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SYNTHESIS AND POLYMERIZATION OF
PERHALOGENATED ACETALDEHYDES AND EPOXIDES

A Dissertation Presented

By

Richard William Campbell

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

DOCTOR OF PHILOSOPHY

May 1980

Department of Polymer Science and Engineering

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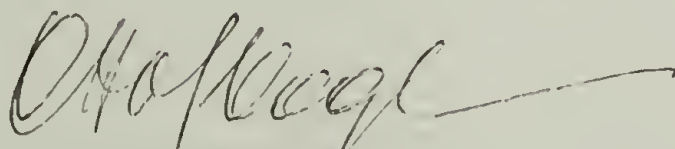
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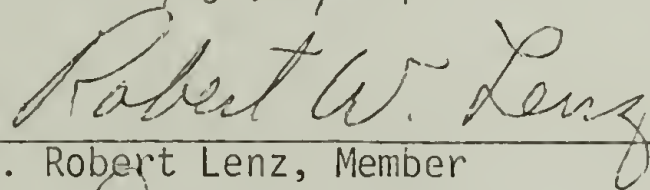
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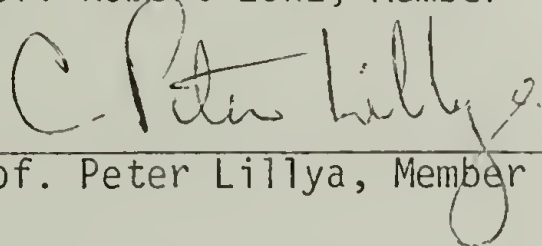
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T0: The late Robert W. Campbell
and Jeannine C. Campbell

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ABSTRACT

Synthesis And Polymerization Of Perhalogenated Acetaldehydes And Epoxides

May 1980

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Four monomers, bromodifluoroacetaldehyde (BDFA), chlorodifluoroacetaldehyde (CDFA) and dichlorofluoroacetaldehyde (DCFA) have been prepared and polymerized with various cationic and anionic initiators. Monomer synthesis was accomplished through reduction of the corresponding methyl trihaloacetate using lithium aluminum hydride. The trihaloacetates were in turn prepared from methyl trichloroacetate and SbF_3 and Br_2 catalyst (DCFA) or SbF_3 and SbCl_5 catalyst (CDFA), by methanolysis of the oxidation products of 1,1-dibromo-2,2-difluoroethylene (BDFA and DBFA) or by bromination of chlorotrifluoroethylene followed by treatment with fuming sulfuric acid plus HgO and methanolysis (BDFA).

The monomers were all found to polymerize to trihalomethyl substituted polyacetals under a variety of conditions with both cationic and anionic initiators. In contrast to polychloral and polybromochloroacetaldehydes, which are wholly insoluble, it was found that under suitable conditions soluble polymers of relatively low molecular weight could be produced from DBFA, DCFA and CDFA, but not BDFA.

Most polymers were, however, insoluble, crystalline and presumably isotactic. Thermal stabilities of all polymers were found to be improved by treatment with either PCl_5 or acid anhydrides. Degradation was quantitative to monomer. Ceiling temperatures for the polymerizations were found to decrease with increasing bromine content and increase with fluorine content. Monomer boiling points varied in the reverse fashion. Relative polymerization rates were measured through copolymerization with chloral, with isocyanates and with one another.

In a separate set of experiments tetrachloroethylene oxide was synthesized by direct oxidation of tetrachloroethylene with oxygen in the presence of ultraviolet light. This preparation resulted in a mixture of tetrachloroethylene oxide and trichloroacetyl chloride in approximately equal amounts under the most favorable conditions. Tetrachloroethylene oxide rearranged readily to trichloroacetyl chloride above 60°C . with an activation energy E_a of 3.0×10^4 cal/mole and a pre-exponential factor A of 1.9×10^{13} . All attempts to polymerize tetrachloroethylene oxide under a variety of conditions failed.

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INTRODUCTION

A. Purpose and Background

Unlike olefins and vinyl ethers which require transition metal initiators whose metal atom must have the proper ligand structure and stability of the coordination complex in order to produce stereoregular polymers, stereoregularity in aldehyde polymerization can be achieved with simple initiators. Especially in the case of aldehydes with long side chains or bulky side groups such as the trichloromethyl group in chloral, stereoregular, isotactic polymers are readily formed. In the case of chloral relative weak nucleophilic anions such as a chloride ion or tetraalkyl ammonium or tetraalkyl phosphonium salts are good initiators to form isotactic polymer. Perhaloacetaldehydes can be prepared with a wide range of size and shape of the side groups and their polymerization can be studied under a variety of relatively simple reaction conditions.

This freedom of selection of side groups is not possible in vinyl compounds because molecules such as 3,3,3-trichloro-1-propene will not polymerize.

Beginning with the work reported by Liebig on polymers of chloral (trichloroacetaldehyde) in 1832 (1) and polyformaldehyde reported by Butlerov in 1859 (2) there has been much interest in the polymerization of aldehydes. Although only polyformaldehyde has been commercially successful (3-5), research has also been carried out on higher aliphatic aldehydes through dodecanal (6-18). Polymers from perhaloacetaldehydes

have also been reported in the literature, but most of the work has centered around chloral and fluoral (trifluoroacetaldehyde) and their polymers. Other perhaloacetaldehydes, the chlorofluoroacetaldehydes and the bromofluoroacetaldehydes are the object of this current research.

Interest in the perhalogenated acetaldehydes has been due in part to their attractive physical properties. Polychloral is self-extinguishing in flammability tests, is insoluble in common organic solvents, is hydrophobic, has high thermal stability, and is unaffected by strong acids even at elevated temperatures. (19-20) The polymer, while insoluble and infusible, can be fabricated into predetermined shapes by a special monomer casting technique called cryotachensic polymerization. (21)

Fluoral has been polymerized to polymers having many of the attractive properties of polychloral with respect to inflammability and chemical resistance. (22-27) In addition it can be polymerized to an amorphous, presumably atactic, polymer which is soluble in organic solvents thus facilitating practical applications through solvent casting techniques.

Tribromoacetaldehyde, bromal, was polymerized only recently to give a polymer which, like polychloral, was infusible and insoluble in all solvents tested. (28, 29)

Since the major difference among the three members of this series is in the physical size and shape of the perhalomethyl side group it was desirable to look at this effect in more detail by synthesizing

and polymerizing perhaloacetaldehydes having side groups of intermediate bulkiness between these three and looking at the effect of these substitutions on the polymerizability of the monomer and the stereoregularity of the polymer obtained. This was accomplished through the synthesis and polymerization of six monomers. These were: dichlorofluoroacetaldehyde, chlorodifluoroacetaldehyde, dibromofluoroacetaldehyde, bromodifluoroacetaldehyde, chlorodibromoacetaldehyde, and bromodichloroacetaldehyde. The latter two monomers were prepared by Dr. David W. Lipp and will only be mentioned here for comparisons. (29-31)

These aforementioned areas of interest arise from the differences in chemical behavior of perhaloacetaldehyde compared to other acetaldehydes and vinyl monomers, and among the perhaloacetaldehydes compared to one another.

The differences in chemical reactivity of the perhaloacetaldehydes effect great differences in ionic polymerization. Fluoral is very difficult to store and trace impurities are sufficient to initiate polymerization. (32) Chloral and bromal can be polymerized with ionic initiators with increasing difficulties requiring rigorous purification of the bromal monomer using antimony trifluoride. (28) Although the differing electron densities and polarizability of the double bonds of the three monomers may be a factor in the observed reactivities, it is believed that the bulkiness of the perhalomethyl pendant groups is the major contributor to this effect.

The stereoregularity of perhaloacetaldehydes and aliphatic

acetaldehydes is unusual. They can be polymerized to stereoregular polymers even with a non-stereospecific initiator. For comparison the stereospecific polymerization of vinyl monomers and epoxy monomers should be considered.

Vinyl ethers and α -olefins can be polymerized by ionic initiators to give polymers having a regular geometrical arrangement of pendant groups along the backbone chain. Their stereospecific polymerization depends on the orientation of the monomer molecule relative to the growing chain end prior to polymerization of that monomer unit. In α -olefins and vinyl ethers this can be accomplished by using stereospecific initiators, usually transition metal complexes with or without co-initiators. These initiators generally depend on their ability to expand their orbitals and complex with the electron cloud of the carbon-carbon double bond of the monomer. Through steric hindrance or electronic polymerization this complexation of the olefinic monomer and the transition metal can occur only in one geometric configuration. This results in a polyolefin or polyvinyl ether in which the monomers are incorporated into the chain backbone in a stereoregular geometry which is caused by the stereoselectivity of the initiator.

Another group of stereoregular polymers which can be prepared depends on a center of asymmetry in the monomer prior to polymerization. These include the ring opening polymerizations such as substituted cyclic ethers, and especially epoxides. Price and Osgan found that 1-propylene oxide could be polymerized by non-stereospecific initiators such as KOH to give optically active, isotactic, polymer.

In this case the stereoregularity of the polymer is dependent on the optical activity of the monomer and polymerization proceeds with retention of configuration, not orientation by the initiator. When a racemic mixture of d and l monomer was polymerized with KOH an atactic polymer resulted. (33)

Aldehydes can also be polymerized to stereoregular polymers but without coordination initiators or optically active monomers. As mentioned chloral was the first aldehyde to be polymerized (1) but, since it was insoluble and infusible, it did not attract immediate interest. Later infrared and x-ray investigations showed it to be isotactic. (34) This is due to the bulkiness of the trichloromethyl pendant side group which allows only the isotactic form.

Polyformaldehyde, since it is not substituted on the carbon atom, can not exhibit tacticity as can the higher aldehydes. Although of commercial significance (35), it will not be discussed.

Acetaldehyde was first polymerized in 1936 by a freeze-thaw procedure without the principles of initiation and ceiling temperature being realized. (36, 37) This lack of understanding caused a twenty year delay before it was discovered that acetaldehyde could be polymerized by BF_3 at -60°C . (38) or later by condensation onto alumina at -80°C . (39) to an amorphous polyacetaldehyde.

Other anionic initiators were found to also be effective and crystalline isotactic polyacetaldehyde was isolated. (40, 41) By similar methods isotactic polyacetals through n-octaldehyde were prepared. (41) The use of aluminum and zinc alkyls (42-44)

provided opportunity for extensive investigation of the initiation step of these polymerizations, (45) and it was found that initiation actually occurred through an aluminum-acetaldehyde complex resulting in high stereospecificity.

The type of initiator has a profound effect on the stereoregularity of the aliphatic polyaldehydes. (46, 47) Anionic initiators generally yield crystalline isotactic polymers, but amorphous, mostly heterotactic, polymers are usually produced from cationic initiators. However, especially in the case of the cationic initiators, the stereoregularity increases as the length of the aliphatic side chain increases. (48)

Therefore it can be concluded that for polymerization of vinyl ethers, α -olefins, cyclic ethers, and many aldehydes the stereochemistry and crystallizability of the resulting polymers are dependent on the initiator. For the vinyl compounds the initiator must form a complex with the monomer in a particular geometry. In the case of the cyclic ethers the monomer must have a center of asymmetry which can be maintained through the polymerization in order to yield stereoregularity in the polymer. Aliphatic polyaldehydes can polymerize to isotactic polymers due largely to the effect of the bulky substituent groups.

Chloral also contains a bulky side group, the trichloromethyl group, which has about the same volume as tertiary butyl groups. Space filling molecular models of polychloral show that the only way these large pendant groups can be accommodated into a polymer

chain is on the outside of a helical conformation, that is an isotactic helix. This arrangement has been supported by x-ray investigations of polychloral. (34, 49) Further evidence arises from the fact that no soluble fraction of polychloral has been isolated. The atactic polymer would be expected to be soluble. The stereoregularity is not dependent on the initiator, but is assumed to be due entirely to the bulkiness of the pendant group. This results in steric crowding of the growing polymer chain allowing new monomers to be added in only one stereospecific configuration.

Because of the electron-withdrawing inductive effect of the trichloromethyl group, the carbonyl bond is readily polarized by nucleophilic initiators. Nucleophiles as weak as chloride ions are sufficient to initiate polymerization to a high molecular weight. (21, 50) Strong acids will also initiate polymerization, and, since no α -hydrogen is present for termination, high DP's might be expected. This is not the case however probably because trace contaminants such as water or dichloroacetaldehyde cause transfer and termination reactions. (50) The fairly rapid polymerization rate at low temperatures does indicate a low Arrhenius energy for cationic polymerization. (50)

The trifluoromethyl pendant group found in fluoral can be accommodated on the polymer chain in configurations other than the isotactic helix, due to its smaller size. For this reason high molecular weight amorphous, presumably atactic, polyfluoral can be extracted from the highly crystalline isotactic polyfluoral, or

under other polymerization conditions the entire polymer may be soluble.

(18) This has been explained as being due to the ability of the smaller monomer to approach the growing chain end in orientations allowing either meso or racemic addition. (18)

B. Preparation and Properties of Haloacetaldehydes

Although Lipp (29) recently reviewed this area, this present work includes references not found therein and is therefore being updated.

1. Chlroactaldehydes. Chloral, first reported in 1832 (1), dichloroacetaldehyde (51) and monochloroacetaldehyde (52), reported in 1882 and 1868, respectively, have become important chemical intermediates. Today they are synthesized by several routes:

a. Preparation of chloral. Chloral has been commercially prepared by the chlorination of ethanol, (53-69) or by the chlorination of acetaldehyde. (70-86)

Ethanol in an enert solvent was reacted with chlorine in an autoclave at 200°C. Under these conditions the ethanol was oxidized to acetaldehyde and chlorination of this acetaldehyde produced chloral. The monomer was purified by distillation from concentrated sulfuric acid at reduced pressure.

Other syntheses involve the production of acetaldehyde separately from ethylene followed by chlorination. Care must be taken in the last step as HCl can catalyze the condensation of acetaldehyde to give chlorination products of crotonaldehyde. (76, 78)

Several patents also describe the one step chlorination

of acetaldehyde to chloral. (72-81) Still others (79-81, 85, 86) describe the chlorination of paraldehyde, the cyclic trimer of acetaldehyde, in the presence of SbCl_5 or a mixture of CuCl_2 , LiCl and $\text{Cu}(\text{OAc})_2$.

b. Preparation of dichloroacetaldehyde. Like chloral, dichloroacetaldehyde has been produced by chlorination of ethanol and acetaldehyde and in most cases a mixture of the two was isolated. (54, 57, 58) Dichloroacetaldehyde alone has been synthesized by the hypochlorination of trans-1, 2-dichloroethane in dioxane. (87)

c. Preparation of monochloroacetaldehyde. Monochloroacetaldehyde has been obtained by the chlorination of anhydrous paraldehyde (88-92) or as a by-product of the commercial oxidation of ethylene using $\text{PdCl}_2\text{-CuCl}_2$ catalysts. (93-95) It was also isolated as the diethyl-acetal by reacting chlorine or hypochlorous acid with vinyl ethers or vinyl esters at low temperatures in the presence of ethanol. (96-103) Chlorination of mixtures of acetaldehyde and alcohols have been reported to yield 1,2-dichloroethylalkyl ethers which, in the presence of water, yielded chloroacetaldehyde. (104)

Addition of water during the chlorination of ethanol has also given monochloroacetaldehyde. (58-63)

2. Bromoacetaldehydes. Most bromoacetaldehydes are synthesized commercially by bromination of ethanol or acetaldehyde. (105)

a. Preparation of bromal. Bromal was synthesized by Lowig in 1832 by brominating either ethanol or diethyl ether in the presence of HBr . (106) It has also been made by reacting paraldehyde with a

mixture of bromine and a small amount of sulfur (107), but commercially is now prepared by treating chloral with AlBr_3 in hexane at 60°C . (108)

b. Preparation of dibromoacetaldehyde and monobromoacetaldehyde.

Both of these monomers have been obtained by brominating acetaldehyde. By changing conditions and/or catalysts one can be formed in preference to the other. Dibromoacetaldehyde is prepared by reacting acetaldehyde (109) or paraldehyde (110) with bromine in chloroform at $25\text{--}40^\circ\text{C}$. Using the same solvent and keeping the reaction at 5°C . (111) or by adding a trace of mercury (112) results in the monobromoacetaldehyde to be the major product of the bromination of acetaldehyde.

3. Fluoroacetaldehydes. Most syntheses of the fluorine containing acetaldehydes involve the oxidation of the appropriate alcohol or reduction of the acid.

a. Preparation of fluoral. Fluoral was first reported by Henne in 1950 by the LiAlH_4 reduction of trifluoroacetamide. (113) Trifluoroacetic acid was also reduced to fluoral with LiAlH_4 . (114-117) Yields were increased to 80% by inverse addition in Et_2O . Hydrogenation of CF_3COF over Pd catalyst at 250°C . (118, 119) and reaction of CF_3COF with PhSO_2Cl followed by hydrolysis of the chlorosulfate (120) also lead to fluoral. Chloral was fluorinated in the vapor phase by over activated $\text{COF}_2/\text{Al}_2\text{O}_3$, $\text{HF}/\text{Cr}_2\text{O}_3$, or chromium oxyfluoride at $200\text{--}400^\circ\text{C}$. in yields to 70%. (121, 122) Liquid vinyl acetate at -50°C . has also been fluorinated by fluorine gas. (123)

Fluoral monomer is difficult to store because it polymerizes spontaneously and is sold commercially as the stable hydrate or

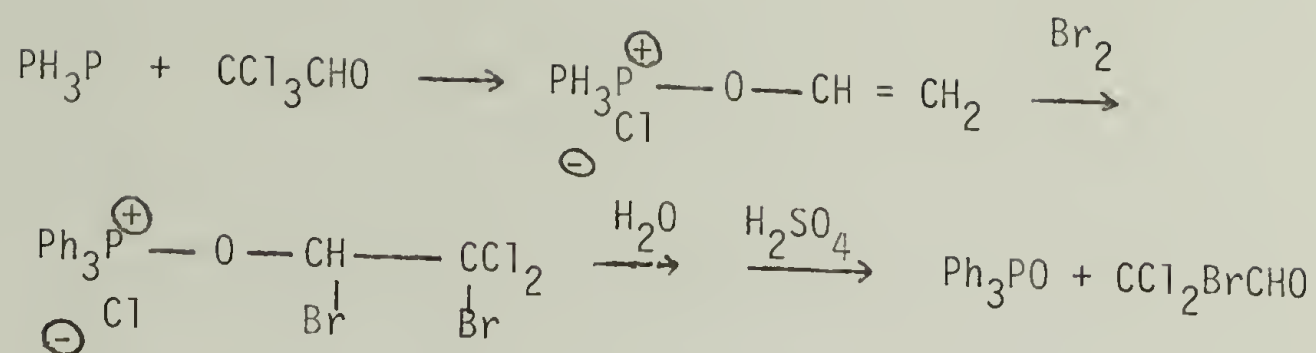
hemiacetal, both of which can be easily decomposed to fluoral by concentrated H_2SO_4 immediately before use.

b. Preparation of difluoroacetaldehyde and monofluoroacetaldehyde.

Difluoroacetaldehyde has been prepared by the reduction of the acid using LiAlH_4 . (124) Monofluoroacetaldehyde also was prepared by the reduction of the acid or acid chloride. (125) In addition synthesis through oxidation of $\text{CFH}_2\text{CH}_2\text{OH}$ by MnO_2 (126, 127) and through oxidation of $\text{CF}_2\text{H}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ by $\text{Pb}(\text{OAc})_4$ or HIO_4 (128) have also been reported. Yakubovich prepared monofluoroacetaldehyde by the fluorination of vinyl acetate at -60°C . in CCl_2F_2 . (129)

A novel synthesis of fluorinated esters was recently reported by Dvorak (130) in which he passed an electrical current through a solution of HF , NaF , F_2O and Cl_2HCOF followed by ethanol addition to give $\text{CF}_2\text{ClCO}_2\text{Et}$, $\text{CFCF}_2\text{CO}_2\text{Et}$ and $\text{CF}_3\text{CO}_2\text{Et}$. The fluorinated perhaloacetaldehydes could be obtained from these, but were not reported.

4. Bromochloroacetaldehydes. Chlorodibromoacetaldehyde and bromodichloroacetaldehyde were first reported in 1882. They were synthesized by the bromination of chloroacetaldehyde and dichloroacetaldehyde, respectively. (131, 132) Lipp prepared chlorodibromoacetaldehyde and bromodichloroacetaldehyde via the vinylphosphonium salts. (19, 30, 31) Bromodichloroacetaldehyde had previously been synthesized by this route but few experimental details were given. (132) Lipp was able to prepare polymerization grade bromodichloroacetaldehyde in good yield by the following sequence

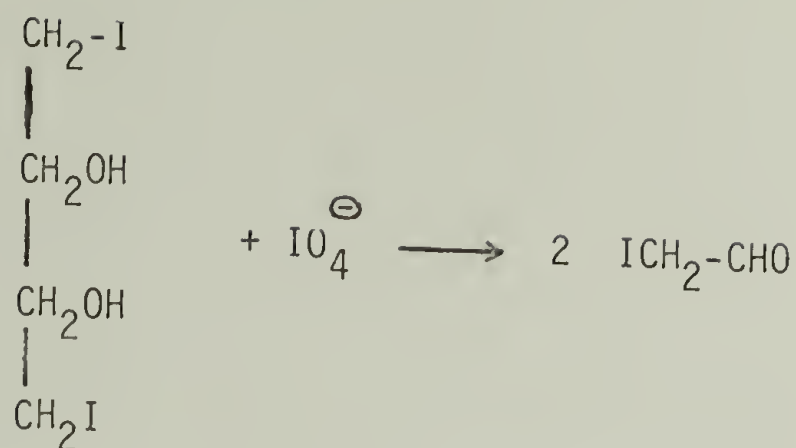


He also prepared dichlorobromoacetaldehyde by bromination of commercial dichloroacetaldehyde diethylacetal. Likewise he synthesized chlorodibromoacetaldehyde from commercial chloroacetaldehyde diethylacetal.

(30)

5. Iodoacetaldehydes.

a. Iodoacetaldehyde. After being first reported by Chautard in 1839 (134), and later made by heating chloroacetaldehyde with KI (135), very little work was done with iodoacetaldehyde for nearly one hundred years. The diethyl acetal was made by reacting acetal with HI and iodine (136-138), but it was not hydrolyzed and dehydrated to the acetaldehyde. The acetal was also produced in very low yields by heating a mixture of bromoacetal and NaI with dry acetone (139) or with ethanol (140) in sealed tubes. The only high yield synthesis of the acetal reported involved the reaction between vinyl acetate with iodine monochloride and conc. HCl to give 85% iodoacetaldehyde diethyl acetal. (141) In 1959 Bose et. al., made iodoacetaldehyde itself by reacting sodium metaperiodate with 1,4-dideoxy-1,4-diiodo-DL-threitol, which was synthesized from cis-but-2-ene-1,4-diol, (142):



The aldehyde was extracted in ether, but it was found that if the ether was removed entirely the aldehyde decomposed. A 2,4-DNP derivate had a melting point 147-148°C. (142)

b. Diiodoacetaldehyde. No references to diiodoacetaldehyde or its acetal were found in the literature.

c. Triiodoacetaldehyde. The only references to iodal are one in which it was believed to have been isolated from seaweed but no characterization or positive identification was made (143) and a second in which an oil formed on iodination of pyruvic acid was speculated to be triiodoacetaldehyde. (144) It again was not purified, characterized or positively identified but decomposed rapidly liberating iodine. It also was immediately hydrolyzed to iodoform in aqueous-methanolic NaOH.

Neither of these citings offer any proof or assurance that iodal has ever indeed been isolated. In view of this and the lack of any reference in the literature to diiodoacetaldehyde, preparations of iodoacetic acids, logical precursors in the syntheses of iodoacetaldehydes, is of interest.

d. Iodoacetic acid. Iodoacetic acid, sold commercially in the form of white crystals, should be handled with extreme care as it has

been reported to be a strong muscle poison with an LD_{50} of 60 mg./Kg. (145) It has been prepared by reacting iodine with chloroacetic acid (146) or the action of NaI on chloroacetic acid or bromoacetic acid in acetone. (147) It was also reported to have been prepared the iodination of acetic anhydride (but not acetic acid) in H_2SO_4 (148) and by the reaction between ketene and iodine monochloride. m.p. $83^\circ C$. (149)

e. Diiodoacetic acid. Diiodoacetic acid has been prepared by treating malonic acid with iodic acid (150), by warming diiodomaleic acid with water at $100^\circ C$. (151) or by treating malonic acid with iodic acid in boiling water. m.p. $100^\circ C$. (152)

f. Triiodoacetic acid. Triiodoacetic acid is commercially available as a fairly unstable yellow crystalline material which decomposes on heating above room temperature to iodine, iodoform and carbon dioxide. (152, 153) It has also been prepared from malonic acid and HI. mp. $150^\circ C$. decomp. (150, 153, 154)

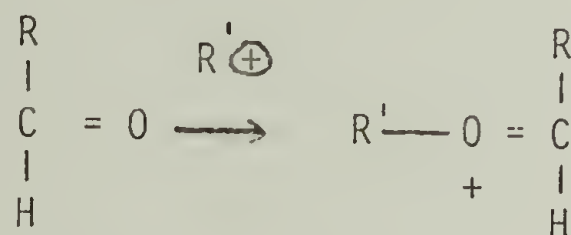
C. Haloacetaldehyde Polymers

Acetaldehyde monomers can be polymerized to high molecular weight polymers by various ionic initiators, either anionic or cationic, and, in the special case of fluoral, it is claimed by free radical initiators. The general mechanism is similar to olefin polymerization in that a double bond is opened to form two single bonds through normal chain growth initiation and propagation. The polarization of the monomer by α -substituted pendant groups determines which initiators will be more effective through the relative stabilities of the propagating

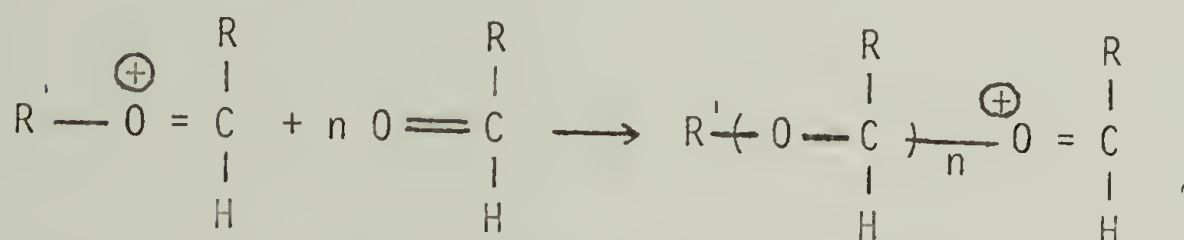
carbenium (carbocations) or carbanions.

As in the case of olefins, e.g., isobutylene, alkyl substituents stabilize the carbenium ion and therefore polymerizations of aliphatic acetaldehydes is more readily carried out by cationic initiators than anionic initiators.

Initiation:



Propagation:



Strong nucleophiles, such as alkoxides can also initiate this polymerizations of aliphatic acetaldehydes.

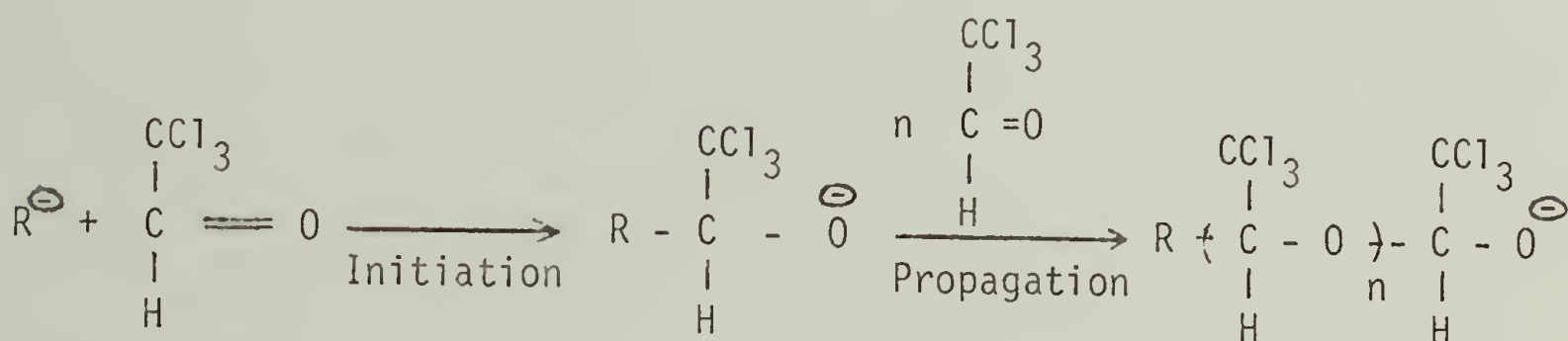
1. Polymerization of chloral. Since most previous work on haloacetaldehyde initiation has been carried out on chloral, it will be used to illustrate many general features of this class of polymerization.

In the polymerization of halogenated acetaldehydes the electron-withdrawing effect of the halomethyl group in the α -position to the aldehyde causes stabilization of the carbanion species resulting in increased facility of anionic initiation. Since the anionic polymerization of chloral predominates it will be reviewed first.

Chloral polymerization has been carried out with anionic initiators of varying nucleophilicities. (19, 20, 133, 155 - 157)

Due to the ease with which nucleophilic attack can take place to give the stabilized alkoxide, even weak nucleophiles such as chloride ions are sufficient to initiate polymerization. Some of the initiations which have lead to high molecular weight polymers are ammonium, phosphonium, and sulfonium halides or carboxylates, tertiary amines and tertiary phosphines. Stronger nucleophiles such as alkali metal and alkaline earth metal alkyls, alkoxides, carboxylates and halides are also good initiators.

The initiator should naturally be soluble in the monomer or solubilized with a complexing agent or solvent.



The concept of ceiling temperature is important for an appreciation of perhaloacetaldehyde polymerization since the ceiling temperature T_c , falls near or below room temperature. For methyl methacrylate, an olefin which also has a ceiling temperature, the T_c is approximately 220°C., (158) and, since this is well above the temperature at which methyl methacrylate is normally polymerized, the T_c becomes inconsequential in a practical sense during polymerization.

In a chain growth polymerization in which the monomer and the growing polymer exist together in solution these can be an equilibrium.



and

$$\Delta G = \Delta H - T\Delta S = -RT \ln K = RT \ln [M]_e$$

at equilibrium where $\Delta G = 0$

$$T_c = \frac{\Delta H}{\Delta S + R \ln [M]_0}$$

By definition T_c is reported at 1 molar initial concentration of monomer so

$$T_c = \frac{\Delta H}{\Delta S}$$

This definition is based on the assumption that the system is under equilibrium conditions; the precipitation of the polymer would cause non-equilibrium. The value of T_c is dependant on the monomer concentration in solution but only slightly on the pressure.

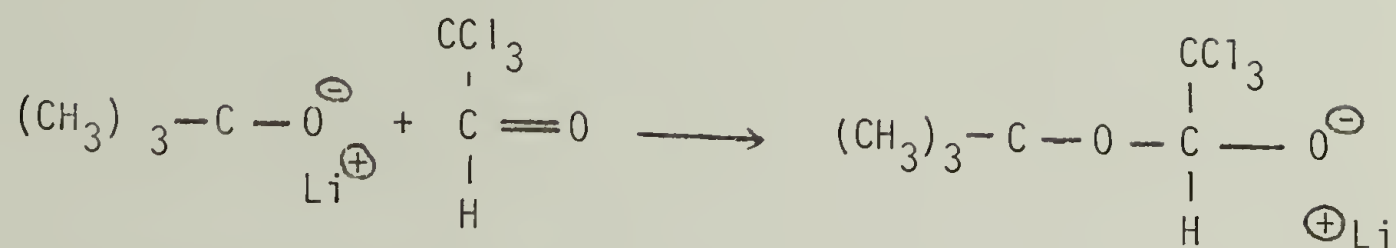
Values of T_c of 11-18°C. for chloral have been reported. (159, 29, 48) The T_c of other perhaloacetaldehydes have been reported as: bromodichloroacetaldehyde, -11°C.; (31) chlorodibromoacetaldehyde, -43°C. (32) and bromal, -75°C. (28) Often, however, a monomer is polymerized in bulk, at concentrations greater than one molar, so that the term polymerization temperature is better used to describe systems where $\Delta G = 0$ at other than 1 molar. For chloral the bulk polymerization temperature has been found to be 58°C. (21)

The practical ramifications of the polymerization temperature are that polymerization will not proceed beyond a DP of 1 at temperature above the polymerization temperature. Since fabrication of chloral is not possible by conventional methods due to its insolubility and

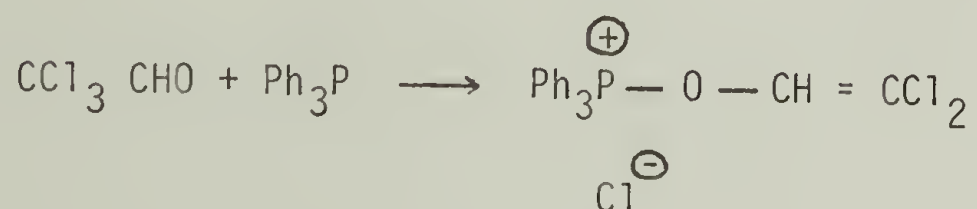
infusibility, the polymerization temperature provides a means of obtaining polychloral objects of a predetermined shape. This is done through the technique of cryotachensic polymerization and is carried out in two distinct steps. (21) First the monomer and initiator are mixed at a temperature above the polymerization temperature. The initiated solution is then transferred to a mold, ensuring that all equipment used in transfer and the mold are maintained above the polymerization temperature. The propagation is then started by cooling the mold. The rate of polymerization is controlled by the rate at which heat is removed from the system. If the internal temperature approaches the polymerization temperature, due to exothermic ΔH_p and ΔH_c and poor heat transfer, the polymerization rate will decrease. This decrease in rate will allow the internal temperature to drop and the reaction tends to accelerate. In this way the polymerization is self controlling. The polymer first becomes a self-supporting gel and then hardens to a coherent object taking the shape of the mold. If chloral is initiated below the polymerization temperature, the homogeneous gel is not obtained and the resulting polymer will be intractable powders, brittle sheets or plugs of poor mechanical properties. The same poor products are obtained under non-anhydrous conditions or in the presence of other protic impurities.

All anionic initiators tested have been found suitable for cryotachensic polymerization of chloral, although the rates of initiation and propagation vary with the initiator. (160) Lithium tertiary butoxide (LTB) was the fastest initiator and has been shown to react with one equivalent of chloral in a reversible equilibrium

favoring the adduct according to NMR studies. (19)



Triphenylphosphine (Ph_3P) is also an excellent initiator, although the initiating species is actually not the phosphine but is the chloride ion produced by the fast 1:1 reaction of Ph_3P with chloral to give the vinyl phosphonium salt. (20, 21)



A reaction of this type is known as the Perkow reaction. (161, 162)

Chloral can also be polymerized by strong cationic initiators. (1, 163-170) Examples of effective initiators are protic acids such as sulfuric and trifluoromethanesulfonic acids and Lewis acids such as AlCl_3 , SbF_5 , and SbCl_5 . These polymerization rates are generally slower than with the anionic initiators. (164, 170) Cationic initiators are not amenable to polymerization by the cryotachensic polymerization technique as the polychloral obtained usually has poor mechanical properties.

Organometallic initiators have also been used to prepare polychloral of high molecular weight. Aluminum alkyls, such as Et_3Al , metal acetylacetonates, and an initiator consisting of 2,6-dimethoxyphenyl lithium plus diethyl zinc have all been reported. (171-185)

2. Properties of polychloral. Conflicts in earlier literature were resolved when it was discovered that the cyclic chloral trimer, or para polymer, was often mistaken for the true linear polychloral, or meta polymer. The meta polychloral from initiation of chloral with pyridine or H_2SO_4 , was shown by polarized infrared spectroscopy to have a regularly substituted polyoxymethylene structure. (49)

The same study showed that in contrast to the planer zig-zag configuration of polyoxemethylene, polychloral crystallizes into a helix of three or more repeat units per turn. Later it was shown that in all cases examined the polymer was isotactic and had four repeat units per turn of the helix. (20)

X-ray diffraction investigations have confirmed that polychloral is stereoregular and semicrystalline. (49) The x-ray diffraction patterns differed slightly among samples prepared by different initiators. An explanation suggested was that the sharper lines associated with anionic initiators were due to the helices being packed into larger crystallites. (49) The infrared spectra differed only in the C-H stretching region near 2900 cm^{-1} . (49)

Since polychloral is both insoluble and infusible it is not amenable to characterization by the methods usually carried out on polymers. One of the most informative means has been through thermal degradation. The thermal stability is very sensitive to the initiators used, the purity of the reactants the end groups on the polymer chain, and the crystallinities. (176) Unstabilizes polychloral, prepared by anionic polymerization, degraded quantitatively to monomer above 140°C . without char formation. (176)

A further increase in thermal stability was achieved by endcapping with acid chlorides or anhydrides (50, 176-179), polymerization in the presence of acid chlorides (180) or with decomposable cations. (181) The thorough study of endgroup and stabilization has recently been reported. (182-185) Another reported method of stabilization of polychloral was the refluxing of the polymer in a 10-15% solution of PCl_5 in CCl_4 for 4-6 hours under nitrogen. (21)

Differential scanning calorimetry and torsion braid measurements show that polychloral has neither a T_g or T_m below its decomposition point. (20)

3. Polydichloroacetaldehyde. Polydichloroacetaldehyde, first reported in 1868 (52), was produced by a slow reaction of HCl with the aldehyde. It was insoluble, but, unlike polychloral, was amorphous and when polymerized under different conditions was soluble in tetrahydrofuran and methyl ethyl ketone. (178) More recently dichloroacetaldehyde was found to polymerize readily in the presence of Lewis acid type cationic initiators, but was unaffected by the usual anionic initiators. (157, 178) The initiator $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at 0°C . produced a polymer having DP_n of more than 400. It was less thermally stable than polychloral, but this was improved by treatment with acetic anhydrides.

4. Polychloroacetaldehyde. Chloroacetaldehyde has been polymerized slowly at room temperature without initiators (51, 108) and in the presence of Lewis acids (47) and organometalics. (32, 163) The polymer was semicrystalline or amorphous, depending on initiators and conditions. The thermal stability was lower than that of polychloral.

5. Polyfluoral. Fluoral is a very reactive monomer which has been polymerized readily under a variety of conditions. The uncatatalyzed (spontaneous) polymerization to a waxy resin was first reported by Schechter and Conrad. (32) Later fluoral polymerization claimed to have been carried out using free-radical (23) anionic and cationic initiators, but the polymers obtained were intractable, infusible, and could not be fabricated. (23) The physical form of these polyfluorals ranged from brittle solids to soft gums depending on polymerization conditions, but were all intractable.

(23, 187, 188)

In 1972 Temple and Thornton reported the polymerization of fluoral to a high molecular weight polyfluoral which was amorphous and tractable thereby allowing practical application of polyfluoral. (25) These polymerizations were carried out using anionic (CsF), cationic (PF_5) initiation or radiation in an inert solvent at -78°C . Polymers soluble in 2,2-bis (trifluoromethyl)-1,3-dioxolane and 2,2,4-tris (trifluoromethyl)-1,3-dioxolane were obtained with inherent viscosities up to 4.0 dl/g. Polymerizations carried out using the same reactants at room temperature resulted in friable, insoluble powders. It was observed that the x-ray diffraction patterns of the insoluble polymers showed then to be a semicrystalline polymer whereas the soluble fractions were amorphous. It was proposed that in the low temperature polymerization the decreased nucleophilicity of both the carbonyl function and the propagating alkoxide anion does not allow a stereospecific polymerization thus producing an atactic,

noncrystalline polyfluoral. (25)

A radical polymerization of fluoral using peroxides was claimed in 1954. (23) This was later supported by Busfield who used ultra-violet light to control the initiation of fluoral with AIBN. (24, 187, 189) The polymerization could be effectively inhibited with known free-radical scavengers such as benzoquinone and diphenylpicrylhydrazil (DPPH) and could be stopped and restarted by turning the UV source off and on, at low conversions. Further evidence for the free-radical mechanism was found by using C^{14} labeled AIBN and finding these fragments as the polymer end groups. (189) The kinetics and thermodynamics of the cationic polymerization of fluoral have been reported by Busfield and McEwen (22, 190-192) and Bird. (193) They also found that polyfluoral could be effectively endcapped with acid chlorides and acid anhydrides to give polymers having a maximum rate of thermal decomposition up to $399^{\circ}C$. This endcapping also provided a convenient means of estimating the molecular weight of the insoluble polymers. (22).

A review of work with mono-, di-, and trifluoroacetaldehydes has been published by Otsu and Yamada. (194)

6. Polydifluoroacetaldehyde. McBee and Pierce found that purified difluoroacetaldehyde slowly polymerized to a white rubbery solid. (195) On further investigation they found that the polymerization rate was increased greatly by addition of a small amount of concentrated sulfuric acid, but at low temperatures even the acid initiated solution did not polymerize. The liquid acetaldehyde was stable for long periods of time

at -78°C . The polydifluoroacetaldehyde obtained softened at 130°C . and depolymerized to monomer above 165°C . It was found to be soluble in acetone but insoluble in water, ethanol, butanol, chloroform, carbon tetrachloride, benzene and n-heptane. It was stable in both cold dilute acids and bases. (195)

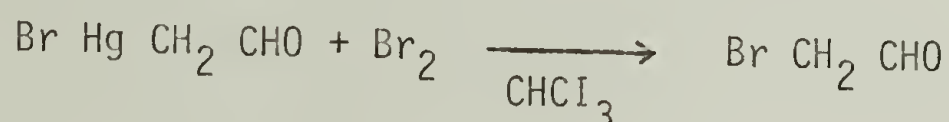
Barney reported the polymerization of difluoroacetaldehyde initiated with triethylphosphite at -80°C . (188)

7. Polyfluoroacetaldehyde. No systematic investigation of the polymerization of fluoroacetaldehyde has been reported, but it was found that when highly purified monomer was allowed to stand it became viscous and then solidified to a white polymer. (196, 197) Since the investigators were interested in the fluoroacetaldehyde synthesis only, no follow up was made to isolate or characterize the polymer or understand the polymerization.

8. Polybromal. Bromal, thought to be non-polymerizable due to the bulkiness of the pendant tribromomethyl groups, was polymerized after careful purification of the monomer. (28) Initiation by both cationic and anionic initiators such as pyridide, quinoline, triethyl amine and LTB gave an intractable polymer. The only cationic initiator, however, found to cause polymerization was trifluoromethane sulfonic acid. The conversion to polymer even using this acid was only 3% after one month at -78°C . The critical requirements for polymerization were found to be monomer purity, dilute monomer solutions in a good solvent (toluene), initiation by dilute solutions of initiator and cooling the monomer solution temperature to -60°C . for a few minutes before lowering the

temperature to the final polymerization temperature of -78°C . and initiating.

9. Polydibromacetaldehyde and polybromoacetaldehyde. Polybromoacetaldehyde was reported by a group of Soviet researchers who obtained the polymer while conducting a study of organo-mercury compounds. They obtained bromoacetaldehyde by the reaction



which rapidly polymerized to give a white solid. (198)

Polydibromoacetaldehyde has not been reported in the literature.

10. Other fully halogenated acetaldehyde polymers.

a. Polydichlorofluoroacetaldehyde. Polydichlorofluoroacetaldehyde was recently prepared from the previously unknown monomer. (199) The polymerization was initiated by both anionic and cationic initiators such as Ph_3P , lithium tertiary butoxide (LTB), H_2SO_4 , TiCl_4 , SbCl_5 , and Et_3Al to give infusible, intractable polymers. The thermal stabilities were dependent on the initiator used and the conditions of polymerization. Due to the incompleteness of this study the research into polydichlorofluoroacetaldehyde was concluded in this thesis.

b. Polychlorodifluoroacetaldehyde. Chlorodifluoroacetaldehyde was first synthesized and reported to polymerize on standing by Woolf in 1959. (200) The monomer was later mentioned in a British patent. (201) A more complete investigation of this polymerization and polymer was recently conducted by Yamada and Vogl who found that under some conditions a partially soluble polymer could be obtained. The initi-

ators employed were Ph_3P , LTB, H_2SO_4 , Et_3Al and SbCl_5 . (199, 202) Again this work was completed in this thesis.

c. Polybromodichloroacetaldehyde. A poorly documented report in 1882 reported obtaining a polymer from bromodichloroacetaldehyde and H_2SO_4 . (131) The chemical nature or structure of the polymer were not confirmed.

Lipp recently reported the synthesis and polymerization of bromodichloroacetaldehyde to give an insoluble semicrystalline polymer similar in structure to polychloral. (31) He found that polymerization could be carried out using anionic or cationic initiators such as Ph_3P , LTB, pyridine, 2,4,6-collidine, triethyl amine, CsF , H_2SO_4 and SbCl_5 at low temperatures. The thermal stability depended on initiator and polymerization conditions but stabilization of the polymers with acid chlorides, acid anhydrides, or PCl_5 was possible to give polymers which were more thermally stable. Vacuum degradation studies showed that polymers produced by anionic initiation (pyridine) degraded quantitatively to monomer, but polybromodichloroacetaldehyde resulting from initiation by H_2SO_4 left approximately 17% of a residue after removal of an orange volatile liquid which was shown by gas chromatography to be a very impure monomer. (31)

d. Polychlorodibromoacetaldehyde. Lipp found that highly purified chlorodibromoacetaldehyde could be polymerized by the same nucleophiles that polymerized chloral with the exception of the tri-alkyl phosphines and bromide or iodide salts. (29, 30) Cationic type initiators were also active in chlorodibromoacetaldehyde polymerization,

but the reaction rates were slower than for chloral. The polymers were isolated as translucent chips which could be stabilized with acetic anhydride or with a PCl_5 in carbon tetrachloride solution. Thermal stabilities were measured using DTA with decomposition maxima to 300°C . recorded for the stabilized polymers. This is somewhat lower than the stabilized chloral polymers. The products of thermal degradation were collected and shown to be at least 98% monomer. (30)

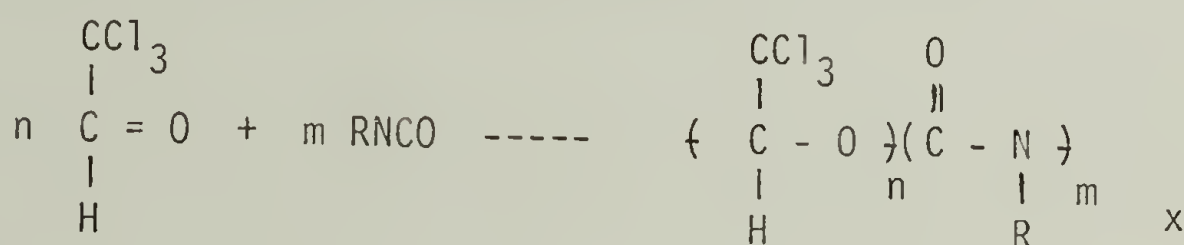
D. Chloral Copolymers

The copolymerizations of chloral have been more carefully studied than those of the other haloacetaldehydes. Only a few copolymerizations of fluoral and bromal have been reported.

