.10-0.12 mm. films stabilized with isopropyl isocyanate. (This method, of course, relies on the assumption that the molar absorptivity  $\epsilon$  is the same for the urethane carbonyl groups derived from isopropyl isocyanate units as for those derived from p-chlorophenyl isocyanate units in the polychloral chain.)

This amount of isopropyl isocyanate was too small to be detected by nitrogen or carbon-hydrogen analysis (outside experimental error), by  $^1\text{H}$  NMR kinetic determinations, or by infrared analysis of

thin ( $\sim 0.02$  mm.) films. If the number-average  $\overline{DP}$  of the polychloral is approximately 1000 (p. 139), then the above data would indicate the presence of from two to four isopropyl isocyanate units per polychloral chain. It is not known as to whether their distribution is random or whether the isocyanate units are clustered at the end of the polychloral chain. In either case, the resultant (opaque) stabilized polymer is essentially the homopolymer of chloral, and use of hindered (secondary or tertiary) aliphatic isocyanates in the polymerization mixture is the key to obtaining quantitatively stabilized chloral "homopolymer" in sections of any thickness and without posttreatment.

Unfortunately, yields of the polymers stabilized with hindered isocyanates were sometimes low and not always reproducible. Table 28 (p. 258) shows yields after extraction (and  $^1\text{H}$  NMR chloral polymerization conversions) for polymers prepared from mixtures of chloral with isopropyl and tert-butyl isocyanates. Yields of the stabilized polymers varied considerably from system to system, with the highest polymer yields found for the LTB-initiated polymers produced from polymerization mixtures containing isopropyl isocyanate.  $\text{Ph}_3\text{P}$ -initiated mixtures gave considerably lower yields, while yields after acetone extraction were generally less than 20% for mixtures containing tert-butyl isocyanate. These yields, in contrast to values obtained earlier for chloral homopolymer (145), are considerably lower than the chloral conversion values observed by  $^1\text{H}$  NMR. Possibly the aliphatic isocyanates (or ureas resulting from their reaction with water in the acetone extractant) promoted polychloral degradation, with the chains degrading down to an isocyanate unit to give a urethane endcap.

TABLE 28

Yields in Polymerization of Mixtures of Chloral with  
Aliphatic Isocyanates

Isocyanate (mole % with respect to chloral)	Initiator	Yield of polymer prepared in test tube, in % (a)	Yield of polymer prepared in NMR tube, in % (a)	Chloral conver- sion to polymer by $^1\text{H}$ NMR, in %
$(\text{CH}_3)_2\text{CHNCO}$ (5)	LTB	58 58	71 64	84 86
$(\text{CH}_3)_2\text{CHNCO}$ (10)	LTB	66 74	73 81	90 90
$(\text{CH}_3)_2\text{CHNCO}$ (5)	$\text{Ph}_3\text{P}$	38 28	42 26	78 73
$(\text{CH}_3)_2\text{CHNCO}$ (10)	$\text{Ph}_3\text{P}$	47 35	46 27	82 81
$(\text{CH}_3)_3\text{CNCO}$ (5)	LTB	15	20	59
$(\text{CH}_3)_3\text{CNCO}$ (10)	LTB	12	23	66
$(\text{CH}_3)_3\text{CNCO}$ (5)	$\text{Ph}_3\text{P}$	20	16	76
$(\text{CH}_3)_3\text{CNCO}$ (10)	$\text{Ph}_3\text{P}$	16	13	84

(a) After Soxhlet extraction with acetone for 2 days.



Table 29 (p. 260) shows polymer yields (after methanol extraction) for mixtures of chloral with different amounts of phenyl, n-butyl, and isopropyl isocyanates initiated with 0.1 mole % LTB. In the case of phenyl isocyanate, which copolymerizes with chloral at a rate similar to chloral itself (Figure 11, p. 252), polymer yield rose progressively from the typical low, irreproducible yield (6-60%) for LTB-initiated chloral homopolymer (p. 198) to a value consistently above 70% for isocyanate levels above 2 mole % with respect to chloral. For chloral copolymerization with n-butyl isocyanate, which enters the copolymer much more slowly (Figure 11) than does chloral itself, a similar trend was noticed, although the data were somewhat more erratic and the highest yields obtained were lower than in the chloral-phenyl isocyanate system. However, when isopropyl isocyanate, which is extremely reluctant to enter the polymer, was used, polymer yields varied erratically with isocyanate concentration over the entire range of isocyanate concentrations. The reason for this irreproducibility in yield is not known; the polymer yields from chloral-isopropyl isocyanate (and chloral-tert-butyl isocyanate) mixtures could possibly be improved and made more consistent by further refinements in experimental technique.

Although the problem of irreproducible yields still remains, the stabilization of chloral polymers with hindered isocyanates remains the most effective method for preparing thick sections of a stable material which is essentially chloral homopolymer.

TABLE 29

Yields in Polymerization of Mixtures of Chloral with Different Concentrations of Isocyanates (a)

Isocyanate	Isocyanate mole percentage with respect to chloral →	Yields of Extracted Polymer, % (b)						
		0	0.06	0.13	0.25	0.5	1	2
$\text{C}_6\text{H}_5\text{NCO}$	11	17	58	56	56	60	71	76
$n\text{-C}_4\text{H}_9\text{NCO}$	47	26	34	49	51	55	61	67
$(\text{CH}_3)_2\text{CHNCO}$	17	14	54	18	61	26	34	39
								50

(a) Initiator: LTB (0.1 mole%)

Sample characteristics: Cylinder, diameter approx. 12 mm.; weight approx. 12 grams.

(b) After Soxhlet extraction with methanol for 2 days.

F. Preparation of Polychloral with Optically Active  
Initiators and Attempted Determination of  
Optical Activity

With the previous problems of mechanism of action of different chloral polymerization initiators, nature of polychloral endgroups, chloral homopolymer stabilization, and preparation of semitransparent systems containing chloral homopolymer having either been solved or brought to a satisfactory conclusion, it was desired to find a system in which optical activity of polychloral could be measured. Since polychloral is infusible and insoluble in all solvents, its optical activity could only be measured in the solid state; indeed, dissolution of polychloral, even if such were possible, would be expected to destroy its optical activity by destroying the helicity. A number of techniques for measuring optical activity of solid polymers were summarized by Bonsignori and Lorenzi (106). These are basically of two types. The first involves suspending a finely divided solid polymer in a solvent mixture having the same refractive index as the polymer; the suspension is then agitated in a polarimeter cell and the optical rotation determined. In this method, contributions to optical rotation from birefringence due to orientation of the polymer particles are averaged to zero because of the large number of polymer particles meeting the polarimeter beam at random angles; the remaining optical rotation is due to the optical activity of the polymer sample. The second method involves polarimetric measurements on polymer films or plates which have been carefully prepared to be free of orientation, which produces birefringence. A requirement in both of these methods is that the

polymer suspension or film be sufficiently transparent that most of the incident light reaches the polarimeter detector without excessive scattering.

Attempts were initially made to determine what liquid-liquid systems and forms of polychloral would be suitable for determination of optical activity in suspension. When the refractive index of a polychloral film was measured microscopically by the Becke line technique (248), it was found to be between the refractive indices of diphenyl ether (1.576) and a mixture of diphenyl ether with 10% of 1-bromonaphthalene (1.658 for 1-bromonaphthalene). However, in diphenyl ether the film-liquid junction was essentially invisible and the film was therefore very close in refractive index to diphenyl ether. This liquid was used in all initial suspension experiments.

A number of different chloral homopolymer and copolymer samples were then prepared by several techniques, including a number of those previously known to give transparent or semitransparent polymers. Polymers were prepared from chloral-p-chlorophenyl isocyanate mixtures containing from 1 to 5 mole % isocyanate in order to determine the minimum amount of isocyanate necessary for satisfactory transparency in suspension. A blend was prepared in large quantities from a mixture of chloral with 20 mole % of styrene, small samples of which had earlier been found to be nearly transparent after acetone extraction (p. 152). Also, quantities of chloral homopolymer were prepared using 1.8 mole % of 1-(dimethoxymethyl)-3,5-dimethylpyrazole as initiator, which had likewise been shown to produce nearly transparent chloral homopolymer (p. 240).



The polymers were then milled on an intermediate-size Wiley mill to pass a 40-mesh screen, followed by extraction and drying. Considerable difficulties were encountered in milling the plugs of chloral-isocyanate copolymers by this technique, and it was found more convenient to mill these polymers first to granules 0.5-1 mm. in diameter with a large Thomas ED-5 Wiley mill and then to mill these granules to powder using the smaller Wiley mill.

When the milled chloral homopolymers and copolymers with 3 or 5 mole % p-chlorophenyl isocyanate were then placed into suspension in diphenyl ether, only translucent turbid suspensions could be obtained. Slow, dropwise addition of 1-bromonaphthalene did not produce visually transparent suspensions even when up to 50 volume percent (relative to diphenyl ether) of 1-bromonaphthalene was added. To test suspension transparency quantitatively, suspensions of copolymers prepared from mixtures of chloral with 3 or 5 mole percent of p-chlorophenyl isocyanate were prepared in 10 ml. of diphenyl ether ( $n_D = 1.576$ ) and placed into a turbidimeter. The agitated suspensions were then titrated with 1-bromonaphthalene ( $n_D = 1.658$ ) or 1,2-dichlorobenzene ( $n_D = 1.551$ ). Titration of a suspension of chloral-3% p-chlorophenyl isocyanate copolymer with 1-bromonaphthalene increased light transmittance from 85% initially to 93% after addition of 3 ml. of 1-bromonaphthalene, but the transmittance did not increase further upon addition of an additional 2 ml. of 1-bromonaphthalene. When 1,2-dichlorobenzene was used instead as the titrant, transparency did not change on titration. When a suspension of chloral-5% p-chlorophenyl isocyanate polymer was instead used, transmission was initially 67% and

rose to a plateau of 78% upon addition of 1-bromonaphthalene.

Hence the reason for the turbidity of suspensions of powders (prepared from transparent blocks of chloral-isocyanate copolymers) in liquid mixtures based on diphenyl ether was not caused by mismatch of refractive index between polymer and solvent mixture. It was felt that the turbidity could be caused by surface orientation of these amorphous polymers produced during milling, with the refractive index on the surface of the polymer particles becoming different from that in the interior. Therefore it was attempted to prepare powders of high molecular weight chloral copolymer without the necessity of milling. Although low-molecular weight polychloral powders can be prepared by using large amounts of "rapid" alkoxide initiators (pp. 69 -72 ), the alkoxide residue is believed to be chemically bound to the polymer in these materials, and the high ratio of initiator residue to polymer could lead to questionable optical activity data from these polymers.

Therefore, preparation of powdered chloral-p-chlorophenyl isocyanate copolymer was attempted by suspension copolymerization. A mixture of chloral with 5 mole % of p-chlorophenyl isocyanate was prepared in perfluoro-2-(n-butyl)tetrahydrofuran, a liquid which is immiscible with chloral. Polymerization was then carried out with LTB initiator by the standard cryotachensic technique, with stirring of the suspension during cooling. However, upon cooling the droplets of chloral-isocyanate mixture suspended in the fluorocarbon did not polymerize to granules of polymer but rather coalesced into a film of copolymer on the surface of the reaction kettle.

Because of the extensive amount of scattering of light in the

chloral homopolymer or copolymer suspensions previously obtainable, it was decided to prepare sheets of chloral homopolymer and copolymers and to attempt to remove orientation in these sheets by solvent annealing to give materials on which optical rotation resulting from optical activity could be determined. A sheet 2.5 mm. thick was prepared from a chloral/15% p-chlorophenyl isocyanate mixture and a number of discs approximately 13 mm. in diameter were cut from the sheet with a hole saw. After extraction and drying, the discs were soaked in diphenyl ether at 40°C. for one week in an attempt at solvent annealing to remove orientation. When a disc was placed between glass plates in the film polarimeter cell, still soaked with diphenyl ether, no optical activity readings could be made with a visual polarimeter. When the disc was placed between crossed polarizers in a device designed for detecting stresses in glassware, the disc showed iridescence, indicating a substantial amount of residual orientation which remained in the disc even after solvent annealing. When a thin film (~0.05 mm. thick) of  $\text{Ph}_3\text{P}$ -initiated unextracted polychloral was solvent annealed by the same procedure as above and several discs cut from the film were laminated together with diphenyl ether in the film polarimeter cell, the resultant "sandwich" of films had an optical rotation of zero and the annealed film did not show colors when held between crossed polarizers. Hence thin films were chosen for further work with optically active polychloral. (Diphenyl ether was used as the annealing solvent because of its close match with polychloral in refractive index and its low vapor pressure at room temperature.)

It was decided to attempt to prepare polychloral using four



types of optically active initiators in order to determine the relative influence of the initiating anion and counteranion on the optical activity of the resultant polychloral. These four initiator types were:

1. A neutral optically active initiator such as a tertiary amine;
2. A salt containing an optically active anion and an optically inactive cation;
3. A salt containing an optically inactive anion and an optically active cation;
4. A salt with both anion and cation optically active.

The representative of the first class of initiator actually used was brucine, a commercially available chiral tertiary amine containing no active hydrogen atoms which would inhibit chloral polymerization. As the source of the optically active anion was chosen (+)-ketopinic acid (2-oxo-7,7-dimethylbicyclo(2.2.1)heptane-1-carboxylic acid), a monocarboxylic acid which contained no active hydrogen groups other than the single carboxyl, which contained an asymmetric center immediately adjacent to the carboxyl group, and which could be easily synthesized by permanganate oxidation of the chloride of the commercially available (+)-10-camphorsulfonic acid (209). As the representatives used of the second class of initiators, benzyltriphenylphosphonium (+)-ketopinate was prepared by reaction of silver (+)-ketopinate with benzyltriphenylphosphonium bromide in methanol, and tetramethylammonium and tetrabutylammonium (+)-ketopinate were prepared by titration of solid (+)-ketopinic acid to a phenolphthalein endpoint with commercially available methanol solutions of tetramethylammonium and tetrabutylammonium



hydroxides. (The tetrabutylammonium (+)-ketopinate was obtainable only as a viscous liquid.)

As the optically active counteranion for use in these experiments was chosen the (+)-methyl-n-propylphenylbenzyl phosphonium ion, which was obtained as the chloride salt by reaction with benzyl chloride of (+)-methyl-n-propylphenylphosphine (see p. iv ). An attempt was made to convert the chloride into the (+)-ketopinate salt by reaction with silver (+)-ketopinate in methanol, but the resultant compound (an initiator of the fourth class) could not be made to crystallize and was used as an oil.

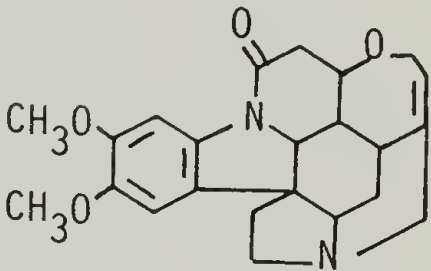
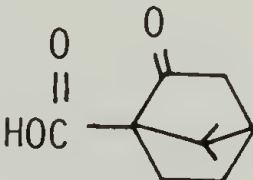
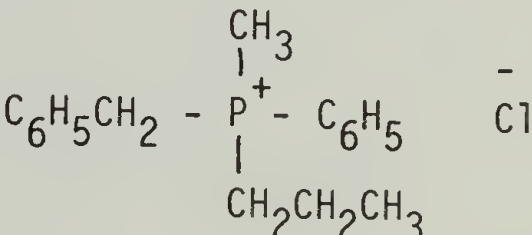
The structures of the initiators used are shown in Table 30, p. 268.

Polychloral films and plugs were prepared by the standard cryotachensic polymerization technique with each of the initiators. Tough films were generally obtained, but the films prepared with the non-crystallizable initiators (tetrabutylammonium (+)-ketopinate and (+)-methyl-n-propylphenylbenzyl phosphonium (+)-ketopinate) and also with benzyltriphenylphosphonium (+)-ketopinate were crumbly and not strong enough for solvent annealing and polarimetric measurement. Tetramethylammonium (+)-ketopinate, however, produced tough polychloral films both when dissolved in chloroform and when dissolved in sulfolane. Other initiators were used as solutions in chloroform and produced tough, coherent polychloral films;  $\text{Ph}_3\text{P}$  and benzyltriphenylphosphonium bromide were used as optically inactive control initiators.

The films and plugs were treated one day with methanol/HCl, extracted with methanol in a Soxhlet extractor for 2 days and dried;

TABLE 30

## Optically Active Initiators Used for Chloral Polymerization

Class (p. 266)	Example(s) used
1. Nonionic optically active molecule	Brucine, 
2. Optically active anion, optically inactive cation	Tetramethylammonium, tetra(n-butyl) ammonium, and benzyl triphenyl-phosphonium salts of (+)-ketopinic acid, 
3. Optically inactive anion, optically active cation	(+)-(S)-Methyl(n-propyl)phenyl-benzyl phosphonium chloride, 
4. Optically active anion, optically active cation	(+)-(S)-Methyl-(n-propyl)phenyl benzylphosphonium (+)-ketopinate

yields are shown in Table 31, p. 270. Polychloral plug yields for most of the initiators were in the 60-80% range typical for triphenylphosphine-initiated chloral homopolymer. Brucine, as an amine, gave a lower yield of polymer after extraction, similar to the results with other amines (p. 203). Benzyltriphenylphosphonium (+)-ketopinate of unknown purity also gave a rather low yield of polychloral. Film yields after extraction were considerably lower than plug yields, because of the increased penetration of the hot methanol into the thin films as compared with the plugs.

The films were then cut into a number of discs of 12 mm. diameter and annealed in diphenyl ether at 50°C. for from two days to one week. The discs were then laminated (with diphenyl ether) within the polarimeter film cell (p. 110) and the thickness of the cell was measured at three points along its perimeter, with an average value taken. The thickness of the laminated film "sandwiches" used was generally 0.5 to 1.5 mm.; in all cases except for the films initiated with brucine, the transparency of the films laminated with diphenyl ether was excellent. The thickness of the individual films used was generally on the order of 0.05 mm.

Polarimetric measurements on the cell containing the laminated films were then performed at three orientations with the latter at 120° and 240° respectively to the first. Average rotations for the films, and average absolute rotations, were determined, together with average specific rotations per millimeter. These data are shown in Table 32, p. 271.

As one can see from the table, even the films initiated with

TABLE 31  
Yields of Polychloral Films and Plugs Prepared With  
Optically Active Initiators (a)

Initiator (b)	Film yield, in %	Plug yield, in %
$\text{Ph}_3\text{P}$	33 (e)	79 78
$\text{PhCH}_2\text{PPh}_3^+\text{Br}^-$	18	72
Brucine	(e)	44
$\text{PhCH}_2\text{PPh}_3^+\text{Ket}^-(\text{c})$	incoherent	13
$(\text{CH}_3)_4\text{N}^+\text{Ket}^-(\text{c})$	(e)	82
$(\text{CH}_3)_4\text{N}^+\text{Ket}^-(\text{c,d})$	incoherent	80
$(+)\text{-(CH}_3\text{)(n-C}_3\text{H}_7\text{)(C}_6\text{H}_5\text{)(C}_6\text{H}_5\text{CH}_2\text{)}^+\text{PCl}_3^-$	4	68
$(+)\text{-(CH}_3\text{)(n-C}_3\text{H}_7\text{)(C}_6\text{H}_5\text{)(C}_6\text{H}_5\text{CH}_2\text{)}^+\text{P}^-\text{Ket}^-(\text{c})$	incoherent	63

- (a) After Soxhlet extraction with methanol for 2 days and drying.
- (b) 0.39 mole% (with respect to chloral) of initiators used as 0.25-0.4M solutions in  $\text{CHCl}_3$ .
- (c) Ket = (+)-Ketopinate.
- (d) Sulfolane used as initiator solvent.
- (e) Not weighed before extraction.



TABLE 32  
Optical Rotation Data for Polychloral Films (a)

Initiator (b)	Thickness of lami- nated films in mm.	Average rotation values at cell angles of			Average rotation (per mm.)	Average absolute rotation (per mm.)
		0°	120°	240°		
Ph <sub>3</sub> P <sup>+</sup> + PhCH <sub>2</sub> PPh <sub>3</sub> Br <sup>-</sup>	0.837	(+)0.17-0.18°	(+)0.05-0.06°	(+)0.26-0.28°	+0.16°(+0.20°)	0.16°(0.20°)
	1.503	(-)0.41-0.43°	(-)0.22-0.24°	(-)0.89-0.91°	-0.52°(-0.34°)	0.52°(0.34°)
Brucine <sup>+</sup> + (CH <sub>3</sub> ) <sub>4</sub> N Ket (c)	1.047	(+)0.35-0.38°	(-)0.62-0.64°	(-)0.75-0.78°	-0.18°(-0.17°)	0.42°(0.40°)
	0.263	(-)0.96-1.03°	(+)1.68-1.74°	(-)0.80-0.74°	-0.11°(-0.42°)	1.16°(4.40°)
(CH <sub>3</sub> ) <sub>4</sub> N Ket (c,d) + (CH <sub>3</sub> ) <sub>4</sub> N Ket (c,d)	0.593	(+)0.18-0.23°	(-)1.45-1.48°	(-)0.59-0.57°	-0.61°(-1.03°)	0.75°(1.26°)
	0.650	(+)62.4-62.5°	(+)42.4-42.45°	(+)32.8-32.9°	+45.9°(+70.6°)	45.9°(70.6°)
(+)-(CH <sub>3</sub> )(n-C <sub>3</sub> H <sub>7</sub> )(C <sub>6</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) + PCl <sup>-</sup>	1.473	(-)50.1-50.16°	(-)55.5-55.85°	(-)48.76-48.3°	-51.4°(-34.9°)	51.4°(34.9°)

(a) Films CH<sub>3</sub>OH extracted, then annealed for 2-6 days in diphenyl ether at 50°C.; optical rotation measured as laminates moistened with diphenyl ether.

(b) 0.39 mole% (with respect to chloral) of initiator used as 0.4M solutions in CHCl<sub>3</sub>.

(c) Ket = (+)-Ketopinate.

(d) Sulfolane used as initiator solvent.

optically inactive initiators such as triphenylphosphine and benzyl-triphenylphosphonium bromide showed small apparent optical rotations, less than  $1^\circ$  per millimeter. These were most likely due to birefringence, because the annealing with diphenyl ether did not completely remove orientation in these extracted polychloral films, in contrast to the earlier experience with unextracted films (p. 265). All of the extracted polychloral films used in this experiment still showed some iridescence between crossed polarizers after being annealed with diphenyl ether at  $50^\circ\text{C}$ . for one week.

Polychloral films initiated with some optically active initiators (brucine, tetramethylammonium (+)-ketopinate in chloroform) showed optical rotations not much larger than those obtained for films initiated with optically inactive initiators. Also, both types of films often showed (small) optical rotations differing in sign with different angle of rotation of the cell.

However, two of the optically active initiators, tetramethylammonium (+)-ketopinate in sulfolane and (+)-methyl-n-propylphenylbenzylphosphonium chloride in chloroform, gave films which could be laminated to materials having very high optical activity of the same sign (though differing somewhat in magnitude) at all three rotation angles of the cell used. Because of the strong optical rotation of the same sign at all three cell angles in cells containing from 10 to 30 laminated film discs, it appears that optically active polychloral may have been formed in these films. However, optical activity is still made uncertain by strong birefringence effects, as shown by the marked changes in optical rotation upon changes in cell position for many of

the samples.

In future work, one could do a number of things in an attempt to reduce further the effects of birefringence:

1. Anneal for a longer time. Longer annealing times may further decrease orientation which causes birefringence. The polychloral film for which annealing with diphenyl ether earlier appeared effective in removing birefringence (p. 265) had not been extracted with a solvent or subsequently dried. Because of the considerable amount of shrinkage often occurring upon drying after extraction, orientation with resultant birefringence might be lessened considerably by transferring the wet films directly from methanol to diphenyl ether. The development of birefringence in the films might be traced by following the polychloral films with crossed polarizers through polymerization, removal from the glass plates, methanol extraction, and diphenyl ether annealing. This following of birefringence could suggest further ways of preventing its formation. (For following the development of birefringence during polymerization, diphenyl ether itself might be the ideal polymerization diluent because of its close refractive index match with polychloral.)

2. For each film, repeat the optical rotation determination performed above, but in several stages using increasing numbers of films in each stage. Optical rotation due to birefringence should show no pattern with increasing numbers of randomly oriented films in the cell. Addition of a new film would be as likely to decrease as to increase observed optical rotation due to birefringence, since the orientation in the new layer would be as likely to be perpendicular to that in the previous layer as to be parallel to it. Optical rotation due to optical

activity, however, should increase linearly with increasing thickness of the film composite measured.

3. Run the above experiment using a cell equipped with an air turbine, which can rotate the films at a speed such that one revolution requires less time than the correlation time of the polarimeter. (For even better accuracy, this experiment could be performed with a time-integrating polarimeter such as the Perkin-Elmer 241MC.) Then the polarimeter would see an average value of the optical rotation over all angles of cell position, canceling the effect of birefringence (106). (The above experiment was performed with readings at only the three cell positions possible with the Perkin-Elmer 141MC polarimeter used, and readings differed markedly with cell position.)