1. Chloral-aldehyde copolymers. Chloral has been readily polymerized with other acetaldehydes through what are believed to be a random copolymerization as there is no particular driving force for stereoelectivity. Insoluble, infusible copolymers of chloral and dichloroacetaldehyde have been produced by initiation of a solution of the monomers in toluene below -40°C . using zinc dialkyls and cadmium dialkyls. (203, 204) Chloral-fluoral copolymers having good mechanical properties were obtained under anionic conditions. (21) By varying the ratios of chloral and a comonomer the relative reactivities may be estimated for a series of comonomers through analysis of the copolymer or of the unreacted monomers. This procedure was used by Lipp to show that the order of reactivities was chloral > bromodichloroacetaldehyde > chlorodibromoacetaldehyde > bromal. (28-31)

Chloral has also been copolymerized with non-halogenated aldehydes such as formaldehyde. Low temperatures and initiators such as Ph_3P , trialkylamines, and triethylaluminium have been reported to yield copolymers of varying compositions. (205-209) Other patents have claimed the copolymerization of chloral and aldehydes or the related cyclic ethers. Examples of these are: acetaldehyde (210), trioxane (211-213), ethylene oxide (214), propionaldehyde (210), 1,3-dioxolane (211, 212), and 3,3-dichloromethyl oxetane. (211)

2. Chloral-isocyanate copolymers. Chloral was copolymerized with isocyanates and found to have improved optical clarity and thermal stability of polychloral even with relatively small amounts of various isocyanates. (21, 204, 215-230) The copolymers had greater solubility as larger amounts of isocyanate were incorporated.



Odian carried out a series of copolymerizations of chloral and phenyl isocyanate using different initiators and solvents to study the reactivity ratios and the effect of counterions. (231, 232) The reactivity ratios were found to be r_1 (chloral) = 1.2, r_2 (phenyl isocyanate) = 0 in hexane and 0.5 and 0, respectively, in ether at -78°C .

II. EXPERIMENTAL SECTION

A. Chemicals1. Sources of commercial chemicals.a. Reagents.

Acetic Anhydride	E
Antimony Pentachloride	Af
Antimony Trifluoride	Ad
Boron Trifluoride Etherate	Af
Bromine	F
Butadiene	Mt
n-Butyl Lithium	Af
CaCl ₂	F
Chloral	DS
Chlorotrifluoroethylene	PCR
15-Crown-5-Ether	PCR
24-Dinitrophenylhydrazine	E
Epichlorohydrin	E
Ethanol	E
Feric Chloride	F
Fluoral Hydrate	PCR
Fuming Sulfuric Acid	F
Lithium Aluminum Hydride (LAH)	Af
Lithium t-Butoxide (LTB)	Af
Maleic Anhydride	A
Methanol	E
Phenyl Isocyanate (PhNCO)	A
Phosphorus Pentachloride	F
Phosphorus Pentoxide	F
Pyridine	E
Sodium Carbonate	F
Sulfuric Acid	F
Tetrachloroethylene (TCE)	A
Tetrahydrofuran	A
Trichloroacetic Acid	A
Triethyl Aluminum (Et ₃ Al)	TA
Trifluoromethane Sulfonic Acid (TFMSA)	A
Trioxane	C
Triphenyl Phosphine (Ph ₃ P)	A

b. Solvents.

Acetone	F
Benzene	F
Chloroform	F
Diethyl Ether (Anhyd)	B
Dioxane	MCB
Freon 113	D

b. Solvents. (Cont'd)

n-Hexane	F
Methylcyclohexane (MCH)	A
Toluene	A

c. Sources.

A	=	Aldrich Chemical Co.
Ad	=	Allied Chemical Co.
Af	=	Alfa Inorganics (Ventron)
B	=	J. T. Baker Co.
C	=	Celanese Co.
D	=	E. I. DuPont
DS	=	Diamond Shamrock Co.
E	=	Eastman Kodak Co.
F	=	Fisher Scientific Co.
M	=	Mallinckrodt Chemical Co.
MCB	=	Matheson, Coleman & Bell
MT	=	Matheson Gas Products
TA	=	Texas Alkyls

2. Purification. All of the distillations except chloral were carried out in a distillation apparatus equipped with a 1 foot jacketed Vigreux column and a Claisen distillation head. Vacuum distillations utilized, in addition, a magnetic stirrer and bar to prevent bumping. A Cartesian diver type manostat was used to stabilize intermediate vacuums.

Chloral was supplied through the courtesy of L. S. Corley and was purified by him. It was refluxed for 24 hours over P_2O_5 under nitrogen. It was then distilled through 100 cm. of glass helices and through an automatic distillation head at a 50:1 reflux ratio. Purity, monitored by GC, was better than 100 ppm. water and 20 ppm. dichloroacetaldehyde.

Tetrachloroethylene was washed several times with dilute hydrochloric acid, water, and sodium carbonate solution and dried over calcium chloride and finally distilled through a packed column.

The following chemicals were distilled prior to use from the suitable drying agents: acetic anhydride, antimony pentachloride, dioxolane ethanol, methanol, pyridine, tetrahydrofuran, benzene, chloroform, n-hexane, methylcyclohexane PhNCO and toluene.

Ph_3P was recrystallized from benzene, trioxane and maleic anhydride from diethyl ether.

LTB was sublimed onto a cold finger at 0.1 mm. Hg.

All other reagents and solvents were used as received, preferably from freshly opened containers. All air or moisture sensitive compounds were stored under nitrogen in sealed containers or in a dry box for brief periods.

B. Measurements

Proton and fluorine nuclear magnetic resonance spectra were obtained on a Perkin-Elmer R-32 90 MHz ^1H variable temperature NMR. Spectra were recorded in the locked mode using internal TMS for PMR at normal temperature, 35°C. Hexamethyldisiloxane (HMDS) was used as an internal lock signal for those spectra recorded at higher temperatures. ^{19}F NMR spectra were measured using trifluoroacetic acid in an external (coaxial) tube as the locking resonance signal. ^{13}C NMR spectra were obtained on a Bruker HFX-90 22.63 MHz instrument on solutions of the polymer in CCl_4 . The solvent also served as the internal standard. The instrument was run in both a coupled and decoupled mode using D_2O as an external lock signal. Other variables were: temperature 40°C.; 90° - =3.0 sec; norm. constant 2; V.F.S. \pm 2 volts; 90° pulse width 45.5 sec.; H.D.S. 8-16 K; stab. ampl. 100;

field width 5,000 Hz.; T1 3; 4096 scans.

Infrared spectra were obtained on either a Perkin-Elmer 257 or 727 Infracord ($4000-600\text{ cm.}^{-1}$) or a 283 ($4000-250\text{ cm.}^{-1}$) Solid samples were measured as KBr pellets and liquid samples were measured between sodium chloride plates. Gaseous samples were measured in closed cells consisting of sodium chloride windows with a 10 cm. path length. The vapors were diluted with nitrogen.

Thermal degradation was measured with a Perkin-Elmer TGS-1 thermo-balance using a sample size of about 10 mg. in a nitrogen atmosphere and a heating rate of 10°C./min. The heating rate was controlled by a Perkin-Elmer UU1 Temperature Program Control. Most data were collected using the differential mode (DTG), but the normal mode (TGA) was also utilized.

Normal melting points were measured on a Mel-Temp capillary melting point apparatus and corrected.

Gas chromatograms were obtained on a Varian Associates Model 920 gas chromatograph. Specific columns and conditions are described in the experimental details.

Wide angle x-ray scattering was carried out on an in-house made instrument with a Norelco power supply. The radiation was from a $\text{Cu K}\alpha$ source having a wavelength of 1.5418 angstroms. The powdered sample was placed in a 7 mm. diameter hole in a 1.5 mm. thick lead plate and secured with a layer of cellophane tape on each side. The sample was placed about 1 cm. from the radiation port and the photographic film plate positioned about 8 cm. behind the sample. All distances were

carefully measured before and after each exposure. The exposure time was controlled by an automatic timer and was about 8 hours for each sample.

All ceiling temperatures were measured on an apparatus constructed for this project. In brief, the method involved, a focused beam of light passed through a solution of the acetaldehyde which was initially heated to a temperature above the polymerization temperature. The solution was cooled slowly. The light beam intensity sharply decreased when the solution began to polymerize. The change was detected by a photocell and plotted graphically on an x-y recorder. The temperature of the bath was measured manually and noted on the recorder trace. A schematic diagram is shown in Figure 20.

The specific components used in the construction of this apparatus were: The light source was a 5.9 V., 5 amp., G.E. Mazda projection bulb. A voltage control was connected between the lamp and outlet. The light beam was focused through a lens having a 50 mm. focal length and a 5 mm. iris condensor. The detector was a selenium photocell, Lafayette Radio Co. No. 99-6243. The recorder was a Linear Instruments Corp. Model 161. To adapt it to the photocell output, a 3,000 ohm resistor was shunted across the input leads. Chart speed was 16 in. per hr. The sample was placed in Pyrex tubes consisting of a cylindrical sample chamber 12 mm. in diameter and 25 mm. high. This was attached to a 8 mm. (O.D.) x 200 mm. filling stem. The purpose of the thinner neck was to allow the sealing of the tube which would be difficult in the 25 mm. tubing needed to get adequate sample in the light beam. The tube was immersed in an oil bath which was made from a 250 ml. reagent bottle with a ground

glass stopper. To ensure a uniform light transmittance, the two opposite sides were flattened to give parallel windows. A one inch magnetic stirring bar was placed in the oil bath to provide a uniform temperature. The oil bath-sample assembly was placed on a stirrer-hotplate. With a sample tube in position, the light source, oil bath sample tube and detector were all aligned to give the maximum initial light intensity through the sample.

The intensity of the ^{60}Co source was measured by FeSO_4 dosimetry. A solution of 0.2000g. FeSO_4 , 0.0300g. NaCl and 11.0 ml. conc. H_2SO_4 was diluted to 500 ml. with distilled water. 10 ml. of the fresh solution were sealed into screw cap vials which were no more than one-half full to provide air for the solution. These were irradiated for varying periods of time. The intensity of radiation was determined by measuring the UV absorbance of the solutions at 3040 \AA^0 to measure the amount of ferric ion generated.

Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

C. Polymerization Procedure

The general method used for the polymerizations of the haloacetaldehydes was carried in sealed ampules as follows.

The initiator or initiator solution was sealed under atmospheric nitrogen pressure into a break tube, a thin walled tear shaped ampule about 8 mm. in diameter made from a melting point capillary tube, and this was placed into a larger, 12 mm. x 100 mm., ampule. A neck was

formed in the middle of the larger tube above the ampule and the monomer and solvent, if any, were vacuum distilled from P_2O_5 into the tube which had been cooled to $-78^{\circ}C$. and it was sealed at 0.1 mm. Hg. The sealed tube was heated to the desired temperature and the initiator released by vigorously shaking the tube until the smaller ampule was broken.

Since the exclusion of moisture is critical all glassware was thoroughly dried overnight at $120^{\circ}C$. and cooled to room temperature under nitrogen just prior to use. This was accomplished by removing the tube from a $120^{\circ}C$. oven, capping it with a rubber septum and inserting two #20 syringe needles, the inlet, reaching the bottom of the tube, and an exit needle near the top, and maintaining a brisk flow of dry nitrogen through the system for several minutes until the tube was cool. The tube was uncovered and the initiator ampule removed from a desiccator and added quickly. The tube was then flushed again with nitrogen. The necking was done while the tube was connected to a very slight positive nitrogen pressure source. During necking the initiator solution was protected by keeping it in the bottom of the tube and cooling this portion of the tube with ice. In this manner no thermal decomposition of the initiator took place.

D. BDFA Monomer Synthesis and Characterization

Experiment 1: Synthesis of dibromofluoroacetyl fluoride and bromodifluoroacetyl bromide by oxidation of 1,1-dibromo-2,2-difluoroethylene.

A dried 100 ml. 3-neck 14/20 flask was fitted with a rubber septum, and oxygen inlet sparge tube and a condenser vented to a trap which in turn was equipped with a drying tube and cooled in Dry Ice/acetone. Into the

flask was placed a magnetic stirring bar and 1,1-dibromo-2,2-difluoroethylene 33.5 g., 0.15 moles, and the flask placed in an ice water bath. Oxygen was introduced at the rate of 2 cc. per minute under the surface of the stirred liquid. The progress of the oxidation was followed by periodically removing samples and analyzing them by gas chromatography using a 6' x $\frac{1}{4}$ " column of Apiezon N on Chromosorb W ($^{100}/200$) with the injection port temperature 70° C., column 55° C. detector 240° C. and a helium flow of 50 ml. per minute. Peaks were recorded at 6.0 and 6.9 minutes. The first corresponded to the unresolved oxidation products, dibromofluoroacetyl fluoride and bromodifluoroacetyl bromide. The later peak was assigned to the olefin starting material. When no more olefin was detected by G.C., after about 6.5 hours, the reaction was stopped, leaving a pale yellow liquid product.

Experiment 2: Preparation of methyl bromodifluoroacetate and methyl dibromofluoroacetate. The mixture of acid halides prepared above were slowly distilled, under nitrogen, directly into a stirred receiver flask containing 40 g. dry methanol which was cooled to 0° C. The mixed halides distilled together over the range $65-80^{\circ}$ C. The reaction with methanol spontaneously gave the two corresponding methyl haloacetates. The methanol solution was washed thrice with a 10% sodium bicarbonate solution, washed with water, and dried overnight over magnesium sulfate. The products were separated by fractional distillation into methyl bromodifluoroacetate (bp. $96-98^{\circ}$ C.; lit. bp. 96° C.) (234) and methyl dibromofluoroacetate (bp. 83° C. @ 71 mm. Hg; lit. bp. 85° C @ 80 mm.) (233) The yields of the two compounds were 7.1 g. and 8.0 g., respec-

tively, for an overall combined yield of 50% from the olefin. The molar ratio of the two recovered products was 1.0:0.85, respectively. The purity of the products was checked by G.C. using a 6' x $\frac{1}{4}$ " Carbowax 20 M on Chromosorb W column with temperatures as follows: injection port 140° C.; column 75° C.; detector 240° C. Using a helium flow of 50 ml./minute the compounds were eluted at 2.25 and 25.5 minutes, respectively, each having impurities of less than 0.5%. The major impurity in each was the other isomer. The infrared spectrum of the methyl bromodifluoroacetate (Figure 1) was identical to that reported in the literature. (235) The neat film of the compound showed peaks at 2970 cm^{-1} vs (C-H stretching), 1780 cm^{-1} vs (C=O stretching), 1445 cm^{-1} vs (C-H bending), 1310 cm^{-1} ms (C-O stretching), 1182 cm^{-1} vs (C-F stretching), 1130 cm^{-1} ms, 988 cm^{-1} ms, 915 cm^{-1} ms, 875 cm^{-1} ms, 815 cm^{-1} vs and 722 cm^{-1} ms. The ^1H spectrum showed a singlet at 3.98 ppm. (TMS) (5% in CDCl_3). The ^{19}F signal was also a singlet located 20.35 ppm. downfield from trifluoroacetic acid.

Experiment 3: Preparation of methyl bromodifluoroacetate from chlorotrifluoroethylene. (235) A 250 ml. 3-neck flask was equipped with a magnetic stirrer, a gas inlet sparge and a Dry Ice/acetone condenser protected by a drying tube. Into this flask was charged Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) 200 ml. and bromine (67.2 g., 0.42 moles). The flask was flushed with nitrogen and placed in a ice water bath. Chlorotrifluoroethylene (b.p. -28° C.) was passed through a safety trap and a flow meter and bubbled into the solution under the surface of the stirred liquid. The flow rate was maintained at about

150 ml. per minute. This rate was not exact since the flow meter was calibrated for air. As long as the mixture was maintained at $0^{\circ}\text{C}.$, all gas was absorbed at this flow rate.

After 95 minutes the solution turned from reddish-brown to clear, indicating that all of the bromine had reacted. The system was flushed with nitrogen prior to opening. The liquid was washed with 10% sodium bicarbonate, then washed with water, and dried overnight over calcium chloride. The reaction mixture was distilled to give the product 1,2-dibromo-1-chlorotrifluoroethane (bp. $91-93^{\circ}\text{C}.$; lit. (235) $92^{\circ}\text{C}.$) in 82% yield. The infrared spectrum was identical to that reported; (235) (neat, NaCl plates) $1196\text{ cm}^{-1}_{\text{s}}$ (C-F), $1172\text{ cm}^{-1}_{\text{s}}$ (C-F), $1123\text{ cm}^{-1}_{\text{s}}$, $1115\text{ cm}^{-1}_{\text{s}}$ (C-F stretching), $1020\text{ cm}^{-1}_{\text{s}}$, $1010\text{ cm}^{-1}_{\text{s}}$, $885\text{ cm}^{-1}_{\text{s}}$, $879\text{ cm}^{-1}_{\text{s}}$, $865\text{ cm}^{-1}_{\text{s}}$, $848\text{ cm}^{-1}_{\text{s}}$, $780\text{ cm}^{-1}_{\text{m}}$, $740\text{ cm}^{-1}_{\text{m}}$. (Figure 2)

The haloethane (115 g., 0.42 moles), 30% fuming sulfuric acid (90 ml.) and yellow mercuric oxide (1.0 g., 0.0046 moles) were charged into a 300 ml. one-neck flask. A condenser on the flask led through a series of two traps cooled to $0^{\circ}\text{C}.$ and into a 100 ml. flask containing a slurry of methanol (80 ml., 2.0 moles) and potassium fluoride (26.0 g., 0.45 moles), plus a magnetic stirring bar and an exit vent protected by a drying tube. On heating, the acidic haloethane solution turned reddish-brown. Bromine and an invisible gas were evolved. The former was collected in the cold traps and the latter, volatile CBrF_2COF , was bubbled under the surface of the stirred methanol-KF suspension. After the reflux had continued for 11 hours, the methanol solution was poured into ice water and the lower oily layer was quickly separated, washed once with water, and dried over magnesium sulfate.

The clear liquid was distilled to give methyl bromodifluoroacetate, bp. 97-98⁰ C. (lit. bp. 96⁰ C.) (234) in 68% yield. The IR and ¹H NMR spectra were identical to those of the material prepared by the oxidation of the olefin in Experiment 2.

Experiment 4: Reduction of methyl bromodifluoroacetate to the hydrate.

CBrF₂CH(OH)₂. The reduction of methyl bromodifluoroacetate was performed by a method similar to that reported by Pierce and Kane for the preparation of fluoral hydrate. (236)

Into a 100 ml. 3-neck flask equipped with a stirring bar, a 25 ml. addition funnel and a reflux condenser was placed methyl bromodifluoroacetate (7.1 g., 0.038 moles) in 15 ml. of anhydrous diethyl ether. The flask was immersed in a Dry Ice/acetone bath and cooled to -78⁰ C. In a separate operation, finely divided lithium aluminum hydride (LAH) (0.38 g., 0.010 moles) was slurried in 25 ml. anhydrous ether in a 50 ml. flask equipped with a magnetic stirring bar and a reflux condenser and maintained under a positive pressure of nitrogen. After stirring for two hours the agitation was stopped and the mixture allowed to settle. The supernatant was decanted into the 25 ml. addition funnel on the acetate flask assembly and added dropwise over 30 minutes with stirring. The LAH sludge was reslurried in fresh anhydrous ether and this suspension also added dropwise with stirring to the acetate solution. The total addition time was limited to not more than three hours.

After all additions had been completed the mixture was stirred for 30 minutes. The mixture was then allowed to slowly warm to room temperature. When this was achieved, the mixture was carefully poured into a

stirred beaker containing 200 ml. crushed ice and 2 ml. conc. sulfuric acid to dissolve the aluminum compounds. The two layers were separated and the aqueous layer extracted twice with ether. The combined ether portions were concentrated by carefully removing volatiles under a reduced pressure of 25 mm. Hg. at room temperature to leave the high boiling bromodifluoroacetaldehyde hydrate in 90% (crude) yield.

Experiment 5: Preparation of bromodifluoroacetaldehyde, BDFA
(CBrF_2CHO). The BDFA was obtained by dehydrating the above hydrate with conc. sulfuric acid. Equal volumes of the crude hydrate (7 ml.) and conc. sulfuric acid (7 ml.) were mixed in a 25 ml. distillation flask equipped with a magnetic stirring bar and 15 cm. Vigreux column distillation head. The distillation was conducted under a blanket of dry nitrogen using thoroughly dried glassware. The hydrate and acid do not mix initially so vigorous stirring was required throughout the distillation in order to maintain effective mixing and reaction. BDFA was collected over the boiling range $43\text{--}44^\circ\text{C}$. in a receiving flask cooled in an ice water bath. The clear liquid had a sharp odor. The yield was 3.4 g. (60% of the theoretical yield based on the methyl bromodifluoroacetate used.)

The infrared spectrum of the BDFA was characterized by absorptions of the aldehydic proton at 2861 cm^{-1} and carbonyl stretching at 1762 cm^{-1} (5% concentration in carbon tetrachloride.) The BDFA spectrum was also recorded neat in the gaseous phase in nitrogen. (Figure 3) Bands were recorded at 3560 cm^{-1} s (overtone), 2861 cm^{-1} s

(C-H stretching), 1762 cm^{-1}_s (C-O stretching), 1371 cm^{-1}_s (C-H bending, in plane), 1312 cm^{-1}_m , 1240 cm^{-1}_m , 1190 cm^{-1}_s , 1150 cm^{-1}_m , 1071 cm^{-1}_m , 1016 cm^{-1}_s (C-C stretching), 1011 cm^{-1}_s , 1005 cm^{-1}_s , 895 cm^{-1}_m (C-H bending, out of plane), 821 cm^{-1}_m , 747 cm^{-1}_s , 663 cm^{-1}_m (C-Br stretching), 591 cm^{-1}_m and 435 cm^{-1}_s .

Nuclear magnetic resonance characterization was also employed. ^1H NMR showed a triplet centered at 9.09 ppm. (TMS) with the coupling constant $J_{\text{H-F}} = 4.0\text{ Hz}$. The ^{19}F spectrum showed a doublet 8.53 ppm. downfield from trifluoroacetic acid (external). The coupling constant was also 4.0 Hz. Both were recorded at 5% concentration in CDCl_3 .

ANAL. Calcd. for $\text{C}_2\text{HBrF}_2\text{O}$: C, 15.11; H, 0.63; F, 23.91.
Found: C, 15.02; H, 0.59; F, 24.10

Experiment 6: 2,4-Dinitrophenylhydrazone of bromodifluoroacetaldehyde:

$[\text{CBrF}_2\text{CH} = \text{NNHC}_6\text{H}_4(\text{NO}_2)_2]$. This derivative was prepared according to the method of Ross and Ring (237) which is specifically used for the preparation of 2,4-dinitrophenylhydrazones of haloacetaldehydes.

A solution of 2,4-dinitrophenylhydrazone (0.77 g., 3.9 m moles, in 20 ml. conc. hydrochloric acid) at 45°C . was added slowly with stirring to a solution of BDFA hydrate (1.23 g., 7.7 mmoles, in 2 ml. conc. HCl). The solution was stirred for two hours at room temperature then cooled in ice water. The yellowish orange crystals which precipitated were collected by filtration, washed with water, recrystallized twice from ethanol, and dried. mp. $136\text{--}138^\circ\text{C}$.

ANAL. Calcd. for $\text{C}_8\text{H}_5\text{BrF}_2\text{N}_4\text{O}_4$: C, 28.34; H, 1.49; N, 16.52.

Found: C, 28.60; H, 1.55; N, 16.30

Experiment 7: ^1H NMR of BDFA hydrate $[\text{CBrF}_2\text{CH}(\text{OH})_2]$. To a 5% solution of BDFA in CDCl_3 in a 5 mm. NMR tube water was added in one microliter increments. The ^1H NMR spectrum was recorded after each addition. The formation of the stable hydrate was indicated by the replacement of the aldehydic proton triplet at 9.09 ppm. by two sets of peaks, a triplet at 5.16 ppm. and a singlet at 3.85 to 4.35 ppm. (TMS), depending on concentration. The integrated intensity of these two absorptions was 1:2, respectively, indicating they were due to the one methine proton and the two hydroxyl protons. Repeating the experiment with deuterium oxide (D_2O) instead of water resulted in the same observations except the resonances due to the hydroxyls were not observed due to the replacement of the protons by the deuterium atoms.

E. Polymerizations of BDFA

Experiment 8: Polymerization of BDFA with Ph_3P 25°C . An initiator tube containing 0.04 ml. of a 0.30 M. solution (0.012 m moles) of Ph_3P in methyl cyclohexane (MCH) was placed in a polymerization ampule. Into this was distilled BDFA (1.36 g., 8.6 mmoles) from P_2O_5 and the system sealed at -78°C . and 0.05 mm. Hg. The tube and contents were allowed to warm to room temperature and the initiator ampule broken to give a homogeneous solution of monomer and initiator.

After three minutes the contents of the tube gelled to a clear mass which solidified within one hour.

After 28 hours the tube was cut open and the polymer, a hard,

light amber glass, was removed. It was triturated and stirred overnight in acetone (50 ml.) The polymer was totally soluble in acetone, but could be reprecipitated by pouring the solution into water. The powder was collected and dried. The yield of acetone soluble polymer was 0.20 g. (15%).

The soluble polymer was characterized by several means. The inherent viscosity was found to be 0.20 dl./g. @ 25° C. in acetone. The infrared spectrum (KBr pellet) (Figure 4) showed absorptions at 3400 cm^{-1} _b (OH), 2950 cm^{-1} _m (C-H stretching), 1385 cm^{-1} _s (C-H bending), 1360 cm^{-1} _s (C-H bending), 1235 cm^{-1} _m, 1165 cm^{-1} _{ms} (C-O stretch), 1055 cm^{-1} _s (C-O stretch), 982 cm^{-1} _s, 958 cm^{-1} _s, 847 cm^{-1} _s. ¹H NMR of a 5% solution in CDCl₃ showed only an unresolvable broad singlet centered at 5.23 ppm. (TMS) at 35° C. Attempted resolution at 90° C. and 105° C., 5% in tetrachloroethylene, still showed only the broad singlet at 5.31 ppm. (HMDS). ¹⁹F NMR was even less well resolved.

The thermal degradation spectrum (DTG) showed a single maximum at 161° C.

ANAL. Calcd. for (C₂HOBBrF₂)_n: C, 15.11%; H, 0.63%; F, 23.91%. Found: C, 15.35%; H, 0.75%; F, 23.64%.

Experiment 9: Isothermal decomposition of poly BDFA. A small amount of the soluble solid polymer (0.159 g.) was placed in an 18 mm. x 100 mm. ampule with a 10 mm. x 300 mm. L-shaped side arm to determine the thermal degradation products formed by isothermal pyrolysis. The ampule was evacuated to 0.1 mm. Hg and sealed. The end of the large

tube, containing the sample, was heated in a sand bath to 250°C . and maintained at this temperature until all solid polymer had disappeared. This took 3.5 hours. Simultaneously the volatile degradation products were collected in the side L-tube which was cooled to liquid nitrogen temperature. A colorless liquid was obtained (0.146 g. or 92% recovery) which was identified by G.C. and ^1H NMR as pure BDFA.

Experiment 10: Stabilization of poly BDFA. Into a dried 25 ml. round bottom flask were placed powdered polymer (0.1 g.) and a solution of 10% PCl_5 in carbon tetrachloride (10 ml.). The flask was fitted with a condenser and nitrogen inlet adapter. The system was flushed with nitrogen and refluxed under a positive nitrogen pressure for five hours. At the end of this time the polymer was precipitated in methanol, washed with methanol, water and dried.

Stabilization was also accomplished by acetylation. Polymer (0.1 g.) and acetic anhydride (2 ml.) were placed in a dried 3 inch test tube which was stoppered and left at room temperature for 24 hours. The soluble polymer was recovered by precipitation in ice water and dried under reduced pressure.

Both methods of stabilization were equally effective in increasing the maximum rate of degradation temperature from 160°C . to 240°C .

Experiment 11: Polymerization of BDFA with Ph_3P at -78°C . In an apparatus described previously BDFA (0.90 g., 5.7 mmol) in 1 ml. n-hexane was initiated by Ph_3P (0.05 ml. of 0.30 M. in MCH, 0.26 mole%). The ampule was sealed at liquid nitrogen temperature at 0.1 mm. Hg and warmed to 70°C . The inner ampule was broken, the contents mixed, and

the tube replaced in the -78°C . bath for polymerization. The polymer gelled in two minutes to give an opaque mass.

The ampule was opened after 40 hours. Liquid unreacted monomer was still present as shown by wettness and odor. The finely divided polymer was slurried in 50 ml. acetone overnight. The mixture was filtered and the filtrate mixed with 150 ml. ice water to precipitate the soluble polymer. The yields, based on the starting monomer, were 20% and 5% for the soluble and insoluble fractions, respectively. Infrared spectra of the two fractions were identical to each other and to Figure 4.

Thermal degradation studies were carried out on each fraction, before and after treatment with PCl_5 as described in Experiment 10. Thermal decomposition measurements recorded maximum rates of degradation at 165°C . and 161°C . for the raw insoluble and soluble portions, respectively, and 240°C . for each after PCl_5 stabilization.

The soluble poly BDFA was further characterized by measuring the inherent viscosity (0.338 dl./g. in benzene at 35°C .) and by vapor phase osmometry. The latter was carried out by dissolving the polymer (0.100 g.) in benzene (2.00 ml.) and by serial dilutions obtaining five solutions of known concentration. Using a Mechrolab 302B Vapor Phase Osmometer under normal operating conditions a number average molecular weight of 3470 g./mole was measured.

Experiment 12: Polymerization of DBFA with LTB at -78°C . Into the standard polymerization ampule were placed BDFA (1.23 g., 7.7 mmoles), 1 ml. n-hexane and a sealed ampule freshly sublimed LTB (0.04 ml. of

0.30 M. in MCH, 0.15 mole%). After the monomer had been vacuum distilled into the ampule at -196°C ., the sealed ampule was heated to 70°C . The initiator ampule was broken and the polymerization allowed to proceed at -78°C .

After 24 hours the polymer, an opaque solid, was removed from the ampule, finely divided, and slurried in acetone (50 ml.). The insoluble product was removed by filtration after stirring overnight. No soluble fraction was recovered by pouring the acetone filtrate into ice water. The yield of insoluble polymer was 0.43 g. (35%).

The polymer was stabilized by reacting it with PCl_5 as described in Experiment 10. The DTG showed maximum rates of thermal degradation at 222°C . and 389°C . for the untreated and stabilized polymers, respectively. The infrared spectra (KBr) of both were found to be identical to each other (Figure 5) and to the poly BDFA spectrum previously described.

Experiment 13: Polymerization of BDFA with LTB at 25°C . BDFA
(1.41 g., 8.9 mmoles) was vacuum distilled into a polymerization tube containing a sealed ampule of freshly sublimed LTB (0.03 ml. of 0.30 M. in MCH, 0.10 mole%). The tube was sealed and warmed to 80°C . The inner tube was shattered to release the initiator and the tube cooled to the polymerization temperature, 25°C . White solid polymer collected in the bottom of the tube within one minute and after two hours the entire tube contained a white granular product.

The tube was opened after 24 hours at 25°C . to give a slightly rubbery granulated product. This was slurried with acetone (50 ml.)

overnight and the insoluble polymer filtered off. (Yield 0.64 g., 45%). The acetone solution was poured into ice water (200 ml.) and the acetone soluble polymer recovered. (Yield 0.07 g., 5%).

A portion of the poly BDFA (0.1 g.) was treated with PCl_5 to stabilize it against thermal degradation. The maximum rates of thermal degradation were 220°C . for the raw polymer and 390°C . for the stabilized sample.

The infrared spectra were identical to those of poly BDFA prepared by other initiators, such as Ph_3P .

Experiment 14: Polymerization of BDFA with Pyridine at 25°C . BDFA (1.10 g., 6.9 mmol) was initiated with pyridine (0.03 ml. of 0.3 M. in MCH, 0.13 mole%) by the method described previously. The initiator ampule was broken at 85°C . and the tube placed in a water bath at 25°C . for polymerization. The solution became cloudy within one minute and after one hour had solidified to a pale yellow opaque solid. The tube was broken after 24 hours and the polymer removed. It was pulverized and slurried overnight in acetone (50 ml.). The acetone soluble and insoluble fractions were separated and found to be 0.04 g. (4% yield) and 0.36 g. (36% yield), respectively, of white, crystalline poly BDFA.

The maximum rates of thermal degradation occurred at 218°C . and 205°C . for the insoluble and soluble fractions, respectively. A portion of the insoluble fraction was treated with PCl_5 to give a polymer having a DTG maximum at 380°C . A second portion of the insoluble polymer was refluxed under the same conditions using only carbon tetrachloride to ascertain that the stabilization was due to the reaction

with PCl_5 and not due to the heating or removal of impurities. The DTG maximum was at 218°C ., the same as the raw polymer.

The infrared spectra of poly BDFA's prepared by other initiators are shown in Figure 5.

Experiment 15: Polymerization of BDFA with sulfuric acid at 25°C .

BDFA (1.79 g., 11.3 mmoles) was vacuum distilled into a polymerization tube containing an ampule of sulfuric acid (0.02 mmoles, 0.2 mole%). The tube was heated to 80°C ., the acid released, and the solution cooled to 25°C . The solution began getting viscous immediately and after five minutes was a solid, clear gel.

After 24 hours the translucent glass was removed from the tube, pulverized, and slurried with acetone (50 ml.) overnight. The conversion was 1.24 g. (70% yield) insoluble polymer and 0.40 g. (21% yield) soluble poly BDFA.

ANAL. Calcd, for $(\text{C}_2\text{HOBBrF}_2)_n$: C, 15.11%; H, 0.63%, F, 23.91%.

Found: C, 15.29%; H, 0.74%; F, 23.53%

The thermal stability was measured prior to and after treatment with PCl_5 . The maxima were observed at 196°C . and 411°C . for the insoluble polymer before and after stabilization, respectively, and 195°C . and 410°C . for the acetone soluble polymer. A sample of the insoluble polymer was also acetylated by allowing it to react for 24 hours with freshly distilled acetic anhydride as described in Experiment 10. This had a maximum rate of thermal degradation at 410°C .

The infrared spectra matched those of other poly BDFA's (Ph_3P , Figure 4) except that hydroxyl region at 3380 cm^{-1} was stronger for

the sulfuric acid initiated polymers. (Figure 5)

The ^1H NMR spectra was recorded for a 5% solution of the soluble fraction in tetrachloroethylene at 105°C . One unresolved peak was observed at 5.23 ppm. (HMDS).

Isothermal pyrolysis was conducted as described in Experiment 9. Acetone insoluble, raw polymer (0.468 g.) was sealed into the sample compartment of the pyrolysis tube. It was slowly heated to 200°C . in a sand bath for four hours and the volatiles collected in the other arm which was cooled in a liquid nitrogen bath. The liquid collected (0.460 g., 98%) was confirmed to be BDFA monomer by gas chromatography and PMR (5% in carbon tetrachloride).

Experiment 16: Attempted Polymerization of BDFA with sulfuric acid at -78°C . Into a polymerization tube was charged BDFA (1.13 g., 7.1 mmol), 1.0 ml. n-hexane and a sealed ampule containing sulfuric acid (0.030 mmol, 0.42 mole%). The tube was heated to 75°C ., the initiator released and mixed, and the tube plunged into a Dry Ice/acetone bath as quickly as possible. No polymer precipitation or increase in viscosity were observed after one week. The experiment was repeated using 0.8 mole% acid and again no polymer formation was observed. The tubes were broken and the solutions poured into ice water but no precipitate or cloudiness appeared.

Experiment 17: Polymerization of BDFA with SbCl_5 at -78°C . BDFA (1.11 g., 7.0 mmol) and 1.0 ml. n-hexane were distilled from P_2O_5 into a polymerization tube at 0.05 mm. Hg pressure. The polymerization

was initiated by breaking an ampule containing SbCl_5 (0.05 ml. of 0.55 M. in CH_2Cl_2 , 0.39 mole%). The tube was quickly cooled to -78°C . in a Dry Ice/acetone bath and allowed to stand undisturbed at this temperature. Gel formation was observed after one minute. After 24 hours the contents of the tube were removed as a soft translucent gel (0.09 g., 8% conversion) which was wholly soluble in acetone.

The infrared spectrum was the same as previously obtained and described for poly BDFA (Figure 4 and Figure 5). The DTG maximum for the acetone soluble raw polymer was located at 201°C . No further characterization was attempted.

Experiment 18: Attempted Polymerization of BDFA with SbCl_5 at -25°C .
BDFA (1.64 g., 10.3 mmol) was mixed with SbCl_5 (0.05 ml. of 0.55 M. in CH_2Cl_2 , 0.27 mole %) in a polymerization tube as described previously. The tube was placed in a refrigerator maintained at -25°C . There was no precipitation observed after six days, but the viscosity of the solution increased to that of a thick syrup. The tube was broken and part of the liquid poured into acetone and the remainder into cold water. In neither case was a precipitate formed and the liquid was totally miscible. No further characterization was attempted.

Experiment 19: Attempted polymerization of BDFA with boron trifluoride etherate at 25°C . Into a polymerization ampule was placed BDFA (1.01 g., 6.4 mmol) and a sealed ampule containing $\text{BF}_3\cdot\text{OEt}_2$ (0.02 ml. of 0.1 M. in n-hexane, 0.31 mole%). The tube was heated to 80°C ., the inner ampule broken and the reactants mixed. No heat or precipitation was observed on mixing and no changes were observed after five days.

The solution was totally miscible with both acetone and water.

Experiment 20: Polymerization of BDFA with Et_3Al at -78°C . BDFA (1.37 g., 8.62 mmol) was initiated with Et_3Al (0.04 ml. of 1 M. solution in benzene, 0.46 mole%) to give a gelled product after one hour in a Dry Ice/acetone bath. After 48 hours the product, a firm, translucent gel was removed from the tube and slurried in acetone (50 ml.) overnight. The insoluble material was isolated. No acetone soluble polymer precipitated when the solution was poured into ice water. The yield was 0.65 g. (45% conversion) of the insoluble polymer.

The polymer was characterized by its infrared spectrum which was indistinguishable from those of other poly BDFA's shown in Figures 4 and 5. The polymer was treated with PCl_5 to give a product having a DTG maximum at 316°C ., compared to 230°C . for the raw material.

Experiment 21: Polymerization of BDFA with Et_3Al at 25°C . In the normal manner BDFA (0.5 g., 3.15 mmol) was initiated with Et_3Al (0.02 ml. of 1 M. in benzene, 0.63 mole%). The formation of a cloudy gel was observed about 20 seconds after initiation. Within 30 minutes an opaque white solid filled the tube. After 24 hours the glassy solid was removed, triturated, and slurried in acetone (50 ml.). A 50% conversion to acetone insoluble material and no soluble fraction were found.

The infrared spectrum was identical to that of poly BDFA. A portion of the polymer was refluxed in a 10% solution of PCl_5 in

carbon tetrachloride under nitrogen for four hours to give a stabilized polymer. The maximum rate of thermal decomposition was observed at 377°C . for the stabilized polymer and 246°C . for the raw polymer.

Experiment 22: Copolymerization of BDFA and chloral with SbCl_5 at -25°C . Using a dry 1 ml. syringe and 12 inch #20 needle freshly distilled BDFA (1.17 g., 7.4 mmoles) and freshly distilled chloral (0.90 g., 6.1 mmoles) (55:45 molar ratio) were transferred to a dry polymerization tube which contained a sealed ampule of SbCl_5 solution (0.06 ml. of 0.55 M. in CH_2Cl_2 , 0.25 mole%). The ampule was heated to 80°C ., shaken to break the inner ampule and to mix the initiator, and placed in a bath which was cooled to -25°C . and kept in a refrigerator at this temperature. After 24 hours the contents of the tube had solidified to a translucent gel. The tube was broken and the semisolid gel was found to be completely soluble in acetone. The product was reprecipitated from water. Yield: 0.5 g. (25% conversion).

The infrared spectrum of the KBr pellet was recorded. It showed peaks at $2951\text{ cm}^{-1}_{\text{m}}$ (C-H stretch), $1400\text{ cm}^{-1}_{\text{w}}$, $1380\text{ cm}^{-1}_{\text{w}}$ (C-H bending), $1354\text{ cm}^{-1}_{\text{w}}$ (C-H bending), $1150\text{ cm}^{-1}_{\text{s}}$ (C-O stretching), $1072\text{ cm}^{-1}_{\text{vs}}$, $1056\text{ cm}^{-1}_{\text{s}}$ (C-O stretching), $1045\text{ cm}^{-1}_{\text{m}}$, $980\text{ cm}^{-1}_{\text{m}}$, $958\text{ cm}^{-1}_{\text{vs}}$, $843\text{ cm}^{-1}_{\text{vs}}$, $817\text{ cm}^{-1}_{\text{s}}$, $742\text{ cm}^{-1}_{\text{ms}}$, and $790\text{ cm}^{-1}_{\text{s}}$.

Thermal stability was measured by the location of the DTG maximum before and after PCl_5 stabilization. These were 205 and 386°C ., respectively.

ANAL. Found: 20.2% F, which corresponds to 87 mole% BDFA content in the copolymer.

Experiment 23: Copolymerization of BDFA with chloral with Ph_3P at -25°C . A polymerization tube was charged with BDFA (0.88 g., 5.5 mmoles) chloral (0.82 g., 5.5 mmole) and an ampule containing a solution of Ph_3P in MCH (0.04 mmoles, 0.36 mole%). The tube was cooled in liquid nitrogen and sealed under a pressure of 0.05 mm. Hg. It was then heated to 75°C . and shaken until the inner ampule was broken, releasing and mixing the initiator solution. The tube was quickly transferred to a bath at -25°C . and maintained at this temperature in a refrigerator.

After 24 hours the tube was broken and a soft gel removed. This was slurried in acetone (50 ml.) overnight and separated by filtration. The filtrate, containing the soluble fraction, was poured into water and a white powder collected. Both fractions were dried overnight in an aspirated oven at 60°C . @ 25 mm. Hg. The yield of insoluble polymer was 0.48 g. (28% conversion) and the soluble polymer was 0.41 g. (24%).

The products were characterized by DTG and IR. The DTG trace showed maximum rates of thermal decomposition at 162°C . and 275°C . for the insoluble fraction before and after treatment with PCl_5 . The maxima for the soluble fraction were 156°C ., and 260°C . for the raw and PCl_5 treated polymers, respectively.

The infrared spectrum was superimposable on the bromodifluoroacetaldehyde chloral spectra from Experiment 21. Figure 6.

Elemental analysis was used to determine the relative amount of the two comonomers which were incorporated into the copolymer.

ANAL. Insoluble: Found: F, 19.93%.

Soluble: Found: F, 19.69%.

Both of these correspond to 82% BDFA in the copolymer.

Experiment 24: Copolymerization of BDFA and Ph NCO with Ph_3P at -25°C . Into a dried polymerization tube were sealed BDFA (1.59 g., 10.0 mmol) and phenyl isocyanate (1.10 g., 9.2 mmol) (52 mole% BDFA in feed). The solution was initiated by rupturing a break ampule containing a Ph_3P solution in MCH (0.06 mmol, 0.3 mole%). The solution was cooled to -25°C and allowed to polymerize in a refrigerator at this temperature. A translucent gel formed in about five minutes. After 24 hours the solid polymer was removed, found to be soluble in acetone, reprecipitated from water and dried. The composition was determined by nitrogen analysis.

ANAL. Found: N, 4.1% This corresponds to 30% phenyl isocyanate in the copolymer.

F. Synthesis of DBFA

Experiment 25: Reduction of methyl dibromofluoroacetate to the hydrate, $\text{CBr}_2\text{FCH}(\text{OH})_2$. Methyl dibromofluoroacetate, isolated in Experiment 2, was reduced in a manner similar to that used in the reduction of BDFA as described in Experiment 4.

Methyl dibromofluoroacetate (10.0 g., 40 mmol) in anhydrous ethyl ether (15 ml.) were charged into a 100 ml. 3-neck flask which had been equipped with a magnetic stirring bar, a 25 ml. pressure equalizing addition funnel and a reflux condenser topped with a CaCl_2 filled drying tube. Using a Dry Ice/acetone bath the solution was cooled to -78°C . In a separate operation, powdered LAH (0.40 g., 11 mmol)

was slurried in 25 ml. anhydrous ether in a 25 ml. flask equipped with a stirring bar and reflux condenser and maintained under a slight positive pressure of nitrogen. The stirring was stopped after two hours and the mixture allowed to settle. The supernatant was decanted into the 25 ml. addition funnel and added to the cold ester solution dropwise with stirring over a 30 minute period. The LAH sludge was reslurried in fresh anhydrous ether (25 ml.) and this suspension was also added dropwise to the acetate solution. The total addition time was one hour.

The acetate solution was stirred for an additional 30 minutes. The Dry Ice/acetone bath was removed and the mixture was allowed to slowly warm to ambient temperature. It was then carefully poured into a stirred mixture of crushed ice (200 g.) and conc. H_2SO_4 (2 ml.) to dissolve the aluminum residue. The aqueous layer was removed using a separatory funnel and extracted twice with ether. The ether portions were combined and the ether removed under a reduced pressure (25 mm. Hg.) at ambient temperature. The nonvolatile crude DBFA hydrate was obtained in good yield (9.3 g., 97% yield, crude).

Experiment 26: Preparation of DBFA. The crude DBFA hydrate (6 ml.) was mixed with conc. H_2SO_4 (6 ml.) in a 25 ml. distillation flask equipped with a magnetic stirring bar and a 15 cm. Vigreux distillation head. The system was blanketed with a slight positive pressure of nitrogen. Heating was accomplished with a 25 ml. heating mantle.