4. Return to use of suspensions. Although the method of (3) would give a considerable improvement over that actually used in the experiment performed above, it still would give merely the value of the rotatory power for a particular direction in an optically anisotropic sample, with the optic axis created artificially by the cell rotation (106). This is not really comparable to optical activity as measured in an isotropic solution. Optical activity determined in suspensions of fine powders, however, would be directly comparable to solution optical activity, because there would be averaging over all optic axes of the sample. This work was not performed above because of problems with turbidity. However, chloral copolymer suspensions could conceivably be used in a standard polarimeter with a specially designed rotating cell to maintain the suspension in an agitated state during measurement, and chloral homopolymer suspensions might be used in a



polarimeter specially designed to measure optical rotations of turbid materials (249).

#### G. Conclusions and Further Work

The work in this dissertation has shown that polychloral of sufficient transparency and stability for optical activity measurements can be prepared. Initiation mechanism studies have shown the cases in which initiator residues in the polymer must be considered, and preparation of blends of polychloral with other polymers has shown one way to obtain nearly transparent chloral homopolymer in bulk. The nature of the end-groups in polychloral prepared by cryotachensic anionic techniques has been characterized, and an effective means of preparing chloral "homopolymer" with little or no thermal degradation below 200°C. has been discovered. Preliminary work with optically active initiators has led to highly promising results, with very high optical rotations (consistently in the same direction at all angles of cell orientation) obtained for polychloral films prepared with two optically active initiators. However, the results remained uncertain because it was not possible to eliminate birefringence completely.

Further work, in the opinion of this author, should concentrate initially on unequivocally proving (or disproving) the existence of optical activity in polychloral by use of the experimental refinements described on pp. 273-275. This unequivocal determination may be made either by eliminating birefringence in polychloral films through improved methods of annealing or by randomizing birefringence, averaging its effects over all angles (pp. 273-275) to determine the net optical

rotation caused by optical activity.

If the above polychloral could be unequivocally proven to be optically active, characterization of the crystal structure by wide-angle X-ray scattering would be indicated in order to determine the pattern of helices in such polychloral. The properties of the optically active polychloral should then be compared with those of standard optically inactive polychloral by all standard means of characterization (tensile testing, Rheovibron, DSC, SEM, TEM, SALS, etc.) used to characterize optically inactive polychloral in the past.

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## A P P E N D I X   A

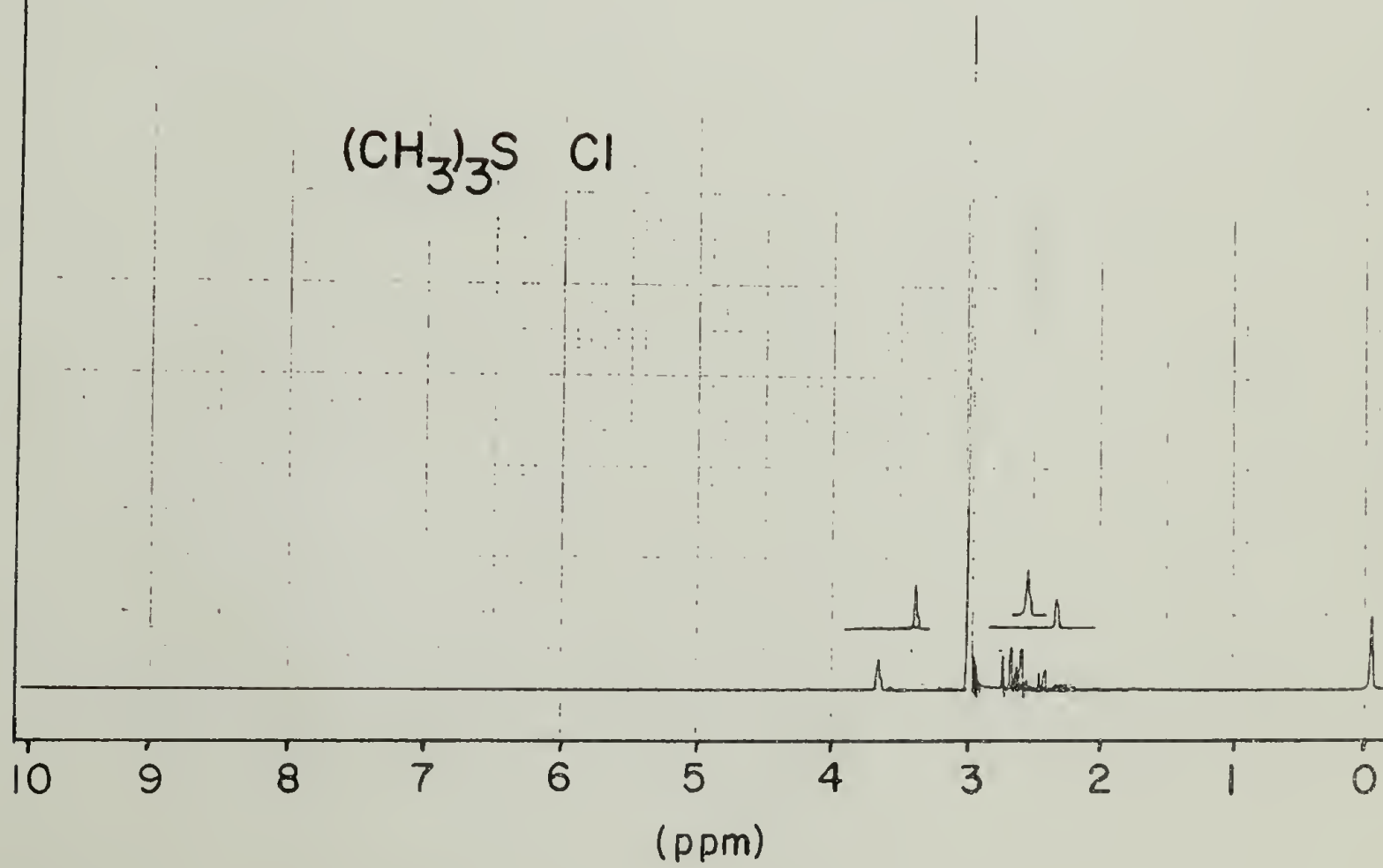
### PROTON MAGNETIC RESONANCE SPECTRA

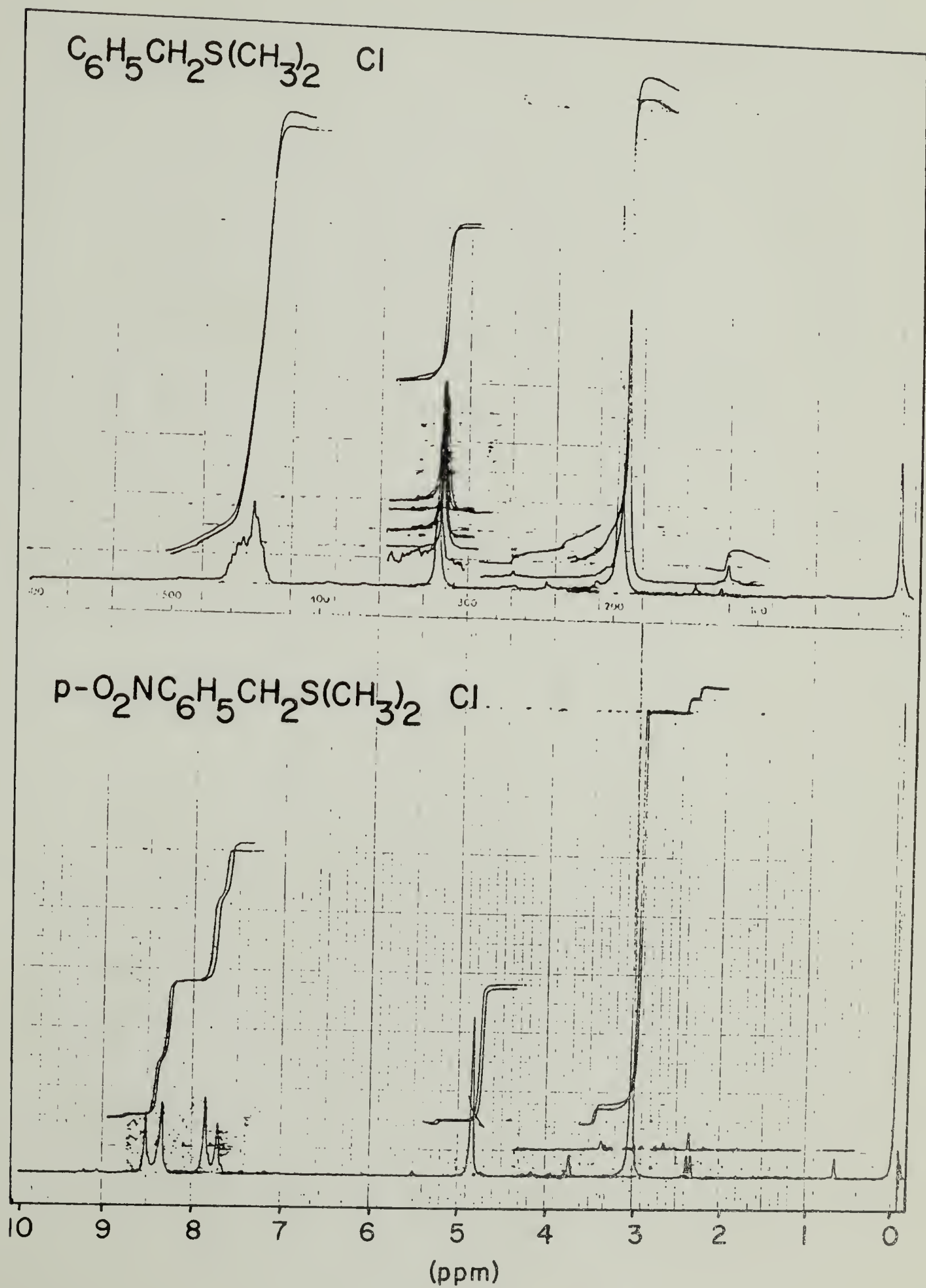


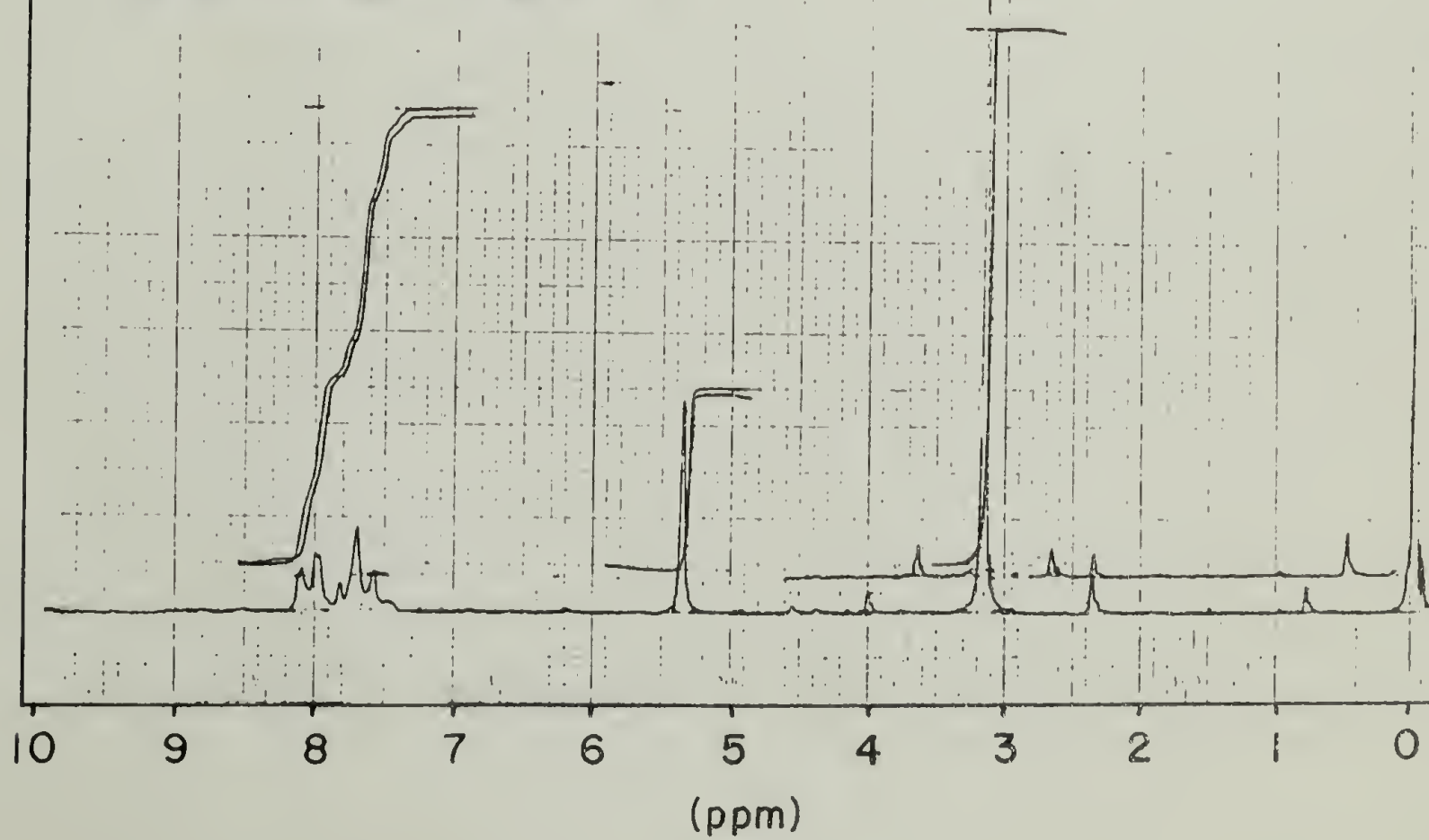
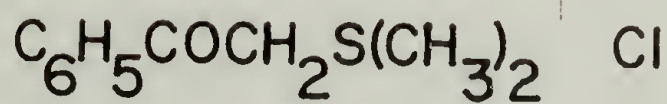
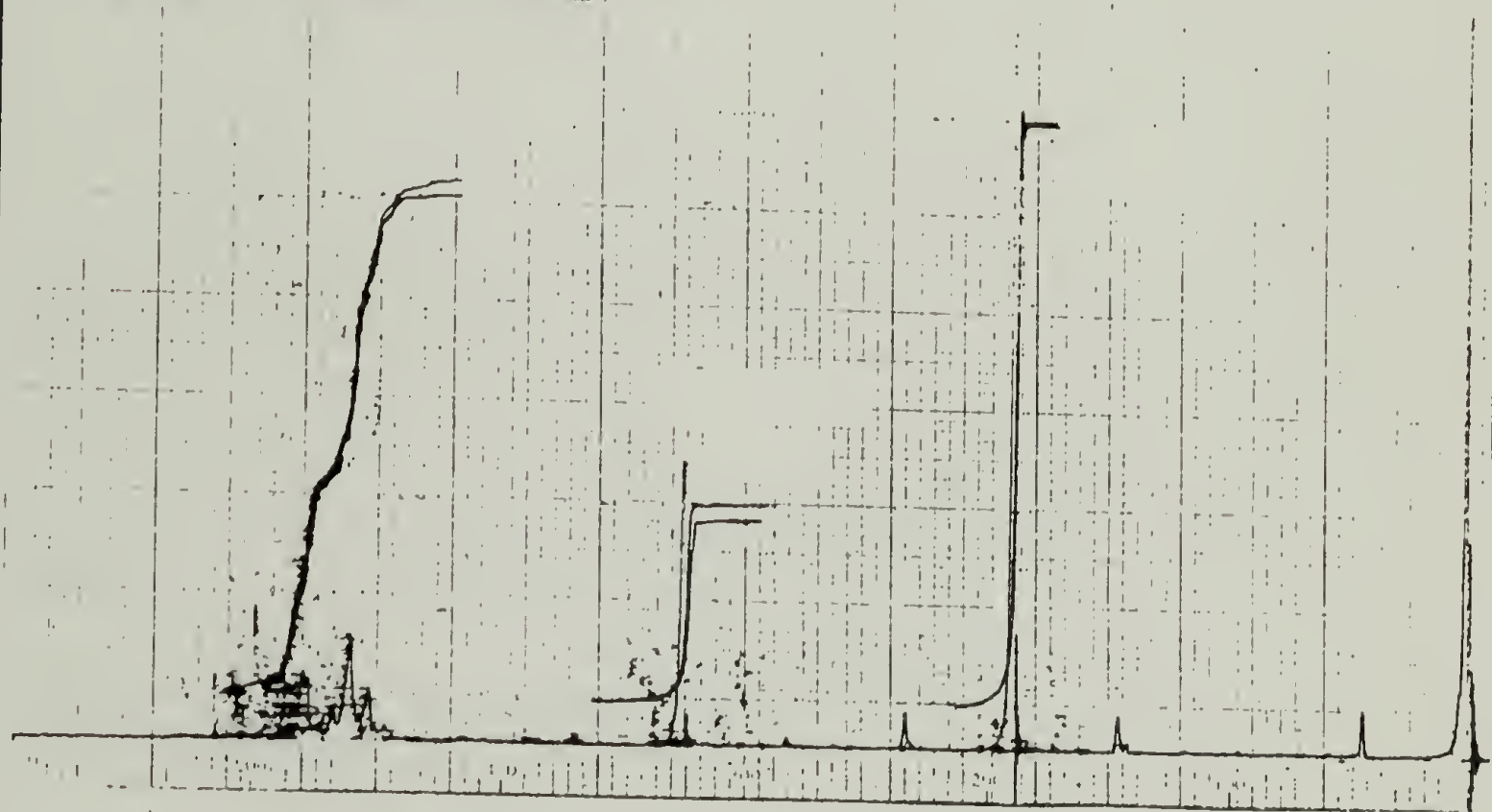
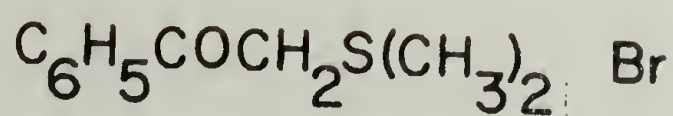
$(C_6H_5)_3P$ , IM in  $C_6D_6$