On heating an orange non-condensable gas was evolved and the stirred solution became deep orange. No DBFA was distilled. Heating was termi-

nated when the solution became dark brown.

A second reaction mixture was prepared identical to the first. This time, however, the pressure was reduced prior to heating by means of a vacuum pump and Cartesian diver type manostat. A clear liquid was distilled in good yield. bp. 66°C . at 105 mm. Hg (6.6 g., 75% yield from the ester).

The purity of the DBFA was checked using GC. A 1 microliter sample was injected onto a 33% diisodecyl phthalate on Chromosorb W column at 115°C . The only peak eluted other than the DBFA monomer (16.5 minutes) was present in less than 25 ppm. level and was assigned to BDFA based on retention time (6.9 minutes).

The DBFA was characterized by its infrared, PMR and FMR spectra and elemental analysis.

The infrared spectra were obtained as a film of the neat liquid on NaCl plates (Figure 7), in the gaseous state and in 2% solutions in CHCl_3 and hexane. In the neat liquid sample bands were recorded at $3497\text{ cm}^{-1}_{\text{s}}$ (overtone), $2861\text{ cm}^{-1}_{\text{s}}$ (C-H stretching), $1751\text{ cm}^{-1}_{\text{vs}}$ (C=O stretching), $1395\text{ cm}^{-1}_{\text{m}}$, $1358\text{ cm}^{-1}_{\text{s}}$ (C-H bending in plane), $1319\text{ cm}^{-1}_{\text{w}}$, $1268\text{ cm}^{-1}_{\text{m}}$, $1165\text{ cm}^{-1}_{\text{s}}$, $1092\text{ cm}^{-1}_{\text{s}}$, $1031\text{ cm}^{-1}_{\text{m}}$, $983\text{ cm}^{-1}_{\text{vs}}$, $930\text{ cm}^{-1}_{\text{vs}}$, $813\text{ cm}^{-1}_{\text{m}}$, $766\text{ cm}^{-1}_{\text{s}}$, $700\text{ cm}^{-1}_{\text{s}}$, and $651\text{ cm}^{-1}_{\text{m}}$.

The NMR spectra were measured on a 2% solution of the acetaldehyde in CDCl_3 . The ^1H NMR showed a doublet centered at 8.86 ppm. ($J_{\text{H-F}} = 7.0\text{ Hz}$). The ^{19}F spectrum was also a doublet, 0.60 ppm. downfield from trifluoroacetic acid (external). $J_{\text{H-F}} = 7.0\text{ Hz}$.

ANAL. Calcd, for C_2HBr_2FO : C, 10.93; H, 0.46. Found: C, 10.98; H, 0.48.

Experiment 27: Preparation and NMR of DBFA hydrate $[CBr_2FCH(OH)_2]$.

Water was added in 4 microliter increments to a solution of DBFA (5% in $CDCl_3$) in a 5 mm. NMR tube and the changes in chemical shifts observed by 1H NMR. The initially present aldehydic doublet at 8.86 ppm. was replaced stepwise by two new peaks which appeared as a doublet at 5.10 ppm. and a singlet at approximately 4 ppm. with an integrated intensity of 1:2. The position of the latter peak, which can be assigned to the hydroxyl protons, is dependent on concentration due to hydrogen bonding. The former peak, the acetalic proton, is not affected by concentration.

When this experiment was repeated using D_2O instead of water the doublet due to the methine was still observed to have a chemical shift of 5.10 ppm., but no peak appeared at 4 ppm. due to the isotopic replacement in the hydroxyls. This provides further evidence for the validity of the peak assignments.

G. Polymerization of DBFA

Experiment 28: Polymerization of DBFA with pyridine at $25^{\circ}C$. Into the previously described polymerization apparatus was sealed DBFA (0.84 g., 3.8 mmols) and a break tube containing pyridine in toluene (0.13 mmols, 3.3 mole%). The tube was heated to $60^{\circ}C$., the inner tube shattered and the contents mixed rapidly. The tube was immersed in an ambient temperature water bath and after less than one minute

the contents of the tube solidified to an opaque white mass.

The tube was broken after 24 hours to give 0.05 g. of a white brittle material which was insoluble in acetone (6% conversion). No acetone soluble polymer was precipitated on mixing the filtrate with cold water.

Thermal stability of the poly DBFA was measured by DTG before and after PCl_5 stabilization. In each case a binodal trace was obtained. The raw polymer had peaks at 153°C . and 222°C . After stabilization the thermal stability was increased to 230°C . and 341°C .

The infrared spectrum of the raw polymer in a KBr pellet was recorded. (Figure 8) It is characterized by peaks at $3380 \text{ cm}^{-1}_{\text{b}}$ (OH), $2945 \text{ cm}^{-1}_{\text{m}}$ (C-H stretching), $1387 \text{ cm}^{-1}_{\text{m}}$ (C-H bending), $1358 \text{ cm}^{-1}_{\text{m}}$ (C-H bending), $133 \text{ cm}^{-1}_{\text{m}}$ (C-H bending), $1155 \text{ cm}^{-1}_{\text{m}}$ (C-O stretch), $1110 \text{ cm}^{-1}_{\text{m}}$, $1059 \text{ cm}^{-1}_{\text{s}}$ (C-O stretch), $1029 \text{ cm}^{-1}_{\text{w}}$, $1004 \text{ cm}^{-1}_{\text{w}}$, $960 \text{ cm}^{-1}_{\text{s}}$, $830 \text{ cm}^{-1}_{\text{vs}}$, and $800 \text{ cm}^{-1}_{\text{w}}$.

Experiment 29: Polymerization of DBFA with sulfuric acid at -25°C .

DBFA (1.64 g., 7.4 mmoles) and concentrated sulfuric acid (0.05 mmoles, 0.73 mole%) were sealed into a polymerization ampule and break tube, respectively. The ampule was sealed as usual at liquid nitrogen temperature and 0.05 mm. Hg. When the inner tube was broken at 60°C . a clear solution resulted. The tube was plunged into an acetone bath which was maintained at -25°C . in a freezer.

No change in appearance had occurred after 12 hours at -25°C . Only after several days the contents were observed to have gelled.

The tube was broken after one week and a grainy gel was removed and found to be wholly insoluble in acetone. The recovered conversion of insoluble polymer was 0.58 g., 35% conversion.

DTG maxima were recorded at 262°C . and 365°C . before and after PCl_5 treatments respectively.

Experiment 30: Polymerization of DBFA with sulfuric acid at 25°C .

Into the standard polymerization ampules were sealed DBFA (0.95 g., 4.3 mmoles) and concentrated sulfuric acid (0.02 mmoles, 0.51 mole%). The monomer was initiated and maintained at room temperature. The contents of the tube were observed to have gelled after only one hour. After 24 hours the tube was opened to give 0.76 g. (80% conversion) of acetone insoluble polymer. No soluble polymer was recovered on mixing the filtrate into cold water.

Thermal characterization by DTG showed the raw and PCl_5 stabilized polymers had maximum rates of thermal decomposition at 259°C . and 363°C ., respectively.

ANAL. Calcd. for $\text{C}_2\text{HBr}_2\text{FO}$: C, 10.93; H, 0.46. Found: C, 11.29; H, 0.55.

Experiment 31: Isothermal pyrolysis of poly DBFA. A sample of the raw polymer obtained in Experiment 30 (0.108 g.) was placed in the sample portion of an h-shaped pyrolysis tube as described in Experiment 9. The tube was cooled in liquid nitrogen and sealed under a vacuum of 0.05 mm. Hg. The sample end was heated slowly in a sand bath to 250°C . It was maintained at this temperature for four hours while collecting any volatile decomposition products in the side arm, which was cooled

in liquid nitrogen for the entire experiment.

After four hours no solid polymer sample remained nor was there any other residue in the sample chamber. The collection tube was sealed off and removed. On thawing a clear liquid was observed. The tube was broken and the liquid was identified by IR and GC as being exclusively monomer in 96% conversion (1.04 g.).

Experiment 32: Polymerization of DBFA with Et_3Al at 25°C . DBFA (0.87 g., 4.0 mmol) and Et_3Al (3M. in hexane) (0.30 mole%) were charged into a polymerization ampule and sealed tube, respectively. The ampule was warmed to 60°C . and shaken to break the inner tube and initiate the polymerization. It was immediately placed in a beaker of water at 25°C . where gelation took place in less than one minute.

After one week the appearance, that of a soft gel, was unchanged. The tube was cut open and the gel stirred with 50 ml. acetone overnight. The white crystalline polymer (0.06 g., 7% conversion) was filtered off and the filtrate mixed with cold water. No precipitation occurred.

The polymer was characterized by its thermal decomposition. DTG maxima were recorded at 279°C . and 360°C . for the product before and after PCl_5 stabilization.

Experiment 33: Polymerization of DBFA with Et_3Al at -78°C . A polymerization assembly was charged with DBFA (1.16 g., 5.3 mmol) and Et_3Al (3M. in hexane) (0.38 mole%) and initiated as usual at 60°C .

The solution was then plunged into a Dry Ice/acetone bath and allowed to stand undisturbed.

After eight hours a clear gel had formed. The tube was opened after one week to yield a soft translucent gel found to be insoluble in acetone (0.11 g., 10% conversion). No soluble polymer was isolated.

The DTG spectra showed the decomposition maxima to occur at 292°C . for the raw polymer and 363°C . for the PCl_5 stabilized material.

Experiment 34: Polymerization of DBFA with TFMSA at 25°C . DBFA (0.97 g., 4.4 mmol) was initiated by breaking a tube of trifluoromethane sulfonic acid (TFMSA) (0.019 g., 0.13 mmol, 2.9 mole%) at 60°C . At first the two liquids were not miscible, but after approximately one minute of shaking a homogeneous solution was obtained. Gelation occurred in five minutes at 25°C .

After one day the tube was cut open to yield a hard translucent gel. Stirring overnight in acetone (50 ml.) failed to dissolve any of the polymer. The yield of insoluble product was 0.26 g. (27% conversion).

Experiment 35: Polymerization of DBFA with LTB at -78°C . A solution of LTB (0.3M. in MCH) (0.61 mole%) was used to initiate DBFA (1.07 g., 4.9 mmol) at 60°C . The tube was quickly cooled by placing it into a Dry Ice/acetone bath. A gel was formed within 30 seconds at -78°C .

The tube still contained some liquid monomer over the precipitated polymer after 10 days when it was cut open. The polymer was slurried in acetone (50 ml.) overnight. Insoluble polymer only (0.17 g., 16%

conversion) was isolated.

The thermal stability was measured by DTG where decomposition maxima were observed at 223°C . and 340°C . for the polymer before and after treatment with PCl_5 , respectively.

Experiment 36: Polymerization of DBFA with LTB at 25°C . Into a standard polymerization apparatus were charged DBFA (1.10 g., 5.0 mmoles) and LTB (0.3M. in MCH) (0.24 mole%). Initiation was carried out by shaking the assembly at 60°C . to break the inner tube and release the LTB. The solution was cooled to room temperature in an ambient water bath. The initiated monomer solution gradually became cloudy but only a small amount of precipitation took place even after two weeks. The viscosity of the monomer solution did not change to any noticeable extent.

The tube was cut open and the cloudy solution poured into acetone (10 ml.). The acetone solution became and remained cloudy, showing that the precipitate which formed during the polymerization was insoluble in acetone, but, due to the very small amount, could not be isolated by filtration. Pouring the filtrate into cold water did not show any soluble polymer to be present.

Experiment 37: Attempted polymerization of DBFA with Ph_3P at -25°C . DBFA (1.28 g., 5.8 mmoles) was initiated with Ph_3P (0.3M. in MCH) (0.26 mole%) using the standard procedure. The mixed solution was cooled to -25°C . in a freezer in an acetone bath. No change in appearance or viscosity of the solution had occurred after two weeks. The tube was broken and the contents poured into cold water. No

precipitate was formed.

Experiment 38: Attempted polymerization of DBFA with Ph_3P at -78°C .

Into a standard polymerization apparatus was charged DBFA (0.83 g., 3.8 mmol) and a sealed break tube containing Ph_3P (0.3M. in MCH) (0.32 mole%). The tube was warmed to 60°C . and the initiator solution released by breaking the inner break ampule. The solution was quickly shaken and placed in a Dry Ice/acetone bath.

As in Experiment 37, no visual changes occurred after two weeks at -78°C . The tube was carefully cut open in a dry box and more Ph_3P to make to total concentration 2.3 mole% with respect to the acetaldehyde. The tube was resealed with an 8 mm. I.D. unpigmented rubber septum and allowed to stand at room temperature for 24 hours. This also failed to produce any polymer, either soluble or insoluble fractions.

Experiment 39: Copolymerization of DBFA and chloral with sulfuric acid at 25°C .

Freshly distilled monomers, DBFA (0.82 g., 3.8 mmol) and chloral (0.55 g., 3.7 mmol), were injected into a polymerization tube and mixed to give a homogeneous solution. The polymerization was initiated by vigorous shaking to break the inner ampule of H_2SO_4 (0.075 mmol, 2.0%). The initiated solution was initially clear, but within 5 minutes of standing undisturbed at 25°C . it became a translucent gel. After 15 minutes the gel was opaque white. The tube was opened following a reaction time of 24 hours to give a white crystalline solid. Extraction with acetone showed it to be wholly insoluble. Yield:

0.22 g., 16%.

The material was characterized by DTG; maxima at 246°C . and 380°C ., before and after PCl_5 treatment, respectively.

ANAL. Found: 4.31% F. which corresponds to 40 mole% DBFA.

Experiment 40: Copolymerization of DBFA and chloral with pyridine at 25°C . DBFA (1.31 g., 6.0 mmoles) and chloral (0.91 g., 6.2 mmoles) were mixed in a polymerization tube and initiated with pyridine (0.36 mmoles, 3 mole%) by breaking an inner ampule inside the sealed tube. Initiation at 85°C . was followed by cooling the clear solution to 25°C . where the contents of the ampule became opaque white within one minute. After 24 hours the tube was cut open to give a white crystalline copolymer. No acetone soluble fraction was found. Yield: 0.22 g., 10%.

Thermal decomposition was studied and the copolymer was found to decompose at the highest rates at 210°C . and 320°C . for the raw and PCl_5 treated copolymers, respectively.

ANAL. Found: F, 5.56%. This corresponds to 56% of DBFA in the copolymer.

Experiment 41: Copolymerization of DBFA and PhNCO with pyridine at 25°C . Into a dried ampule containing a sealed initiator tube of pyridine (0.046 mmoles, 3.0 mole%) was charged DBFA (1.68 g., 7.7 mmoles) and PhNCO (0.90 g., 7.5 mmoles). The solution was warmed to 85°C . and shaken until the inner ampule was broken, releasing and mixing the initiator. The sample was then placed in a bath at

25⁰ C. where it solidified to a clear gel within 10 minutes. The tube was cut open after 24 hours. The copolymer was found to be completely insoluble in acetone. Yield 0.33 g., 13%.

The DTG spectra showed maxima at 230⁰ C. and 350⁰ C. for the raw and PCl_5 treated copolymer, respectively.

ANAL. Found: N, 0.11%. This corresponds to 1.4 mole% PhNCO incorporated into the copolymer.

H. Synthesis of DCFA

Experiment 42: Preparation of methyl trichloroacetate. Trichloroacetic acid (432 g., 2.64 moles), methanol (254 g., 7.92 moles), sulfuric acid (13 ml.), and benzene (600 ml.) were charged into a 2 l. one neck flask on which was mounted a 10 inch Vigreux column topped with a condenser. The mixture was stirred using a magnetic stirrer and refluxed overnight. After 16 hours reflux, a Dean-Stark trap was inserted between the column and condenser and water was removed by azeotropic distillation with the benzene. The refluxing mixture turned from cloudy to clear after most of the water had been removed (total 47 ml. -99% of theoretical). The mixture was cooled, washed 3 times with distilled water and dried overnight over CaCl_2 . After removal of the CaCl_2 by filtration, the liquid was distilled through a 10 inch Vigreux column to give methyl trichloroacetate, bp. 153⁰ C., lit. 154⁰ C. (238) Yield: 348 g., 74%. Gas chromatography showed traces (less than 100 ppm.) of benzene and methanol but no other impurities. (5 foot Carbowax 20M on Chromosorb W column at 100⁰ C., injector 160⁰ C., detector

220⁰ C.)

Experiment 43: Preparation of methyl dichlorofluoroacetate. Methyl trichloroacetate (347 g., 2.0 moles), 50% excess antimony trifluoride (174 g., 1.0 moles) and bromine (8.0 g., 0.10 moles) were placed into a 500 ml. one neck flask and refluxed for 24 hours while stirring vigorously with a mechanical stirrer. (239) The insoluble sludge was removed by filtration and the filtrate distilled through a 12 inch Vigreux column to give crude methyl dichlorofluoroacetate. This distillate, which contained sublimed antimony halides, was washed with water and dried over anhydrous sodium sulfate. Redistillation using the same column gave 99% pure methyl dichlorofluoroacetate, bp. 114-116⁰ C. lit. 114-116⁰ C. (239) Yield: 202 g., 64%. The impurity was shown by GC to be the starting ester. (Carbowax 20M on Chromosorb W at 95⁰ C.)

Experiment 44: Reduction of methyl dichlorofluoroacetate. The reduction of methyl dichlorofluoroacetate was carried out by a method similar to that reported by Pierce and Kane for the preparation of fluoral hydrate. (236)

Into a 1 l. three neck flask equipped with a stirrer, a 500 ml. addition funnel and a reflux condenser protected with a drying tube was placed methyl dichlorofluoroacetate (70 g., 0.44 moles) in anhydrous ethyl ether (100 ml.). The flask was immersed in a Dry Ice/acetone bath and cooled to -78⁰ C. In a separate operation, LAH (4.54 g., 0.12 moles) was suspended in anhydrous ethyl ether (100 ml.) and stirred

under dry nitrogen at 30°C . The stirring was stopped after three hours and the mixture allowed to settle. The supernatant was decanted into the addition funnel which was connected to the reaction flask containing the ester solution and added dropwise with stirring. The hydride sludge was reslurried with fresh anhydrous ethyl ether and this suspension was also added dropwise to the reaction solution. Total addition time was less than two hours. The mixture was stirred an additional one hour at -78°C .

95% ethanol (20 ml.) was added to the reaction flask and the mixture was allowed to warm slowly to room temperature. The reaction mixture was poured into a 2 l. beaker containing crushed ice (300 g.) and conc. sulfuric acid (50 ml.) to dissolve the aluminum compounds. Two layers were obtained which were separated using a separatory funnel and the aqueous layer extracted twice with ether. The ether fractions were combined and distilled without drying through a 1 ft. Vigreux column. The fraction boiling between 57°C . and 60°C . at 50 mm. Hg was collected in 75% yield. It was found to contain a mixture of hemiacetal and the hydrate of dichlorofluoroacetaldehyde.

Experiment 45: Preparation of DCFA. DCFA was prepared by dehydration of the above mixture with sulfuric acid. Equal volumes (10 ml.) of the hydrate mixture and conc. sulfuric acid were mixed in a 50 ml. round bottom flask and heated under nitrogen. Vigorous stirring was required to effect mixing and the formation of a high yield of DCFA. The aldehyde was distilled through a 8 inch Vigreux column and collected in 65% yield: bp. 56°C . Prior to polymerization DCFA was further

purified by trap to trap distillation from phosphorus pentoxide under a reduced pressure of 0.2 mm. Hg. Gas chromatography showed the aldehyde to contain less than 20 ppm. of water. This determination was made using a diisodecyl phthalate column (35% on Chromosorb W) 6 foot in length. The column conditions were: column temperature 90°C ., injector temperature 170°C ., detector temperature 280°C ., flow 45 cc/min.

The infrared spectra were recorded neat and in solutions with hexane, CCl_4 and CHCl_3 . Figures 9-12. The spectra of a film of the neat liquid DCFA was characterized by peaks at $3500\text{ cm}^{-1}_{\text{m}}$ (overtone), $2878\text{ cm}^{-1}_{\text{s}}$ (aldehydic proton) $1770\text{ cm}^{-1}_{\text{s}}$ (carbonyl stretching), $1363\text{ cm}^{-1}_{\text{s}}$ (in plane C-H bending), $1182\text{ cm}^{-1}_{\text{s}}$, $1104\text{ cm}^{-1}_{\text{s}}$, $1058\text{ cm}^{-1}_{\text{s}}$, $1000\text{ cm}^{-1}_{\text{s}}$, $967\text{ cm}^{-1}_{\text{s}}$, $877\text{ cm}^{-1}_{\text{m}}$, $783\text{ cm}^{-1}_{\text{s}}$, $623\text{ cm}^{-1}_{\text{s}}$.

The ^1H and ^{19}F NMR spectra were recorded for a 10% solution of DCFA in carbon tetrachloride. The aldehydic proton was split by the fluorine of the adjacent dichlorofluoromethyl group into a doublet at 9.15 ppm., relative to TMS. The coupling constant $J_{\text{H-F}}=5.0\text{ Hz}$. The ^{19}F NMR spectrum was also a doublet 0.32 ppm. downfield from an external trifluoroacetic acid lock signal; $J_{\text{H-F}}=5.0\text{ Hz}$.

ANAL. Calcd. for $\text{C}_2\text{HCl}_2\text{FO}$: C, 18.35; H, 0.77; F, 14.51 Found: C, 18.61; H, 0.77; F, 14.45.

Experiment 46: Preparation of DCFA 2,4-dinitrophenylhydrazone

$[\text{CCl}_2\text{FCH=NNHC}_6\text{H}_3(\text{NO}_2)_2]$. The hydrazone of DCFA was prepared according to the method of Ross and Ring which is specifically used for the preparation of 2,4-dinitrophenylhydrazones of haloacetaldehydes. (237)

A solution of 2,4-dinitrophenylhydrazine (1 g. in 20 ml. conc. HCl) at 45° C. was added to a stirred solution of DCFA hydrate (1.3 g. in 2 ml. conc. HCl). After stirring for 2 hours at room temperature, the mixture was chilled and the yellow crystalline precipitate was collected by filtration, washed with water, recrystallized from ethanol, and dried, mp. 127° C. lit. mp. 135° C. (201)

ANAL. Calcd. for $C_8H_5Cl_2FN_4O_4$: C, 30.67; H, 1.61; N, 17.88.
Found: C, 30.45; H, 1.93; N, 17.79.

Experiment 47: NMR of DCFA hydrate. Water was added in one microliter increments to a 10% solution of DCFA in chloroform in a 5 mm. NMR tube and the 1H NMR spectra recorded. The resulting product was the stable hydrate as shown by the appearance of two peaks; a doublet at 5.27 ppm. ($J_{H-F}=3.0$ Hz.) and a singlet in the range 4.5-5.2 ppm., depending on concentration, corresponding to the hydroxyl protons. The integrated intensity of the two absorptions was 1:2, respectively. Each injection of water caused the aldehydic proton signal to decrease and the two hydrate resonances to increase in amplitude. Substitution of deuterium oxide (D_2O) for the water resulted in the same observations except the hydroxyl resonances were not observed due to the replacement of their protons by deuterium. The ^{19}F spectra in each case consisted of a doublet 1.58 ppm. upfield from an external lock of trifluoroacetic acid. $J_{H-F}=3.0$ Hz.

I. Polymerization of DCFA

Experiment 48: Polymerization of DCFA with Ph_3P at 30° C. The initiator

solution of Ph_3P (0.013 g., 0.050 mmoles, in 0.2 ml. toluene) was sealed in a small vial (5 mm. x 20 mm.) which was then placed into a clean flamed-out polymerization ampule (18 mm. x 200 mm.). DCFA (1.50 g., 11.5 mmoles) was distilled at 0.1 mm. Hg into the ampule which was cooled in liquid nitrogen and the ampule was sealed. The ampule was then heated to 75°C . and shaken vigorously in order to break the initiator ampule. Because the initiator ampule had been sealed under a nitrogen atmosphere at room temperature, it broke readily and dispersed the initiator solution immediately in the monomer and gave a homogenous solution. The reaction was kept at 30°C . for 24 hours after which time the contents of the ampule had solidified. The tube was opened and the contents poured into acetone (25 ml.) and stirred for 16 hours. The suspension was filtered and the insoluble polymer was collected on a sintered glass funnel and dried under reduced pressure.

The filtrate was poured into ice water (200 ml.) to precipitate any acetone soluble polymer. The recoveries were 55% and 16% for the insoluble and soluble polymers, respectively.

ANAL. (for the insoluble fraction) Calcd. for $\text{C}_2\text{HCl}_2\text{FO}$: C, 18.35; H, 0.77; F, 14.51 Found: C, 18.48; H, 0.89; F, 14.39.

The IR spectrum of the raw insoluble polymer (KBr) showed absorptions at: 3380 cm^{-1} (hydroxyl end groups); 2948 cm^{-1} (C-H stretching); $1360\text{ cm}^{-1}_{\text{w}}$ and $1338\text{ cm}^{-1}_{\text{s}}$ (C-H bending); plus carbon-halogen vibrations at $1158\text{ cm}^{-1}_{\text{w}}$, $1120\text{ cm}^{-1}_{\text{m}}$, $1060\text{ cm}^{-1}_{\text{m}}$, $975\text{ cm}^{-1}_{\text{s}}$, $870\text{ cm}^{-1}_{\text{s}}$ and $703\text{ cm}^{-1}_{\text{s}}$. The spectra of the soluble and insoluble fractions are indistinguishable. (Figures 13 and 14)

Experiment 49: Stabilization of polyDCFA. Acetylation of the poly-DCFA was carried out with acetic anhydride in order to increase the thermal stability of the polymer. In a dried test tube, powdered polymer (100 mg.) and freshly distilled acetic anhydride (2 ml.) were allowed to react at room temperature for 48 hours to achieve acetylation. Acetone insoluble polymer was also insoluble in acetic anhydride and was isolated by filtration through a sintered glass funnel. The polymer was further purified by extraction with acetone in a Soxhlet apparatus for 48 hours and was then dried under reduced pressure. The acetone soluble polymer was isolated from the acetylation mixture by pouring it into ice (100 g.) and the polymer was filtered and purified by an additional precipitation from an acetone solution with water.

An alternative means of stabilization was also used as described in Experiment 10 by refluxing polyDCFA (100 mg.) in a 10% solution of PCl_5 in carbon tetrachloride under a positive nitrogen pressure for 5 hours. The insoluble polyDCFA was also insoluble in this reaction mixture and was removed by filtration and dried. The acetone soluble fraction dissolved in the PCl_5 solution was recovered by precipitation in methanol, washed with methanol and water and dried. Both methods of stabilization were equally effective as the DTG maximum was increased from 162°C. for the raw polyDCFA to 190°C. for the polymer stabilized by acetylation and 195°C. for the PCl_5 treated polyDCFA. The IR spectrum of the acetylated polymer was identical to that of the raw polyDCFA except for the addition of a weak absorption band at 1740 cm.^{-1} arising from the acetyl group.

Experiment 50: Isothermal decomposition of polyDCFA. Unstabilized poly-DCFA (0.20 g.) was placed in an "h" shaped tube and sealed at 0.05 mm. Hg as described in Experiment 9. The large end of the tube containing the sample was heated to 250⁰ C. in a sand bath. Volatiles were collected in the side arm of the tube which was cooled in a liquid nitrogen bath. Heating was continued until all of the solid polymer had decomposed, approximately 3 hours. The volatiles were analyzed by GC and ¹H NMR and found to be pure monomer, DCFA, in 96% recovery.

Experiment 51: Polymerization of DCFA with Ph₃P at -5⁰ C. DCFA (1.1 g., 8.4 mmoles) was initiated with Ph₃P (0.4 mole%) and polymerized at -5⁰ C. After 24 hours a white solid was recovered which was found to be partially soluble in acetone. The conversions were 70% acetone insoluble and 10% acetone soluble polyDCFA. Identification of product was made through the IR spectra which were found identical to that of poly-DCFA made in Experiment 48.

DTG spectra were recorded for the polyDCFA for both fractions before and after PCl₅ treatment. These were: insoluble, 121⁰ C. and 230⁰ C.; soluble 108⁰ C. and 240⁰ C.

Experiment 52: Polymerization of DCFA with Ph₃P at -78⁰ C. As described earlier DCFA (1.15 g., 8.8 mmoles) was initiated with Ph₃P (0.4 mole%) and the solution plunged into a Dry Ice/acetone mixture for 24 hours to polymerize. This time, in contrast to polymerizations at higher temperatures, no acetone soluble product was recovered. The conversion of acetone insoluble polymer was 75%. The infrared spectra matched that of polyDCFA.

The thermal stability was used for characterization of the polymer. The DTG maxima were 150°C . and 235°C . before and after treatment with the PCl_5 solution.

Experiment 53: Polymerization of DCFA with LTB at 25°C . A polymerization tube was charged with DCFA (0.88 g., 6.7 mmole) and an internal break tube of LTB (1 M. in MCH, 0.36 mole%). The tube was sealed at 0.1 mm. Hg in liquid nitrogen. The assembly was warmed to 75°C . and the initiator ampule was then broken. The solutions were mixed to give a homogenous clear liquid which on cooling to 25°C . quickly formed a white opaque solid. After 24 hours, the white solid was broken up in acetone (25 ml.) and stirred 16 hours. The insoluble material was separated. No acetone insoluble polymer was found on pouring the filtrate into cold water. The recovery was 85%.

Characterization by DTG showed maximum rates of degradation at 225°C . and 385°C . before and after stabilization with PCl_5 , respectively. The IR spectrum was identical to that described in Experiment 48 for polyDCFA.

Experiment 54: Attempted polymerization of DCFA with LTB at -78°C . DCFA (1.02 g., 7.8 mmoles) and an ampule containing LTB (1M. in MCH, 0.3 mole%) were sealed in a polymerization tube, heated to 75°C ., initiated, and cooled in a Dry Ice/acetone bath. After 24 hours since no precipitate was observed, the tube was maintained at -78°C . and checked daily. After one week, the experiment was terminated when the solution was still clear and no precipitate formed on pouring the solution into water.

The experiment was repeated doubling the LTB concentration to 0.6 mole %. Again the solution remained clear through one week at -78°C .

Experiment 55: Polymerization of DCFA with pyridine at -78°C . The monomer (1.07 g., 8.1 mmole) and pyridine (0.3 mole %) were charged in the standard manner and the initiation carried out at 75°C . The clear mixture was immediately placed in a Dry Ice/acetone bath for 24 hours. At the end of this time the tube was removed and found to contain a white opaque mass. The solid was broken up and stirred overnight in acetone (25 ml.). The polymer was entirely acetone insoluble (14% conversion). DTG maxima were recorded at 240°C . and 370°C . for the raw and PCl_5 stabilized polymer, respectively.

Experiment 56: Polymerization of DCFA with Et_3Al at 25°C . Into a polymerization tube was charged DCFA (1.06 g., 8.1 mmole) and an ampule of Et_3Al (1.25 M. in hexane, 0.7 mole %). The DCFA was initiated at 80°C . and cooled to room temperature. The polymerization began within five minutes to give a solid white plug. After 24 hours the tube was broken and the plug broken up and stirred in acetone overnight. No acetone soluble polymer was recovered. The conversion was 93% insoluble polyDCFA.

DTG maxima for the raw polymer were 177°C . and 317°C . (the latter was the major peak). Acetic anhydride stabilization was not fully effective in that the DTG maxima were only increased to 237°C . and 342°C . PCl_5 stabilization resulted in a single maximum at 385°C . The IR spectrum for the raw polymer was identical to that of polyDCFA

recorded in Experiment 48.

Experiment 57: Polymerization of DCFA with Et_3Al at -78°C . The same procedure and quantities of reagents as were described in Experiment 55 were used except that the initiated monomer was plunged into a Dry Ice/acetone bath for the 24 hour polymerization period. The polymer was again wholly acetone insoluble (62% recovery).

The thermal stability was improved over the product of the room temperature polymerization. The low temperature peak was absent and only a single peak at 305°C . was observed for the raw polyDCFA. On stabilization with PCl_5 the DTG maximum increased to 385°C .

Experiment 58: Polymerization of DCFA with H_2SO_4 at 25°C . DCFA (0.99 g., 7.6 mmoles) was charged into a polymerization tube with an ampule containing H_2SO_4 (0.3 mole %). The tube was heated 75°C ., initiated, and cooled in a water bath at 25°C . The contents of the tube quickly solidified to a white mass, which after 24 hours polymerization time, was found to be acetone insoluble (79% recovery).

The IR spectrum matched that of polyDCFA (Experiment 48). Thermal stability characterization by DTG showed peaks at 257°C . and 380°C . before and after treatment with PCl_5 .

Experiment 59: Attempted polymerization of DCFA with H_2SO_4 at -78°C . A polymerization tube was charged with DCFA (0.92 g., 7.0 mmoles) and an ampule containing H_2SO_4 (0.4 mole %). The tube was heated to 75°C ., shaken to break the inner ampule and mix the contents, and plunged into a Dry Ice/acetone bath. No precipitated polymer was present after 24

hours. After eight days, the solution was still transparent, thus the experiment was terminated.

The experiment was repeated using twice the H_2SO_4 concentration (0.8 mole %). Again the solution remained clear for a period of eight days, at which time the experiment was stopped.

Experiment 60: Copolymerization of DCFA and chloral with Ph_3P at 25°C .

A polymerization tube was charged with DCFA (1.43 g., 10.9 mmoles) and freshly distilled chloral (1.39 g., 9.4 moles) to give a 54-46 molar feed ratio of the two monomers. An ampule of Ph_3P (0.3 M. in benzene, 0.4 mole %) was also sealed into the polymerization tube. The tube was heated to 80°C . and shaken to release the Ph_3P and mix the contents. The polymerization tube was then placed in a water bath at room temperature. After one hour the tube was broken open and the waxy solid removed. It was cut into small pieces and stirred in acetone for 18 hours. The insoluble polymer was removed (72% recovery) and the acetone filtrate poured into water. No precipitate formed.

Elemental analysis found the insoluble polymer to contain 60.73% Cl. This corresponds to 36.5% chloral in the copolymer. Vacuum thermal degradation of the copolymer followed by GC analysis of the volatiles showed that the copolymer contained 40% chloral. Agreement is good between the two methods.

The IR spectrum was recorded (KBr) and showed bands at $3375\text{ cm}^{-1}_{\text{s}}$ (hydroxyl end groups); $2948\text{ cm}^{-1}_{\text{s}}$ (C-H stretching); $1360\text{ cm}^{-1}_{\text{w}}$; $1338\text{ cm}^{-1}_{\text{w}}$; $1323\text{ cm}^{-1}_{\text{s}}$ (C-H bending); $1155\text{ cm}^{-1}_{\text{w}}$; $1123\text{ cm}^{-1}_{\text{m}}$; $1075\text{ cm}^{-1}_{\text{w}}$, $1057\text{ cm}^{-1}_{\text{m}}$; $1018\text{ cm}^{-1}_{\text{w}}$; $965\text{ cm}^{-1}_{\text{s}}$; $880\text{ cm}^{-1}_{\text{s}}$; $820\text{ cm}^{-1}_{\text{s}}$;

740 $\text{cm}^{-1}_{\text{w}}$; and 698 $\text{cm}^{-1}_{\text{s}}$. (Figure 15).

Thermal stability was also used to characterize the copolymer. DTG maxima were recorded at 172 $^{\circ}$ C. and 207 $^{\circ}$ C. for the raw and PCl_5 treated copolymers, respectively.

Experiment 61: Copolymerization of DCFA and chloral with SbCl_5 at 0 $^{\circ}$ C. DCFA (1.41 g., 10.7 moles) and freshly distilled chloral (1.59 g., 10.8 mmoles) (50-50 feed) were transferred to a polymerization tube. SbCl_5 (0.5 M. in tetrachloroethylene, 0.35 mole %) was sealed in a break ampule and this in turn sealed in the monomer tube. The tube was heated to 75 $^{\circ}$ C., SbCl_5 released and mixed and the solution cooled to 0 $^{\circ}$ C. It formed a gel after one minute which became firm within one hour. After two hours it was removed, cut up and soaked in acetone. 87% acetone insoluble. No soluble fraction was isolated.

The copolymer was characterized by DTG and volatiles analysis. The thermal degradation curves showed maxima at 262 $^{\circ}$ C. and 392 $^{\circ}$ C. for the raw copolymer and 392 $^{\circ}$ C. for the PCl_5 treated product. A sample of the copolymer was placed in an evacuated "h" tube and pyrolyzed at 300 $^{\circ}$ C. for two hours, at which time no solid residue remained. The liquid, which had been collected in the cold side arm was analyzed by GC and found to contain 40% chloral.

Experiment 62: Copolymerization of DCFA and PhNCO with Ph_3P at 25 $^{\circ}$ C. DCFA (1.09 g., 8.3 mmoles) and PhNCO (1.10 g., 9.2 mmoles) 53:47 feed ratio were charged into a polymerization tube with a break tube containing Ph_3P (0.3 M. in benzene, 0.3 mole %). The tube was heated to 75 $^{\circ}$ C., initiated, and placed in a water bath at 25 $^{\circ}$ C. The solution

became cloudy in one to two minutes and gelled in less than five minutes. After two hours, the thick grease-like mass was removed from the tube, washed overnight with acetone and dried to a white powder, 16.5% acetone insoluble. Needles were observed to have formed on the sides of the acetone filtrate beaker. These were collected, recrystallized from ethanol and found to have a melting point of 242-244⁰ C. The IR spectrum did not resemble the polymer or any of the starting materials and showed no carbon-halogen absorptions. It was identified as diphenyl urea.

The acetone insoluble copolymer was fairly thermally unstable in that the DTG maxima were 152⁰ C. and 187⁰ C. before and after PCl₅ treatment. Elemental analysis indicated that the copolymer contained 0.67% N, or 6.6 mole % PhNCO.

Experiment 63: Attempted copolymerization of DCFA and trioxane with SbCl₅ at 25⁰ C. DCFA (0.51 g., 3.9 mmoles) and freshly recrystallized trioxane (0.40 g., 4.4 mmoles) (47-53 feed ratio) were initiated by the standard procedure with SbCl₅ (0.3 mole %). The solution quickly became viscous at 25⁰ C. but after 24 hours was still a viscous oil. The tube was opened and the oil found to be totally soluble in acetone, but on addition of water reverted to an oil. IR was inconclusive beyond showing a mixture of starting materials.

J. Synthesis of CDFA

Experiment 64: Synthesis of methyl chlorodifluoroacetate. Methyl trichloroacetate was made from trichloroacetic acid and methanol by repeat-

ing Experiment 42.

SbF_3 (300 g., 1.68 moles) and SbCl_5 (46.5 g., 0.156 moles) were thoroughly mixed in a 1 l. reaction flask. Freshly distilled dry methyl trichloroacetate (270 g., 1.52 moles) was added. (240) The flask was equipped with a mechanical stirrer, condenser and thermometer. The receiving flask was cooled in ice water. After the system had been purged with nitrogen, it was maintained under a slight positive nitrogen pressure and heated rapidly by means of a Variac and heating mantle. The color of the stirred mixture soon changed to a deep muddy purple. When the mixture began to boil the Variac setting was reduced to control the distillation rate. The crude product obtained (151.7 g.) was washed successively with dilute HCl , water and dilute Na_2CO_3 . It was dried overnight over MgSO_4 . Distillation gave two pure fractions: bp. $80-82^\circ \text{C}$. (the desired product, methyl chlorodifluoroacetate in 17% yield) and bp. $115-116^\circ \text{C}$. (the side product, methyl dichlorofluoroacetate in 23% yield). The literature boiling points for these two esters are: $79-81^\circ \text{C}$. (240) and 116°C . (239) respectively.

Experiment 65: Reduction of methyl chlorodifluoroacetate. The method reported by Pierce and Kane (236) for the formation of fluoral hydrate was used to make the CDFA hydrate.

A 500 ml. flask equipped with a stirrer, a 125 ml. addition funnel and a reflux condenser fitted with a drying tube was charged with methyl chlorodifluoroacetate (50 g., 0.35 moles) and anhydrous ethyl ether (100 ml.). The flask was cooled in a Dry Ice/acetone bath to -78°C . In a separate operation, LAH (3.94 g., 0.10 moles) was slurried in

anhydrous ethyl ether (100 ml.) and stirred under a slight positive nitrogen pressure. After three hours, the slurry was allowed to settle and the ether layer decanted into the addition funnel on the reaction flask. The hydride solution was added dropwise to the stirred ester solution over a one hour period. The hydride residue was reslurried in fresh anhydrous ether and this suspension was also added dropwise to the reaction flask. The stirring was continued at -78°C . one hour after the final addition.

Ethanol (95%, 20 ml.) was added through the addition funnel and the Dry Ice/acetone bath removed to allow the stirring mixture to warm to room temperature. The entire mixture was then poured into a 1 l. beaker containing crushed ice (300 g.) and conc. H_2SO_4 (20 ml.) The aqueous layer was removed and extracted three times with ether. The combined ether fractions were placed in a 100 ml. flask and the ether vacuum stripped through a 1 ft. Vigreux column at room temperature. The residue was distilled and the fraction boiling at $52-55^{\circ}\text{C}$. at 70 mm. Hg was collected. (lit. bp. $104-106^{\circ}\text{C}$. at 760 mm. Hg.) (200) GC showed the distillate to be a mixture of several compounds including the hemiacetalized and hydrated forms of CDFA.

Experiment 66: Dehydration of hydrate to CDFA. Chlorodifluoroacetaldehyde was prepared by dehydrating the crude distillation mixture with sulfuric acid. Equal volumes of the distillation mixture (10 ml.) and concentrated sulfuric acid (10 ml.) were mixed in a 100-ml. round-bottomed flask and heated in a nitrogen atmosphere under vigorous stirring. The distillate did not mix immediately with sulfuric acid and

formed a separate layer. Consequently, vigorous stirring was necessary to maintain effective mixing which resulted in obtaining CDFA in high yields. CDFA was collected after being distilled through a 10 inch Vigreux column into a flask which was cooled in a Dry Ice/acetone trap; bp. 18°C .; lit. bp. $17\text{--}18^{\circ}\text{C}$. (200); yield 8.5 g., 69%. The distillation was easily carried out in a cold room at 0°C . The aldehyde was further purified by ampule-to-ampule distillation from phosphorus pentoxide under reduced pressure (0.2 mm. Hg) three times (cooling with liquid nitrogen). The aldehyde was then sufficiently pure for polymerization. On the basis of GC analysis, purified CDFA contained less than 20 ppm. of water.

ANAL. Calcd. for C_2HOCIF_2 : C, 20.98%; H, 0.88%. Found: C, 21.59%, H, 1.50%. (Too volatile for halogen analysis).

The IR spectrum of the CDFA (Figure 16) had absorptions (neat, gaseous) at $2860\text{ cm}^{-1}_{\text{s}}$ (C-H stretch); $1760\text{ cm}^{-1}_{\text{vs}}$ (C=O stretch); $1366\text{ cm}^{-1}_{\text{m}}$ (in plane C-H bending); $1310\text{ cm}^{-1}_{\text{w}}$; $1245\text{ cm}^{-1}_{\text{s}}$; $1183\text{ cm}^{-1}_{\text{w}}$; $1143\text{ cm}^{-1}_{\text{vs}}$; $1020\text{ cm}^{-1}_{\text{s}}$; $911\text{ cm}^{-1}_{\text{s}}$; $776\text{ cm}^{-1}_{\text{s}}$.

The infrared spectrum of CDFA showed bands of the aldehyde hydrogen at 2857 cm^{-1} and the carbonyl group at 1770 cm^{-1} in carbon tetrachloride or hexane. The corresponding absorptions for chloral were at 2850 and 1767 cm^{-1} .

The chemical shift of the aldehyde proton of the ^1H NMR spectrum of CDFA (10% in carbon tetrachloride) was 9.25 ppm. relative to TMS. It was split by the two fluorine atoms of the adjacent chlorodifluoromethyl group into a triplet with a coupling constant, $J_{\text{H-F}}$, of 3.0 Hz. The ^{19}F NMR spectrum recorded on the same instrument showed a doublet shifted

5.52 ppm. downfield from an external trifluoroacetic acid lock. The coupling constant was also 3.0 Hz.

Experiment 67: CDFA-2,4-dinitrophenylhydrazone $[\text{CClF}_2\text{CH}=\text{NNHC}_6\text{H}_3(\text{NO}_2)_2]$

The hydrazone of CDFA was prepared from chlorodifluoroacetaldehyde hydrate according to the method reported by Ross and Ring (237) which is specifically used for the preparation of 2,4-dinitrophenylhydrazones of haloaldehydes. A solution of 2,4-dinitrophenylhydrazine (1 g.) in concentrated HCl (20 ml.) at 45° C. was added to a stirred solution of CDFA hydrate (1.3 g.) in concentrated HCl (2 ml.). After stirring for two hours at room temperature, the mixture was cooled to 0° C. and the yellow crystalline precipitate was filtered, washed with water, recrystallized from ethanol, and dried; yield 80%; mp. 148° C.

ANAL. Calcd. for $\text{C}_8\text{H}_5\text{ClF}_2\text{N}_4\text{O}_4$: C, 32.60%; H, 1.71%; N, 19.01%.
Found: C, 32.54%; H, 1.50%; N, 18.58%.

Experiment 68: NMR of CDFA hydrate. CDFA was dissolved in chloroform (10%) in a 5 mm. NMR tube. Was added in one microliter increments by using a microliter syringe and the ^1H NMR spectra observed. The initial aldehyde proton resonance decreased in amplitude with each aliquot of water and a triplet appeared at 5.21 ppm. ($J_{\text{H-F}}=4.0$ Hz.) plus a singlet in the range 4.7-5.2 ppm., depending on the concentration, corresponding to the hydroxyl protons. The integration showed the peaks to be in the ratio 1:2, respectively.

The experiment was repeated using deuterium oxide (D_2O) in place of the water. Only the triplet at 5.21 ppm. resulted.

The ^{19}F spectra in each case showed a doublet 0.79 ppm. downfield

from an external trifluoroacetic acid reference; $J_{H-F}=4.0$ Hz.

K. Polymerizations of CDFA

Many polymerizations of CDFA were originally carried out by B. Yamada and described in part elsewhere (199, 202), consequently, the details will not be repeated here. His data will, however, be summarized in the tables of data, with proper acknowledgements.