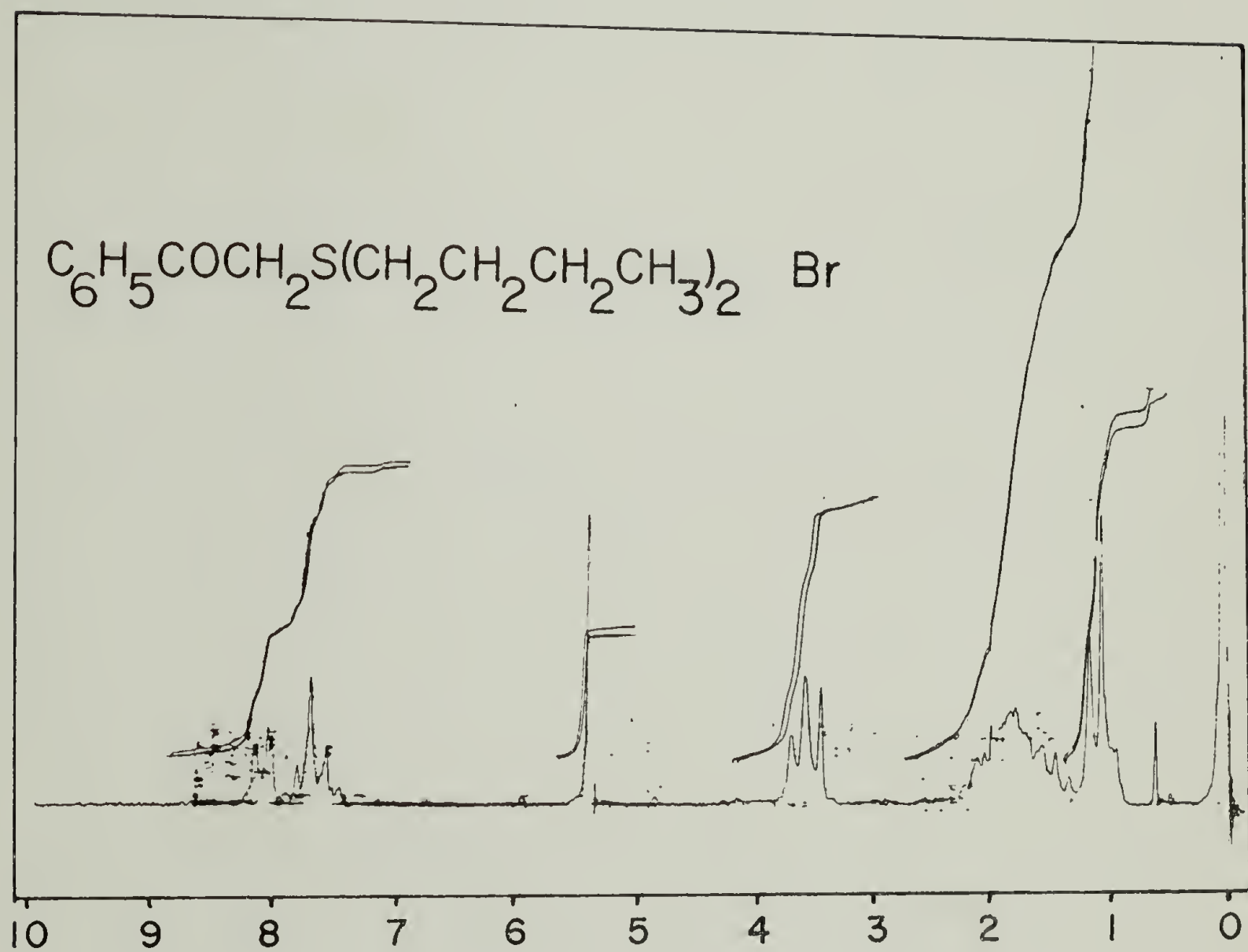


$(CH_3)_3S^+ Cl^-$

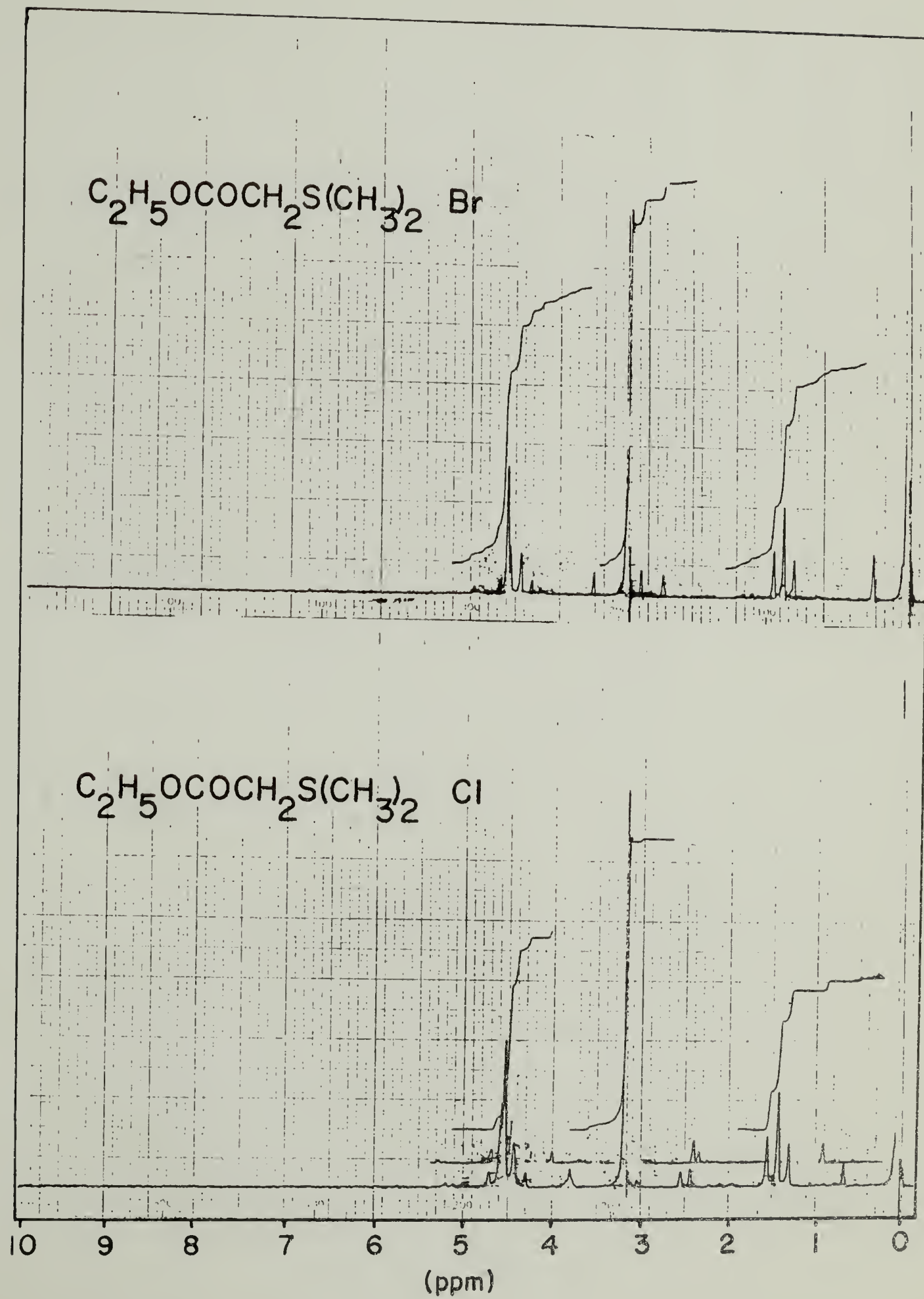


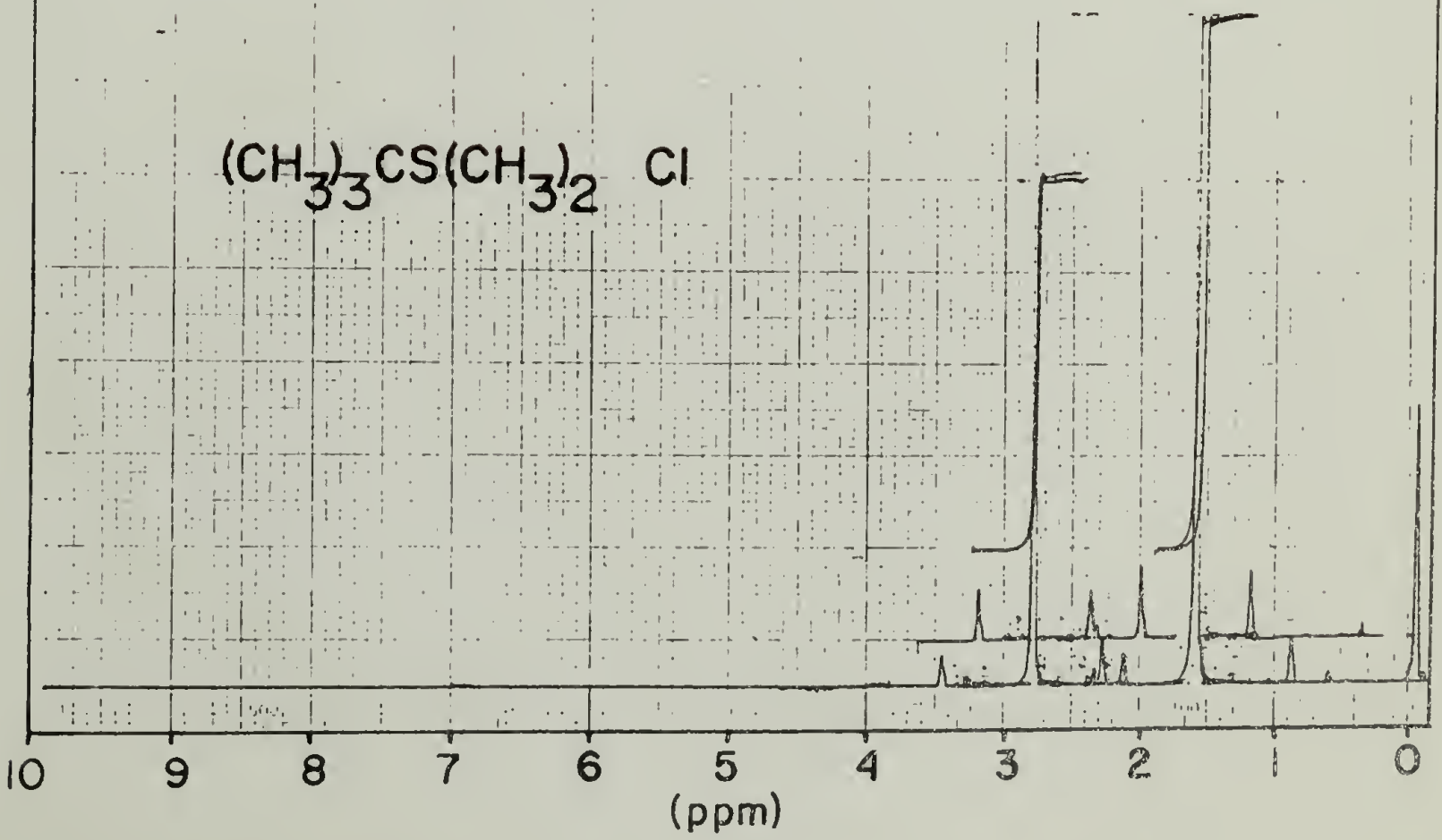
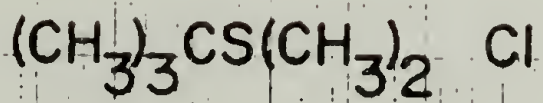
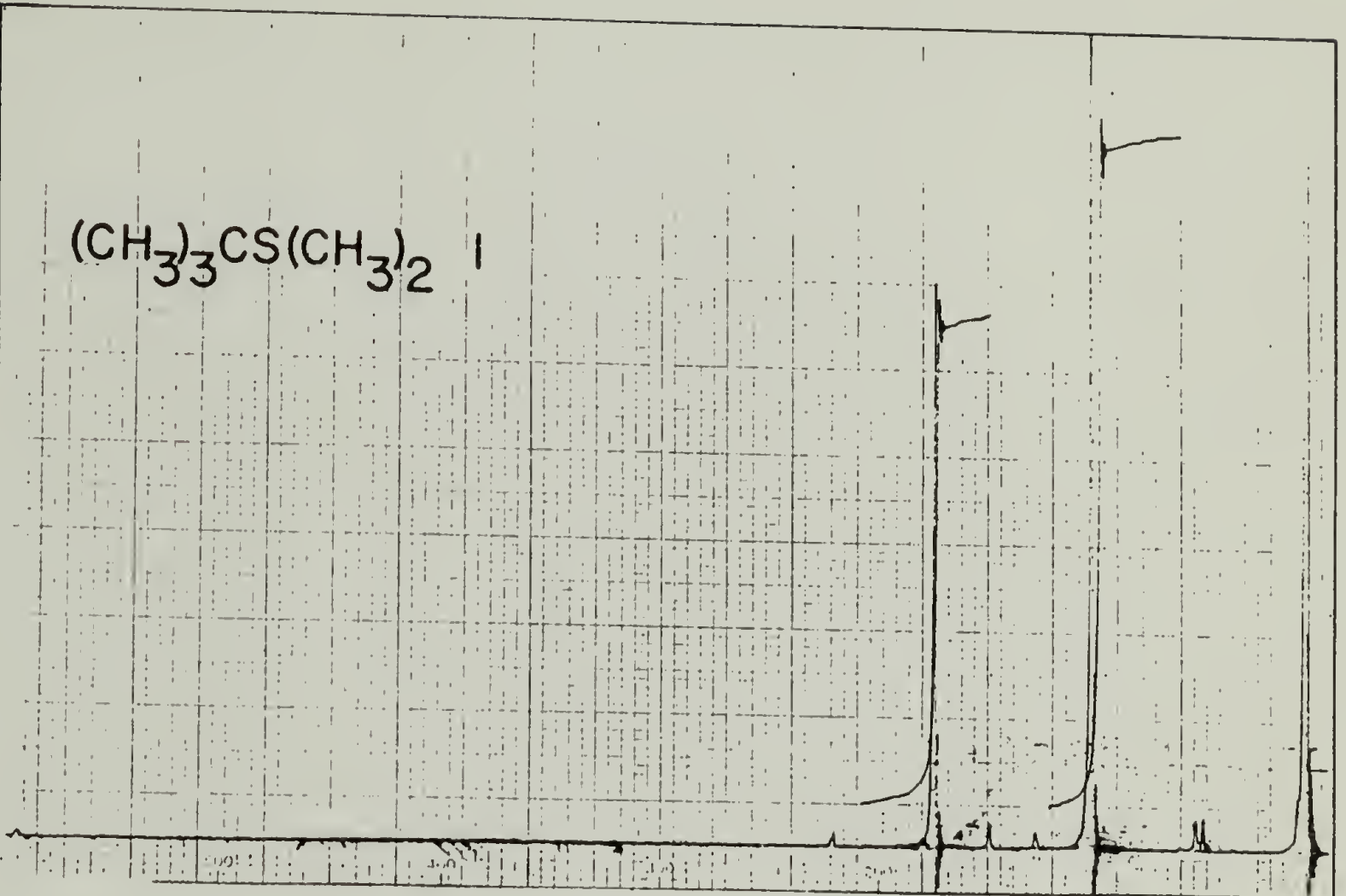
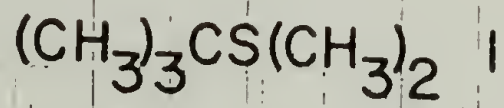


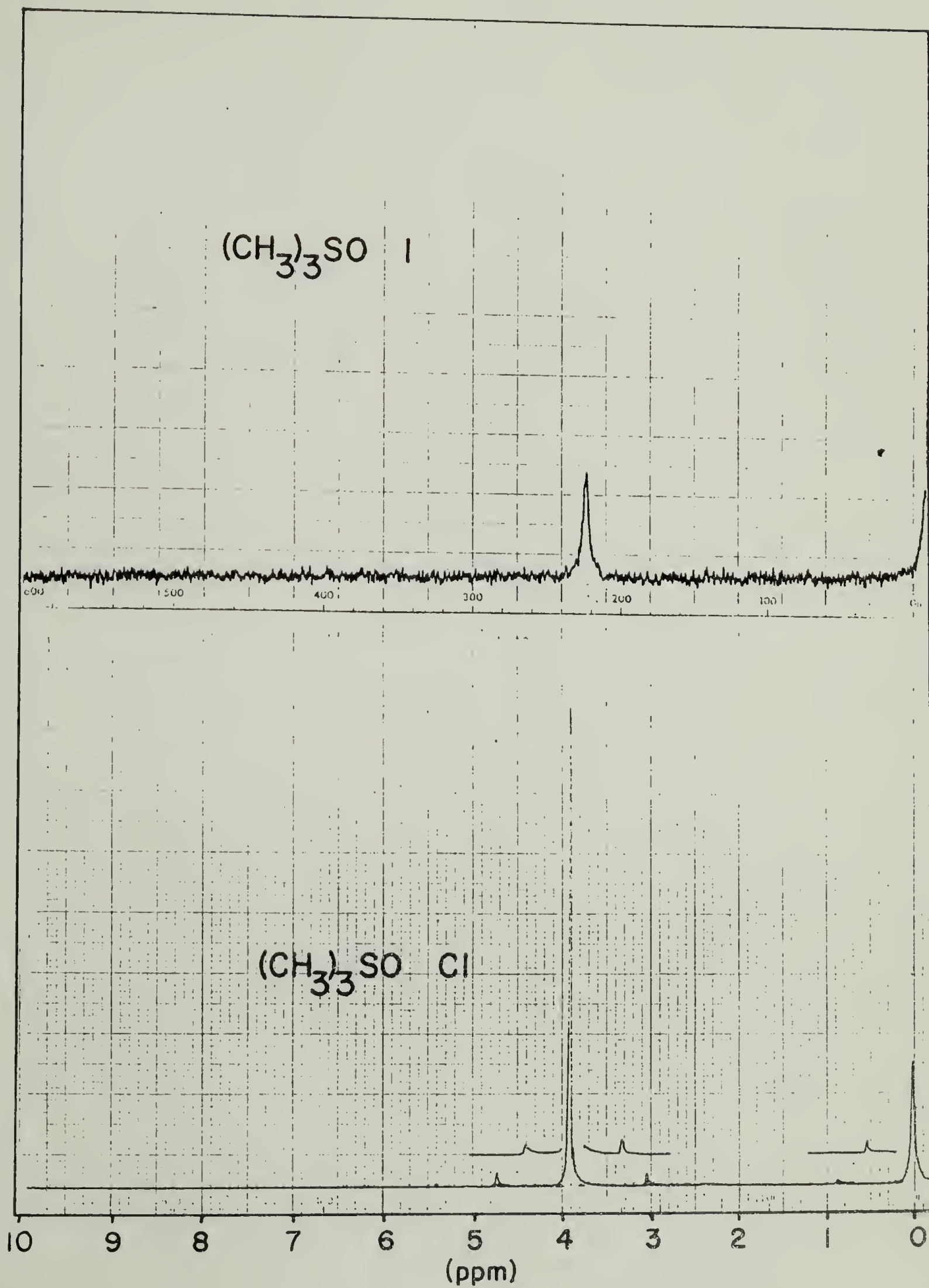


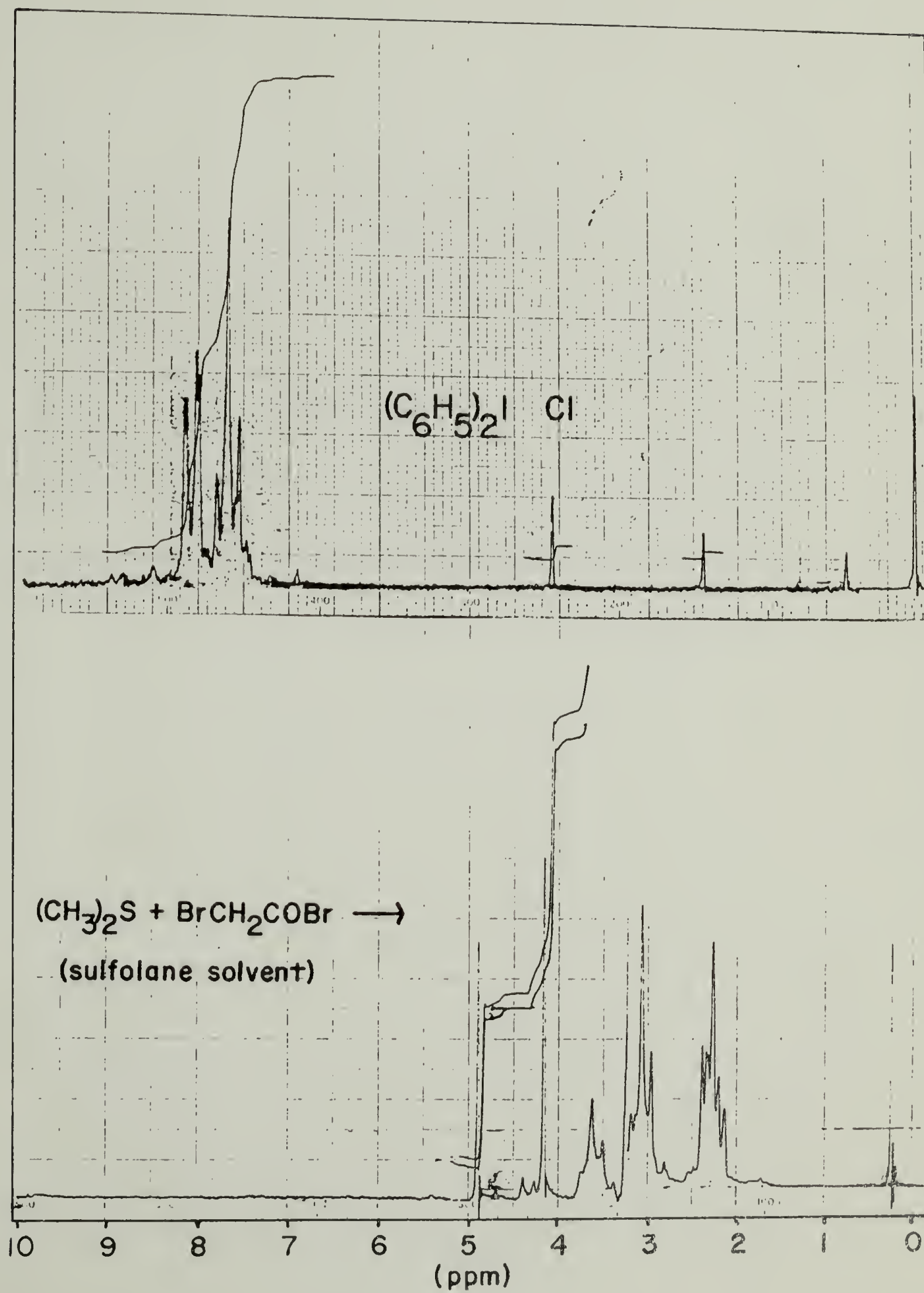




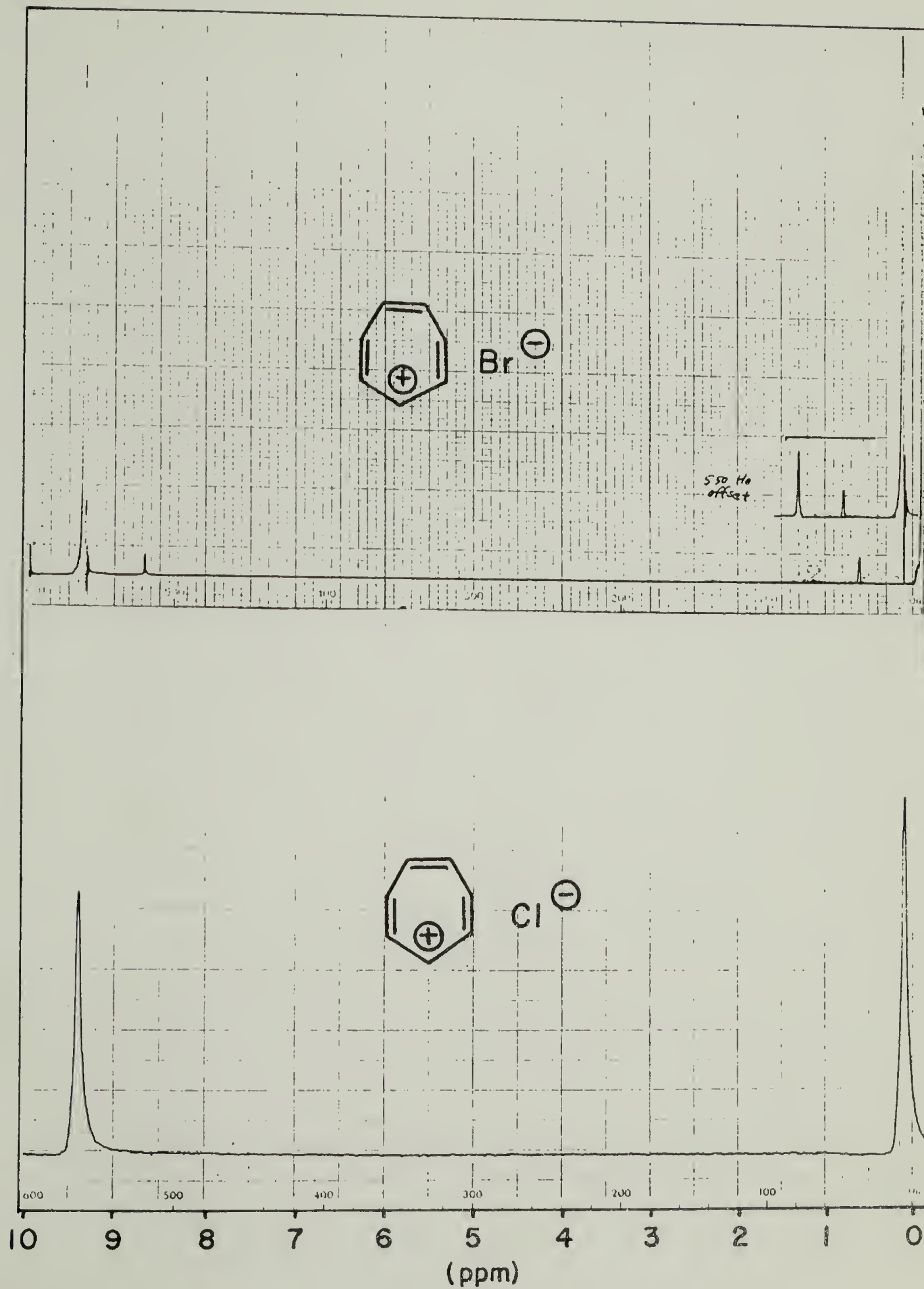


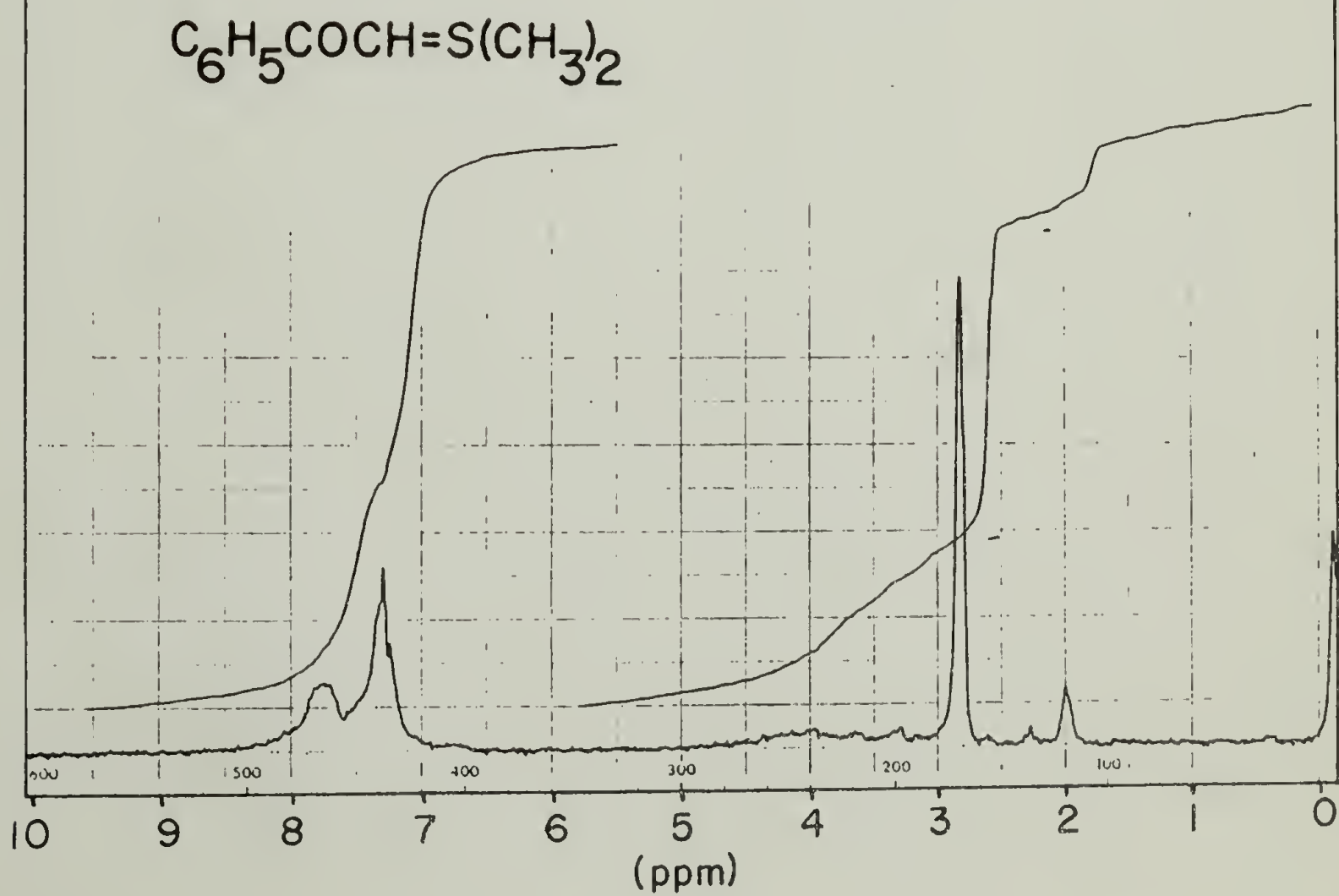
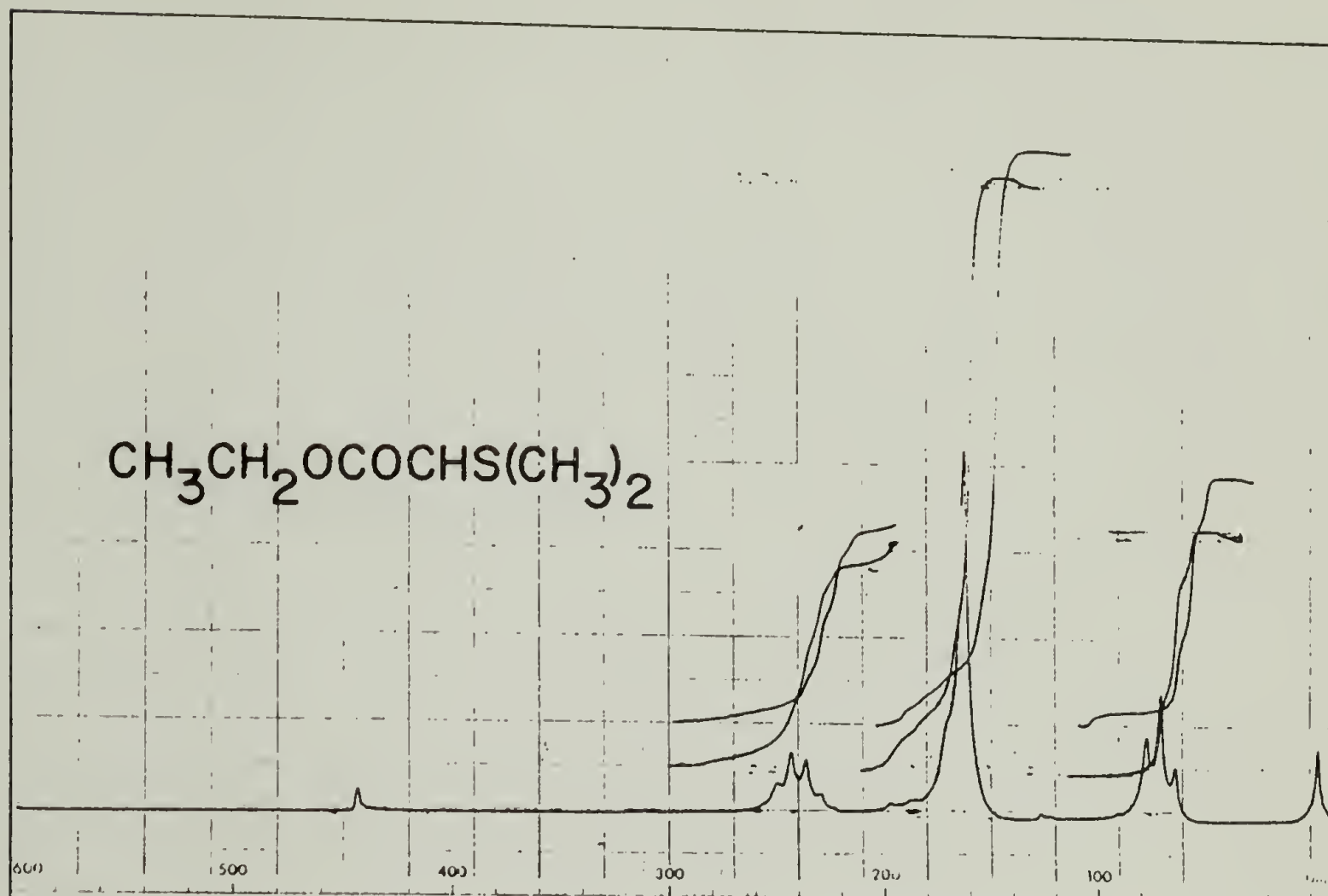