Experiment 69: Polymerization of CDFA with Ph_3P at $-78^{\circ}C$. A polymerization tube was charged with CDFA (0.86 g., 7.5 mmoles) and an ampule containing $SbCl_5$ (0.1 mole %). The tube was warmed to $100^{\circ}C$., the inner ampule broken, and cooled to $-78^{\circ}C$. in a Dry Ice/acetone bath. Within minutes, the monomer solution had solidified to an opaque white solid. It was opened after 24 hours, broken into pieces and soaked overnight in acetone. The polymer was found to be entirely soluble in acetone but could be reprecipitated from cold water.

Recovery: 52%.

An infrared spectra of the polyCDFA was obtained by casting a film on NaCl plates. Absorptions were: 3340 cm^{-1}_w (hydroxyl ends); 2958 cm^{-1}_{vw} (C-H stretch); 2926 cm^{-1}_s (C-H stretch); 2853 cm^{-1}_m (C-H stretch); 1460 cm^{-1}_w , 1380 cm^{-1}_m and 1350 cm^{-1}_w (C-H bending); 1230 cm^{-1}_s ; 1150 cm^{-1}_s ; 1053 cm^{-1}_m ; 986 cm^{-1}_s ; 848 cm^{-1}_s ; 730 cm^{-1}_m and 699 cm^{-1}_w (C-halogen). (Figure 17).

Further characterization was done by vapor phase osmometry (VPO) of the polyCDFA in benzene. A Mechrolab model 302B VPO was used according to its normal operating procedures. The number average

molecular weight determined was approximately 1300 g./mole which would indicate an oligomer of 11 repeat units per chain.

Thermal stabilities were measured by DTG and found to be 110⁰ C. and 254⁰ C. before and after acetylation with acetic anhydride respectively.

¹H NMR showed a broad singlet at 5.37 ppm. (TMS) at 35⁰ C. for a 20% solution of polyCDFA in CCl₄. ¹⁹F NMR showed two broad singlets, 6.85 ppm. and 5.25 (downfield from TFA) in approximately a 6:1 ratio. The splitting is larger than would be expected to originate from the heterotacticity so is assigned to internal and terminal acetal groups.

The ¹³C NMR spectrum was recorded as described in the Measurements Section in both the decoupled and coupled mode. In the broad band decoupled spectrum of four peaks were observed. Their frequencies, downfield from CCl₄ were: 41.16, 28.10, 14.94 and a broader peak at 0 ppm. The interpretation was clarified through the coupled spectrum which had six peaks: 41.21, 28.10, 15.16, 3.99, 0.00 and -4.96 ppm. There were more clearly a triplet centered at 28.10 ppm. downfield from CCl₄ and a doublet centered at 0.49 ppm. upfield from the reference CCl₄ signal (0 ppm.). The peaks can be assigned to the backbone and pendant carbons, respectively.

Experiment 70: Polymerization of CDFA with Et₃Al at 25⁰ C. CDFA

(1.03 g., 9.0 mmoles) and a sealed ampule of Et₃Al (0.5 mole %) were charged into a polymerization tube and sealed at 0.1 mm. Hg. in liquid nitrogen. The tube was heated to 100⁰ C., the inner ampule broken and cooled to 25⁰ C. Within one minute, the solution gelled and after 24

hours, a hard solid plug was removed. The acetone extraction yielded 86% insoluble polymer; no soluble fraction was recovered. The IR was identical to that of polyCDFA observed in Experiment 69. DTG measurements showed an increased thermal stability: maxima at 220°C . and 348°C ., raw and after PCl_5 treatment, respectively.

Experiment 71: Polymerization of CDFA with SbCl_5 at -78°C . Into a polymerization tube was charged CDFA (0.9634 g., 8.4 mmoles) and a break ampule containing SbCl_5 (0.1 mole %). The tube was heated to 100°C ., mixed, and cooled quickly to -78°C . After 24 hours, a gel-like mass was removed from the polymerization tube and found to be wholly soluble in acetone. 46% recovery. The IR spectrum matched that of polyCDFA described in Experiment 69. DTG measurements showed maxima at 230°C . and 350°C ., for the soluble polyCDFA before and after PCl_5 treatment.

ANAL. Calcd. for C_2HOCIF_2 : C, 20.98%; H, 0.88%. Found: C. 21.21% H, 1.06%.

Experiment 72: Copolymerization of CDFA and chloral with SbCl_5 at 25°C . CDFA (1.10 g., 9.6 mmoles) and chloral (1.54 g., 10.5 mmoles) (48-52 ratio) were charged into a polymerization tube containing a sealed ampule of SbCl_5 (0.2 mole %). The SbCl_5 tube was broken and mixing took place at 100°C . The initiated solution was placed in a 25°C . water bath for polymerization. Within less than one minute, the solution started to gel, becoming a firm pale yellow solid after two minutes. At the end of one hour the tube was broken and the plug slurried in acetone. No acetone soluble copolymer was recovered. The

conversion to insoluble polymer was 61%.

The copolymer was stabilized by treating with PCl_5 solution to increase the DTG maximum from 250°C . to 375°C .

The IR spectrum was recorded (KBr): $3450\text{ cm}^{-1}_{\text{b}}$ (O-H stretch); $2955\text{ cm}^{-1}_{\text{m}}$ (C-H stretch); $1368\text{ cm}^{-1}_{\text{w}}$, $1358\text{ cm}^{-1}_{\text{m}}$, and $1323\text{ cm}^{-1}_{\text{m}}$ (C-H bending); $1234\text{ cm}^{-1}_{\text{w}}$; $1158\text{ cm}^{-1}_{\text{w}}$; $1170\text{ cm}^{-1}_{\text{m}}$; $1080\text{ cm}^{-1}_{\text{w}}$; $1062\text{ cm}^{-1}_{\text{w}}$; $1025\text{ cm}^{-1}_{\text{w}}$; $982\text{ cm}^{-1}_{\text{w}}$; $962\text{ cm}^{-1}_{\text{s}}$; $840\text{ cm}^{-1}_{\text{s}}$; $828\text{ cm}^{-1}_{\text{s}}$; $798\text{ cm}^{-1}_{\text{s}}$; $714\text{ cm}^{-1}_{\text{w}}$; $672\text{ cm}^{-1}_{\text{s}}$; $579\text{ cm}^{-1}_{\text{s}}$; $490\text{ cm}^{-1}_{\text{m}}$; and $360\text{ cm}^{-1}_{\text{m}}$.

ANAL. 13.54% F. This indicates that the copolymer contains 60 mole % CDFA.

Experiment 73: Copolymerization of CDFA and chloral with Ph_3P at 25°C . CDFA (1.302 g., 11.4 moles) and freshly distilled chloral (1.66 g., 11.3 mmoles) were mixed in a polymerization tube, initiated with Ph_3P (0.3 mole %) and cooled to 25°C . The solution quickly gelled and was removed as a solid plug after one hour. It was found to be totally soluble in acetone with a 45% recovery.

DTG maxima were measured at 150°C . and 230°C . for the raw and PCl_5 treated polyCDFA, respectively.

The IR spectrum was identical to that of the copolymer reported in Experiment 72. Isothermal decomposition at 250°C . followed by GC analysis of the volatiles showed the copolymer to contain 85% CDFA.

L. Ceiling Temperature Measurements

Experiment 74: Ceiling temperature of DCFA. Three tubes were prepared

by washing in dil. HCl, rinsing with distilled water four times and drying overnight at 120° C. Each tube was then cooled by purging with nitrogen with an inlet and outlet needle through an amber rubber septum. DCFA was then added by dry syringe to each tube, and the tubes weighed to measure the amount of monomer. Dry toluene was then transferred to each tube such that the volumes were all nearly equal but the concentrations varied. The exact amount of toluene was determined by reweighing. The break ampules were then prepared. An amount of pyridine equivalent to 3 mole % (3 M. in toluene) of the monomer was sealed in the break ampules and these plus a glass breaker bead were placed into each polymerization tube. The apparatus used was described in Section II-B. Figure 20.

Tube one was charged with DCFA (1.14 g., 0.85 ml., 8.7 mmoles), toluene (1.04 g., 1.20 ml.) (4.25 M.) and pyridine (0.26 mmoles), and sealed under 0.1 mm. Hg pressure at -196° C. It was heated in the oil bath to 105° C., shaken to break the ampule, and quickly replaced in the oil bath. The light beam was aligned and the recorder chart started. The bath was allowed to cool at approximately 1° C. per minute. The light intensity was constant until the temperature reached 62° C. The recorder trace indicated a rapid decrease in intensity at this point.

The experiment was continued using the other tubes which had been sealed with different monomer concentrations. The procedure was identical to that already described.

A 2.4 M. solution was made by mixing DCFA (0.57 g., 0.40 ml., 4.4 mmoles) with toluene (1.39 g., 1.60 ml.) with an ampule of pyridine (1.5 mole %). The polymerization temperature was found to be 53° C.,

after initiation at 95° C.

The 2.0 M. DCFA solution was made by mixing monomer (0.52 g., 0.39 ml., 4.0 mmoles, toluene (1.39 g., 1.60 ml.) and pyridine (2.5 mole %) at 90° C. Its light transmittance decreased sharply at 50° C.

Experiment 75: Ceiling temperature of CDFA. Solutions were prepared and polymerized as described in Experiment 74. Pyridine concentration was maintained at 3 mole % of the CDFA.

<u>Conc.</u>	<u>CDFA</u>	<u>Toluene</u>	<u>T_p</u>
1.8 M.	0.45 g., 4.0 mmoles	1.64 g., 1.89 ml.	73° C.
2.75 M.	0.63 g., 5.5 mmoles	1.36 g., 1.57 ml.	80° C.
3.6 M.	0.87 g., 7.6 mmoles	1.30 g., 1.50 ml.	87° C.

Experiment 76: Ceiling temperature of BDFA. Same procedure as before. Monomer and 3 mole % pyridine mixed at 85° C.

<u>Conc.</u>	<u>BDFA</u>	<u>Toluene</u>	<u>T_p</u>
1.02 M.	0.36 g., 2.2 mmoles	1.74 g., 2.00 ml.	49° C.
2.05 M.	0.68 g., 4.3 mmoles	1.48 g., 1.72 ml.	61° C.
2.4 M.	0.76 g., 4.8 mmoles	1.37 g., 1.58 ml.	68° C.

Experiment 77: Ceiling temperature of DBFA. The same apparatus as before except that the bath medium was changed to isopropyl alcohol and cooling was achieved with small additions of Dry Ice. Streams of dry nitrogen were directed against the bath windows to prevent fogging by moisture in the air. Monomer was mixed with pyridine at 50° C.

<u>Conc.</u>	<u>DBFA</u>	<u>Toluene</u>	<u>T_p</u>
1.60 M.	0.77 g., 3.52 mmoles	1.61 g., 1.86 ml.	5° C.
2.35 M.	1.14 g., 5.17 mmoles	1.47 g., 1.69 ml.	13° C.
3.58 M.	1.73 g., 7.88 mmoles	1.24 g., 1.43 ml.	23° C.

Experiment 78: Ceiling temperature of fluoral. Fluoral was prepared by the H_2SO_4 dehydration of commercial fluoral hydrate. Fluoral monomer was collected in a Dry Ice/acetone trap (lit. bp. -18°C .¹²) and purified by trap to trap distillation from P_2O_5 . The IR matched that reported by Schechter and Conrad for fluoral. (32) ^1H NMR showed a quartet centered at 9.36 ppm. (TMS).

The determination of the ceiling temperature of fluoral was carried out as before except that the higher boiling xylene replaced benzene as the solvent due to the anticipated higher ceiling temperature. The fluoral solution and pyridine were mixed at 120°C .

<u>Conc.</u>	<u>Fluoral</u>	<u>Xylene</u>	<u>T_p</u>
1.5 M.	0.31 g., 3.15 mmoles	1.64 g., 1.90 ml.	90° C.
2.0 M.	0.41 g., 4.2 mmoles	1.49 g., 1.70 ml.	95° C.
3.3 M.	0.68 g., 6.9 mmoles	1.23 g., 1.42 ml.	106° C.

M. Wide Angle X-ray Scattering

Experiment 79: X-ray pattern of polyDCFA.

79-A. Raw, insoluble polymer prepared in Experiment 56 (Et_3Al at 25°C .) was examined by placing the sample holder 10 mm. from the source port and positioning the film plate 100.0 mm. behind the sample. The

source was activated and the automatic timer preset to give eight hours exposure.

At the end of the exposure time the film plate was developed. No rings could be observed.

79-B. The experiment was repeated with the insoluble acetylated fraction of polyDCFA from Experiment 46 (Ph_3P at 25°C). The film was positioned 95.3 mm. behind the sample and exposed for eight hours. Again no rings were visible.

79-C. Experiment 76-B was repeated with two changes. The film was removed to 365 mm. behind the sample in order to improve the resolution of any rings which might be located near the center of the photograph and therefore may have been hidden by the lead center stop. The exposure time was increased to 16 hours. However, still only a very faint ring was visible in the developed photograph.

79-D. Raw, insoluble polyDCFA made in Experiment 58 (H_2SO_4 at 25°C .) was examined by x-ray. The film was positioned 76.2 mm. behind the sample and exposed for 15 hours. This gave a photograph consisting of at least six concentric rings. The diameters of these were measured on the photographic plate (negative) and found to be 15, 27, 48, 54, 60 and 78 mm. Figure 23.

Experiment 80: X-ray pattern of polyCDFA. A sample of ray, insoluble polyCDFA from Experiment 70 (Et_3Al at 25°C .) was mounted in the lead sample holder and positioned in the x-ray. A photographic plate was placed 76.2 mm. behind it and exposed for 12 hours.

Only two rings were produced: 26 and 51 mm. in diameter.

Figure 24.

Experiment 81: X-ray pattern of polyDBFA. A sample of raw, insoluble polyDBFA from Experiment 30 (H_2SO_4) at 25°C.) was mounted 76.2 mm. in front of a film plate and irradiated 15 hours to give a set of five rings. The spacings on the negative were 24, 42.5, 48.5, 54 and 70 mm. in diameter. Figure 25.

Experiment 82: X-ray pattern of polyBDFA.

82-A. Raw, insoluble polyBDFA from Experiment 15 (H_2SO_4) at 25°C.) was placed in the sample holder and positioned 79.4 mm. in front of a film plate which was then exposed for 14 hours. A set of four rings of 16.5, 28, 55 and 62.5 mm. in diameter resulted. Figure 26.

82-B. A different sample of polyBDFA was also examined. It represented Experiment 15 (H_2SO_4 at 25°C.) also, but had been treated with PCl_5 . The film to sample distance was set at 76.2 mm. After 15 hours, a set of very sharp rings was obtained 24, 48, 54 and 70 mm. in diameter. Figure 27.

N. Attempted Synthesis of Bromochlorofluoroacetaldehyde (BCFA).

Experiment 83: Attempted synthesis of BCFA. Following an adaptation of Lipp's (31) procedure used in his synthesis of bromodichloroacetaldehyde (BDCA) from chloral, DCFA (18.2 g., 0.14 moles) was dissolved in dry CH_2Cl_2 (40 ml.) and added dropwise over a one hour period to a vigorously stirred solution of Ph_3P (36.0 g., 0.137 moles) in dry CH_2Cl_2 (75 ml.) in a 3 neck 500 ml. flask. The temperature was maintained at

ambient by occasional cooling with an ice water bath. A nitrogen blanket was maintained over the carefully predried system. All reagents had been rigorously dried.

At the end of the aldehyde addition n-hexane (100 ml.) was added to precipitate the phosphonium salt. Instead of a crystalline salt, a red oil separated.

The mixture was cooled to 0°C . with stirring, and anhydrous ether (50 ml.) added. The product remained a gum or thick oil.

CH_2Cl_2 (100 ml.) was added to redissolve the oil. Bromine (21.8 g., 0.139 moles) in CH_2Cl_2 (45 ml.) was added very slowly while maintaining the reaction under a nitrogen blanket and at 0°C . The solution was stirred for two hours after the 2.5 hour Br_2 addition was completed. The solvent was stripped off by warming the reaction flask to room temperature and maintaining a flow of nitrogen over the solution and vented through a CaCl_2 drying tube.

The flask was equipped with an addition funnel, a reflux condenser, and a nitrogen inlet tube. Dioxane (60 ml.) was added to redissolve the oil. The product was hydrolyzed by slow addition of water (2.4 ml.) in dioxane (35 ml.). This resulted in a suspension of the red oil in the aqueous dioxane. The mixture was refluxed for two hours to form the acetaldehyde hydrate. Dioxane (90 ml.) was distilled out. It contained no hydrate by GC. Conc. H_2SO_4 (25 ml.) was added to dehydrate the product and the material distilled. The fractions (2 g. total) distilled over a very broad range ($50\text{--}130^{\circ}\text{C}$.) with no distinct steps to give a very acidic smelling product. (Extrapolation from other haloacetaldehyde would suggest a bp. of approximately 95°C .)

No characterization was made of the very impure mixture.

Experiment 84: Preparation of DCBA. In order to check the techniques and quality of reagents used in Experiment 83, Lipp's (31) synthesis was repeated. Chloral (33.4 g., 0.226 moles) in CH_2Cl_2 (45 ml.) was added dropwise to a vigorously stirred solution of Ph_3P (59.4 g., 0.226 moles) in CH_2Cl_2 (75 ml.). The procedure followed was identical to Experiment 83. The addition of the n-hexane (100 ml.) caused a precipitation of a copious amount of white salt, instead of the previous oil. The remainder of the process went as described by Lipp with the final product distilled at 125-127° C. lit. bp. for DCBA 127° C. in 65% yield.

Experiment 85: Repeated attempt to prepare BCFA. Extreme care was taken to dry all glassware and ensure that all chemicals were as dry as possible.

DCFA (21 g., 0.16 moles) in CH_2Cl_2 (50 ml.) was again added to Ph_3P (42.1 g., 0.16 moles) in CH_2Cl_2 (100 ml.) in a 500 ml. 3 neck flask. The addition was carried out over three hours with the reaction flask maintained at 0° C. in an ice water bath.

The addition of n-hexane (125 ml.) again resulted in the formation of a red oil. Attempts to crystallize the oil; cooling, scratching and changing solvents; all failed. The experiment was terminated at this point.

Experiment 86: Attempt to prepare BCFA using ether as solvent. DCFA (4.73 g., 36.1 mmoles) in anhydrous ethyl ether (25 ml.) was added drop-

wise to a stirred solution of Ph_3P (9.48 g., 36.1 mmol) in anhydrous ethyl ether (30 ml.). The Ph_3P -ether solution was refluxed during the addition while being maintained under a slight positive nitrogen pressure. The solution turned pale yellow during the 15 minute aldehyde addition and, after about 70% of the addition, turned slightly cloudy. Refluxing was continued for one hour during which time the solution cleared to a transparent pale yellow.

The ether was removed under a slight vacuum leaving pale yellow crystals in good yield. Dry CH_2Cl_2 (40 ml.) was added to dissolve the crystals. The resulting solution was a transparent reddish-brown. Dry n-hexane (40 ml.) added to reprecipitate reddish-brown crystals.

The salt was redissolved in CH_2Cl_2 (25 ml.), cooled to 0°C ., and Br_2 (5.78 g., 36.1 mmol) in CH_2Cl_2 (25 ml.) was added dropwise to the cold solution. (The addition of bromine to the double bond could not be confirmed due to the already reddish-brown color). The solution was stirred for 2.5 hours after the addition of the bromine was completed. The CH_2Cl_2 was removed under vacuum to give a very thick oil. This was crystallized by washing it with anhydrous ether.

The salt was hydrolyzed by dropwise addition of aqueous dioxane (0.65 g., 36 mmol H_2O) to a solution of the salt in dioxane (20 ml.) H_2SO_4 (5 ml.) was added to dehydrate the product. The dioxane was removed by distillation. The flask was placed in an oil bath and heated slowly. As the bath temperature increased, the vigorously stirring product became darker in color, without any volatiles being evolved. At a bath temperature of approximately 150°C . (well above

the predicted bp.) the contents of the flask were a thick, black sludge, but no volatiles had been collected. The distillation was terminated.

III. RESULTS AND DISCUSSION

A. Purpose

This work was undertaken to prepare four perhaloacetaldehydes, bromodifluoroacetaldehyde (BDFA), dibromofluoroacetaldehyde (DBFA), chlorodifluoroacetaldehyde (CDFA) and dichlorofluoroacetaldehyde (DCFA), and study the influence of the side group size in the stereoregularity, solubility and thermal stabilities of the resulting polymers. In addition, copolymers were also prepared to determine the effect of the chemical influence of the side groups on reactivity.

B. Monomer Synthesis and Purification

1. Bromodifluoroacetaldehyde (BDFA). BDFA was synthesized by two routes, the first one being a four step synthesis starting with chlorotrifluoroethylene (235) and gave BDFA in about 30% yield (Figure 28). Chlorotrifluoroethylene was brominated at 0° C. in Freon 113 to give 1,2-dibromo-1-chloro-1,2,2-trifluoroethane in 85% yield. This compound was treated with fuming sulfuric acid and HgO to give in 75% yield bromodifluoroacetyl fluoride which was esterified with methanol at 0° C. in 75% yield.

In a separate synthesis, the same compound was also obtained starting from 1,1-dibromo-2,2-difluoroethylene. Oxidation at 0° C. gave a mixture of bromodifluoroacetyl bromide and dibromofluoroacetyl fluoride as indicated in (Eqn. 1B Figure 28). (233) This oxidation goes presumably via the 1,1-dibromo-2,2-difluoroethylene oxide which could not be isolated although several attempts were made to do so. The mixture of the bromodifluoroacetyl bromide and dibromofluoroacetyl fluoride was

treated with methanol and the resulting methyl bromodifluoroacetate and dibromofluoroacetate could be separated by fractional distillation. Although the boiling points are sufficiently far apart, trace amounts of the methyl dibromofluoroacetate were always present in methyl bromodifluoroacetate as was found by gas chromatography in the final product.

Methyl bromodifluoroacetate was reduced by reverse reduction with LAH at -78°C . The aluminum salts were decomposed with concentrated sulfuric acid and the pure BDFA rectified.

BDFA isolated in 60% yield from the reduction of methyl bromodifluoroacetate had a boiling point of $43-44^{\circ}\text{C}$. The 2,4-dinitrophenylhydrazone of BDFA prepared by the method developed for haloaldehydes melted at $136-138^{\circ}\text{C}$.

1,1-Dibromo-2,2-difluoroethylene oxide is a most likely intermediate of the oxidation of 1,1-dibromo-2,2-difluoroethylene in view of the fact that we have recently shown that tetrachloroethylene oxide is the intermediate of the oxidation of tetrachloroethylene to trichloroacetyl chloride. (241) 1,1-Dibromo-2,2-difluoroethylene oxide is much less stable than tetrachloroethylene oxide and could not be isolated in spite of our repeated efforts based on experience in the oxidation of tetrachloroethylene and isolating the oxide.

In the preparation of the BDFA, a crude "hydrate" was isolated after the lithium salts obtained in the reduction with LAH were decomposed in water. This material, although it gave pure BDFA upon dehydration with concentrated sulfuric acid, is in actual fact not a pure hydrate but contains also hemihydrate which can be readily seen in the

^1H NMR spectrum of the "crude" hydrate. The hydrate was subsequently reconstituted from BDFA and water. The ^1H NMR spectrum showed a triplet at 5.16 ppm. for the acetal proton split by the fluorine atoms and OH protons had a chemical shift of 3.85 to 4.35 ppm. depending on the concentration of BDFA. When D_2O was used instead of water and the BDFA deuterate rather than the hydrate was prepared, only the triplet of the acetal proton at 5.16 ppm. was observed.

2. Dibromofluoroacetaldehyde (DBFA). DBFA was prepared by oxidation of 1,1-dibromo-2,2-difluoroethylene with oxygen to give a mixture of dibromofluoroacetyl fluoride and bromodifluoroacetyl bromide acid. The mixture was treated with methanol and gave the methyl esters. Methyl dibromofluoroacetate was separated by distillation from bromodifluoroacetate and was reduced with LAH to DBFA. Figure 29.

The synthesis of DBFA was accomplished in an overall yield of 15-20%. Initially 1,1-dibromo-2,2-difluoroethylene was air oxidized at 0°C . (233) The oxidation apparently goes through the unstable 1,1-dibromo-2,2-difluoroethylene oxide which could not be isolated but rearranged directly to a mixture of dibromofluoroacetyl fluoride and bromodifluoroacetyl bromide. These products were not separated but were immediately treated with methanol at 0°C . and gave an approximately 50:50 molar mixture of methyl dibromofluoroacetate and methyl bromodifluoroacetate. The boiling points of these two compounds were far enough apart that methyl bromodifluoroacetate, boiling much lower, could be distilled as the foreshot. The residual methyl dibromofluoroacetate was rectified and then reduced with LAH at 0°C . Aluminum

compounds formed were directly decomposed with water to the hydrate and semiacetal of DBFA and then dehydrated with conc. sulfuric acid to DBFA. The crude DBFA hydrate actually consists not only of the hydrate but also of the methylhemiacetal as the hydrate showed several peaks in the PMR spectrum which were not assignable to pure DBFA hydrate. The overall DBFA yield for this preparation was nearly 20%. DBFA was purified by careful distillation and showed, by GC analysis, only one impurity which was found at the 25 ppm. level and identified as BDFA.

DBFA hydrate was regenerated from DBFA by adding water to a solution of DBFA in CDCl_3 . The initially present aldehyde doublet at 8.86 ppm. was replaced by two new peaks which appeared as a doublet at 5.10 ppm. and a singlet at approximately 4 ppm. The first chemical shift peak was clearly identified as the CH frequency of the hydrate while the other peak was, according to its integration intensity ratio of 1:2, identified as the proton of the hydroxyl group. The latter peak did not exist if the hydration was done with D_2O instead of H_2O .

3. Dichlorofluoroacetaldehyde (DCFA). DCFA has been prepared in a sequence of four steps in an overall yield of 20%. Figure 30

Trichloroacetic acid was esterified in 75% yield with methanol catalyzed by sulfuric acid. Methyl trichloroacetate was converted to methyl dichlorofluoroacetate with SbF_3 in the presence of bromine as the catalyst in more than 50% yield. The hydrate was then dehydrated with sulfuric acid and the aldehyde purified by repeated distillation from phosphorus pentoxide to obtain polymerization grade monomer.

Impurities were shown by CG to be less than 20 ppm. and, based

on retention times, believed to be less than fully halogenated acetaldehydes.

4. Chlorodifluoroacetaldehyde (CDFA). CDFA was synthesized by a route which has been established for the preparation of fluoral. (236)

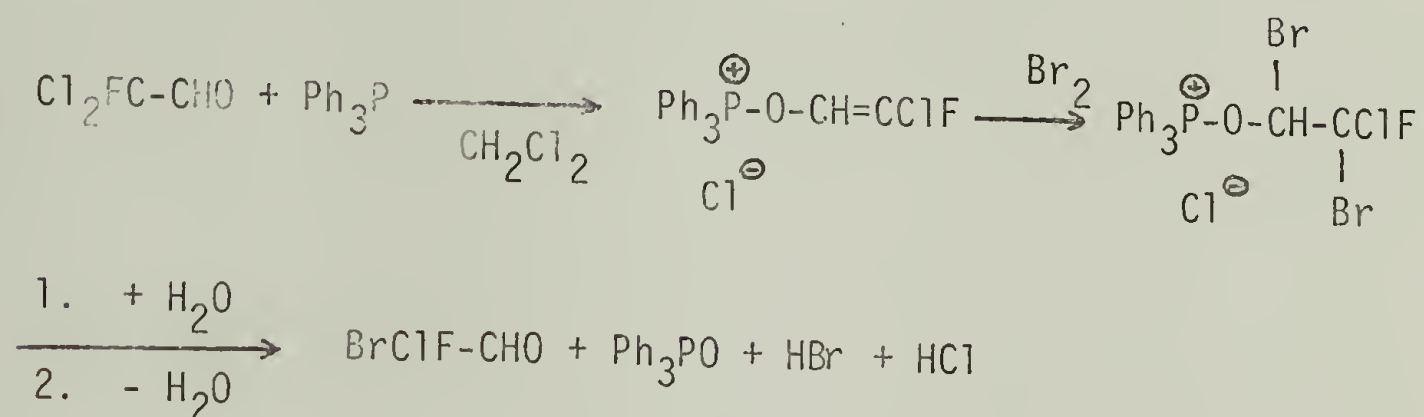
Figure 31.

Methyl chlorodifluoroacetate was synthesized by reacting methyl trichloroacetic acid with SbF_3 in the presence of SbCl_5 catalyst in a 17% yield. (The selectivity of the catalyst is shown by the replacement of two chlorines, whereas monosubstitution is achieved with bromine catalyst.) Methyl chlorodifluoroacetate was reduced with lithium aluminum hydride at -78°C . The reaction had to be carried out at low temperatures and with the exact amount of LAH in order to avoid undesirable side reactions, primarily the reduction of halogens from the trihalomethyl group.

The reduction product of methyl chlorodifluoroacetate was hydrolyzed to a mixture of CDFA derivatives including the hydrate and the methyl hemiacetal. This mixture was isolated by the distillation in almost 80% yield. Attempts to identify the species which were present in the distillation mixture did not allow any conclusions to be drawn as to the exact nature of the products. The mixture was treated with sulfuric acid and phosphorus pentoxide to give the free aldehyde which was then purified by trap-to-trap distillation.

5. Attempted synthesis of bromochlorofluoroacetaldehyde (BCFA). The attempted synthesis of this monomer was modeled after the Perkow reaction. (138, 142) Lipp has reported the synthesis of BDCA by reacting

chloral with Ph_3P to give the phosphonium chloride. Bromine was added across the double bond, the salt hydrolyzed, then dehydrated to the DCBA in 60% overall yield. (31) A similar reaction would be expected to yield BCFA from DCFA:



However, when the same procedure was followed with DCBA as with the chloral, a red oil was formed instead of the crystalline phosphonium chloride. This oil was not characterized but did not undergo the other reactions leading to BCFA. Technique and reagent purity and dryness were confirmed through the successful synthesis of DCBA. Variations in temperature and solvent offered no improvement in the outcome of the synthesis.

Further work on this compound should include characterizations of intermediates and products to better assess the problems involved and suggest solutions.

C. Monomer Characterization

The monomers were characterized by their elemental analyses, infrared spectra, nuclear magnetic spectra (both ^1H NMR and ^{19}F NMR) and their physical properties.

1. Elemental analysis.TABLE 1
ELEMENTAL ANALYSIS OF MONOMERS

BDFA			DBFA		
	<u>Theory</u>	<u>Found</u>		<u>Theory</u>	<u>Found</u>
C	15.11	15.02		10.93	10.98
H	0.63	0.59		0.46	0.48
F	23.91	24.10		----	----

CDFA			DCFA		
	<u>Theory</u>	<u>Found</u>		<u>Theory</u>	<u>Found</u>
C	20.98	21.59		18.35	18.61
H	0.88	1.50		0.77	0.77
F	----	----		14.51	14.45

Although the CH analysis for CDFA is not within our accepted limits of \pm of 0.3, other methods of analysis, spectral and chromatographic, leave no doubt as to its identity and structure.

2. Physical constants. The following boiling points and densities were determined, or reported, for perhaloacetaldehydes.

TABLE 2
BOILING POINTS AND DENSITIES FOR HALOACETALDEHYDES: R-CHO

R	Boiling Point in ° C.	Densities in g./cc.
CF ₃	-18 ^a	1.47 ^a
CF ₂ Cl	18	1.45
CFCl ₂	56	1.43
CCl ₃	98	1.45
CF ₂ Br	43	1.80
CFBr ₂	52 @ 90 mm. Hg ^b	2.25
CCl ₂ Br	127 ^c	1.87 ^c
CCLBr ₂	148 ^c	2.27 ^c
CBr ₃	174 ^c	2.73 ^c

(a) Ref. 32.

(b) Decomposes on distillation at 760 mm. Hg. observed bp. would correspond to ca. 115° C. at 760 mm. Hg using a P-T nomograph.

(c) Ref. 28-31.

The boiling points increase linearly with increasing bromine, and, to a lesser extent, with increasing chlorine. The densities are not greatly affected by substitution of chlorine for fluorine, probably due to the compensation of the slightly higher atomic mass by the smaller size of the molecules and lower repulsions therefore allowing more fluorine containing molecules to occupy a given volume.

This trend is observed in both the chloro-fluoro and the bromo-fluoroacetaldehydes and with fluoral. Substitution of bromine with its very much higher mass more than offsets its greater bulkiness.

3. Nuclear magnetic resonance. Both ^1H NMR and ^{19}F NMR were used to characterize monomers. Figures 32-39.

TABLE 3
 ^1H NMR AND ^{19}F NMR SHIFTS FOR MONOMERS: R-CHO

R	^1H NMR (TMS)	^{19}F NMR (TFA ext.)	Coupling Constant ($J_{\text{H-F}}$ in Hz.)
CF_3	9.36	N/A	N/A
CF_2Cl	9.25	5.52	3.0
CFCl_2	9.15	0.32	5.0
CCl_3	8.95	N/A	N/A
CF_2Br	9.09	8.53	4.0
CFBr_2	8.86	0.45	7.0
CCl_2Br	8.85 ^a	N/A	N/A
CClBr_2	8.70 ^a	N/A	N/A
CBr_3	8.45 ^a	N/A	N/A

(a) Ref. 28-31.

These data illustrate the effect of shielding by halogens of higher atomic number. Due to the polarizability of the halogen ($\text{Br} > \text{Cl} > \text{F}$), the electrons are able to better shield the aldehyde protons in the order $\text{Br} > \text{Cl} > \text{F}$.

This trend is evident in both ^1H NMR and ^{19}F NMR.

4. Infrared spectra. The infrared spectra of all four monomers synthesized have been described in the Experimental Section and are shown in Appendix 1. In addition to unique patterns in the fingerprint region, differences exist in both the aldehydic C-H stretching absorbance frequency and in the carbonyl C=O frequency which can be related to the electronic environments surrounding these bonds. These data are presented in Table 4.

TABLE 4
ALDEHYDE CARBONYL INFRARED STRETCHING FREQUENCIES (cm^{-1})

R	Gas	n-Hexane Solution	Neat
CF_3	1785	1780	---- ^a
CF_2Cl	1770 ^c	1770 ^c	---- ^a
CFCl_2	1760	1772	1770
CCl_3	1777	1768	1760
CF_2Br	1770 ^c	1762 ^c	1755
CFBr_2	1760	1775	1751
$\text{CCl}_2\text{Br}^{\text{b}}$	1774	1763	1754
$\text{CClBr}_2^{\text{b}}$	1768	1758	1750
CBr_3^{b}	1765	1754	1742

(a) Too volatile to measure neat.

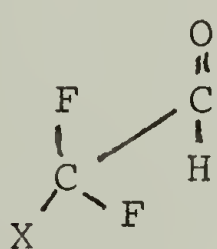
(b) Ref. 28-31.

(c) Broadened or split peaks. See text.

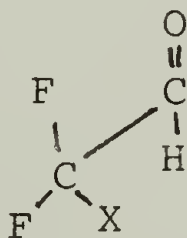
The trends observed can be explained in terms of electronegativity and polarizability of the substituents on the pendant methyl groups. Increasing substitution of more electron withdrawing groups has the effect of increasing the double bond character of the carbonyl. This results in a shift to higher frequency vibrations (lower wavenumbers).

A further observation can be made. In IR spectra of BDFA and CDFA, the carbonyl band is slightly broader than normal or even split in spectra of the monomers in the gaseous phase and in hexane that is not observed in the neat liquid (for BDFA) or CCl_4 . This is not observed for the other monomers, all of which have very sharp characteristic carbonyl peaks. These splittings have been reported for several α -halogen alkyl ketones and due to rotational isomers. (243, 244) The carbonyl bond vibration is therefore affected by a field effect operating across space in addition to the already mentioned inductive effects operating along the bonds. (245, 246) It would be expected that the field effect would be greatest for fluorine and decrease from chlorine through bromine, indeed Lipp does not report this observation for the BDCA nor CDBA. See Figures 3, 7, 9-12 and 16.

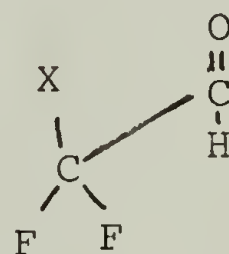
Three rotational isomers can be drawn for either BDFA or CDFA.



I



II



III

where X is either Cl or Br.

The two structures in which F is coplanar with the carbonyl, I

and II, should be the most polar conformations and therefore have the higher frequency vibrations.

As it has been observed for other rotational isomers (245, 246), the relative intensity of the bands vary with solvent. In polar solvents such as CHCl_3 , CCl_4 or in the liquid monomer itself, these frequency shifts are not observed.

D. Homopolymerization of BDFA, DBFA, CDFA and DCFA

Each of the four monomers prepared was homopolymerized under a variety of conditions using compounds known to be anionic or cationic initiators.

1. Ceiling temperature measurements. In order to establish the most favorable reaction conditions for the polymerizations the ceiling temperatures were determined. As described in detail in Section II-B, these measurements were made by diluting the monomers to known concentrations with toluene, heating to a temperature above the expected polymerization temperature and then introducing the initiator. The solution was then cooled at $1^{\circ}\text{C. per minute}$. The onset of polymerization was determined by a decrease in measured intensity of a focused beam of light passing through the solution onto a photocell detector. The measured polymerization temperatures could then be plotted against concentration. The ceiling temperatures was reported as the temperature at which this line crossed 1.0 M. concentration.

The measured ceiling temperatures are presented in Table 5.

TABLE 5
CEILING TEMPERATURES OF PERHALOACETALDEHYDE MONOMERS

<u>Monomer (R-CHO)</u>	<u>T_c (in ° C.)</u>
CF ₃	86
CF ₂ Cl	67
CFC1 ₂	46
CCl ₃	18
CF ₂ Br	48
CFBr ₂	-3
CCl ₂ Br	-15 ^a
CClBr ₂	-40 ^a
CBr ₃	-75 ^a

(a) Ref. 28-31.

The ceiling temperatures for chloral (159) and fluoral (192) have been determined by other workers under different conditions to be 11° C. and 85° C., respectively. Although the ceiling temperature may depend on experimental conditions, it is clear that the substitution of chlorine atoms on the α -carbon atom of chloral by fluorine increased the polymerization ceiling temperature of the haloaldehyde. At the same time, the boiling point of the fluorochloro-substituted acetaldehyde decreased. The same trend is observed through the substitution of bromine into chloral or fluoral. These data are summarized graphically in Figures 21 and 22. A direct consequence of this relationship is the fact that cryotachensic polymerization (21, 47) cannot be effectively

carried out at atmospheric pressure with fluorinated haloaldehydes because this polymerization requires a liquid range of approximately 30-40° C. between the threshold temperature of polymerization for neat monomer and the boiling point of the monomer. In the case of fluoral, the boiling point of the monomer is approximately 120° C. lower than the threshold temperature of polymerization. As a consequence, cryo-tachensic polymerization could be attempted only for the fluorochloroaldehydes and bromofluoroaldehydes in sealed tubes at high pressures.

The values of the thermodynamic quantities ΔS_p^0 and ΔH_p can be calculated from the slope and intercept of the polymerization temperature-concentration curve using the equation: (10)

$$T_c = \Delta H_p / (\Delta S_p^0 + R \ln [M]_c)$$

$$\text{thus: } \frac{1}{T_c} = \frac{\Delta S_p^0}{\Delta H_p} + \frac{R}{\Delta H_p} \ln [M]_c$$

or, alternatively,

$$\frac{\Delta H_p}{RT_c} = \frac{\Delta S_p^0}{R} + \ln [M]_c$$

$$\ln [M]_c = \frac{\Delta H_p}{R} \left(\frac{1}{T_c} \right) - \frac{\Delta S_p^0}{R}$$

These data are shown in Table 6.

TABLE 6
ENTROPIES AND ENTHALPIES OF POLYMERIZATION FOR R-CHO

R	ΔH_p		ΔS_p^0	
	cal/mole ($\times 10^4$)	joules/mole ($\times 10^4$)	eu/mole	joule/mole 0K
BrF ₂	-1.00	-4.17	-31.2	-130
Br ₂ F	-0.73	-3.03	-27.1	-113
ClF ₂	-1.24	-5.19	-37.2	-155
Cl ₂ F	-1.36	-5.67	-43.4	-181
Chloral ^a	-1.05	-4.38	-37.2	-156
Fluoral	-1.75	-7.29	-48.7	-203
BrCl ₂ ^b	-0.87	-3.63	-33.4	-139
Br ₂ Cl ^b	-1.23	-5.13	-52.6	-219
Bromal ^b	-2.99	-12.5	-163	-678

(a) Ref. 247.

(b) Calculated from data-ref. 28-31.

Kambe et.al. (159) found that for the series of acetaldehydes in which the substituent on the methyl group varied from trimethyl (pivaldehyde) to trichloro (chloral) the polymerization entropies and enthalpies became more negative, thus favoring polymer stability, as more chlorines were added. This would be consistent with the ceiling temperature order for this series. Steric hinderance should also favor polymerization of those monomers having smaller side groups.

2. Polymerization of BDFA. BDFA has been polymerized with many ionic initiators to give substituted polyoxymethylene type polymers. In contrast to chloral, with its bulky trichloromethyl group, BDFA can polymerize under certain conditions to a polymer which is soluble in acetone and presumably somewhat heterotactic. This supposition can be supported by space filling molecular models which show that while poly-chloral chains can exist only rigidly in an isotactic helix, poly BDFA, due to the reduced size of the pendant group, has more flexibility.

Both anions and cations were effective initiators for BDFA polymerization.

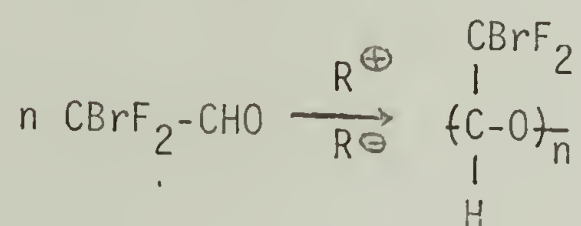


Table 7 summarizes initiators, reaction conditions, and yields of soluble and insoluble polyBDFA.

TABLE 7
POLYMERIZATION OF BDFA
Polymerization Time: 1 Day

Type	Initiator	Polymerization Bath Temp., in ° C.	Conversion to Polymer, in %	
	Amount, in mole%		Total Conversion	Insoluble Fraction (% of total conversion)
LTB	0.15	-78	35	100
LTB	0.10	25	50	90
Ph ₃ P	0.26	-78	25	20
Ph ₃ P	0.14	25	15	0
Pyridine	0.13	25	40	90
H ₂ SO ₄	0.42	-78	0	0
H ₂ SO ₄	0.18	25	91	77
Et ₃ Al	0.46	-78	45	100
Et ₃ Al	0.63	25	50	100
SbCl ₅	0.39	-78	8	0

Polymerization of BDFA has been carried out with cationic and anionic initiators (Table 7). After it was established that the ceiling temperature of polymerization was 48° C., polymerizations were carried out from -78° C. to +25° C. with initiator amounts of 0.1 to 0.6 mole% and acetone soluble and insoluble polymers were obtained.

With Ph₃P as the initiator, added in the amount of 0.14 mole%, and the mixture polymerized at 25° C., a 15% of polyBDFA was obtained which was completely soluble in acetone but could be precipitated into water. The polymer had an inherent viscosity of 0.20 dl./g. When the

polymerization was carried out at -78°C . with 0.26 mole% Ph_3P and the polymerization was terminated after 40 hours, a 25% yield of polymer was obtained, 20% of which was insoluble polyBDFA. The soluble polyBDFA had an inherent viscosity in benzene of 0.34 dl./g. at 45°C . and a molecular weight as measured by VPO of 3,470. With LTB as the initiator (0.15 mole%) and a reaction temperature of -78°C ., an opaque solid polymer was obtained after 24 hours which after washing with acetone and water gave an insoluble polymer (35% yield). At 25°C . and LTB as the initiator (0.10 mole%) after 24 hours, a 50% yield of polyBDFA was obtained which had a 10% acetone soluble fraction.

BDFA could also be polymerized with pyridine as the initiator. At a 0.13 mole% initiator level and a mixing temperature of initiator and monomer of 85°C ., polymerization was carried out at room temperature and gave a 40% yield of polymer which had a small portion (10%) of acetone soluble fraction.

A generally accepted typical cationic initiator, sulfuric acid, at 0.2 mole% and a 25°C . reaction temperature (mixing temperature of monomer and initiator 80°C .) after 24 hours reaction time, gave more than 90% yield of polyBDFA which consisted of a 70% insoluble polymer fraction. At -78°C . and initiator concentration of 0.42 mole%, no polymer was obtained even though the experiment was repeated with 0.8 mole % acid and a mixing temperature of 75°C . With SbCl_5 at -78°C . and a concentration of 0.39 mole % initiator, a small amount of polyBDFA (8% conversion) was obtained after 24 hours which was entirely soluble in acetone. At -25°C . with SbCl_5 initiator of similar con-

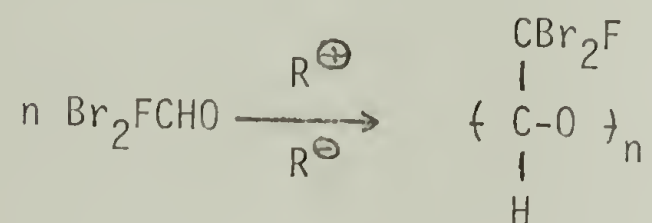
centration, no polymer was obtained. BDFA was also mixed with 0.31 mole% of $\text{BF}_3 \cdot \text{OEt}_2$ at 80°C . and the mixture was allowed to stand at 25°C ., but even after five days no polymer was formed.

Aluminum alkyls, typically Et_3Al , are good initiators for the polymerization of cyclic ethers and oxides and have been frequently used for the polymerization of aldehydes (7). BDFA was initiated with a benzene solution (0.46 mole%) of Et_3Al and the polymerization was allowed to proceed at -78°C .; a 45% yield of insoluble polymer was obtained without any acetone soluble material. With a 0.63 mole% initiator, BDFA polymerized rapidly and gave, after 24 hours, a 50% conversion to acetone insoluble polymer. The polymerization was actually complete after a 30 minute reaction.

As indicated in the last paragraph, the actual polymerization rate for the polymerization of BDFA is quite fast. The polymerization rates of perhaloacetaldehydes with anionic and cationic initiators have been studied more extensively in the case of the polymerization of chloral, bromal and the chlorobromo substituted acetaldehydes. (28-31) It was found that the polymerization depended very much of the extent of initiation, the mechanism of polymerization and the morphology of the polymer formed during the polymerization. In favorable cases the polymerization is complete after about 2-3 minutes but, especially when the initiation is slow and incomplete, it might take hours to complete the polymerization. (247) The reaction times reported here are the times after which the workup of the reaction was carried out and we were sure that no further reaction occurred. It is quite conceivable,

and most likely, that under slightly different conditions, a difference in yield could be obtained. Where no polymer was obtained, it can be assumed that under these conditions no initiation occurred.

3. Polymerization of DBFA. DBFA has been polymerized in the presence of both anions and cations, however, cation initiators result in significantly higher conversions.



PolyDBFA differs from polyBDFA in that regardless of initiators or conditions used no acetone soluble polymer was obtained. This can be accounted for by the increased size of the trihalomethyl group of the DBFA. Space filling molecular models show that the geometry is restricted to an isotactic helix.

The data are presented in Table 8.

TABLE 8
POLYMERIZATION OF DBFA

Polymerization Time: 24 hours

<u>Initiator</u> <u>Type</u>	<u>Amount</u> <u>in mole%</u>	<u>Polymerization</u> <u>Bath Temp., in ° C.</u>	<u>Conversion (a)</u> <u>In %</u>
LTB	0.24	25	0
LTB	4.9	-78	16
Ph ₃ P	0.26	-25	0
Ph ₃ P	0.32	-78	0
Pyridine	3.3	25	6
H ₂ SO ₄	0.51	25	80
H ₂ SO ₄ (b)	0.73	-25	35
Et ₃ Al	0.38	-78	10
Et ₃ Al	0.30	25	7
TFMSA	2.9	25	27

(a) Entire Product was Acetone Insoluble

(b) Polymerization Time: 1 Week

In terms of overall yield, cationic initiation appeared to be the more effective way of initiating this polymerization. Sulfuric acid at 0.5 mole% initiator concentration and 25° C. gave an 80% conversion to polyDBFA. The polymer is completely insoluble in acetone, which is very typical for DBFA polymerization as none of the initiators which we have studied produced any soluble fraction of polyDBFA. At -25° C.

with 0.7 mole% of H_2SO_4 , a 35% conversion of polymer was obtained after one week. The initiation of the polymerization was very slow, especially at lower temperatures, and it appeared that after 12 hours very little or no polymerization had occurred. At room temperature, 80% conversion of polyDBFA was obtained after 24 hours.

TFMSA was also an effective initiator for the DBFA polymerization. The initiator was used at 2.0 mole% concentration and the mixing of initiator and monomer was carried out at 60°C . Although the two liquids (TFMSA and DBFA) were initially immiscible, they became homogeneous after a few minutes of shaking. After five minutes of reaction gelation occurred and after one day at 27% conversion of the polyDBFA was obtained.

Et_3Al has been used in the past for oxide and cyclic ether polymerization; it was also used effectively for various aspects of aldehyde polymerizations either unmodified or modified. (7) As it is known, Et_3Al can act as an anionic or cationic initiator depending on the modifier and is often called a coordinative initiator.

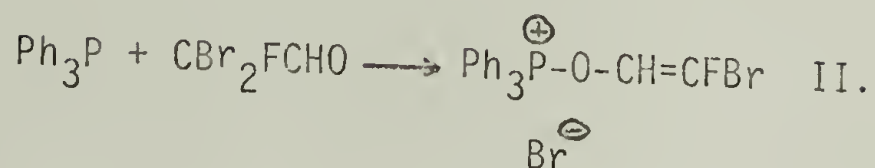
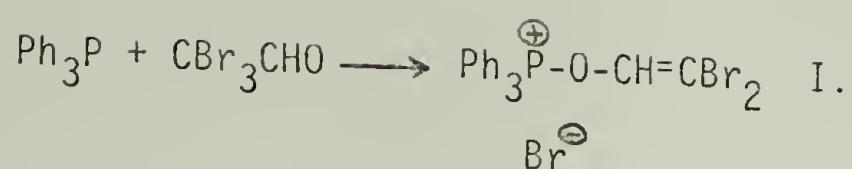
It was found that Et_3Al is a moderately active initiator for the polymerization of DBFA. At 0.3 mole% of initiator at 25°C . and at -78°C . and an approximately 10% conversion of DBFA to the polymer was obtained.

Pyridine is a common initiator for perhaloacetaldehyde polymerization and for most of the rate studies of the haloaldehyde polymerizations it was used as the standard anionic initiator. (46) As initiator for bromal polymerization pyridine had to be used under very

Carefully controlled conditions or no polymerization occurred. It was consequently believed that a similar problem might arise for the DBFA polymerization which was indeed observed. With 3 mole% of pyridine at room temperature, a low conversion of 6% of DBFA to polyDBFA was obtained.

LTB has also been a very active initiator for many aldehyde polymerizations, although it was not very effective for bromal polymerization. (28) Apparently a side reaction occurred which was believed to be bromide extraction from a bromal molecule. In separate experiments it was shown that bromide ion was not an initiator for bromal polymerization, and indeed not for any other perhaloacetaldehyde polymerization. As a consequence, it was not expected that DBFA polymerization initiated with bromide or a nucleophile of lesser activity would initiate DBFA polymerization. At best one would expect low yields of polymer.

When LTB was used at 0.24 mole% and the polymerization was carried out at 25° C. bath temperature, no polyDBFA was obtained; with a large amount, (4.50 mole%) of LTB and a polymerization bath temperature of -78° C., a yield of 16% was obtained. This reaction yield was very low in that under normal conditions, LTB produced 85% of perhaloaldehyde polymers when the substituent X of the -CX₃ groups was chlorine and fluorine. As in the case of bromal, Ph₃P at -25° C. or at -78° C. did not give polymer when it was used as an initiator for the DBFA polymerization. This is not surprising in that Ph₃P reacted with bromal to give I (28) and presumably with DBFA to give II. The bromide anion would be expected to be a poor initiator.



The polymerization of DBFA produced polyDBFA in various physical forms. In many cases a gelatinous mass was obtained which was worked up by stirring the gel in acetone whereby it was broken up and was easy to filter. On some occasions, polyDBFA was also obtained in a powdery form, but the polymer was always infusible and insoluble in all the solvents tried; no soluble fraction of DBFA has ever been isolated.

Because of the relatively small amount of DBFA available as compared to the polymerization studies using commercially available chloral and bromal, the experiments were done and the polymer yields determined with limited sample sizes. The morphology of the precipitating polymer determined the availability of the growing ends during the polymerization reactions and consequently the yields of the polymers. When they become occluded, a active but dormant polymer chain is no longer available for further polymerization because the polymers, even in the gel form, are essentially insoluble.

4. Polymerization of CDFA. In Table 9 the polymerization results of CDFA with a number of initiators are tabulated.

TABLE 9
POLYMERIZATION OF CDFA

Initiator		Polym temp., ° C.	Polym. time, hr	Polymer yield %	
Type	Amount mole%			Acetone- soluble	Acetone- insoluble
Ph_3P^a	0.8	25	1	0	54
Ph_3P^a	0.5	-78	1	19	21
Ph_3P^a	0.1	-78	1.5	46	0
Ph_3P	0.1	-78	24	0	52
Ph_3P^a	0.02	-78	50	73	0
$\text{Al}(\text{C}_2\text{H}_5)_3^a$	0.8	-78	1	0	91
$\text{Al}(\text{C}_2\text{H}_5)_3$	0.5	25	24	0	86
$\text{LiOC}(\text{CH}_3)_3^a$	0.2	-78	1	11	81
Pyridine ^a	0.3	-78	1	1	15
DMF ^a	0.3	-78	1	0	21
SbCl_5^a	0.3	-78	1	56	0
SbCl_5	0.1	-78	24	46	0
TiCl_4^a	0.3	-78	20	0	5
H_2SO_4^a	0.4	25	20 days	3	0

(a) Ref. 199.

Ph_3P , LTB, triethylamine, pyridine, and dimethylformamide were found to be active initiators when the polymerization of DCFA was carried out at a bath temperature of -78°C . after being mixed at 70°C . Ph_3P was added in 1M. toluene solution and LTB in 1M. MCH

solution. The effectiveness of dimethylformamide as an initiator is somewhat in question because of the uncertain purity of dimethylformamide after it was distilled from phosphorus pentoxide. (199)

Presumably the polymerization with these initiators proceeds via an anionic mechanism. In all cases, acetone insoluble, presumably isotactic, polymer was obtained at high yields. The initiator concentration varied from 0.8 mole% to less than 0.1 mole%. In addition to the insoluble polymer of CDFA, a noticeable fraction of soluble polymer was also obtained with LTB as the initiator.

Ph_3P was more extensively studied as the initiator for CDFA polymerization because of extensive experience with Ph_3P as initiator for chloral polymerization. Insoluble crystalline polychloral was obtained at all initiator levels of Ph_3P used.

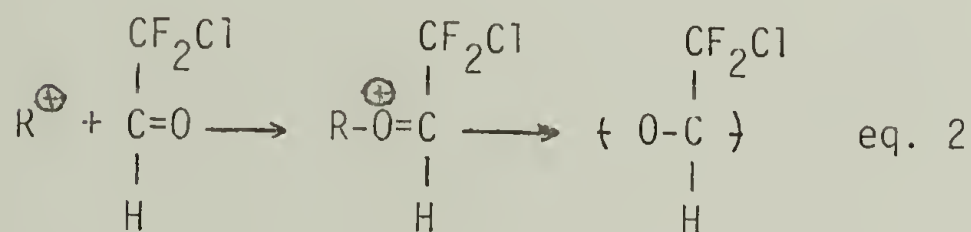
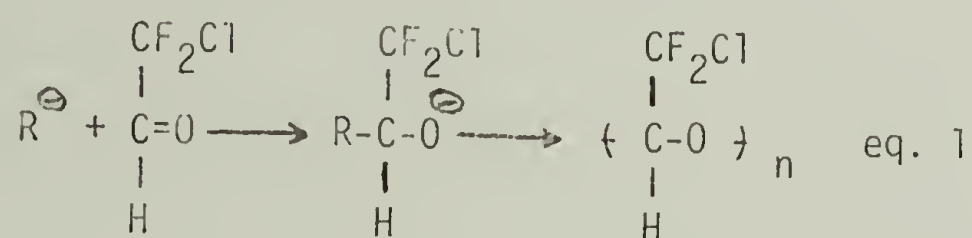
CDFA, however, polymerized with varied amounts of Ph_3P initiator to polyCDFA which was either soluble in acetone or which contained a significant soluble fraction. At high Ph_3P initiator concentration (0.8 mole%) and a polymerization temperature of 25°C ., the polymer obtained was insoluble while at low initiator concentration (0.02 mole%) and at much lower polymerization temperature, a completely acetone soluble polymer with no insoluble fraction was isolated. At initiator amounts of 0.5 mole% but at low reaction temperatures, polymer was obtained which consisted of approximately equal amounts of soluble and insoluble polyCDFA.

The polymerization results with initiators which are normally used for cationic polymerization gave somewhat inconclusive results.

TiCl_4 and sulfuric acid as initiators for the CDFA polymerization gave only small amounts of polymers after very long reaction times. However, SbCl_5 as initiator at a level of 0.3 mole% and a bath temperature of -78°C ., gave a good yield of completely soluble polyCDFA.

Fast polymerization of DCFA and fluoral (22) with SbCl_5 as initiator at a bath temperature of -78°C . had been reported previously. The polymers were insoluble in acetone in contrast to polyCDFA obtained with SbCl_5 as initiator.

According to infrared analysis, soluble and insoluble polyCDFA's have a polyoxymethylene structure regardless of the polymerization initiator used. The polymerization mechanism seems to be similar to the mechanisms proposed for the polymerization of chloral. Anionic polymerizations have a growing alkoxide as the propagating species (eq. 1), and the cationic polymerization is believed to have the oxonium ion (eq. 2) as the propagating species.



The general structure of a substituted polyoxymethylene was confirmed by the determination of the infrared spectra of polyCDFA prepared by a number of initiators and the ^1H NMR spectra of the soluble polymers.

5. Polymerization of DCFA. Polymerization of DCFA to polyDCFA was attempted with initiators which have been known to give polychloral from chloral by an anionic or cationic mechanism. Table 10 summarizes these data.

TABLE 10
POLYMERIZATION OF DCFA

Initiator		Polymerization		Conversion
Type	Amount (in mole%)	Temp. (in ° C.)	Time (in hr.)	Percent
Ph_3P	0.2	-78	48	55, (16) ^a
Ph_3P	0.4	- 5	48	70, (10) ^a
Ph_3P	0.2	30	48	77
LTB	0.2	-78	48	5
LTB	0.8	25	2	85
$\text{Al}(\text{C}_2\text{H}_5)_3$	0.5	-78	24	62
Pyridine	0.5	-78	1	12
DMF	0.5	-78	1	29
SbCl_5	0.6	-78	1	79
TiCl_4 (b)	0.2	25	2	32
H_2SO_4 (b)	0.7	25	46	82
$\text{BF}_3\text{O}(\text{Et})_2$ (c)	3.0	- 5	48	13
AlCl_3 (d)	1.2	- 5	72	24

(a). Acetone soluble polymer

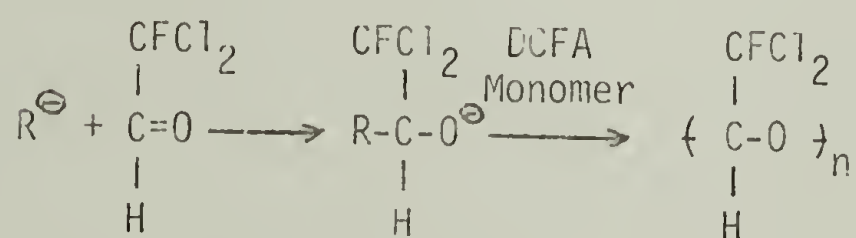
(b). No polymer after 5 days at -78° C.

(c). 50° C. methylene chloride solution.

(d). Initiator not soluble in reaction mixture.

Using LTB, an apparent anionic initiator, at an initiator concentration of 0.8 mole% at 25⁰ C. gave insoluble polyDCFA at 80% conversion when the reaction was terminated after five days. No soluble fraction was observed. A more extensive study of the polymerization of DCFA was done with Ph₃P as the initiator. At 30⁰ C. and an initiator concentration of 0.2 mole%, a 77% yield of acetone insoluble polymer was obtained. At -5⁰ C. the total yield was 80% of which 10% was acetone soluble. At -78⁰ C. and with 0.2 mole% Ph₃P, the total yield of polyDCFA was 70% of which 15% was acetone soluble.

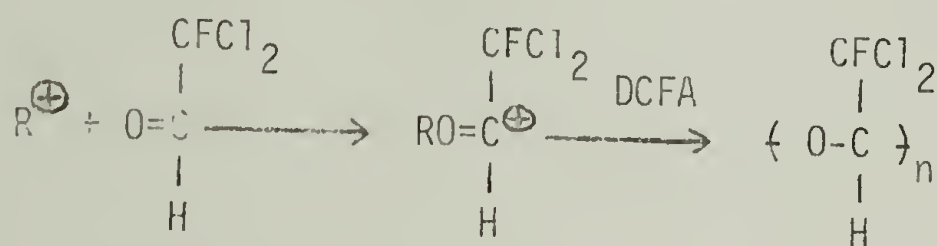
It is believed that the polymerization of DCFA with these initiators is caused in a similar way to the polymerization of chloral. The initiation step, therefore, would be the addition of tertiary butoxide ion to the carbonyl carbon of DCFA in the case LTB and the addition of chloride ion to DCFA in the case of Ph₃P (248). The propagation of this polymerization is undoubtedly via the alkoxide ion to form the polyacetal:



No attempts have been made to identify specifically the termination of this polymerization other than to characterize the final polymer before and after acetylation by thermal degradation.

Polymerization of DCFA with typical cationic initiators has also been studied. These initiators gave exclusively acetone insoluble polymers. With antimony pentachloride at 0.6 mole% concentration at -78⁰ C.,

approximately 80% yield of insoluble polyDCFA was obtained after one hour. However, with TiCl_4 as the initiator at 0.2 mole% at 30°C . an insoluble polymer was isolated in 32% yield after two hours but no polymer was observed after eight days at -78°C . Likewise with H_2SO_4 82% of insoluble polymer was isolated after 48 hours at 25°C . but no polymer was obtained after five days at -78°C . Boron tri-fluoride etherate at 3 mole% concentration at -5°C . gave, after 48 hours, 13% of insoluble polyDCFA. Cationic polymerization is believed to initiate and propagate through the oxocarbenium ion.



When the initiating species was a proton, for example when sulfuric acid was used on the initiator, at least one end of the polymer chain was known to be hydroxyl group. This was confirmed by infrared and end capping studies.

PolyDCFA is a polyoxymethylene substituted with a dichlorofluoromethyl group. It has been shown that cationic initiators as well as anionic initiators are effective for the polymerization of DCFA. The rate of polymerization, or better, the rate of conversion of DCFA to polyDCFA was not determined but it seems to be slower and more erratic than in the case of the polymerization of chloral. Our studies of polymerization conditions, the selection of the type and concentration of initiators are qualitative investigations and no specific effort was made to produce optimum yields.

E. Copolymerization

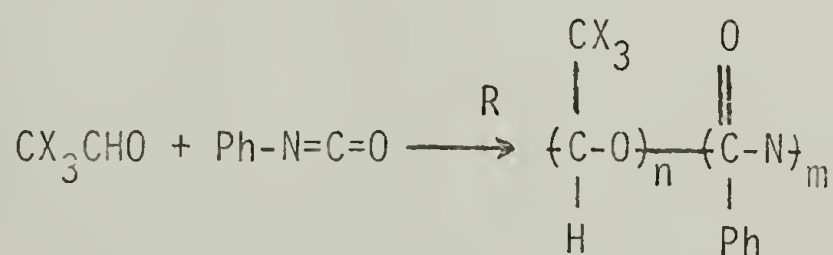
1. Copolymerization with perhaloacetaldehydes. Copolymerization of the set of monomers with one another followed by analysis of the product formed was useful in determining the relative reactivities of the monomers. Each of the four monomers was polymerized with chloral using at least one cationic and one anionic initiator. The data are presented in Table 11.

Infrared spectra indicate that the products are true copolymers and not mixtures of homopolymers.

CDFA and DCFA were copolymerized with one another at -5°C . with Ph_3P to further establish the relative reactivities. Although 48% of the feed was CDFA, 67% of the soluble polymer (2% conversion) and 59% of the acetone insoluble fraction (35% conversion) was found to be CDFA.

These data indicate that the presence of fluorine in an acetaldehyde increases the relative reactivity whereas bromine reduces it, relative to chloral.

2. Copolymerization with PhNCO . Each of the four monomers was copolymerized with phenyl isocyanate (PhNCO).



The amount of PhNCO in the copolymer was determined by elemental analysis for nitrogen.

TABLE 11
COPOLYMERIZATION OF PERHALOACETALDEHYDES WITH CHLORAL

Comonomer	% Chloral in Feed	Polym. Temp. (° C.)	Polym. Time (Hrs.)	Initiator	Conversion % Sol. Insol.	Comonomer in Product Sol. Insol.
DCFA ^a	52	30	1	TiCl ₄	0 50	--- 100
DCFA ^a	50	- 5	1	Ph ₃ P	10 70	68 64
DCFA	54	25	1	Ph ₃ P	0 72	--- 73
DCFA ^a	52	-78	1	SbCl ₅	0 57	--- 55
DCFA	50	0	1	SbCl ₅	0 87	--- 60
CDFA ^a	48	- 5	1	Ph ₃ P	2 67	35 59
CDFA	50	25	1	Ph ₃ P	45 0	85 ---
CDFA	48	25	1	SbCl ₅	0 61	--- 60
DBFA	50	25	24	H ₂ SO ₄	0 16	--- 40
DBFA	49	24	24	Pyridine	0 10	--- 56
BDFA	55	-25	24	SbCl ₅	25 0	87 ---
BDFA	50	-25	24	Ph ₃ P	24 28	82 82

(a) Ref. 199.

TABLE 12
COPOLYMERIZATION OF PERHALOACTALDEHYDES WITH PhNCO

2 mole% Ph_3P

Comonomer	Mole % PhNCO In Feed	Temp. ($^{\circ}\text{C}$)	% Conversion		% PhNCO	
			Sol.	Insol.	Sol.	Insol.
CDFA	40	25	0 ^a	25	---	2
DCFA	50	25	0 ^a	17	---	7
DCFA ^b	50	- 5	0	0	---	---
BDFA	48	-25	20	0	30	---
DBFA	50	25	0	13	---	1.4

(a) In addition to copolymer, diphenyl urea was formed.

(b) Ref. 199.

PhNCO does not copolymerize well with these monomers, as reflected both in the overall conversion to polymer and in the amount of PhNCO found in the copolymers. Lipp found higher conversions in PhNCO copolymers with bromal and bromochloroacetaldehydes and also that the incorporation of PhNCO decreased with the increasing reactivity of the comonomer. (28-31) Therefore the low PhNCO content of copolymers from these even more reactive monomers might be expected.

Both of the chlorofluoroacetaldehyde-PhNCO copolymerizations produced diphenyl urea as a side product. This of course is soluble in acetone and may be confused for a soluble fraction. The material however was highly crystalline and the IR was unlike that of a polyacetal copolymer. It was identified through the IR and melting point,

both of which confirmed it to be diphenyl urea, or carbanilide.

F. Homopolymer Characterization

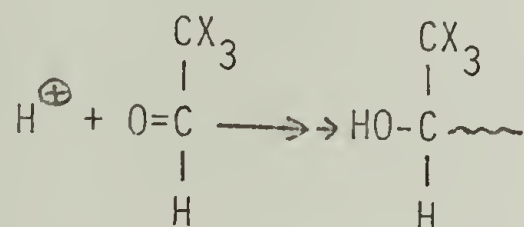
Since most of the homopolymers of perhaloacetaldehydes are insoluble in organic solvents, the methods available for their characterization are extremely limited. They can be classified as acetone soluble or insoluble, KBr pellet infrared spectra may be recorded, thermal stabilities measured, and degradation products collected, empirical elemental analysis determined and x-ray diffraction patterns photographed. In addition, for the few soluble polymers NMR (^1H , ^{19}F and ^{13}C) and such molecular weight determinations as V P O and I V are possible.

1. Infrared spectroscopy. Each of the homopolymers examined exhibited an IR spectrum characteristic of polyacetaldehydes. Further information on the assignment of absorbance frequencies can be obtained by comparison to the spectrum of polychloral analyzed in detail by Takida and Noro (155), Table 13. The infrared spectra of homopolymers made in this study are described in the experimental sections and illustrated in Appendix I.

TABLE 13 (155)
INFRARED SPECTRUM OF POLYCHLORAL

Wave number cm.^{-1}	Intensity	Motion
3500	vs	OH stretching
3360	w	OH stretching
2945	m	C-H stretching
2910	w	C-H stretching
1386	w	combination 803+852
1360	m	C-H bending
1325	s	C-H bending
1122	vs	C-O stretching
1085	vs	C-O stretching
1070	vs	C-O stretching
1028	m	C-H bending
975	vs	C-O stretching
842	vs	
830	vs	C-C and C-Cl
803	vs	Stretching
681	s	C-Cl stretching
675	s	C-Cl stretching
630	w, sh	skeletal non cryst.
582	s	C-Cl stretching

It can be seen that there are obvious similarities between polychloral and polychlorofluoroacetaldehydes and polybromofluoroacetaldehydes. There were no observable differences in absorption frequencies between the soluble and insoluble fractions of either polyBDFA or polyCDFA. In addition, the nature of the initiator does not affect the IR spectrum of the polymers with the exception of the size of the hydroxyl band at approximately 3000 cm^{-1} . This is increased, for example, with a protic initiator such as H_2SO_4 where the mechanism of initiation generates a terminal hydroxyl group.



Acetylation, used as a thermal stabilization technique, also is evident in an IR spectra by replacing the hydroxyl absorption at 3500 cm^{-1} with a carbonyl band at 1750 cm^{-1} . PCl_5 treatment causes no observable spectral changes. These observations agree with data from a careful analysis of the IR spectra of chloral made by Corely and Vogl to determine the effects of various endcapping treatments. (181, 182)

2. Nuclear magnetic resonance. Due to the insolubility of most of the homopolymers only soluble fractions of polyCDFA and polyDCFA could be examined by NMR. The ^1H NMR spectra obtained are shown in Figures 34 and 40. ^1H NMR spectra were unresolved singlets even at temperatures as high as 105° C . in TCE. This suggests that although the polymer is soluble the chains are still fairly rigid

resulting in long relaxation times and poor resolution of the NMR.

^{19}F NMR spectra were extremely broad bumps only and not at all resolved.

3. Vacuum degradation and analysis. As described in the experimental sections at least one sample from each homopolymer was vacuum degraded to the monomer which was then analyzed by GC and NMR. Since these polymers have relatively low ceiling temperatures reversal of the polymerization equilibrium can be carried out without molecular degradation of the monomers. The ability to revert to monomers in high conversion and purity supports the polyacetal structure. Both soluble and insoluble fractions underwent depolymerization quantitatively to monomers.

4. Thermal stability analysis by DTG. Due to the insolubility of most polyperhaloacetaldehydes most methods of characterization are not applicable. Careful interpretation of the thermal stability data, therefore, is essential for an insight into the structure of these polymers.

Thermal stabilities were measured by heating 10 mg. of the sample at 10^0 C./min. in a nitrogen atmosphere in a DTG. The derivative mode was recorded to find the temperature at which decomposition occurred at the highest rate. These data are summarized in Tables 14-17.

TABLE 14
MAXIMUM DEGRADATION RATE TEMPERATURE OF POLYDCFA

Initiator Type	Polymerization Temperatures(^o C.)	Max. Degr. Rate Temp.(^o C.)	
		Raw	PCl ₅ Stabilized
LTB	25	255	385
Ph ₃ P	-78	150	235
Ph ₃ P	- 5	sol. 108	240
		insol. 121	230
TiCl ₄ *	30	280	320
SbCl ₅ *	-78	255	370
Et ₃ Al	-78	305	385
Et ₃ Al	25	177,317	385
H ₂ SO ₄	25	257	380

* Ref. 199, 202; stabilization with acetic anhydride.

TABLE 15
MAXIMUM DEGRADATION RATE TEMPERATURE OF POLYCDFA

Initiator Type	Polymerization Temperature(^o C.)	Max. Degr. Rate Temp. (^o C.)			
		Insoluble Fraction		Soluble Fraction	
		Raw	PCl ₅ Stabilized	Raw	PCl ₅ Stabilized
Ph ₃ P	-78	---	---	115	250
Ph ₃ P	25	---	---	125	240
LTB *	-78	235	370	220	380
H ₂ SO ₄ *	25	---	---	165,230	375
Et ₃ Al *	-78	160,215	370	---	---
Et ₃ Al	25	220	348	---	---
SbCl ₅	-78	---	---	270	350

* Ref. 199,202. Stabilization by acetic anhydride.

TABLE 16
MAXIMUM DEGRADATION RATE TEMPERATURE OF POLYDBFA

Initiator Type	Polymerization Temperature(^o C.)	Max. Degr. Rate Temp. (^o C.)	
		Raw	PCl ₅ Stabilized
Pyridine	25	153,222	230,341
LTB	-78	223	340
H ₂ SO ₄	-25	262	365
H ₂ SO ₄	25	259	363
Et ₃ Al	25	279	360
Et ₃ Al	-78	292	363
TFMSA	25	220	358

TABLE 17
MAXIMUM DEGRADATION RATE TEMPERATURE OF POLYBDFA

Initiator Type	Polymerization Temperature(° C.)	Max. Degradation Rate Temp., in ° C.			
		Insol. Polymer Fraction		Sol. Polymer Fraction	
		Raw	PCl ₅ Treated	Raw	PCl ₅ Treated
LTB	-78	222	389	---	---
LTB	25	220	390	---	---
Ph ₃ P	-78	165	240	161	240
Ph ₃ P	25	---	---	160	240
Pyridine	25	218	380	205	---
H ₂ SO ₄	25	196	411	195	412
Et ₃ Al	-78	230	316	---	---
Et ₃ Al	25	246	377	---	---
SbCl ₅	-78	---	---	201	---

From these data it can be concluded that in general the thermal stabilities of chlorofluoroacetaldehydes and bromofluoroacetaldehydes polymerized with Ph_3P are lower than those polymers from other initiators. This observation is in agreement with data for chloral and bromochloroacetaldehydes. Maximum degradation rate temperatures for the raw Ph_3P initiated polymers are in the range of 110-150° C. depending on the polymerization conditions. After acetylation the maximum degradation rate temperature increased only to a range of 190-240° C., depending on the individual sample. It is however, important to realize that the maximum degradation rate temperature of the stabilized polymers obtained from the polymerizations with Ph_3P , or more correctly triphenyl divinyloxy phosphonium chloride, as the initiator were almost in the same range as the polymer obtained directly with cationic initiators without acetylation. This result indicates that the polymer obtained with Ph_3P as the initiator has one end group which is relatively labile but could not be acetylated.

It can be concluded that polymers as prepared by anionic or cationic initiators give polymers with unstable endgroups. Polymers prepared with sulfuric acid as initiators have hydroxyl endgroups. Samples prepared with other initiators have unstable endgroups of unknown structure or have hydroxyl endgroups which are introduced during the workup of the reaction (precipitation with hydroxylic solvents). In both cases samples could be acetylated. Once stabilized all of the haloacetaldehydes polymers, except those polymerized with Ph_3P , had nearly the same highest maxima. The instabilities therefore

are associated with the endgroups and not inherent in the polymer backbone.

DTG spectra of raw and stabilized polymers are shown in Figures 41-51.

5. Stabilization of polymers. As polymerized all of the perhaloacetaldehyde polymers were found to have low to marginal thermal stabilities. This of course limits the utility of the products derived from these materials. However, it was found that these polymers could be stabilized by post-polymerization treatments which included acetylation with acetic anhydride or reaction with PCl_5 in carbon tetrachloride. Starting with any given sample both methods were found to impart equivalent thermal stability to the polymers as measured by DTG. It has been reported that the addition of up to 2 mole% of acetyl chloride to a polymerization mixture initiated by Ph_3P resulted in a stabilized polychloral without affecting the polymerization or necessitating post-polymerization treatment. (249) Similarly, hindered aliphatic isocyanates, unlike aromatic isocyanates which form copolymers, react slowly with the polychloral to give stable endgroups. (182)

The fact that the polymers are effectively stabilized through alterations of the endgroups indicates that the endgroups as polymerized are the source of instability. The hydroxyl endgroups are sufficiently acidic that they will react with even weak bases such as pyridine or piperidine to form alkoxide groups which unzip readily to monomer. Even without added base the monomer and polymer are in equilibrium as is evidenced by the ever present odor of monomer even in acetone

extracted insoluble fractions. Endcapping of the unstable polymer greatly increases both its thermal stability by DTA and its chemical stability in the presence of bases. This probably results from replacement of the liable hydroxyl endgroup by an acetoxy (acetic anhydride) or chlorine (PCl_5).

6. Solubilities of organic solvents. Each of the polymers was ground to a fine powder and slurried overnight in acetone. The mixture was filtered and the filtrate poured into ice water to precipitate any acetone soluble polymer fraction. Previously only fluoral had been found to give a soluble polymer. (25) It has now been found that polyBDFA and polyCDFA can give soluble and/or insoluble polymer fractions depending on polymerization initiators and conditions. It can therefore be concluded that the space filling size of the trihalomethyl substituent of the perhaloacetaldehyde (which after polymerization) becomes the side group of the polyacetal chain) determines the solubility of the polymer. This is most probably due to the greater spatial requirements of the larger (non-fluorine containing) groups preventing polymerization in any configuration other than isotactic through meso placement of the incoming monomer unit as the exclusive stereochemistry of propagation of polymerization. The diameters of the trihalomethyl side groups have been calculated: CF_3 group: 3.3 \AA , CCl_3 group: 4.3 \AA , CBr_3 group: 4.8 \AA . (46)

7. Wide angle x-ray diffraction patterns. Using the $\text{CuK}\alpha$ source as described in the experimental section, Debye-Scherrer x-ray diffraction

patterns were obtained from powdered samples of the insoluble poly-perhaloacetaldehydes. The photographs are shown in Figures 21-25. The diameters of the concentric circles were measured and the interplanar crystalline spacings were calculated. These data are shown in Table 18.

These data show that all of the polymers examined are at least semicrystalline. The spacings for the DCFA, CDFA, BDFA and DBFA homopolymers were found to be larger than those for chloral and bromal. This must be due to a less densely packed crystalline structure due to less rigidity in the backbone. This can be correlated with space filling molecular models in which the small side groups allow more flexibility of the backbone and in turn more distance between atoms of adjacent pendant side groups than is possible with chloral and bromal.

TABLE 18
INTERPLANAR SPACINGS OF POLYACETALDEHYDES

<u>Polychloral^a</u>	<u>Poly ClF₂ CHO (insoluble)</u>	<u>Poly Cl₂F CHO</u>	<u>Poly Br₂F CHO</u>	<u>Poly Br F₂ CHO (insoluble)</u>	<u>Polybromal^a</u>
8.70	9.14	15.72	9.88	9.88	9.30
5.00	4.80	8.80	5.69	5.07	5.40
3.30		5.07	5.02	4.55	3.60
2.73		4.55	4.55	3.61	2.80
2.40		4.13	3.61		
		3.28			

(a) Ref. 28.

A more detailed interpretation of the diffraction patterns would require a rigorous and systematic study of the patterns of a series of polyacetaldehydes beginning with polyacetaldehyde, polychloroacetaldehyde, etc., through the higher members of the series.

G. Copolymer Characterizations

1. Copolymers with perhaloacetaldehydes. Copolymers of perhaloacetaldehydes were made by polymerizing known amounts of two monomers and determining the compositions of the copolymers obtained by elemental analysis and/or GC analysis of the vacuum degradation products. Further characterization including IR and DTG provides evidence that the products are true copolymers and not mixtures of homopolymers.

Both soluble and insoluble fractions were obtained. Rate data were determined.

a. Relative rates of copolymerization. Relative rates of copolymerization were obtained from a comparison of the monomer feed ratios to the copolymer composition. Chloral was used as the reference comonomer with which the other comonomers were polymerized. The results are summarized in Table 19.

In addition, a copolymerization of CDFA and DCFA (48:52) was carried out using Ph_3P as the initiator. Both soluble and insoluble polymer were obtained (2 wt % soluble, 67 mole % CDFA and 35 wt % insoluble, 59 mole % CDFA).

The data show that the reactivities of the monomers are $\text{BDFA} > \text{CDFA} > \text{DCFA} > \text{Chloral} > \text{DBFA}$. Lipp also copolymerized chloral

TABLE 19
 PERHALOACETALDEHYDE COPOLYMER COMPOSITIONS
 Copolymers with Chloral

<u>Comonomer</u>	<u>Mole % Comonomer in feed</u>	<u>Initiator</u>	<u>Mole % Comonomer in Copolymer</u>
BDFA	55	SbCl ₅	87
	50	Ph ₃ P	82'
DBFA	50	H ₂ SO ₄	40
	49	Pyridine	56
DCFA	50	SbCl ₅	60
	54	Ph ₃ P	61
CDFA	48	SbCl ₅	60
	50	Ph ₃ P	85

' 28% conversion to insoluble fraction,
 24% to soluble fraction. Both had the
 same chemical composition. All other
 copolymers were insoluble only.

with BDCA and CDBA using pyridine as the initiator. (30, 31) He found for a 50-50 feed the copolymers contained 25% BDCA and 12% CDBA, respectively, with chloral. These data are consistent with those presented in Table 19 showing that fluorine containing acetaldehydes are more reactive than chlorine substituted ones which are more reactive than bromine containing monomers. It can also be noted that the relative rates of copolymerization of difluoro substituted monomers are greater with anionic initiators than with cationic initiators. Dibromo and dichloro monomers are relatively insensitive to the type of initiator. This would be expected from the higher electronegativity of the difluoromethyl group and its inductive effect toward anionic initiation.

b. Vacuum degradation to monomer. In the methods described each of the copolymers was degraded quantitatively to comonomers. These monomer mixtures were characterized by GC to determine the ratios of monomers and thereby the compositions of the copolymers shown on Table 19. NMR's were also recorded for selected monomer mixtures and found to show mixtures of the two monomers as expected.

c. Infrared spectra of copolymers. Infrared spectra of the various copolymers were recorded to ascertain that they were not a mixture of two homopolymers. The spectra obtained were found not to be superpositions of the spectra for the two homopolymers so were concluded to be of true random copolymers. See Figure 6, 15 and 19.

The infrared spectra of mixtures of two homopolymers show several distinct differences from the spectra of the copolymers which makes

differentiation possible. The most easily observed of these is in the aldehydic proton stretching band at $2940 - 2955 \text{ cm}^{-1}$. For example, the aldehydic proton stretching frequencies are: polychloral, 2945 cm^{-1} ; polyBDFA, 2950 cm^{-1} and copoly(BDFA-chloral), a single sharp peak at 2951 cm^{-1} . Differences were also observed in the "fingerprint region", 1000 cm^{-1} to 600 cm^{-1} which differentiated between the homopolymer spectra superposition of the mixtures and the spectra of the copolymers.

There were, however, similarities between the spectra of the copolymers and the homopolymers which indicate similarities in conformational structure. All of the copolymers are likely to be in a helical structure like polychloral.

d. Thermal analysis of copolymers. The DTG spectra also indicated, through the observation of one peak instead of two, that the copolymers were true copolymers and not mixture of two homopolymers.

TABLE 20
THERMAL STABILITIES OF COPOLYMERS WITH CHLORAL

<u>Comonomer</u>	<u>Initiator</u>	<u>DTG Max., Raw</u>	<u>DTG max., Stabilized</u>
BDFA	SbCl ₅	205 ° C	386 ° C
	Ph ₃ P	156	260
DBFA	H ₂ SO ₄	246	380
	Pyridine	210	320
DCFA	SbCl ₅	262,392	392
	Ph ₃ P	172	207
CDFA	SbCl ₅	250	375
	Ph ₃ P	150	230

These data are summarized in Table 20. The thermal stabilities of the copolymers follow the same trends as the homopolymers in that the stabilities are increased significantly by treatment with PCl_5 and the copolymers resulting from Ph_3P initiation are much less stable than those resulting from other initiators. The overall stabilities of the copolymers are, in general, similar to those of the homopolymers. (Tables 15-17). The same conclusions can therefore be drawn as for the homopolymers relating stability and structure.

2. Copolymers with isocyanates.

a. Conversions and solubilities. Copolymers with 50 mole % PhNCO feed were made as described and characterized. These copolymers unlike the chloral- PhNCO copolymers, were all opaque. The BDFA gave a wholly soluble copolymer whereas the CDFA copolymer had both soluble and insoluble fractions. Both of the monofluoro substituted copolymers were totally insoluble. This is most likely due to the smaller spacial volume of the pendant side group giving the molecular chain increased flexibility. This is consistent with the earlier observations that the homopolymers of BDFA and CDFA also gave soluble fractions under proper conditions.

TABLE 21
CONVERSIONS AND SOLUBILITIES OF COPOLYMERS OF PERHALOACETALDEHYDES AND PhNCO

<u>Comonomer</u>	<u>Total Conversion</u>	<u>% Soluble</u>
BDFA	25	100
DBFA	13	0
DCFA	17	0
CDFA	36	30

b. Rates of copolymerization. Copolymers with PhNCO were analyzed by elemental analysis. The copolymers, unlike chloral - phenyl isocyanate copolymers were opaque and in general the reactivity rates were reduced relative to chloral.

TABLE 22
COPOLYMERIZATION OF ALDEHYDES WITH PhNCO

<u>Comonomer</u>	<u>Mole % in Feed</u>	<u>Initiator</u>	<u>Analysis for % N</u>	<u>% Isocyanate in polymer</u>
BDFA	52	Ph ₃ P	4.0	30
DBFA	50	Pyridine	0.11	1.4
DCFA	47	Ph ₃ P	0.67	6.6
DDFA	1	Pyridine	0.85	8.4

' Analysis of the insoluble fraction.

The values obtained for PhNCO incorporation obtained by nitrogen analysis were supported by infrared spectral intensities of the carbonyl stretching absorption at 1740 cm^{-1} in the copolymers. The absorption strengths varied in the same order as the nitrogen contents.

c. Thermal stabilities of PhNCO copolymers. The thermal stabilities of the copolymers were measured by DTG.

TABLE 23
THERMAL STABILITIES OF PhNCO COPOLYMERS

<u>Comonomer</u>	<u>DTG Maxima, ° C.</u>			
	<u>Insoluble</u>		<u>Soluble</u>	
	<u>Raw</u>	<u>PCl₅</u>	<u>Raw</u>	<u>PCl₅</u>
BDFA	---	---	150	210
DBFA	230	350	---	---
DCFA	152	187	---	---
CDFA	226	277	274	320

The data show little or no increase in thermal stabilities of the raw copolymers compared to the homopolymers. This suggests that for these products the presence of the isocyanate linkages in the chain does not prevent unzipping to monomer. Corley reported increased stability of chloral through endcapping by terminating the polymerization with hindered aliphatic isocyanates such as isopropyl isocyanates (182), but this was not investigated in this study.

A. Abstract

Tetrachloroethylene oxide has been synthesized by direct oxidation of tetrachloroethylene with oxygen in the presence of ultraviolet light. This preparation resulted in a mixture of tetrachloroethylene oxide and trichloroacetyl chloride in approximately equal amounts under the most favorable conditions. Tetrachloroethylene oxide rearranges readily to trichloroacetyl chloride above 60° C. with an activation energy E_a of 3.0×10^4 cal./mole and a pre-exponential factor A of 1.9×10^{13} . All attempts to polymerize tetrachloroethylene oxide under a variety of conditions failed.

B. Introduction

The literature on the preparation and polymerization of epoxides is extensive. (250, 251) It includes studies of ethylene oxide (252), propylene oxide (253), 2-butene epoxide (254-256), epichlorohydrin (257), 1,4-dichlorobutene-2 epoxide (258), as well as other halogenated epoxides which are basically derivatives of ethylene oxide. (259-269) The polymerizations of these epoxides are carried out with electrophiles, Lewis and Bronsted acids, and to a smaller extent with nucleophilic initiators. In recent years coordinative anionic initiators derived from aluminum alkyls and zinc alkyls by reaction with water and alcohols, have been used extensively for the polymerization of epoxides.

The preparation and polymerization of completely halogenated

epoxides, mostly perfluorinated epoxides (261-269), is published primarily in the patent literature. Tetrafluoroethylene (TFE) was oxidized to tetrafluoroethylene oxide (TFEO) directly with oxygen in the presence of γ -irradiation or ultraviolet light (267) or with H_2O_2 or KMnO_4 . (269) TFEO rearranged readily to trifluoroacetyl fluoride and could be pyrolyzed to carbonyl fluoride and difluorocarbene (270); it hydrolyzed slowly to oxalic acid and HF. With fluoride ions TFEO was polymerized to oligomers. (263) At -195°C . TFEO was polymerized to high molecular weight crystalline polyTFEO which has a melting point of 42°C . (264) Hexafluoropropylene oxide (HFPO) has been synthesized from hexafluoropropylene (HFP) by a number of chemical oxidation methods as well as by direct photochemical oxidation with oxygen. (271) HFPO did not react with radicals or ultraviolet light. However, it could be pyrolyzed to difluorocarbene and trifluoroacetyl fluoride. (272) With ionic catalysts it rearranged to hexafluoroacetone or pentafluoropropionyl fluoride, depending upon the exact reaction conditions. (273) With anionic initiators, preferably with fluoride ions, rubbery polymers of a molecular weight up to 10,000 with unusually good thermal stability have been obtained; cesium fluoride in tetraglyme at relatively low temperatures was the preferred initiator system. (275, 276) The molecular weight of these polymers is limited because of the ease of chain transfer by the fluoride ion which caused chain termination by the formation of acid fluoride end groups and initiation of a new chain.

The direct oxidation of tetrachloroethylene (TCE) was known to

IV. OTHER RESEARCH - A PRACTICAL SYNTHESIS
OF TETRACHLOROETHYLENE OXIDE

result in the formation of trichloroacetyl chloride and phosgene. (274) Kirkbride (275) was able to identify, in addition to trichloroacetyl chloride (TCAC), tetrachloroethylene oxide (TCEO); he oxidized TCE with oxygen in the presence of a mercury arc and chlorine gas at 50-60° C. After partial oxidation the mixture was treated with water which hydrolyzed TCAC to trichloroacetic acid and left a solution of TCEO in TCE. TCEO was not actually isolated but was converted with aluminum chloride to TCAC. This preparation was later repeated, and TCEO was isolated in a yield of 0.9%. (276) In addition to a considerable amount of TCAC, hexachloroethane was found in this residue. It was found that TCEO rearranged to TCAC with an activation energy of 51.4 kcal./mole. TCEO boiled at 110° C./760 "mm" and melted at -59° C. TCEO was hydrolyzed with sulfuric acid or 1 N potassium hydroxide/methanol solution to oxalic acid. The isolation of TCEO from the reaction mixture was difficult and could not be effected readily because the boiling points of TCEO, TCAC, and TCE are 110, 118, and 121° C., respectively at 760 "mm". The range of boiling points is even less at 40 "mm", at which pressure it was necessary to distill the mixture in order to avoid rearrangement of TCEO to TCAC during the distillation.

The infrared spectrum of TCEO was studied in detail by Derkosch and co-workers. (277)

Dobrov and Poluektov (278, 279) studied the oxidation of TCE to TCEO in the presence of Co-60 γ -radiation and obtained TCEO in 20% yield. They also developed and used for the first time a gas

chromatographic analysis for the characterization of the reaction mixtures. They did not, however, make an effort to optimize the yield of the oxidation nor did they isolate preparatively TCEO. They postulated a mechanism for the formation of TCEO in an attempt to explain all the observed products and rate equations. In addition to TCAC and TCEO they identified phosgene and hexachloroethane as by-products of the oxidation of TCE. Other workers had also found that the photochemical decomposition of TCAC can lead to the formation of phosgene and hexachloroethane. (280)

Jeffrey (281) also investigated more recently the oxidation of TCE and found that it can be accomplished with either oxygen or air in the presence of free radical initiators such as azo compounds and peroxides. He also found that this oxidation could be carried out at 60-100⁰ C. and at pressures of 200-300 psi. in the absence of commonly used inhibitors in TCE. Jeffrey found that at 80⁰ C. and approximately 20% TCE conversion, a reaction mixture was obtained which contained 50% TCAC, 40% TCEO, and 10% phosgene. It was not convenient for him to carry out the reaction to more than 20-25% TCE conversion. Above a reaction temperature of 100⁰ C., the yield of TCEO dropped rapidly. The yield of TCEO was not very dependent on the AIBN concentration or the reactor pressure. Most yields of TCEO were about 20% according to their analysis.