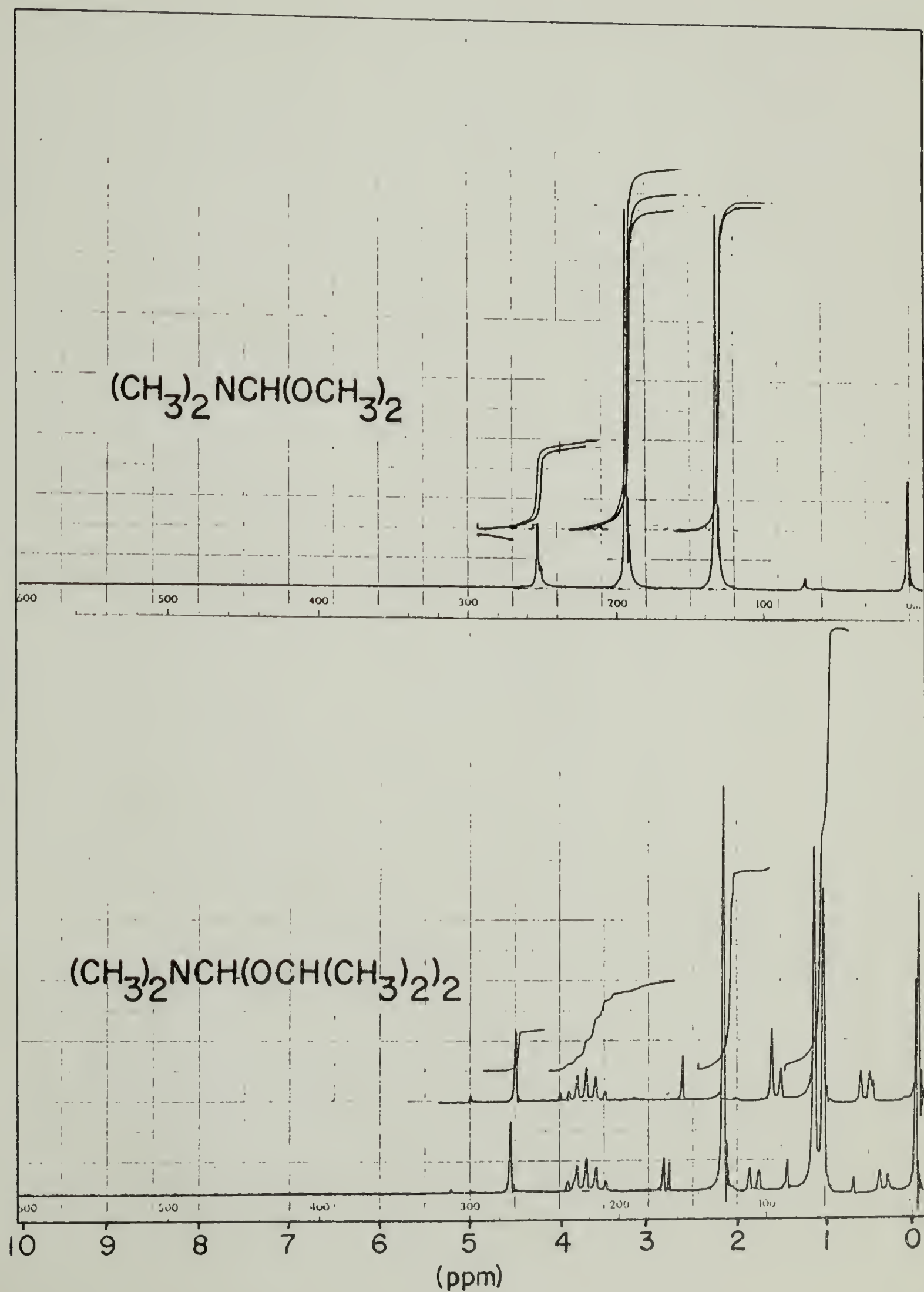


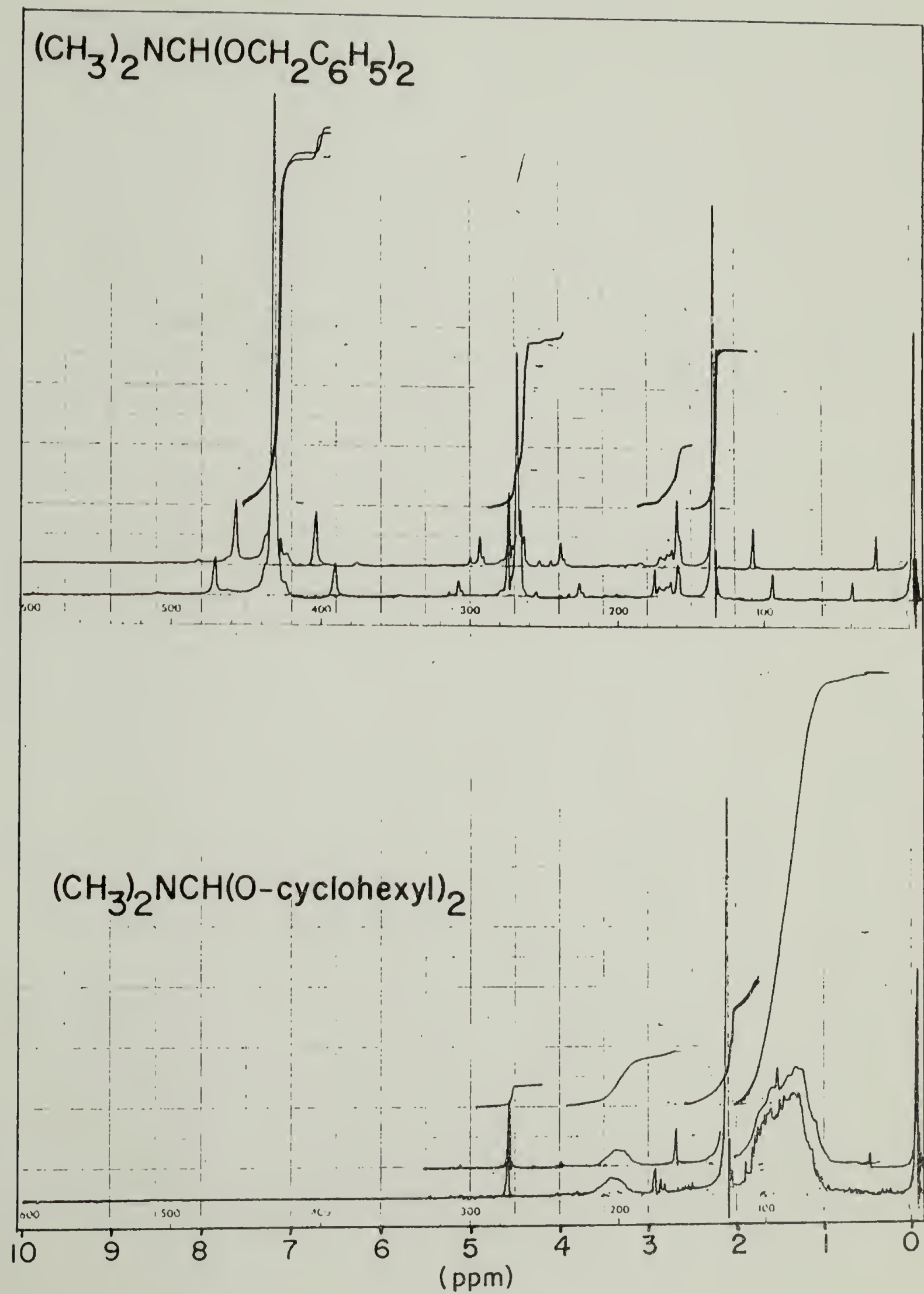




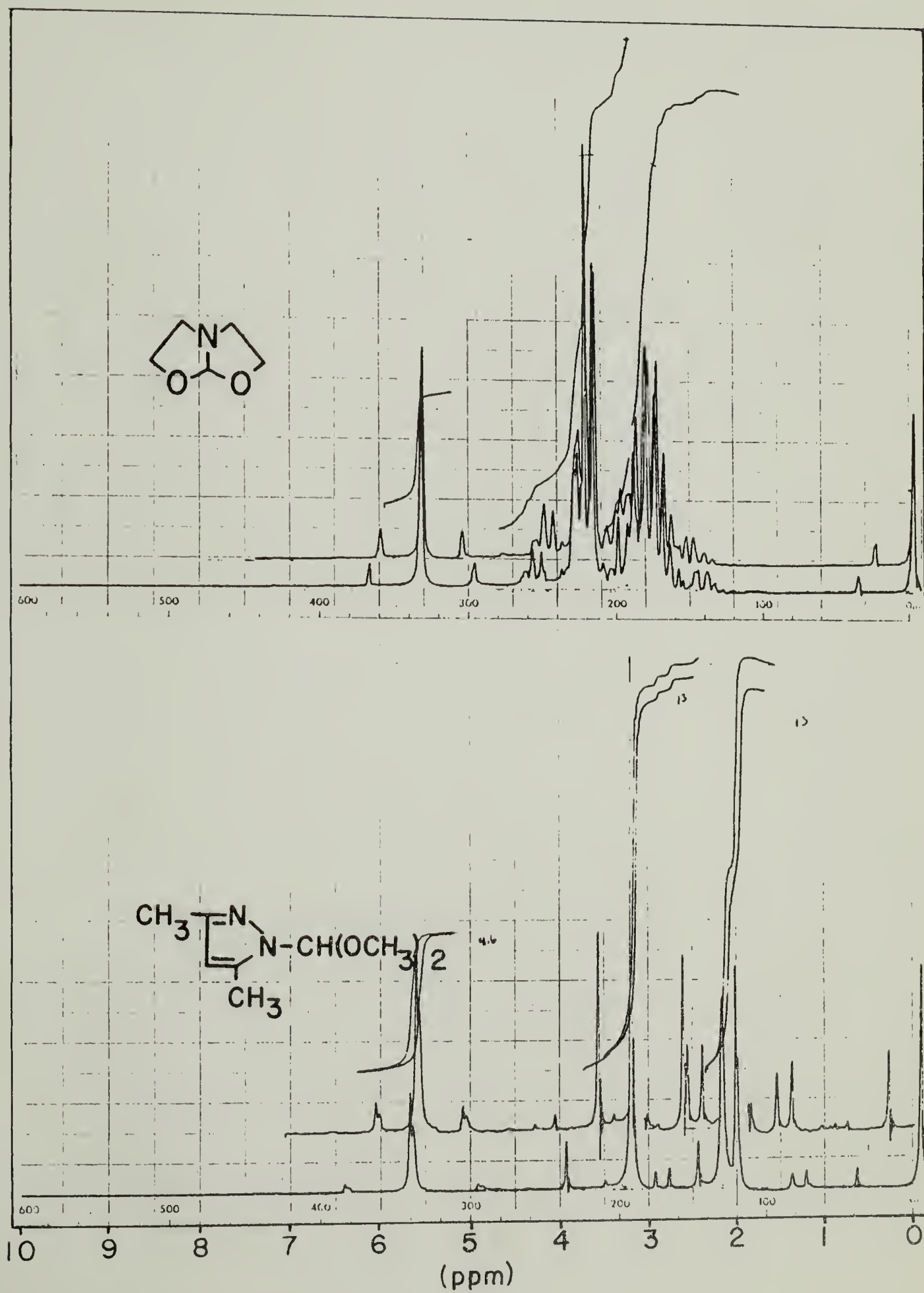


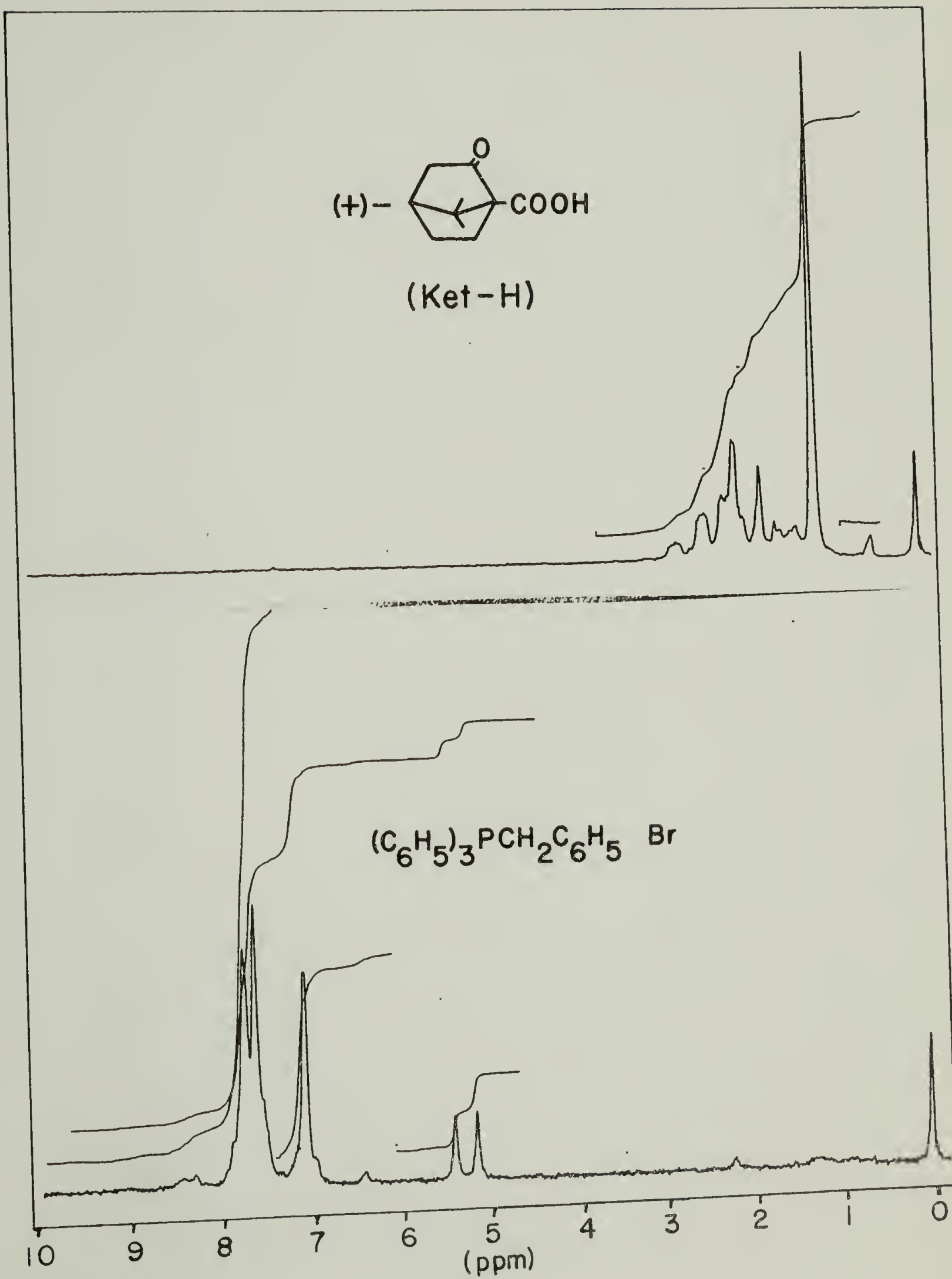