It was the purpose of this work to investigate the preparation of TCEO from TCE and optimize the reaction conditions, to study the thermal decomposition of TCEO, and to carry out typical reactions

of TCEO with particular emphasis on attempts to use TCEO as a monomer for homo- and copolymerization.

C. Experimental

1. Preparation of TCEO and attempted polymerization.

a. Oxidation of TCE. TCE (700 g.) was placed in a 500 ml photochemical reaction vessel which surrounded a quartz immersion well containing a Hanovia 450-W medium-pressure ultraviolet light source filtered by a sleeve of Pyrex or Vycor. The vessel was equipped with a thermometer, condenser, and sparge to introduce oxygen at the center of the bottom of the TCE cavity which also provided agitation. Water was circulated from a constant temperature bath through the jacket surrounding the TCE cavity and also around the immersion well. The water heated the TCE and cooled the lamp (Figure 52). In a typical experiment the reaction was carried out at 80⁰ C. and oxygen was bubbled through the reaction mixture at the rate of 300 ml./min. After the mixture was sparged sufficiently with oxygen (10 min.) the lamp was turned on, and samples were taken at intervals and analyzed by gas chromatography (GC). For the preparative synthesis of TCEO, the photooxidation was stopped when it was determined, by GC, that all TCE had been oxidized; this took approximately 10 hr. at 80⁰ C. After the reaction was completed, oxygen was bubbled through the solution for a few additional minutes in order to remove phosgene. The solution was then poured onto ice, and the TCAC was allowed to hydrolyze at 0⁰ C. It is essential that the temperature not rise

substantially because TCEO might rearrange to TCAC or hydrolyze to oxalic acid at higher temperatures. As the acid chloride was hydrolyzed, 10% sodium hydroxide solution was added to maintain a pH of 7. After the hydrolysis was complete, the product was washed three times each with ammonium carbonate, ammonium hydroxide solution, and finally with water. TCEO was dried over magnesium sulfate and distilled at $46^{\circ}\text{C./68 mm.}$ yield, 120 g. A distillation residue remained which was identified as hexachloroethane by infrared spectra and a melting point of $185\text{--}186^{\circ}\text{C.}$ (lit. (282) mp. $183\text{--}184^{\circ}\text{C.}$).

TCEO should be stored below 0°C. in sealed ampules in order to avoid rearrangement of the compound. TCEO showed a single peak in the ^{13}C spectrum at 129.4 MHz (5.72 ppm.) upfield from the carbon tetrachloride resonance. The infrared spectrum was identical with that described in the literature. (276) Figure 61.

b. Thermal rearrangements of TCEO. Approximately 0.05 g. of TCEO was sealed into each of several ampules, 4 mm.x 30 mm., which had been dried and flushed with nitrogen prior to their use. Before the sealed ampules were used they were stored at -20°C. (no rearrangement was detected by GC). An equal number of ampules were also prepared which contained TCEO and 5 mole % LTB (1.25 M. in MCH). A few tubes contained TCEO and 30 vol.% MCH as diluent to study concentration effects.

For the study of the rate of rearrangements, each of the three groups of ampules were placed in a thermostatted oil bath at 80, 95, and $100 \pm 0.2^{\circ}\text{C.}$ The ampules were withdrawn at intervals and

analyzed by GC.

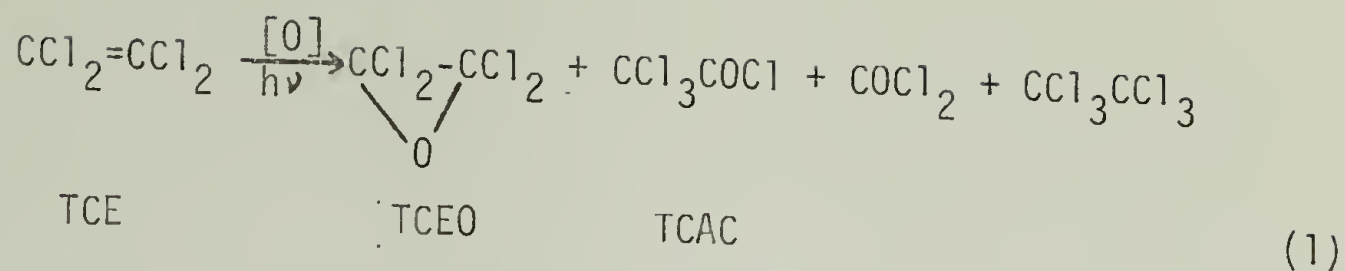
c. Attempted polymerizations of TCEO. Ampules were prepared from 8 mm. ID Pyrex tubing and had a capacity of 2-3 ml. One end was sealed and a constriction was made between the ends to give a 1-2 mm. ID neck for easier sealing. Typically, the initiator was placed in the dried, nitrogen flushed ampule by injecting it through a septum in the case of liquids or solutions, or by adding a solid quickly under nitrogen. The tube was then transferred to a vacuum line and the ampules were evacuated using liquid nitrogen as the coolant. Degassed TCEO was transferred under vacuum of 0.025 mm. into the ampule. The individual ampules were sealed, weighed and placed in the baths of appropriate reaction temperatures: -78, -25, or 25° C.

After the specified time, the tubes were opened, volatile liquids were transferred under vacuum to another ampule and the presence of nonvolatile materials was noted. The volatile products were then analyzed by gas chromatography.

Copolymerizations were attempted in the same manner. Both monomers were distilled into the ampule at 0.025 mm. and the relative volumes estimated from the liquid heights in the ampule.

D. Results and Discussion

1. Synthesis and rearrangements. TCEO was synthesized directly by photooxidation of TCE in good yield and the optimum conditions were determined [Eq.(1)].



Earlier work (275-281) on the synthesis of TCEO consisted of oxidation of TCE in the presence of ultraviolet light with or without additional sensitizer such as chlorine or oxidation with radical initiators. It was found that the use of chlorine produced a substantial amount of hexachloroethane as a by-product and the yield of TCEO was lowered.

Photooxidation to TCEO does not occur at a reasonable rate below 60° C., and above 80° C. the rearrangement to TCAC becomes significant. Figure 53 shows the relative concentrations of TCE, TCEO, and TCAC for a typical photooxidation at 80° C. It can be seen initially that the TCEO concentration exceeded that of TCAC. As a consequence, it appeared that TCAC was produced primarily by the rearrangement of TCEO to TCAC.

A better comparison for the relative formation of TCEO and TCAC can be obtained when the yield of TCEO and the conversion of TCE are plotted as functions of oxidation time. In Figure 54, on using a Pyrex filter at 60° C., it is shown that the initial yield of TCEO was nearly 60% at low conversion of TCE. After 24 hr. the yield of TCEO had dropped below 45% at a conversion of 70% of TCE. At 80° C., with the use of a Pyrex filter, the initial yield of TCEO was near 60% at a conversion of 10% of TCE and decreased after

12 hr. to approximately 40% to 80% conversion of TCE (Figure 55). Figure 56 shows a slightly higher rate, but similar tendency, when using a Vycor filter.

As earlier investigators have pointed out, much of the problem of isolation of TCEO was the separation of three compounds with very close boiling points where one of the compounds is thermally unstable and cannot be held at the boiling point for an extended period of time. Some investigators (276) first hydrolyzed TCAC, isolated the solution of TCEO in TCE, chlorinated TCE, and then isolated TCEO which is much lower boiling than the hexachloroethane.

TCEO was isolated preparatively by oxidizing TCE completely to a mixture of TCAC and TCEO. TCAC could then be removed by hydrolyzing the mixture in ice water to HCl and trichloroacetic acid (water soluble); TCEO could be isolated and distilled directly. The initially high yield of TCEO at low TCE conversion was ultimately reduced at high TCE conversions. Nevertheless, a 20% distilled yield of TCEO could be realized at 100% conversion after a relatively simple work-up procedure.

It has been known that TCEO rearranged thermally to TCAC. From the work on HFPO and TFE0 it was suspected that this rearrangement is ionic in character and was probably catalyzed by trace amounts of nucleophilic or electrophilic compounds present as impurities. As a consequence, TCEO was purified for the degradation studies to a high degree until the GC chromatogram showed less than 100 ppm. of impurities. The thermal rearrangement of TCEO at

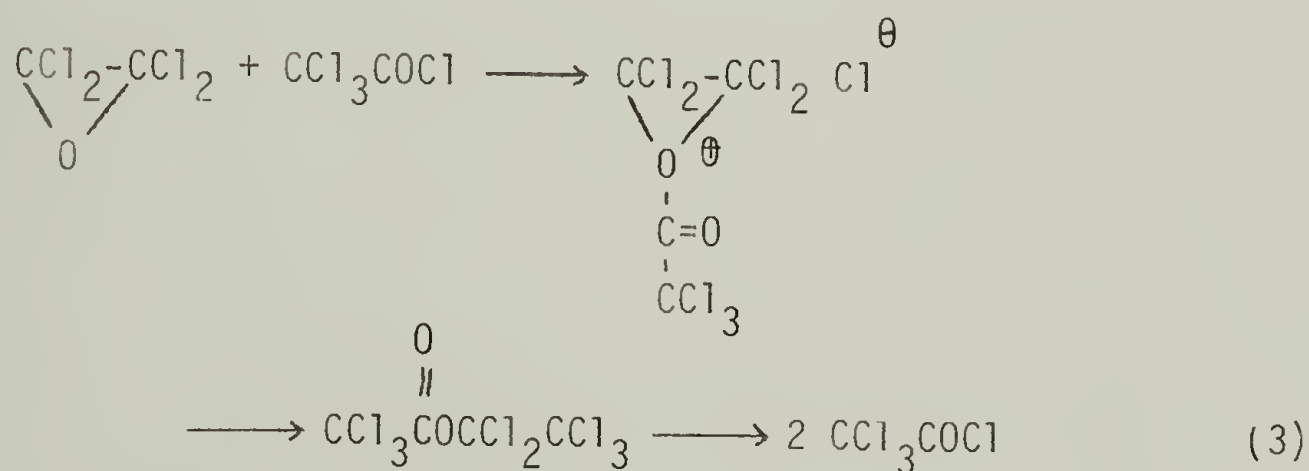
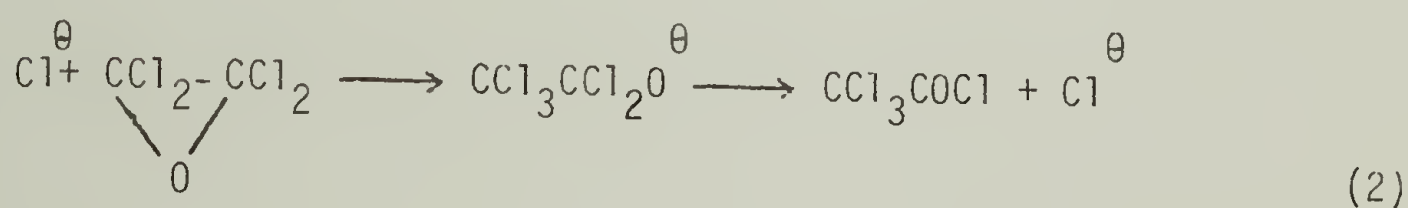
80, 95, and 110⁰ C. is shown in Figures 32, 33 and 34. (57-59). Thermal rearrangement of TCEO at 80⁰ C. (Figure 57B) and at 95⁰ C. (Figure 58B) was also carried out in the presence of LTB in an attempt to neutralize acidic impurities.

It was expected that if the general rearrangement was influenced by nucleophiles, the rearrangement of TCEO to TCAC should have been accelerated in the presence of LTB. On the other hand, if it were influenced by acidic impurities, the presence of LTB should have retarded the thermal rearrangement reaction. As it may be seen from Figures 57B and 58B, the thermal rearrangement of TCEO was not substantially influenced by the presence of LTB although it could be argued that LTB reacted relatively rapidly with the TCEO and was rendered useless after a brief period. The position of the second data point in both Figures 57B and 58B could be interpreted as indicating that there is an inhibition of the thermal reaction which might indicate that this thermal reaction is actually acid catalyzed. The effect of the diluent, MCH, was found negligible.

TCEO probably rearranges to TCAC by the following mechanism. Trace chloride ion impurities cause the initial formation of TCAC from TCEO [Eq.(2)], but the "uncatalyzed" rearrangement is actually catalyzed by TCAC [Eq.(3)], which was formed by the reaction of Eq. (2).

The thermal rearrangement of TCEO followed first-order kinetics with a rate constant of $9.2 \times 10^{-6} \text{ sec}^{-1}$ at 80⁰ C., 5.35×10^{-5} at 95⁰ C., and 2.5×10^{-4} at 110⁰ C. The rate constants could be

plotted on an Arrhenius plot, and the activation energy E_a and the pre-exponential factor A were determined (Figure 60) as $E_a = 3.0 \times 10^4$ cal./mole and $A = 1.9 \times 10^{13}$, in very good agreement with Frankel's results. (276) A similar study was made for the thermal rearrangement of TFE0 by Lenzi and Meli. (270) They measured the rates of rearrangement between 119 and 141⁰ C. and found them to be first order in this temperature range. They calculated values for E_a of 3.36×10^4 cal./mole and $A = 5 \times 10^{13}$. Gozzo and Camaggi (283) also studied the reactivity of TFE0 and found that liquid TFE0 did not react with butyllithium but did rearrange to the acid fluoride with BF_3 . This observation seems to be similar to our observation that LTB was also unreactive toward TCE0.



2. Reactions of TCE0. It was also found, as Frankel (276) reported earlier, that TCE0 reacted with methanol to give methyl trichloroacetate. In addition, dimethyl oxalate was also identified by its gas chromatographic retention time as well as by its infrared spectrum after isolation. (284) Ginsberg (285) had also isolated diethyl

oxalate from the reaction of TFE0 with ethanol.

When TCE0 was allowed to react with equimolar amounts of ethanol, ethyl trichloroacetate was obtained as the primary reaction product, and ethyl oxalate as a by-product. After 12 hr. reaction time at room temperature, TCE0 reacted with isopropanol to give the two expected esters, but in the case of tertiary butyl alcohol and TCE0 after 24 hr. only the tertiary butyl trichloroacetate, but no oxalate, was isolated.

TCE0 reacted with a number of primary, secondary, and tertiary amines to form water-soluble salts which were not characterized further.

Dimethyl sulfoxide reacted readily with TCE0 to form a gel. On addition of water, a white solid deposited which was identified by its infrared spectrum as paraformaldehyde. The 2,4-dinitrophenylhydrazine was also prepared and was identical with formaldehyde 2,4-dinitrophenylhydrazone (mp. 164-165⁰ C., pure or mixed).

3. Attempted polymerization and copolymerizations of TCE0. Attempts were made to carry out the homopolymerization of TCE0. Compounds which are known to act as either cationic or anionic initiators were added to TCE0 and were allowed to react at various temperatures for up to 4 weeks. Up to 2 mole% of the potential initiators were used at temperatures of -78, -25, and 25⁰ C. In no case has any polymer of TCE0 been observed although some compounds caused the rearrangement of TCE0 to TCAC even at -78⁰ C. SbCl₅, FeCl₃, Ph₃P, and Pruitt's catalyst (FeCl₃/epichlorohydrin) (286) gave a 100% yield

of TCAC at 25° C. TCEO was also quantitatively converted to TCAC with SbCl_5 at -25 and at -78° C. In the presence of CsF (with pentaglyme or 1 vol. % 15-crown-5 crown ether) at 25 and at -78° C., an 80% TCEO to TCAC transformation was obtained. $\text{CF}_3\text{SO}_3\text{H}$ gave only 5% rearranged TCAC at -25 and -78° C. TCEO remained unchanged with LTB at 25° C., with butyllithium and LTB at -25° C., and with Ph_3P , butyllithium, and LTB at -78° C. With Et_3Al and $\text{Et}_3\text{Al}:\text{H}_2\text{O}$ (1:1) at -78° C. no rearrangement was observed, but at 25° C. a reaction of TCEO with the aluminum alkyls was noticed which caused the formation of TCAC. The same mixture of 60% TCEO and 40% TCAC was also obtained when an ethereal solution of EtMgBr was added to TCEO. The results of these attempted polymerizations are shown in Table 24.

TABLE 24
ATTEMPTED HOMOPOLYMERIZATIONS OF TCEO
(Reaction Time: 2 Weeks)

Potential Initiator	Composition of product		
	25° C.	-25° C.	-78° C.
SbCl ₅	100% TCAC	100% TCAC	100% TCAC
FeCl ₃	100% TCAC	-	-
Pruitt's Catalyst	100% TCAC	-	100% TCAC
CF ₃ SO ₃ H	-	95% TCEO + 5% TCAC	95% TCEO + 5% TCAC
CsF (Pentaglyme or 15-crown-5-ether)	20% TCEO + 80% TCAC	-	30% TCEO + 70% TCAC
Ph ₃ P	100% TCAC	-	100% TCEO
BuLi	-	100% TCEO	100% TCEO
LtB	100% TCEO	100% TCEO	100% TCEO
Et ₃ Al or Et ₃ Al:H ₂ O (1:1)	60% TCEO + 40% TCAC, dark brown solution	-	No reaction until warmed to 25° C.; then same product mixture as at 25° C.
EtMgBr (ether)	60% TCEO + 40% TCAC	-	-

Attempts were also made to polymerize TCEO with ultraviolet and γ -irradiation. TCEO samples (0.5 ml.) were sealed into a quartz tube under vacuum. The sealed tubes were cooled to -80° C. and placed 8 cm. from the ultraviolet lamp. No filter sleeve was used, and the TCEO received the full spectrum of light. After 40 min. the solution had turned pale yellow, and after 1.5 hr., a reddish brown. No further changes occurred until the reaction was stopped after 16 hr. GC analysis of the liquid showed that about 80% of TCEO had rearranged to TCAC.

TFEO had been successfully polymerized to high molecular weight, crystalline polyTFEO by γ -irradiation from a Co-60 source. It was reported that the highest rate of polymerization was achieved a few degrees below the melting point of TFEO and no polymer was formed in the liquid state. (264)

A number of samples of TCEO were vacuum sealed and placed in a Dewar flask containing Dry Ice and chloroform to maintain the temperature below the melting point of TCEO. The Dewar was then placed in a radiation field with an intensity of 72,000 rad./hr. as measured by ferrous sulfate dosimetry. (287) Two samples were removed at each of three intervals after receiving the indicated amount of radiation. In 6.25, 23.5 and 28.5 hr. the samples were exposed to 0.45, 1.70, and 2.05 Mrad., respectively. No polymers were formed in either case, and the volatile material was shown by GC to be identical to the original TCEO in all cases.

Attempts were also made to use TCEO as comonomer with various

monomers. Solid polymers were found in some copolymerization attempts as shown in Table 25. When the material was isolated, the infrared spectrum in each case showed it to be homopolymer of the starting monomer without evidence of incorporation of any TCEO. This information was useful and demonstrated that there were no impurities in the sample of TCEO which terminated polymerization. The lack of polymerizability was inherent in TCEO.

TCEO with an equimolar amount of epichlorohydrin with Et_3Al at 25°C . gave an oily liquid, but at -25°C . a solid amorphous polymer was formed in good yield. The infrared spectra showed these to be polyepichlorohydrin with no incorporation of TCEO. Propylene oxide and TCEO at a 3:2 ratio with $\text{Et}_3\text{Al}:\text{H}_2\text{O}$ at -25°C . gave a low yield of amorphous polymer which was identified as poly(propylene oxide) homopolymer. TCEO with trioxane at a ratio of 1:1, 3:1, and 1:3 with SbCl_5 in TCE at 45°C . gave a high yield of polyoxymethylene homopolymer, and gas chromatographic analysis of the mother liquid showed that TCEO had remained unchanged. Butadiene and TCEO at the ratio of 1:1 and 1:5 with butyllithium in hexane at 25°C . gave no polymer but a small amount of water-soluble residue which was identified as lithium chloride. Homopolymerizations of epichlorohydrin, propylene oxide, trioxane, and butadiene were carried out under the same conditions as the attempted copolymerization in order to see if TCEO had interfered with the polymerization in any way. This did not seem to be the case. In all cases, the homopolymers were obtained in good yield.

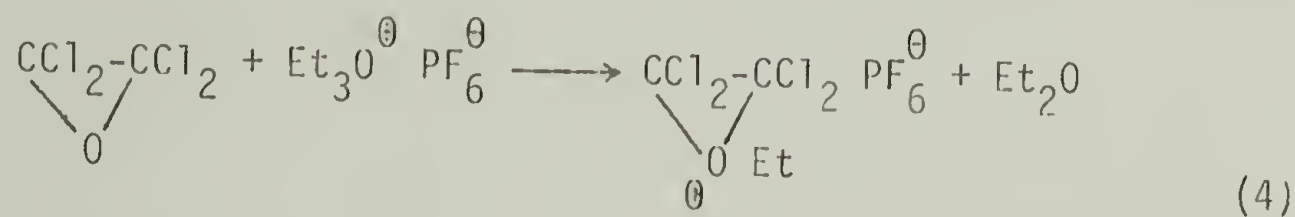
TABLE 25
ATTEMPTED COPOLYMERIZATION OF TCEO
(Reaction Time: 2 Weeks)

Comonomer (ratio) ^a	Initiator ^b (solvent)	Temperature (° C.)	Observations
Epichlorohydrin, 1:1	Et ₃ Al (Hexane)	25	Oily Liquid
		-25	Solid amorphous polymer formed in good yield; shown by IR to be pure PECH with no TCEO incorporated
Propylene oxide	Et ₃ Al:H ₂ O	-25	Low yield of amorphous polymer shown by IR to be PPO homo- polymer
Trioxane 1:1 3:1 1:3	SbCl ₅	45	High yield of POM homopolymer; GC shows TCEO unchanged
Maleic anhydride 1:15	SbF ₅ (Neat)	55	No change; GC showed 5% TCEO, 95% TCAC
Phenyl isocyanate 2:1	Ph ₃ P (Hexane)	-78	No change; GC showed only unchanged starting materials
Butadiene 1:1 1:5	BuLi (Hexane)	25	No polymer; small amount of water-soluble residue (LiCl)
Tetrahydrofuran 1:1	Et ₃ Al	-25	No change
Dioxane 1:1	Et ₃ Al	25	No change

^aTCEO: comonomer ratio ^bInitiator concentration 1.0 mole%.

Attempts at copolymerization of TCEO were made with PhNCO at a 2:1 ratio with Ph_3P in hexane at -78°C . and at a 1:1 ratio with Et_3Al at -25°C . No physical change was observed, and the gas chromatographic analysis showed that TCEO had not rearranged.

TCEO was also treated with triethyloxonium hexafluorophosphate, an initiator for cationic polymerization of cyclic ethers. There was no change either in the physical appearance or in the GC analysis of the mixture on standing 3 hr. at 25°C . The ^1H NMR spectrum of equimolar solutions of TCEO and the triethyloxonium salt in dichloromethane showed no detectable interaction between the triethyloxonium cation and the oxygen of TCEO. Such a reaction would liberate diethyl ether, which would be detectable by NMR in concentrations as low as 3 mole% of the oxonium salts (289) [Eq. (4)]. It was therefore concluded that TCEO is stable to cationic attack by this initiator.



From these experiments it can be concluded that TCEO could readily be prepared in good yield and at high polymerization grade purity. It did not polymerize or copolymerize under a variety of conditions, nor did it undergo an alkylation reaction on the oxygen atom of the tetrachlorooxirane ring. The electron deficiency of the oxygen seems to be responsible for this behavior. The electron deficiency of the carbonyl oxygen of chloral is also responsible for the poor performance of chloral in cationic polymerization. (290)

Rearrangement of TCEO to TCAC was readily accomplished with acids or thermally by an apparently ionic mechanism. This would allow TCEO to be used as an acylating agent at the end of a reaction. TCEO could be used as an inert solvent or diluent for an ionic polymerization. The reaction could be carried out without interference of the acylation reagent and the acylating agent could be simply generated by heating after the polymerization was completed.

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APPENDIX

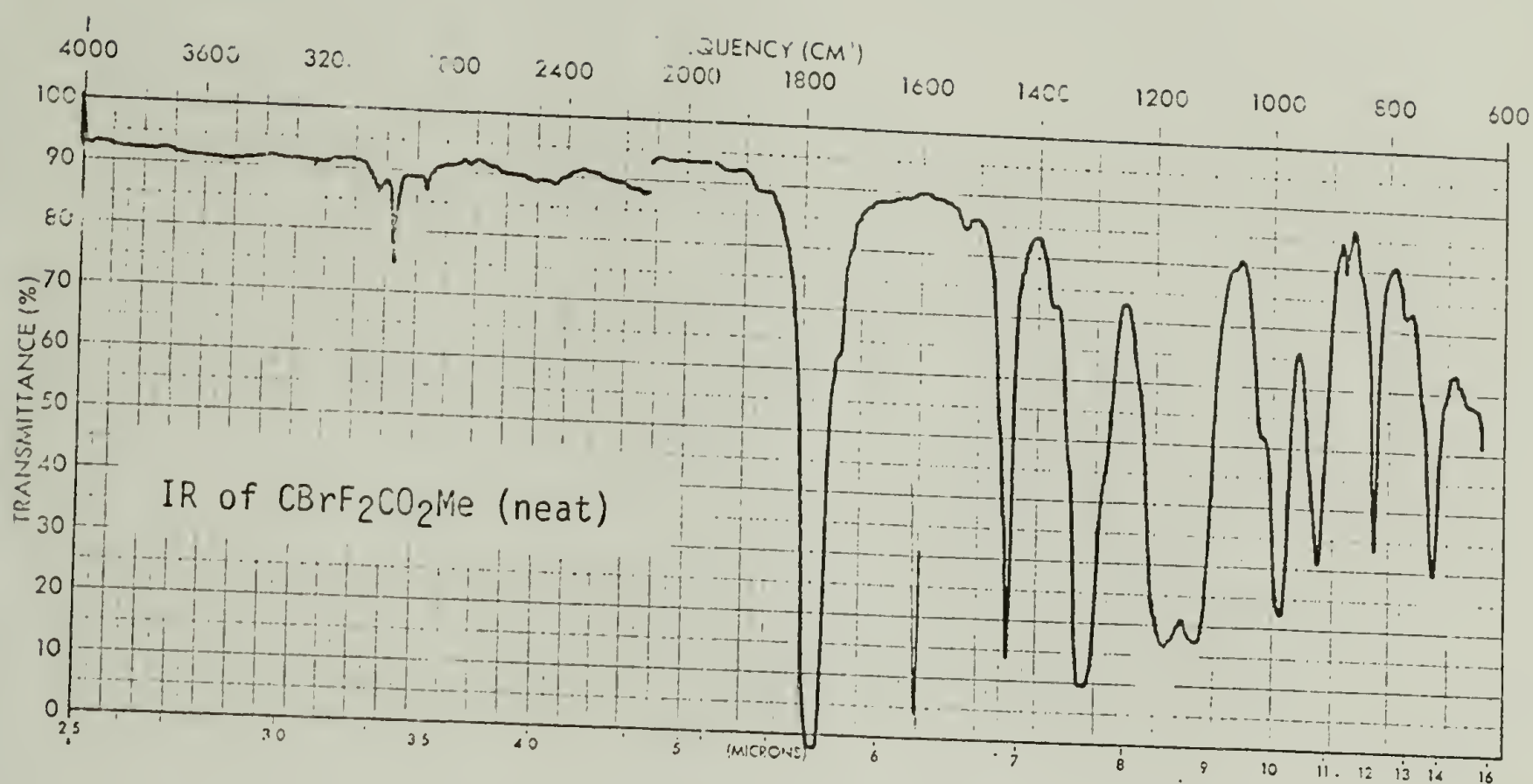


FIGURE 1

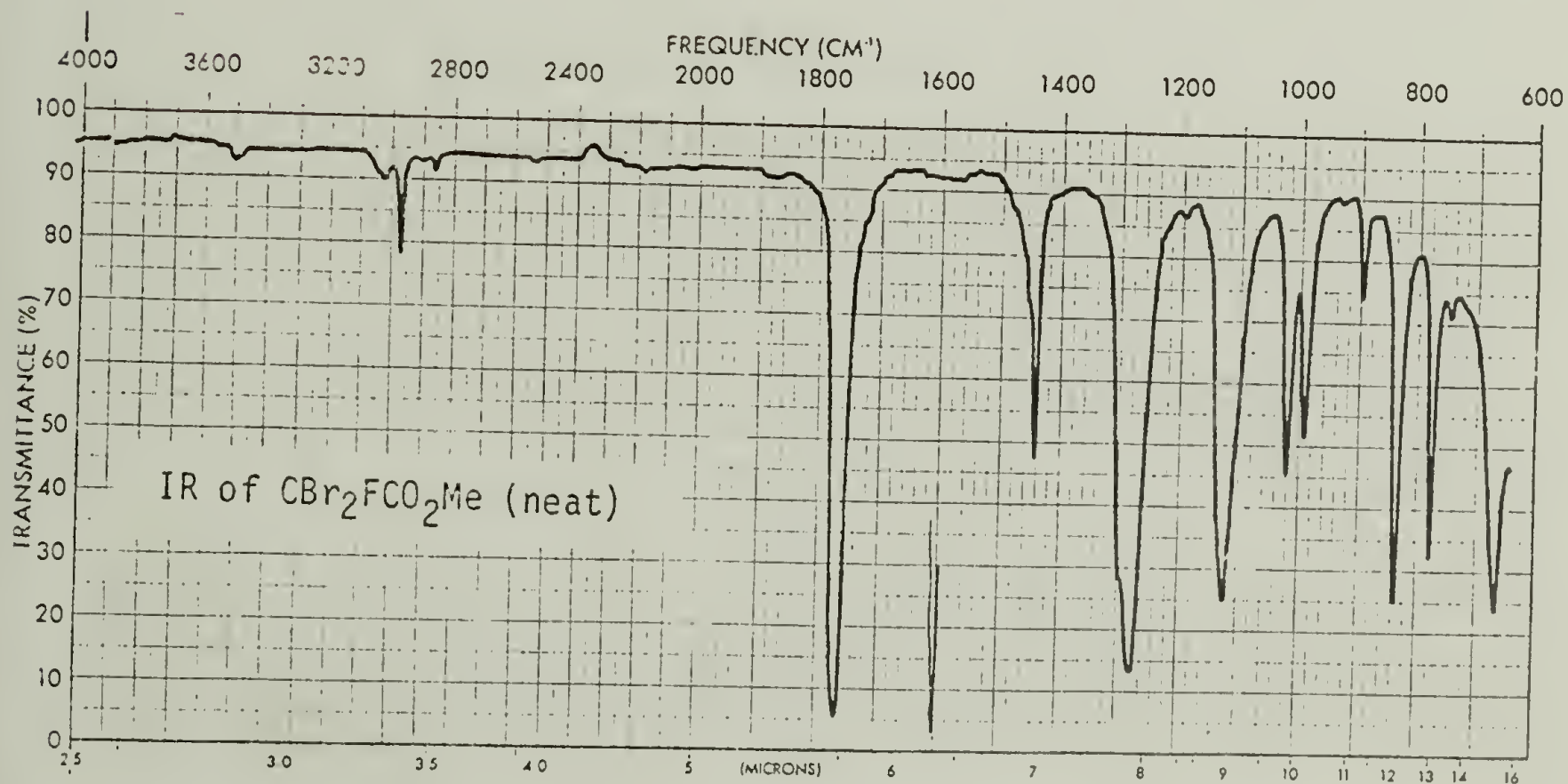


FIGURE 2

IR Spectrum of Bromodifluoroacetaldehyde

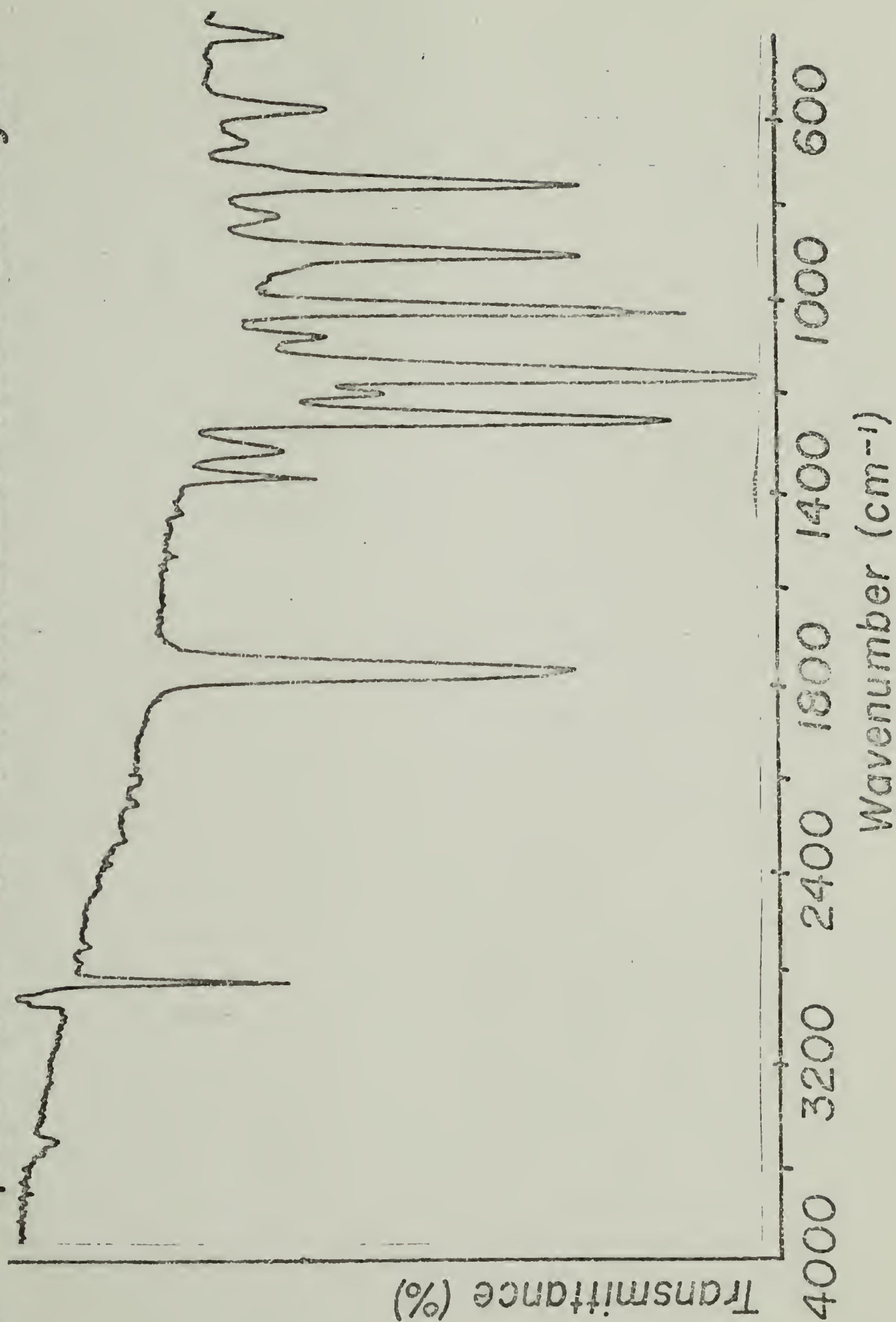


FIGURE 3

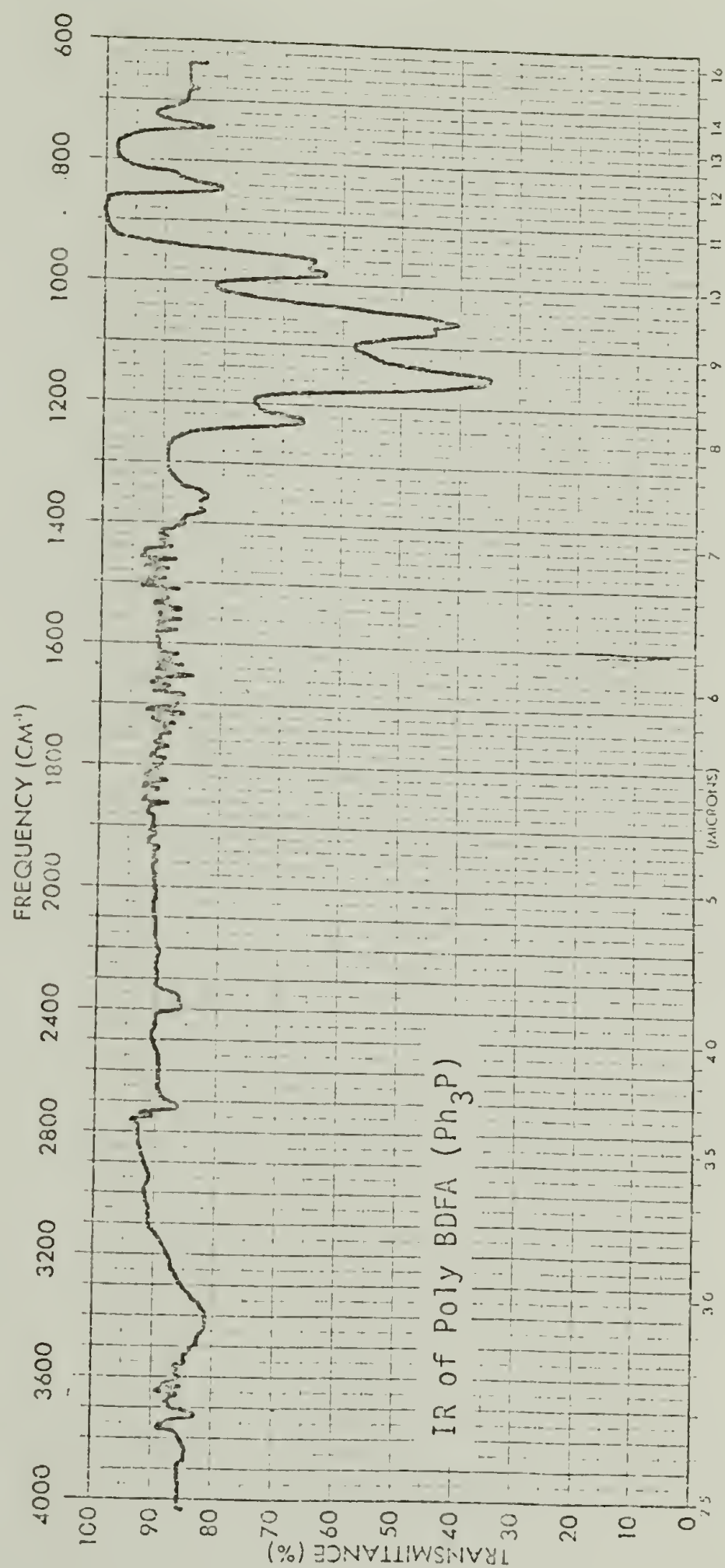


FIGURE 4

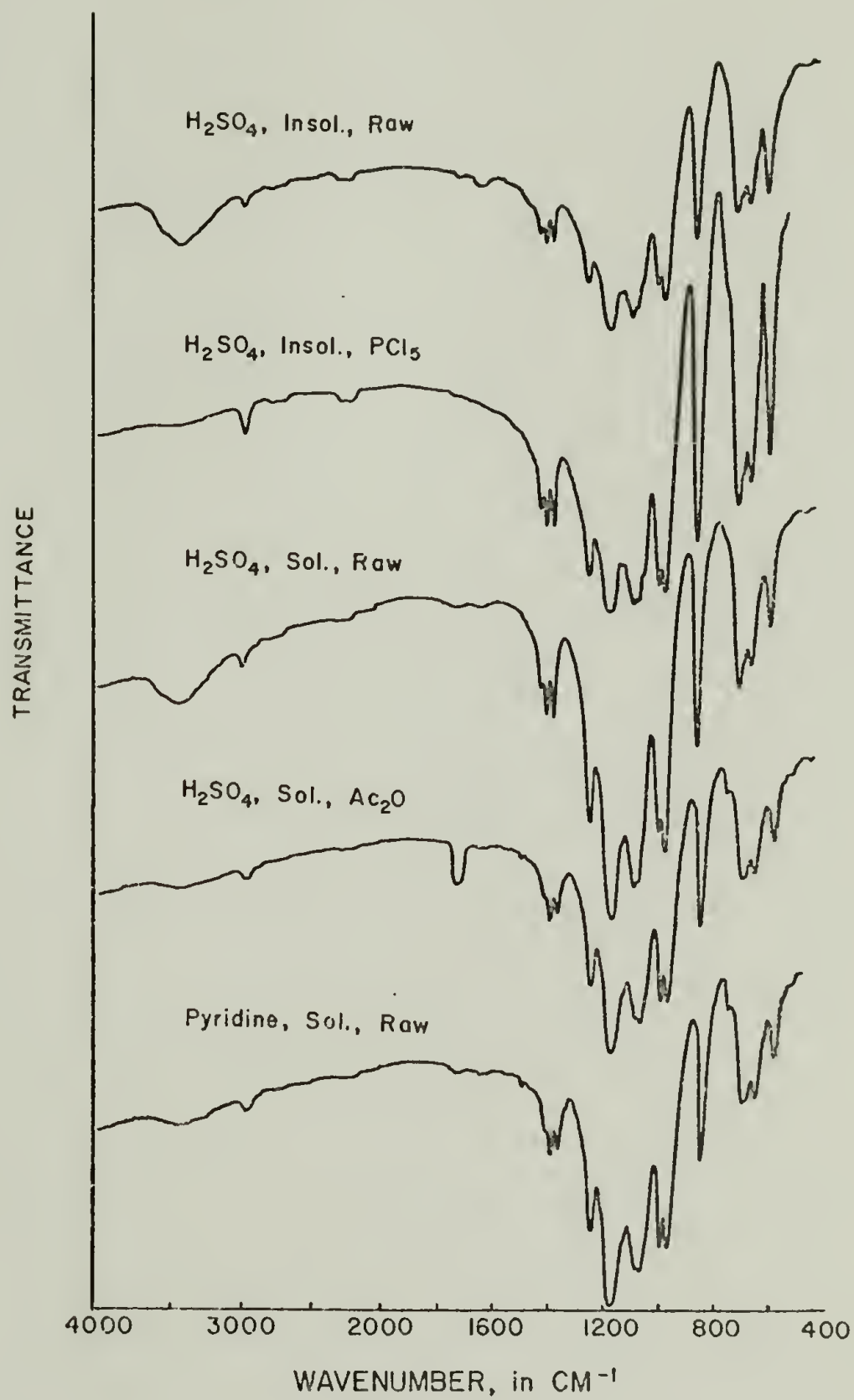
IR SPECTRA OF POLY-CBrF₂CHO

FIGURE 5

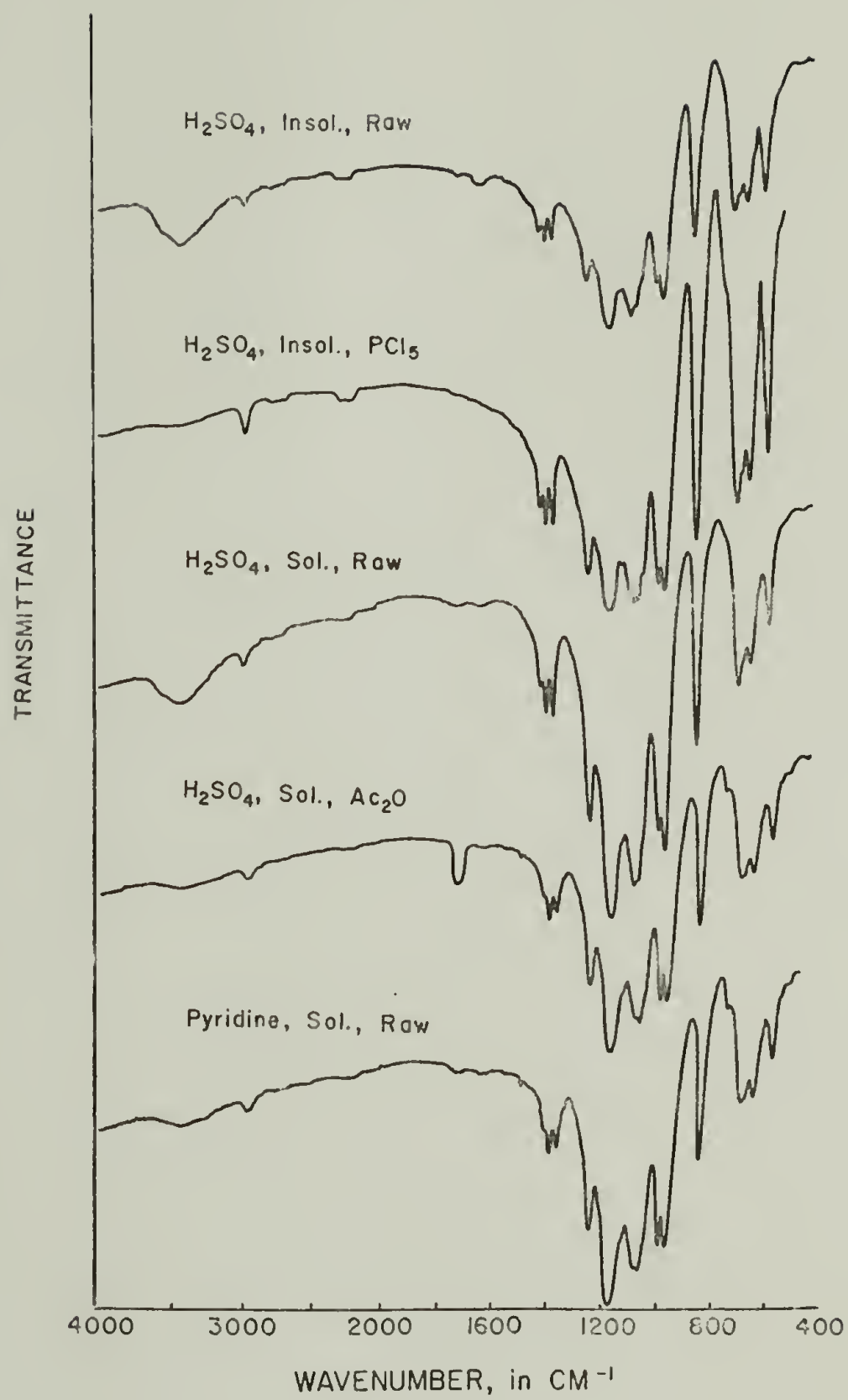
IR SPECTRA OF POLY-CBrF₂CHO

FIGURE 5

IR Spectrum of Chloral + BDFA Copolymer (Ph₃P)

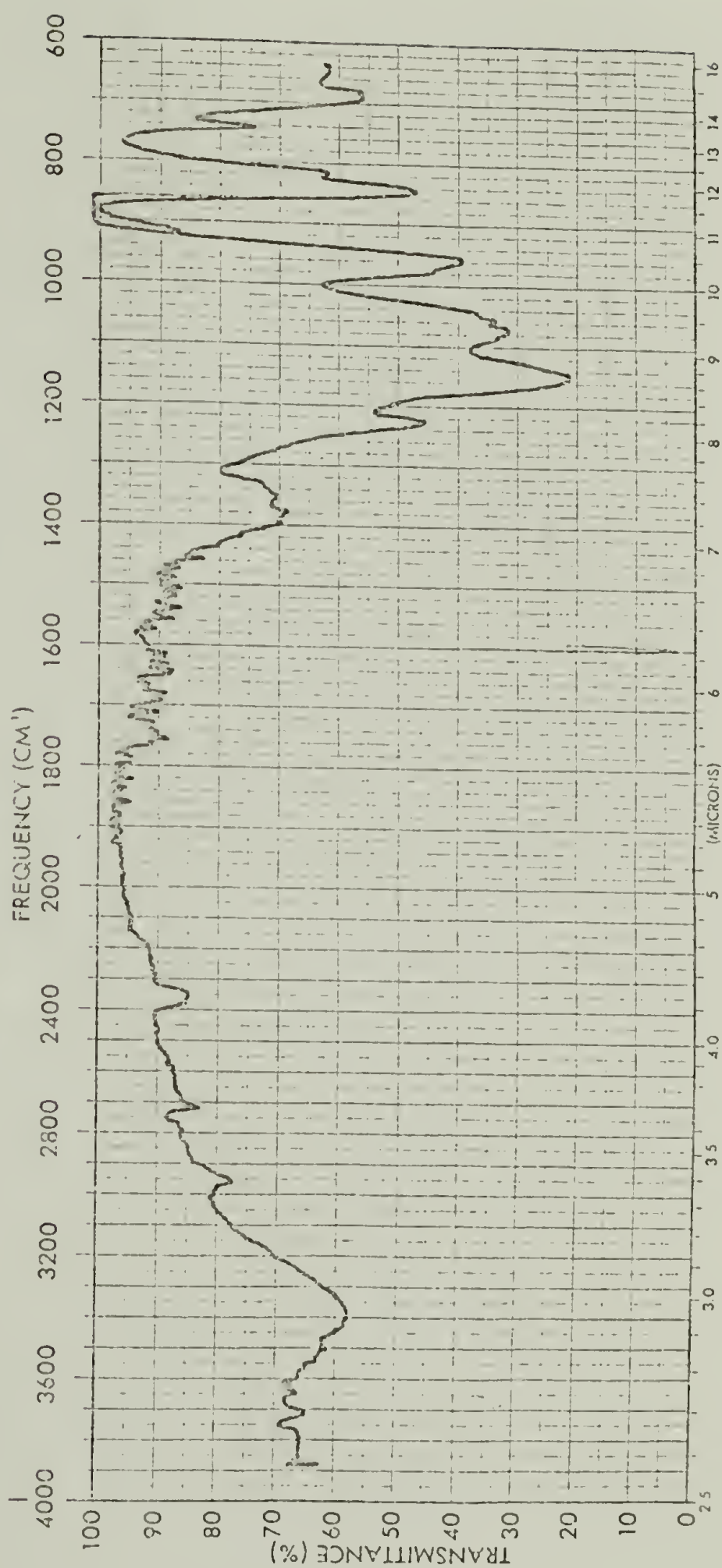


FIGURE 6

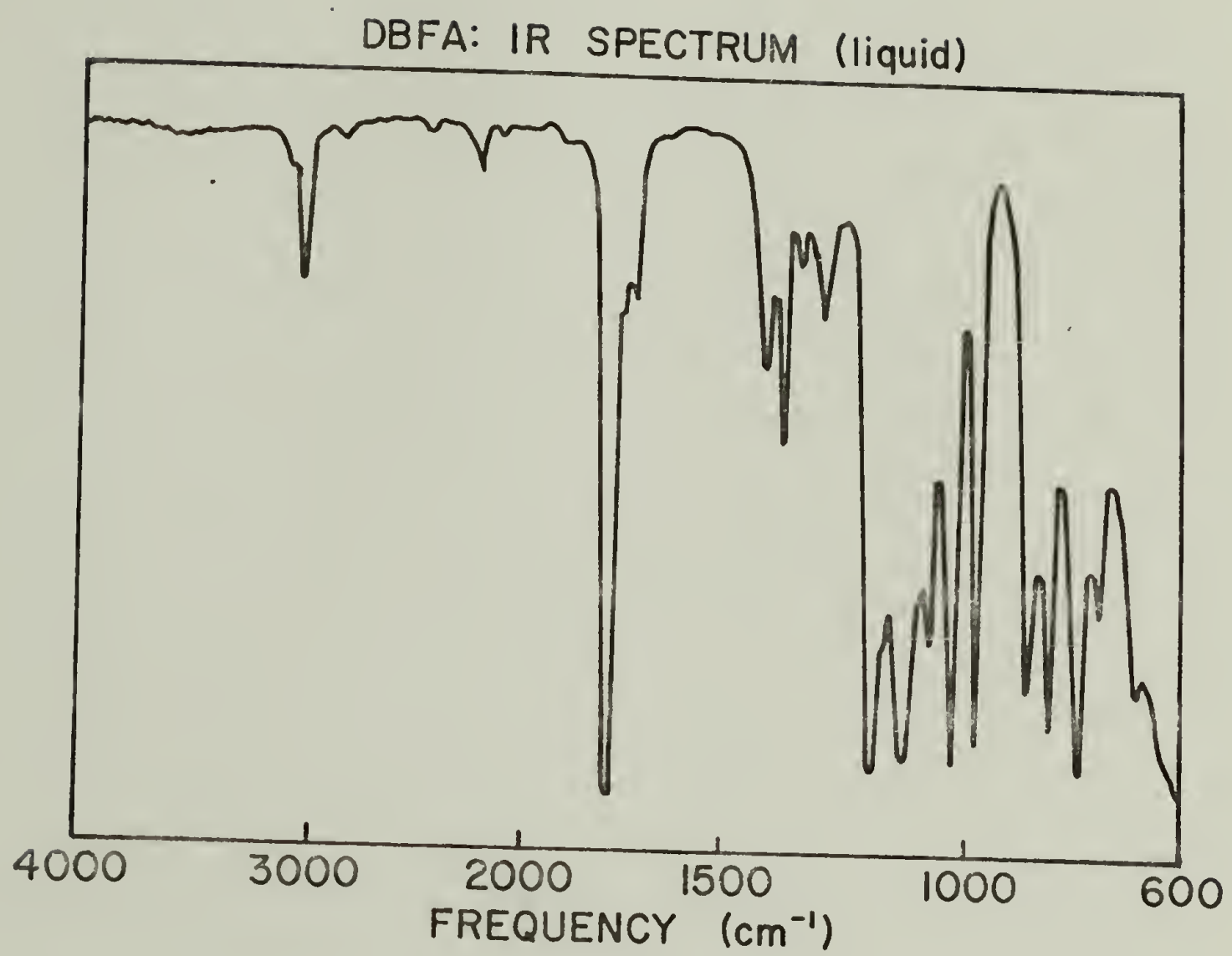


FIGURE 7

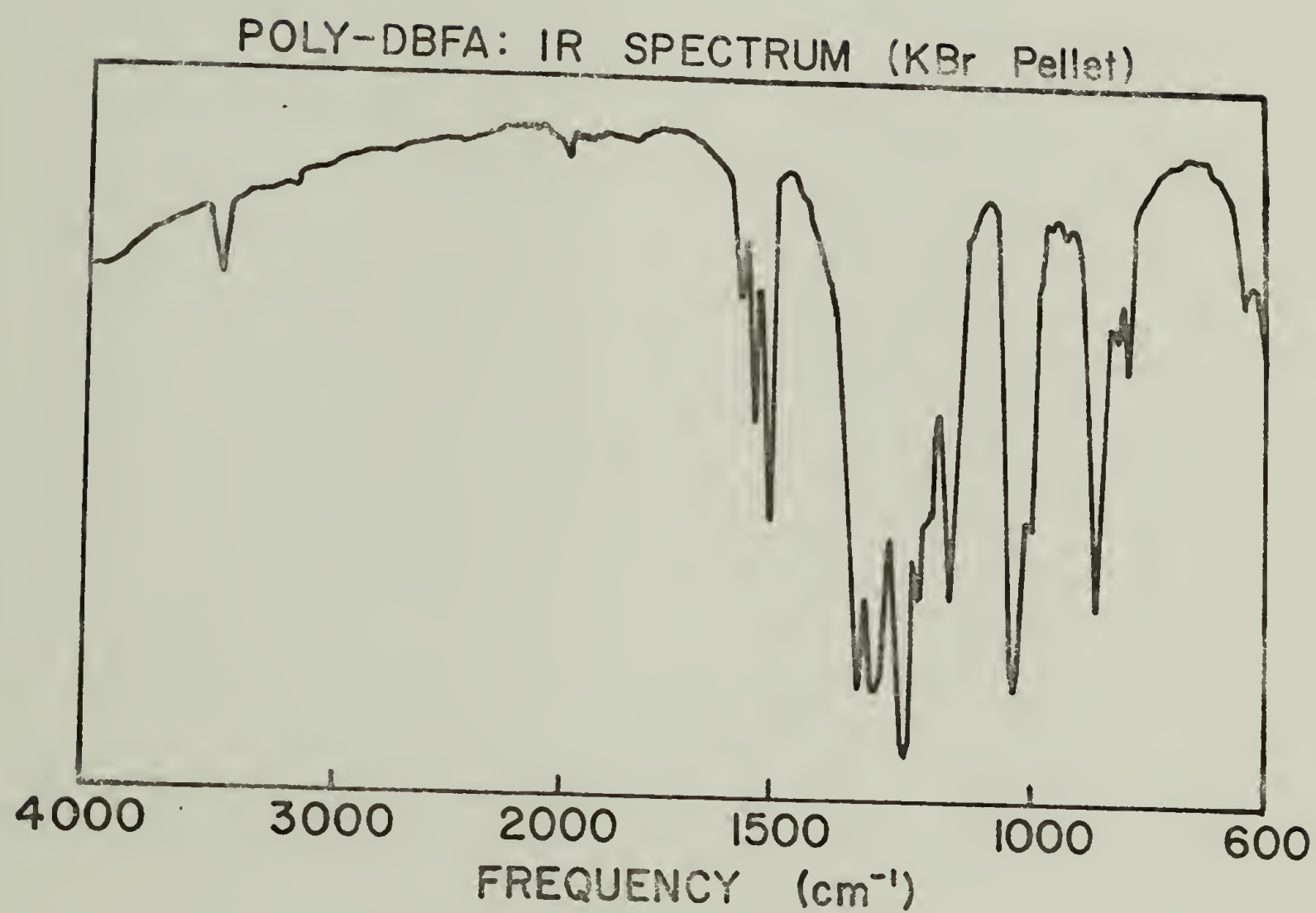


FIGURE 8

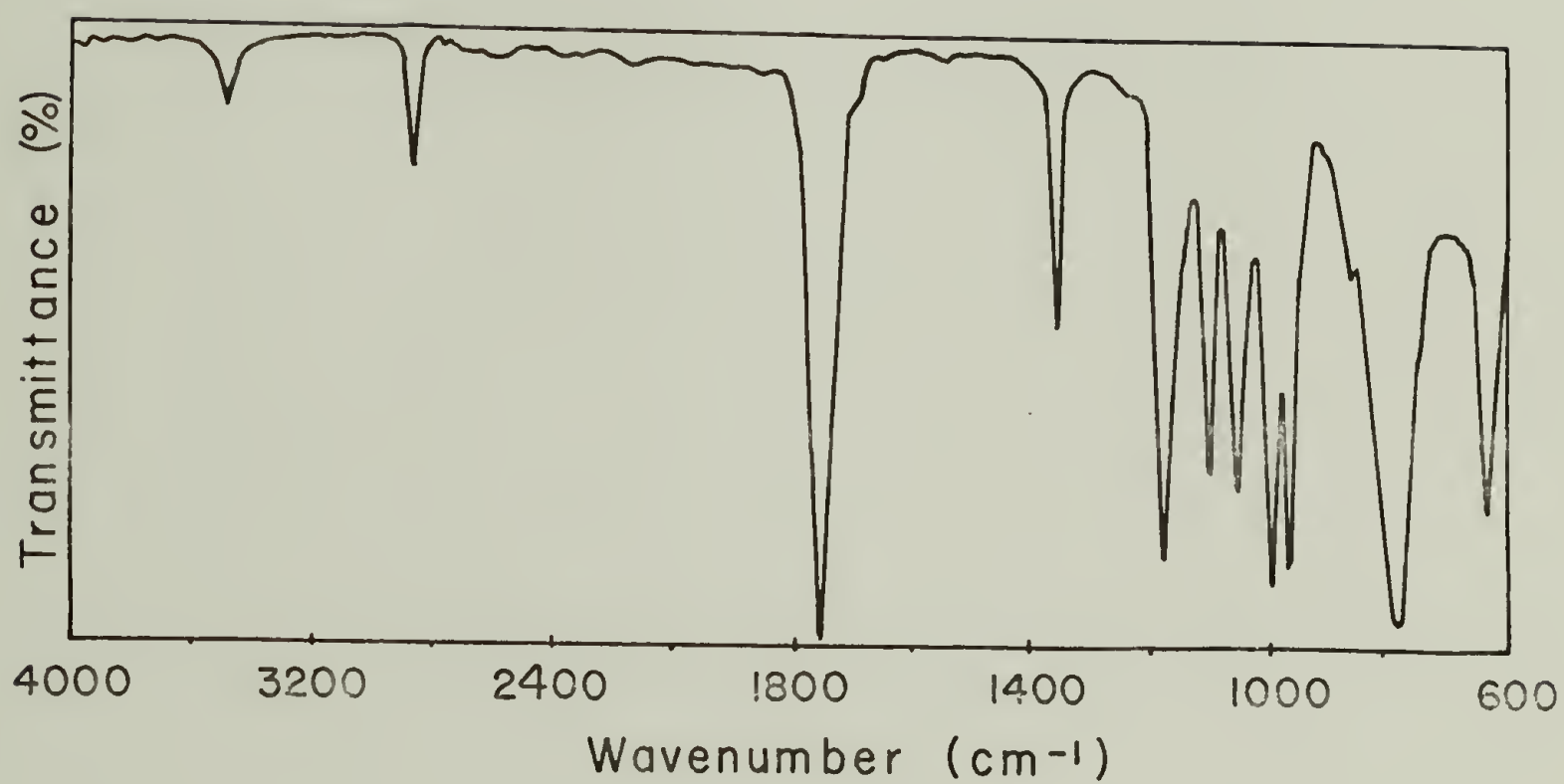
IR Spectrum of FCCl_2CHO 

FIGURE 9

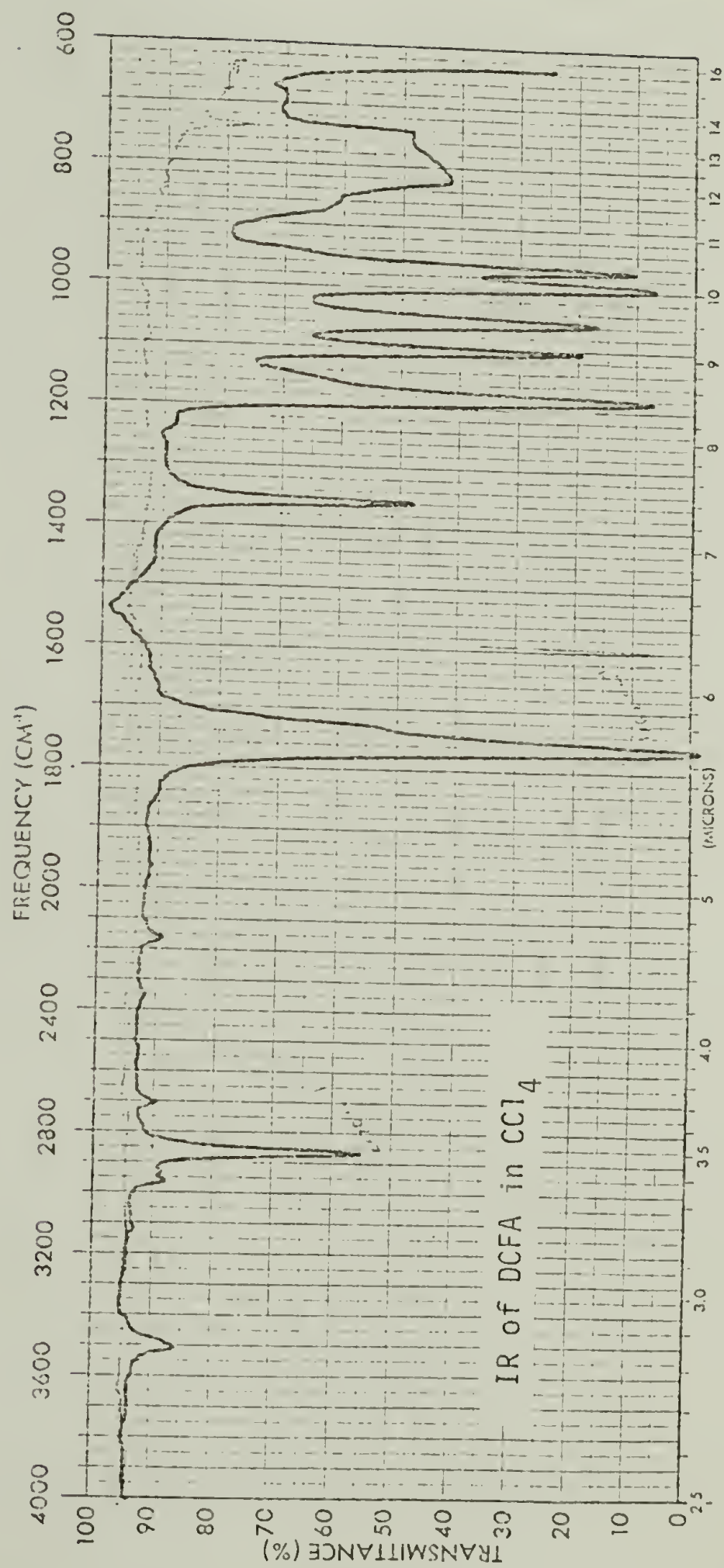


FIGURE 10

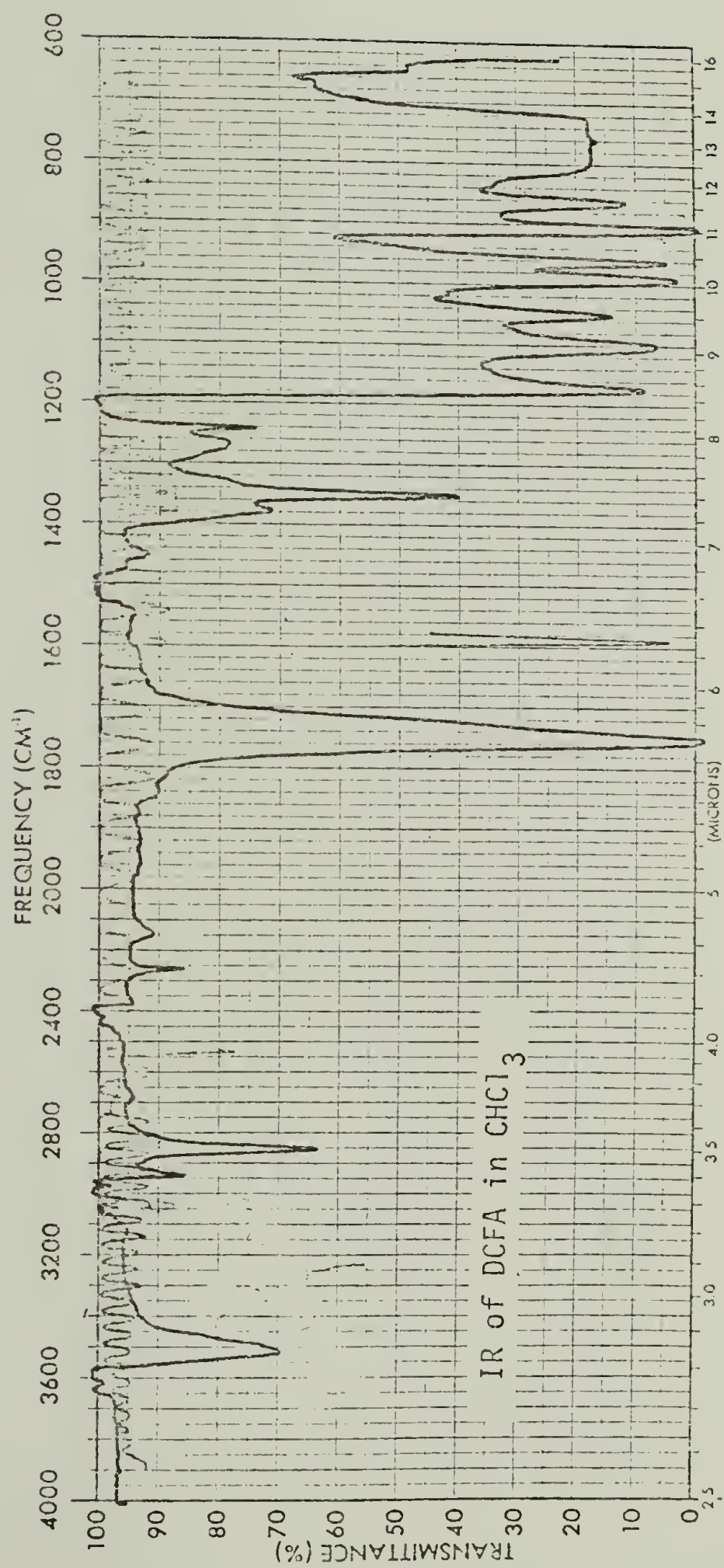


FIGURE 11

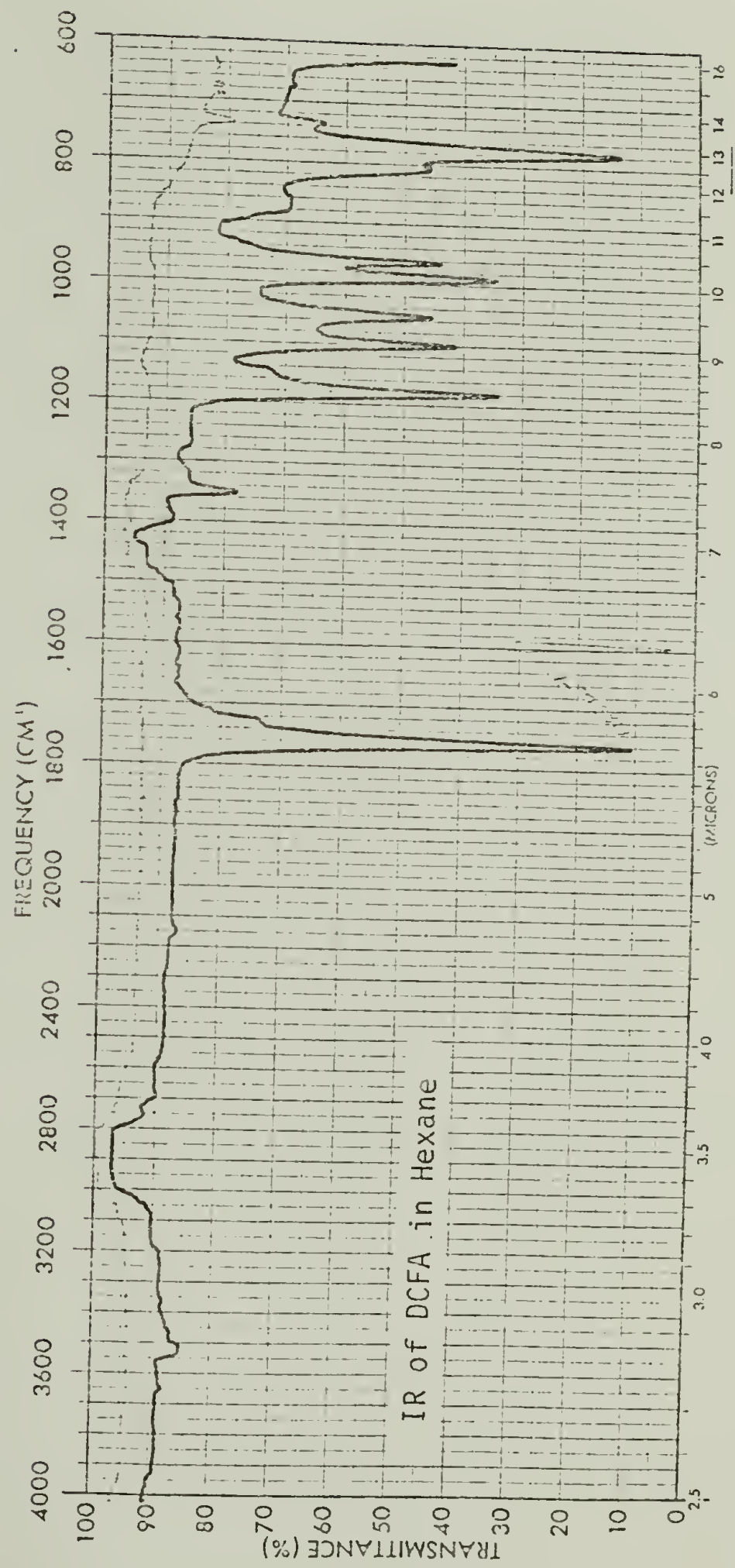


FIGURE 12

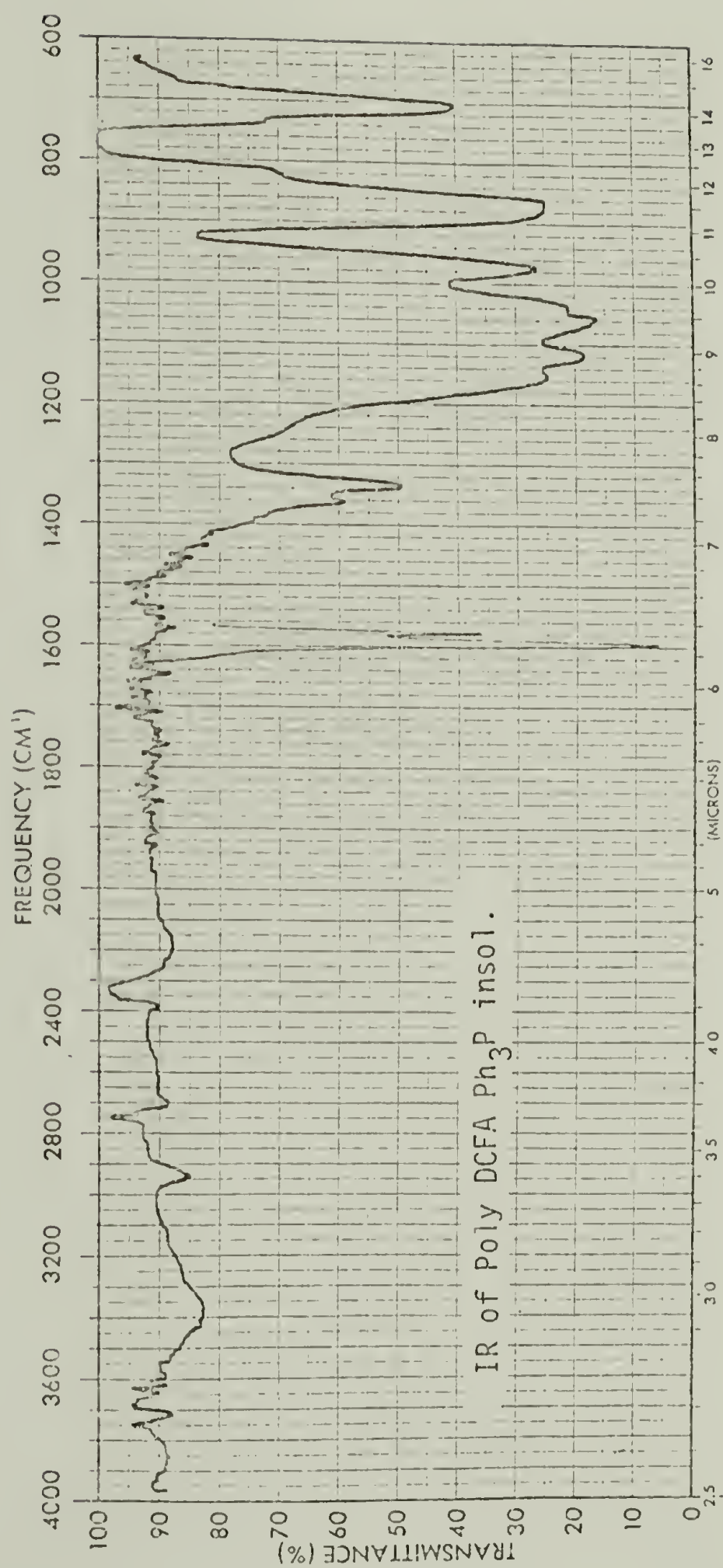


FIGURE 13

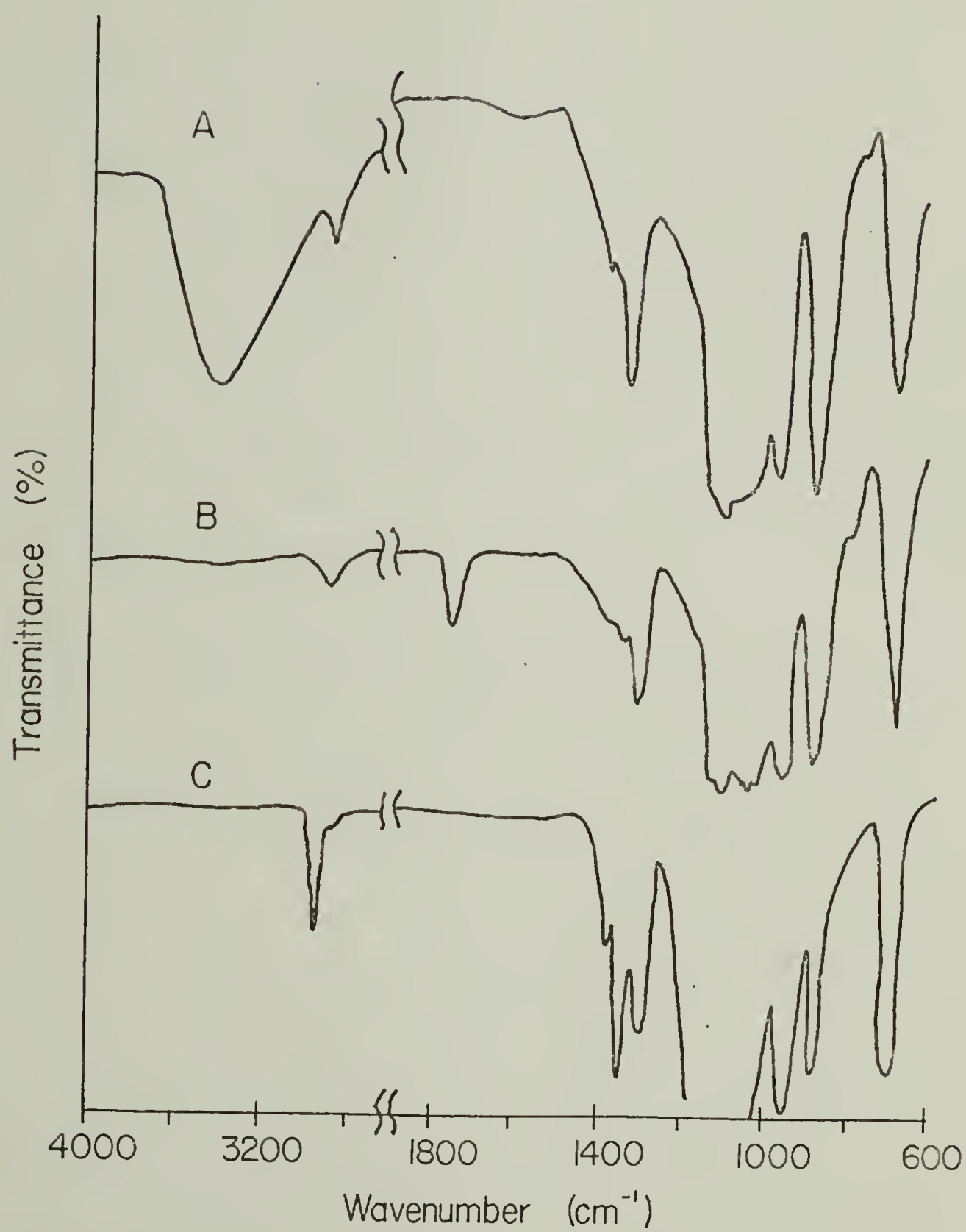
IR Spectra of Poly-FCCl₂CHO

FIGURE 14

IR Spectrum of Chloral + DCFA Copolymer

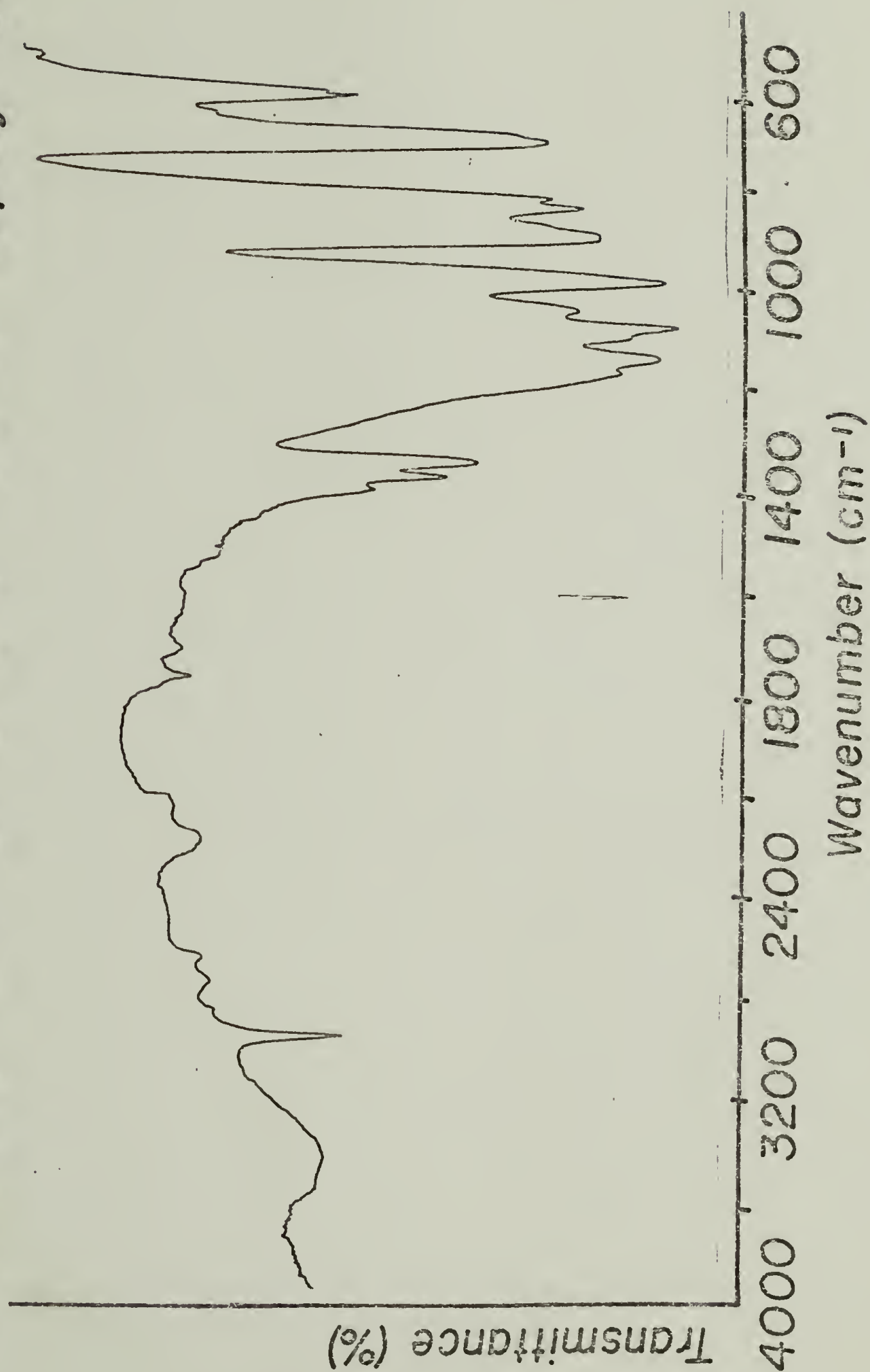


FIGURE 15

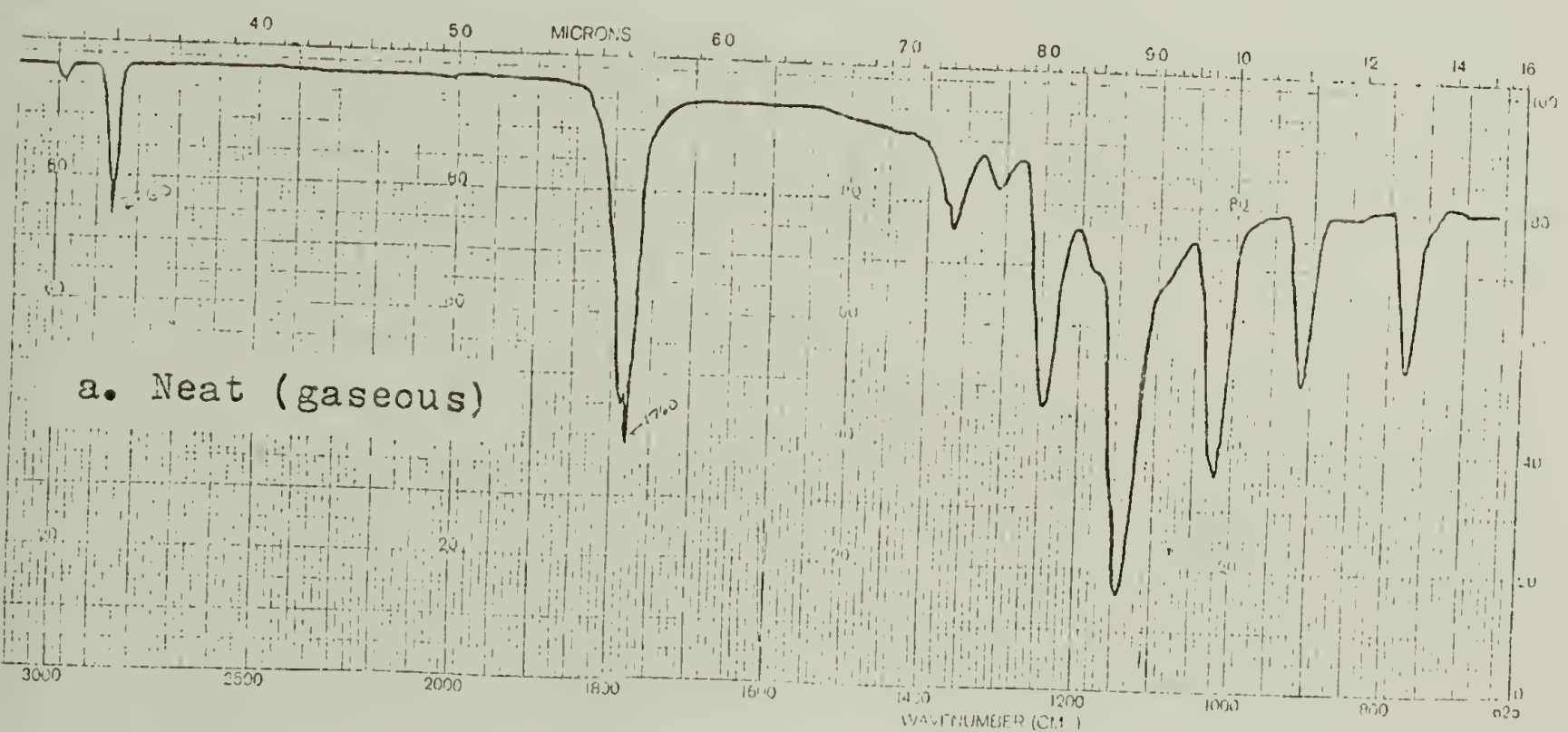
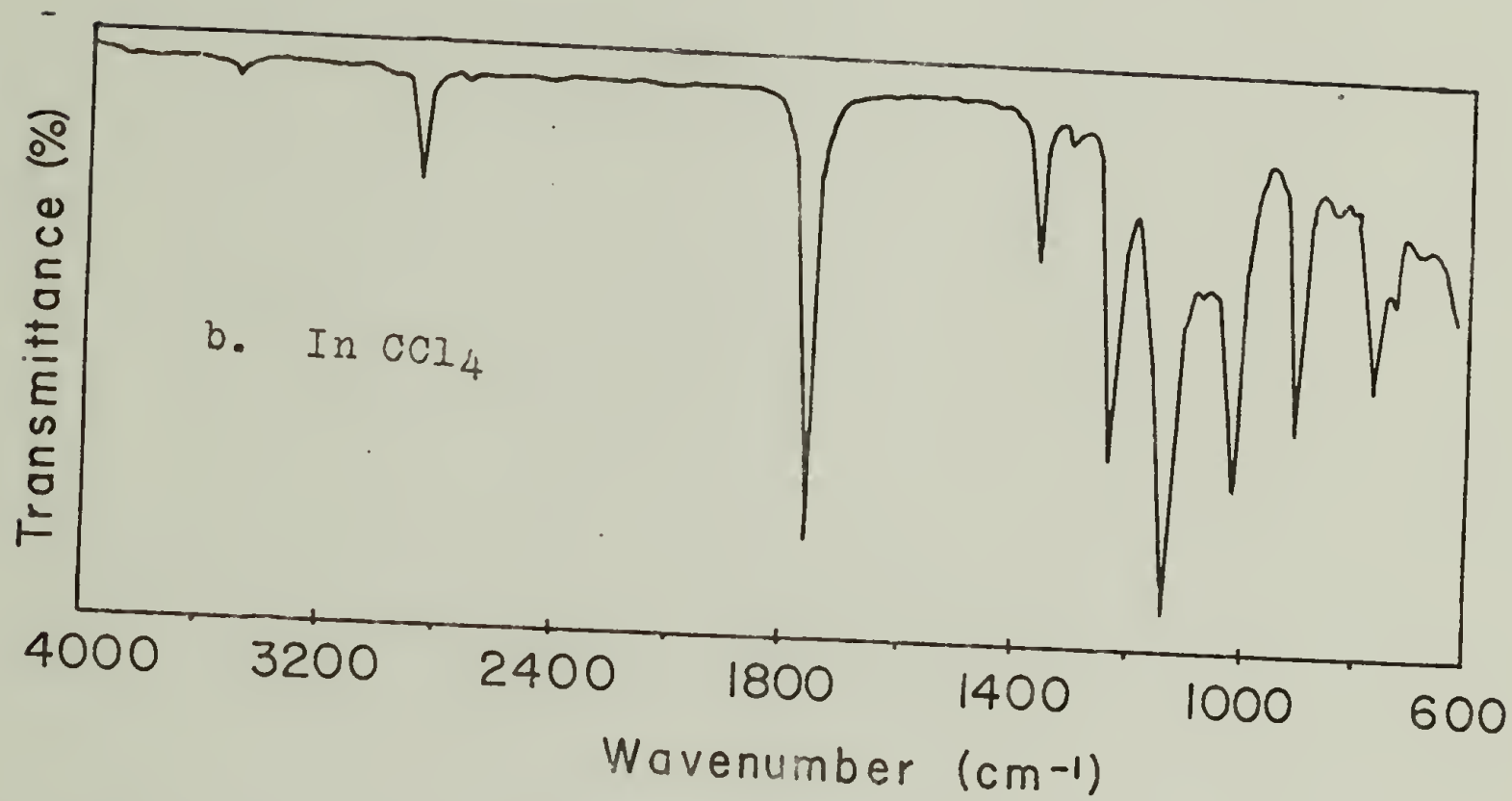
IR Spectrum of ClCF_2CHO 