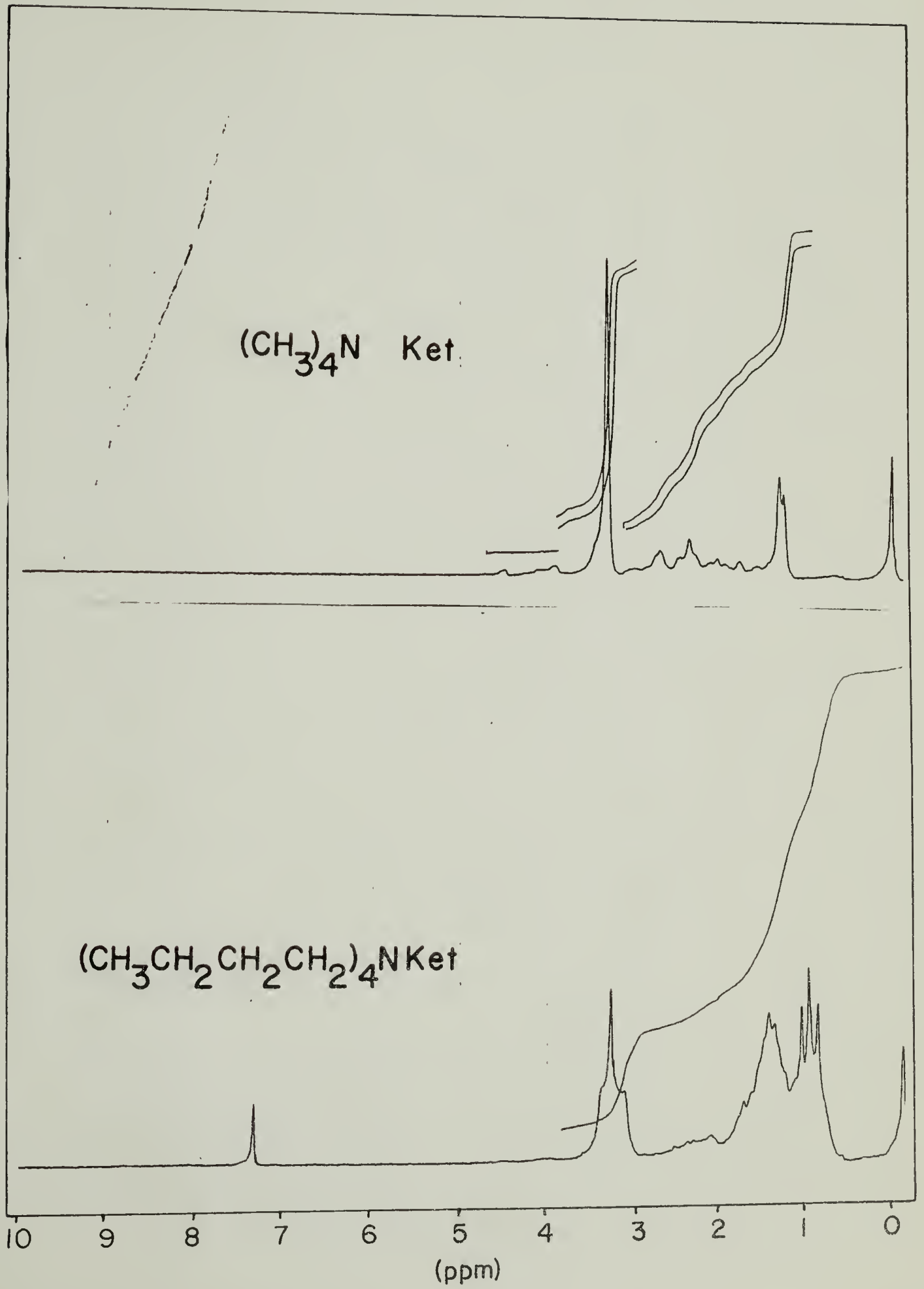


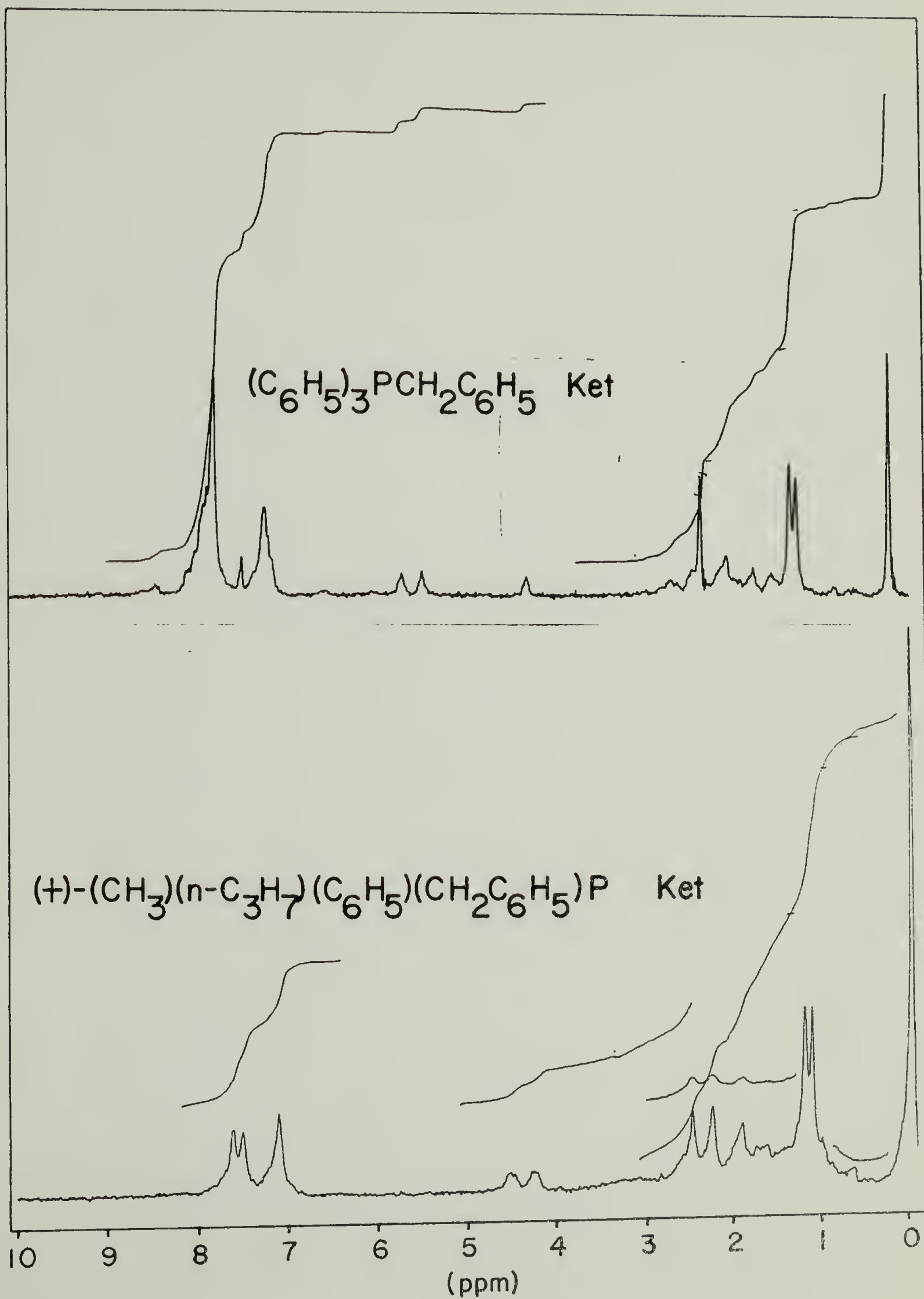














## A P P E N D I X   B

### INFRARED SPECTRA