FIGURE 16

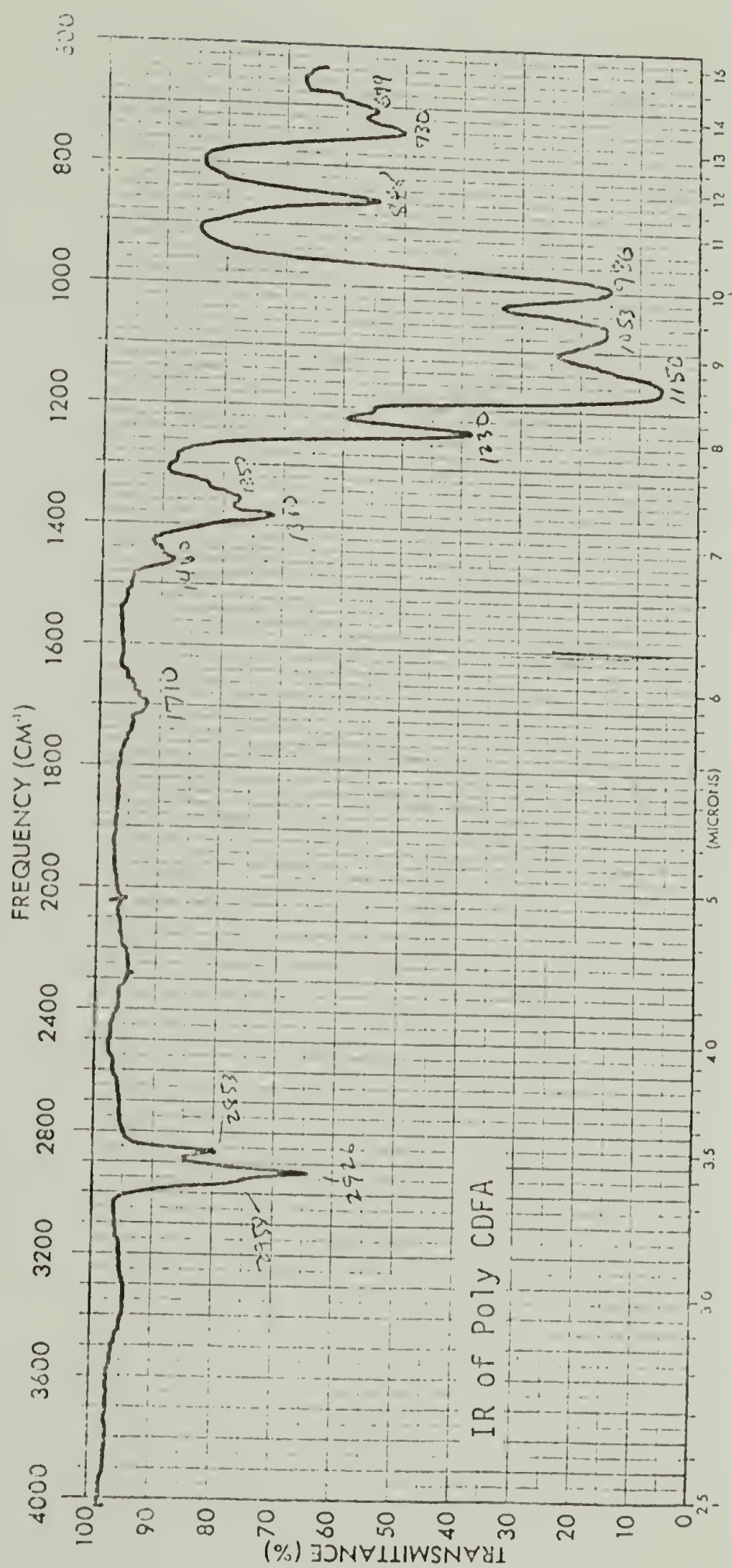


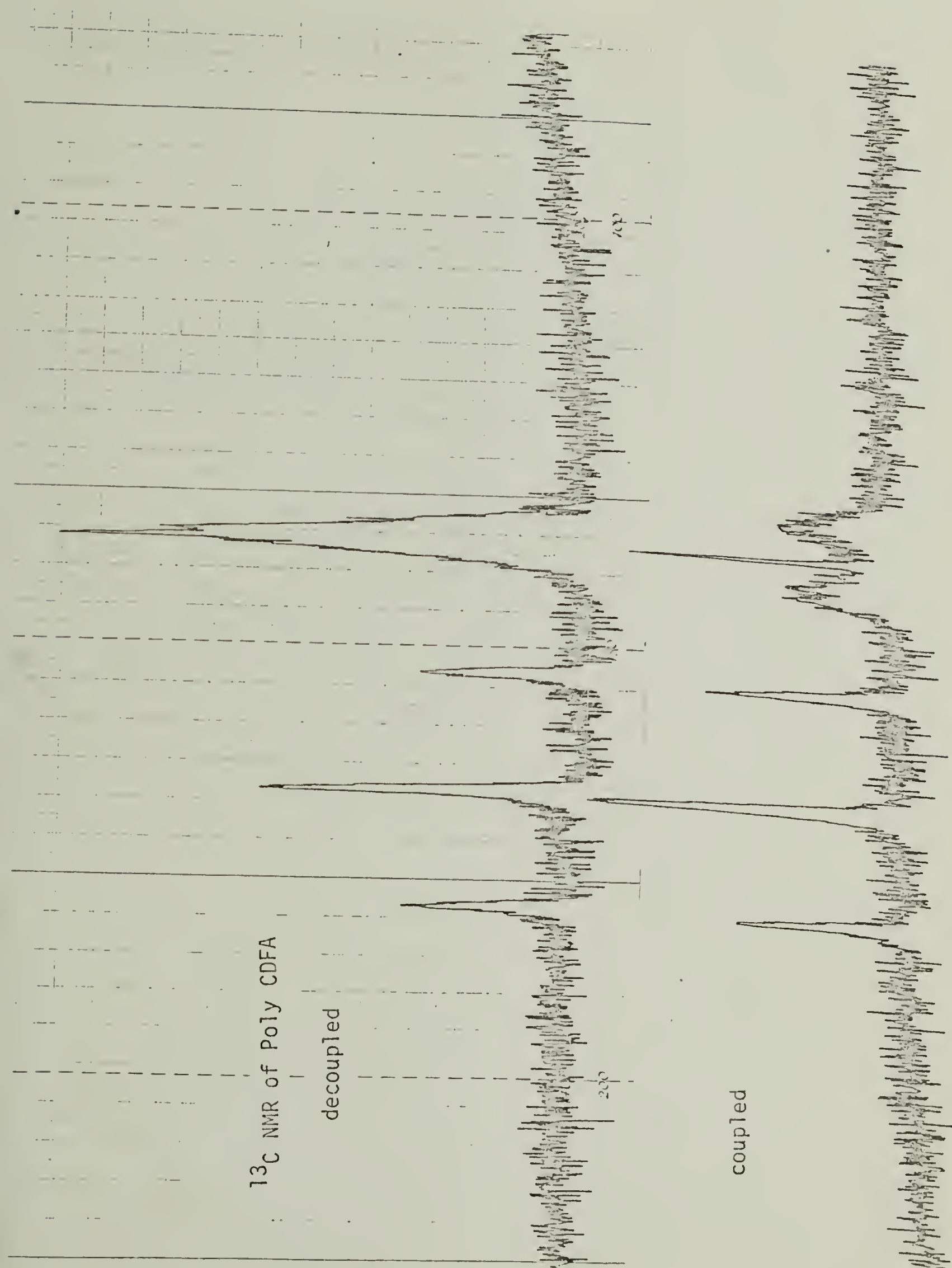
FIGURE 17

^{13}C NMR of Poly CDFA

decoupled

coupled

FIGURE 18



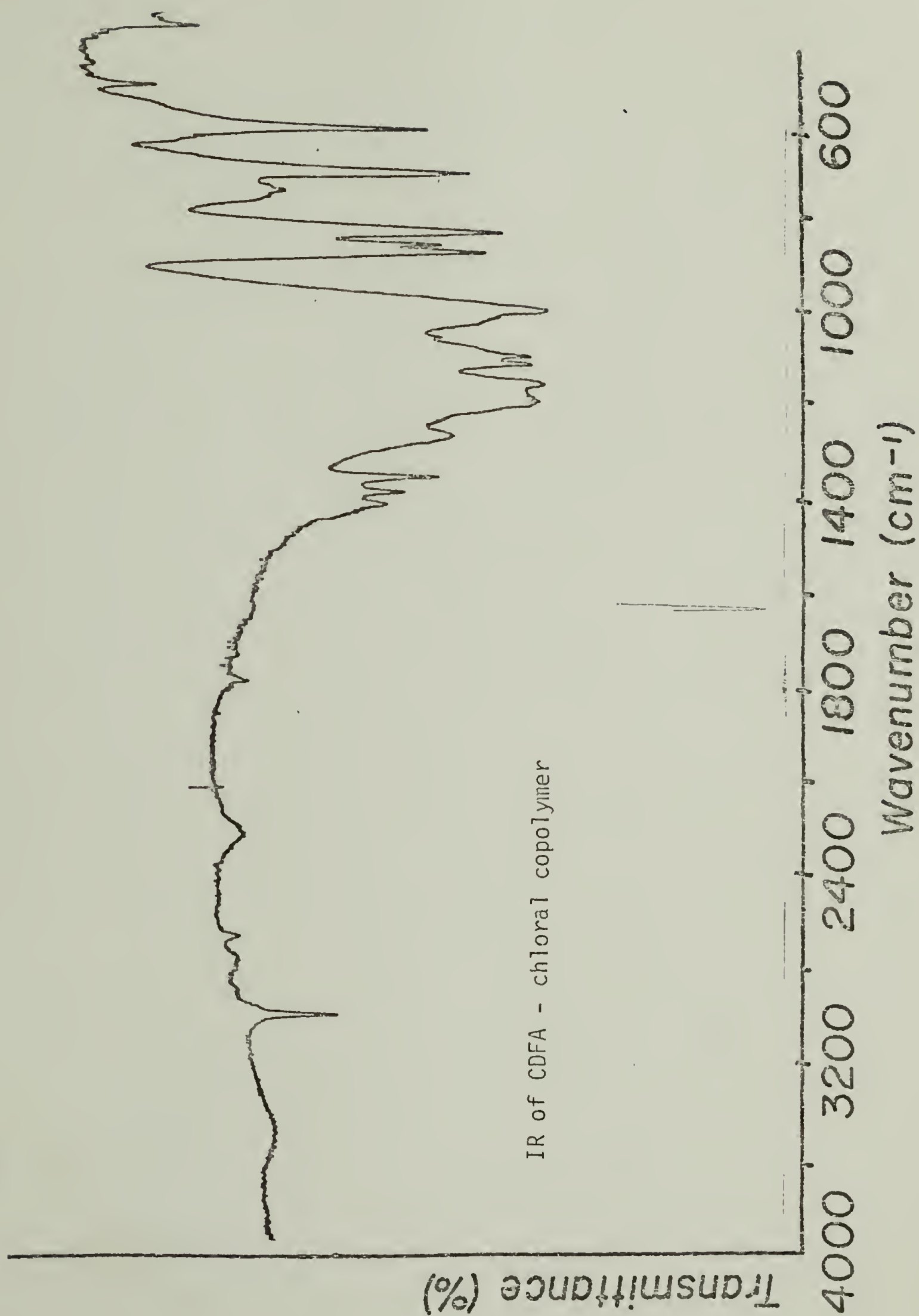


FIGURE 19

CEILING TEMPERATURE APPARATUS

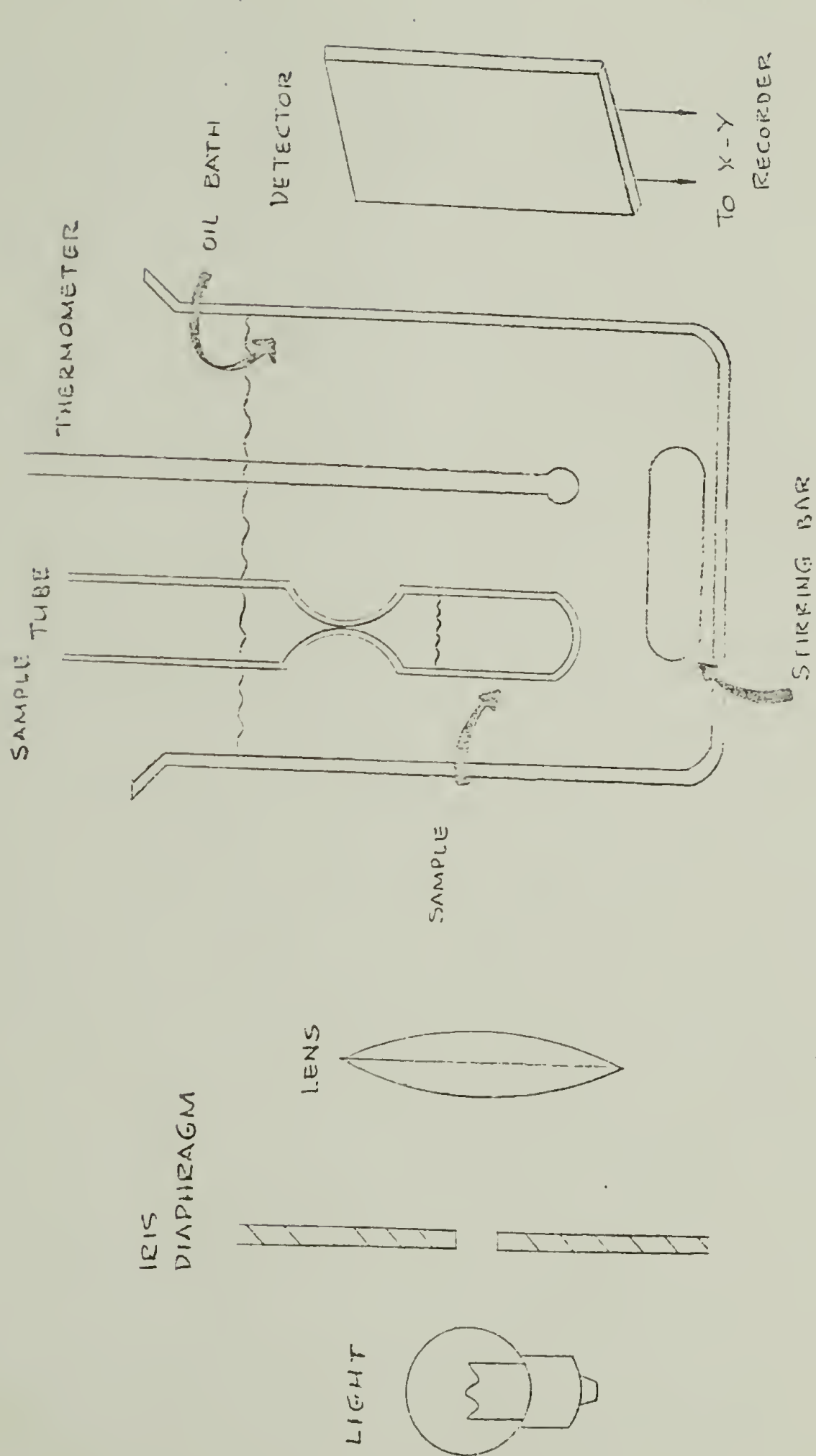


FIGURE 20

6w 211112
12 SEP 19

CEILING TEMPERATURES and BOILING POINTS
of BROMOFLUOROACETALDEHYDES

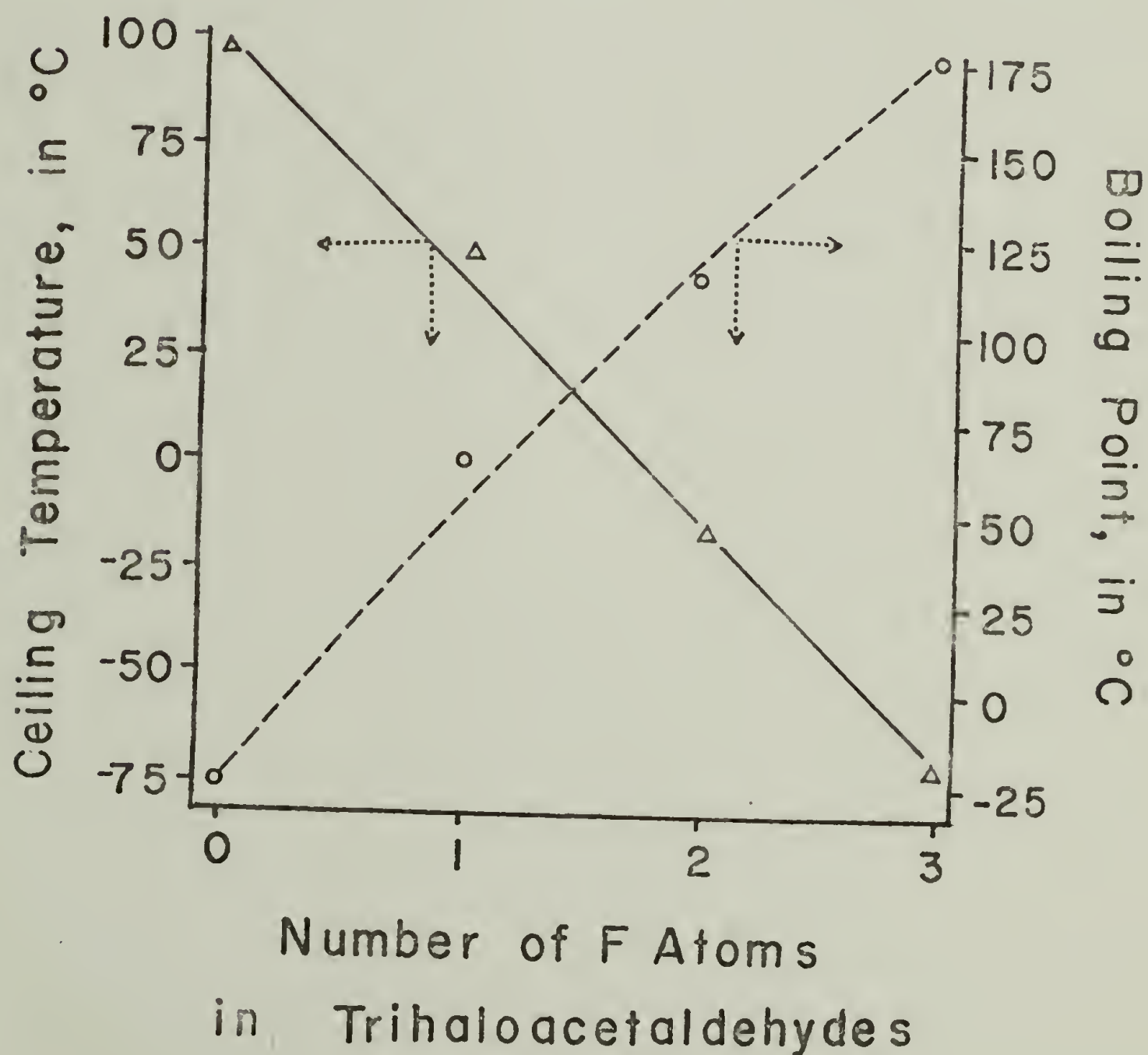


FIGURE 21

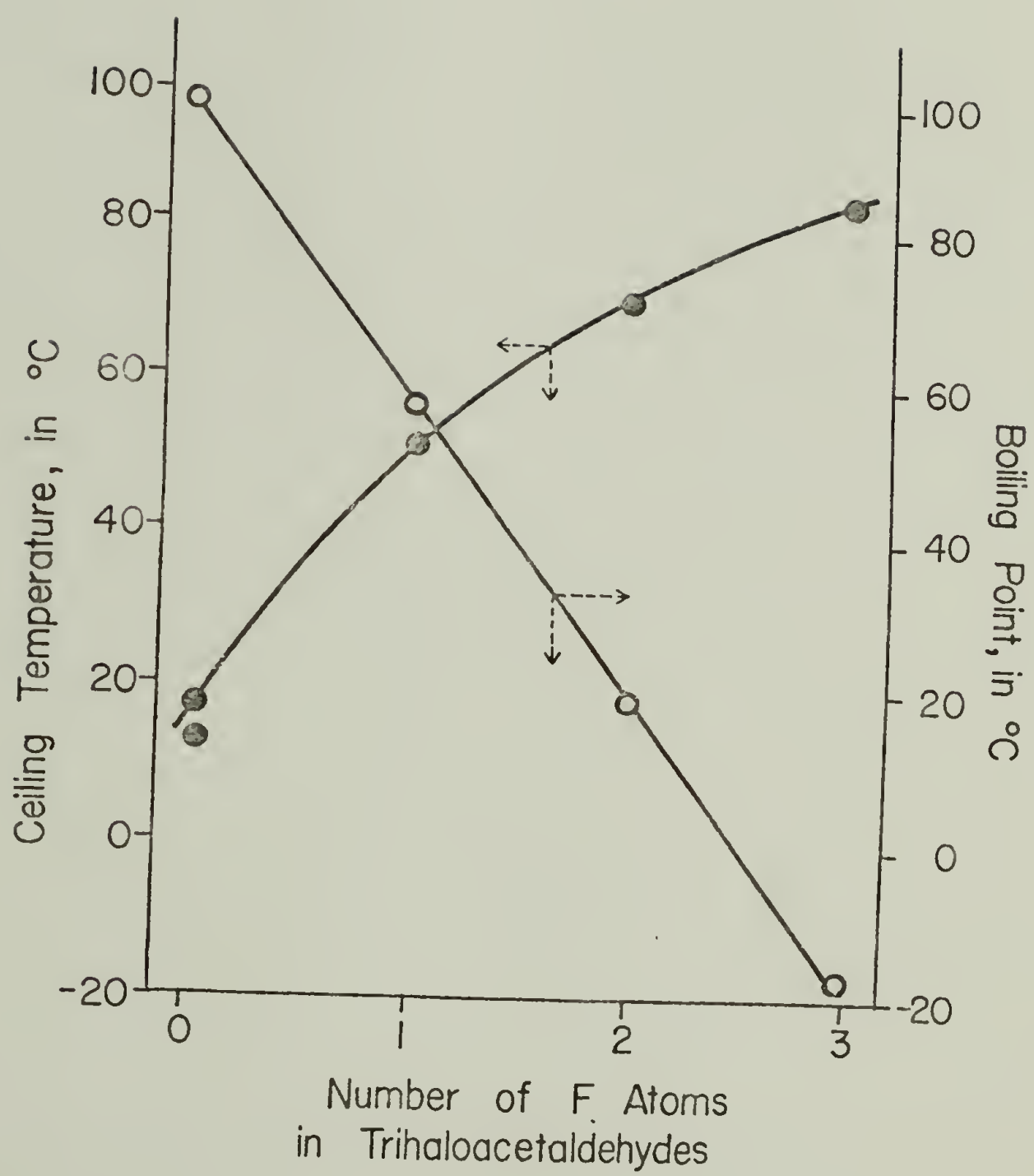


FIGURE 22

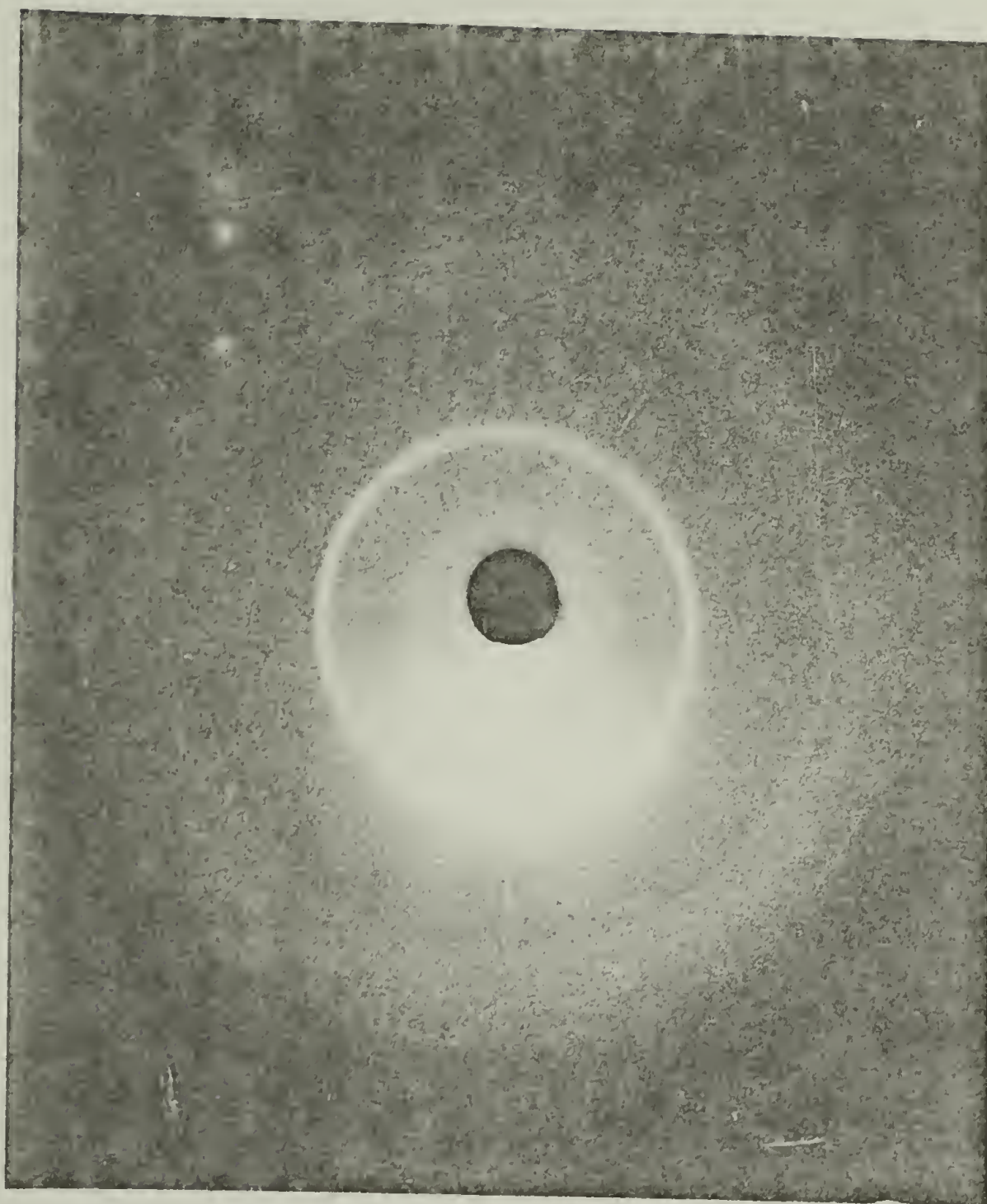


FIGURE 23

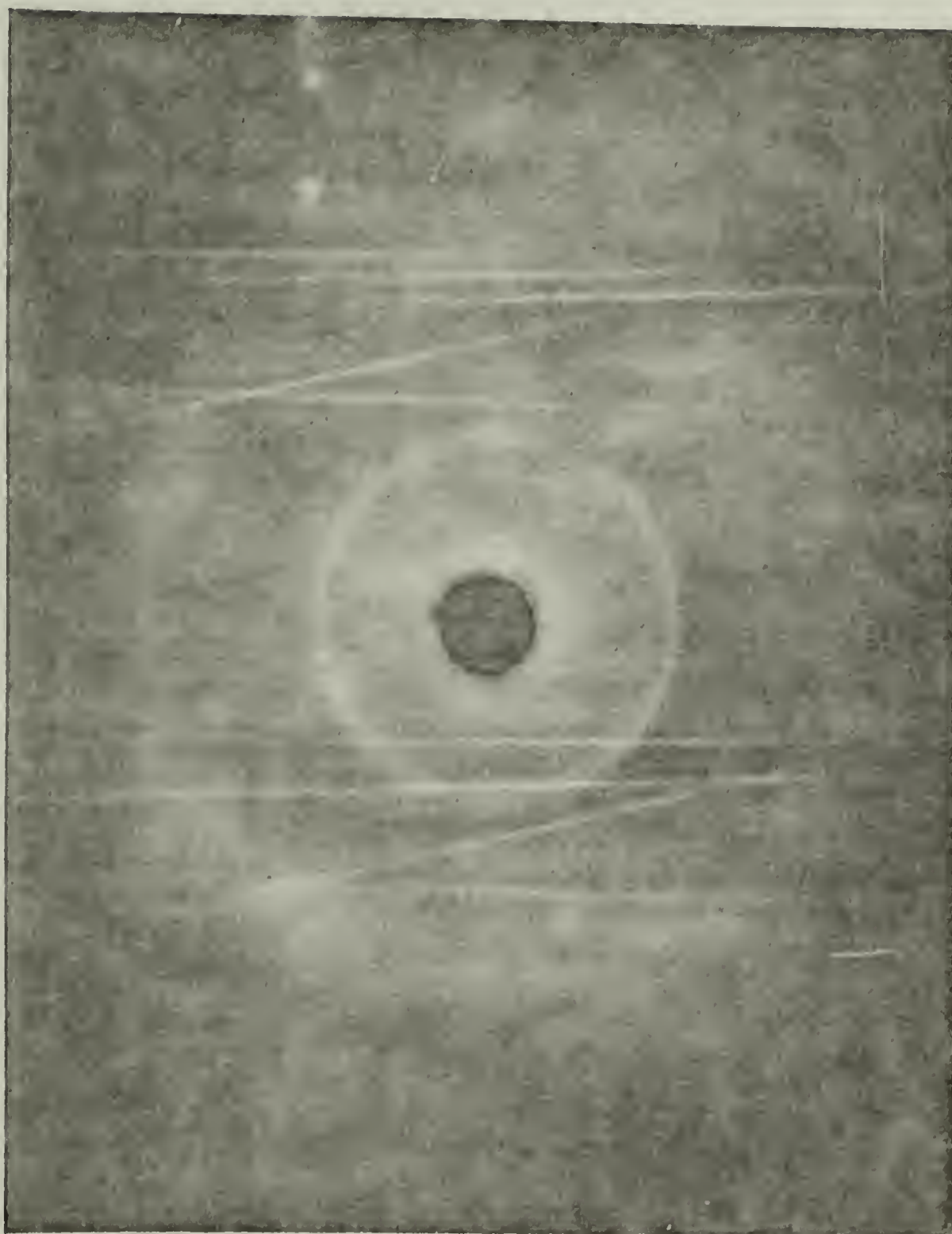


FIGURE 24

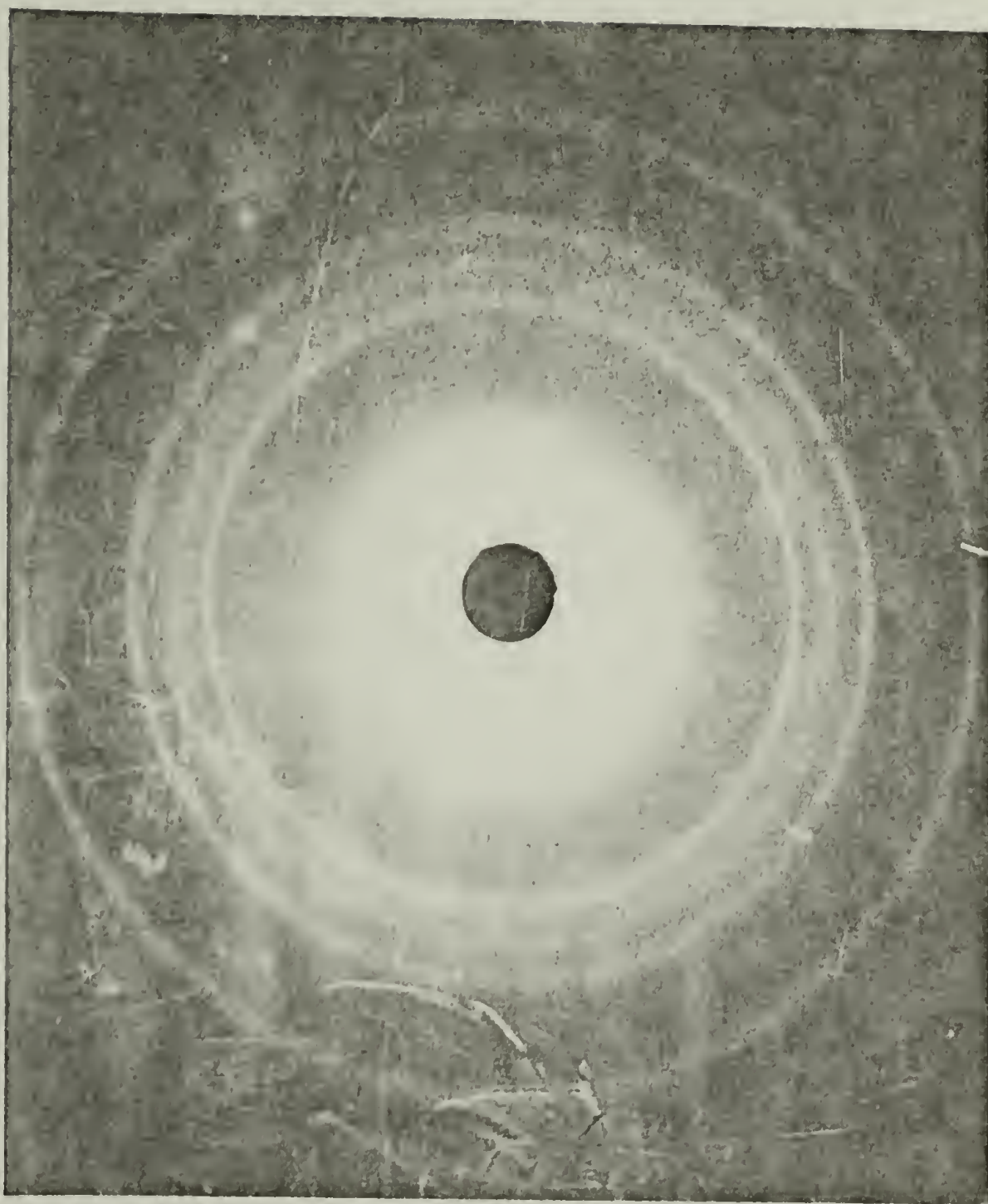


FIGURE 25

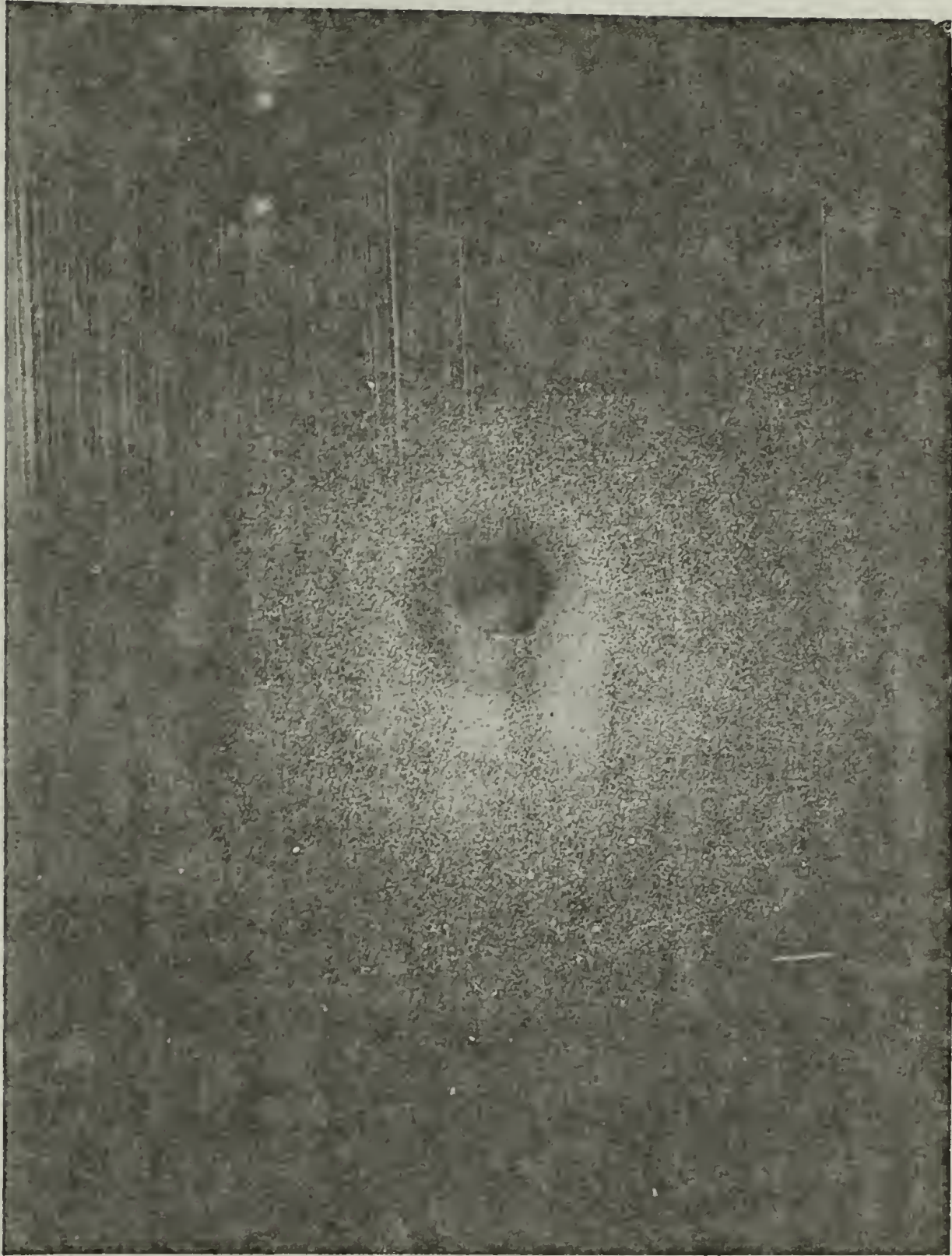


FIGURE 26

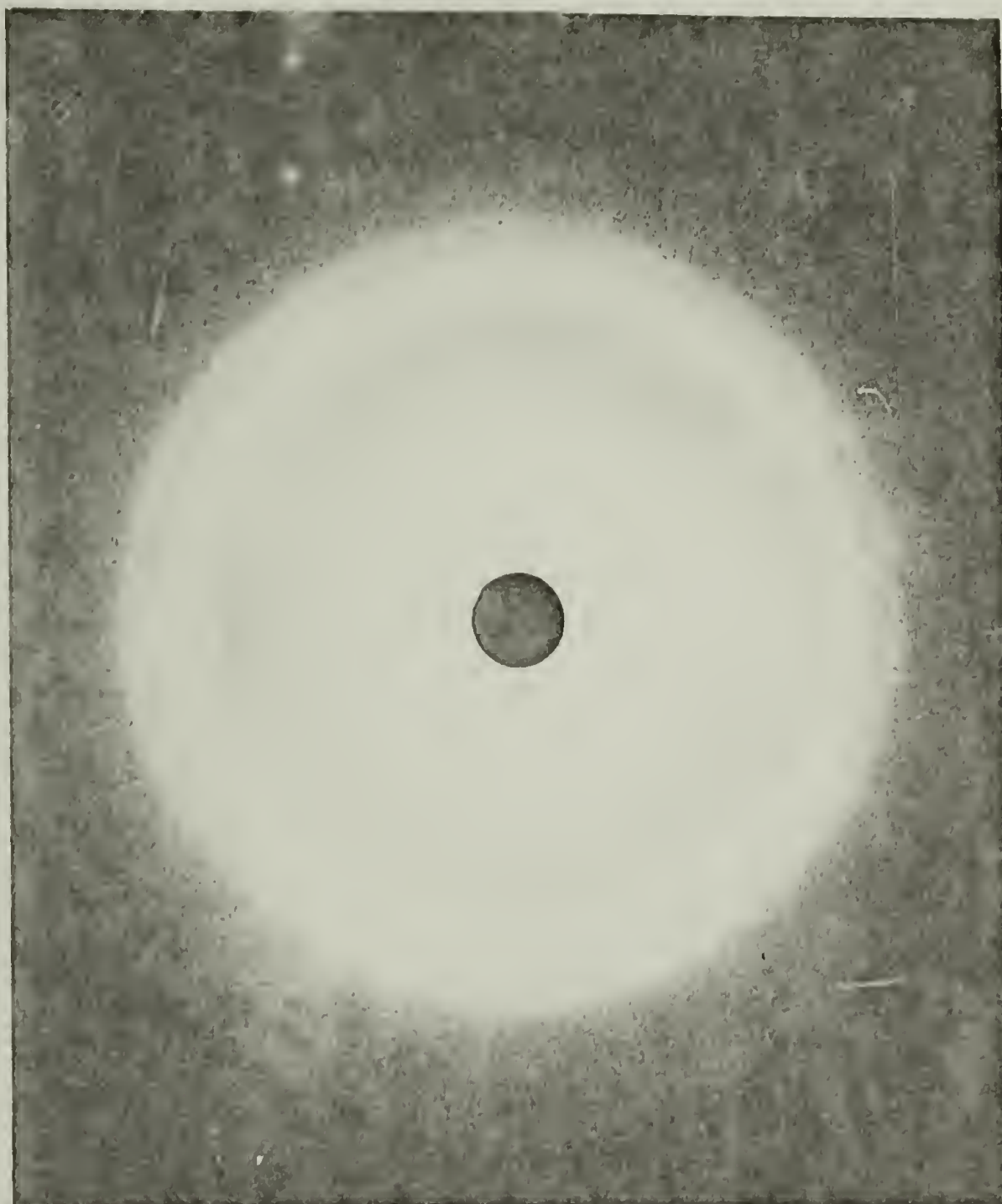


FIGURE 27

SYNTHESIS OF CBr_2FCHO and CBrF_2CHO

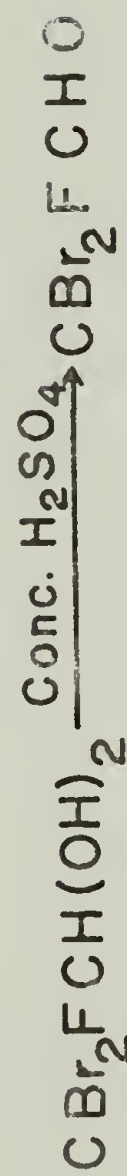
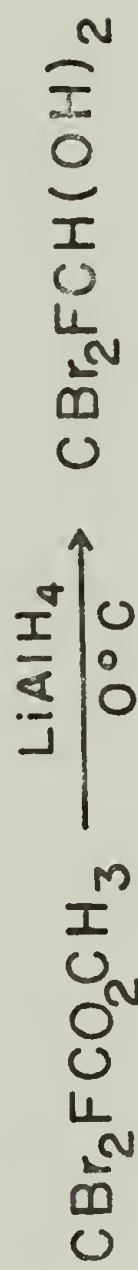


FIGURE 28

ALTERNATIVE SYNTHESIS OF CBrF_2CHO

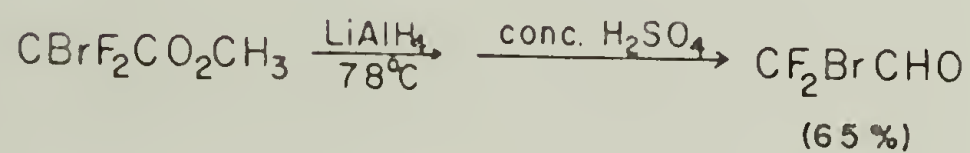
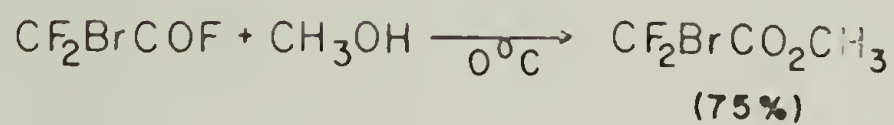
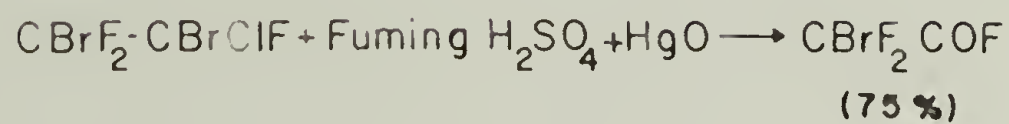
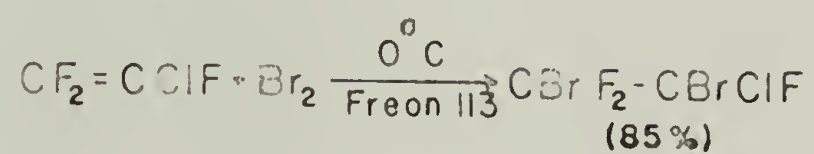


FIGURE 29

SYNTHESIS OF DCFA

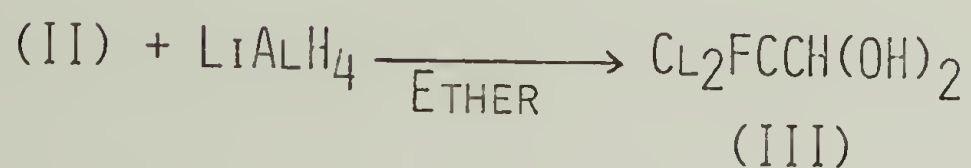
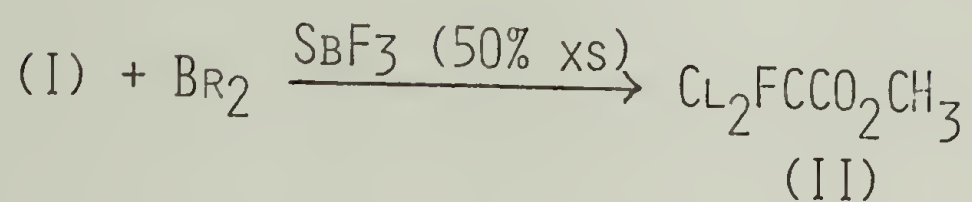
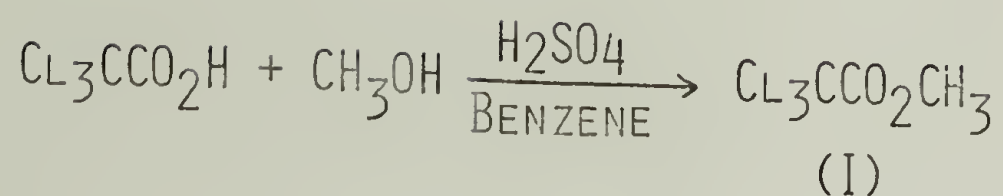


FIGURE 30

SYNTHESIS OF CDFA

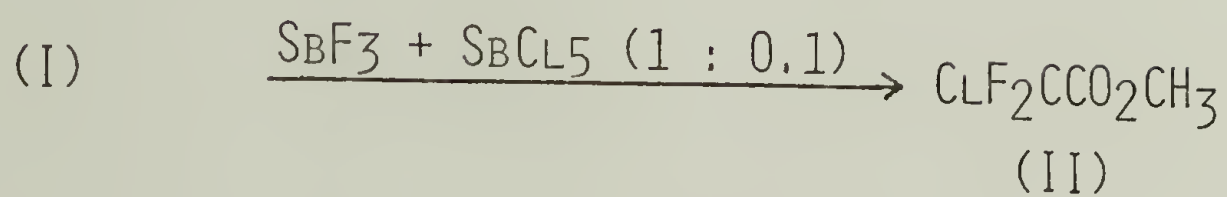
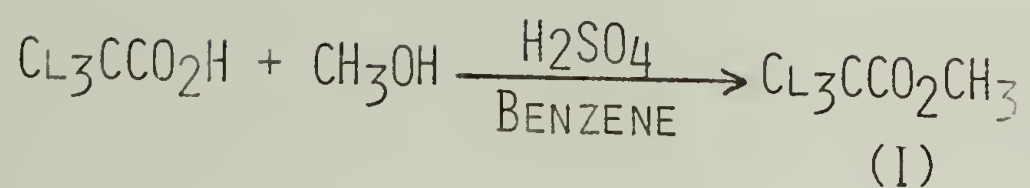


FIGURE 31

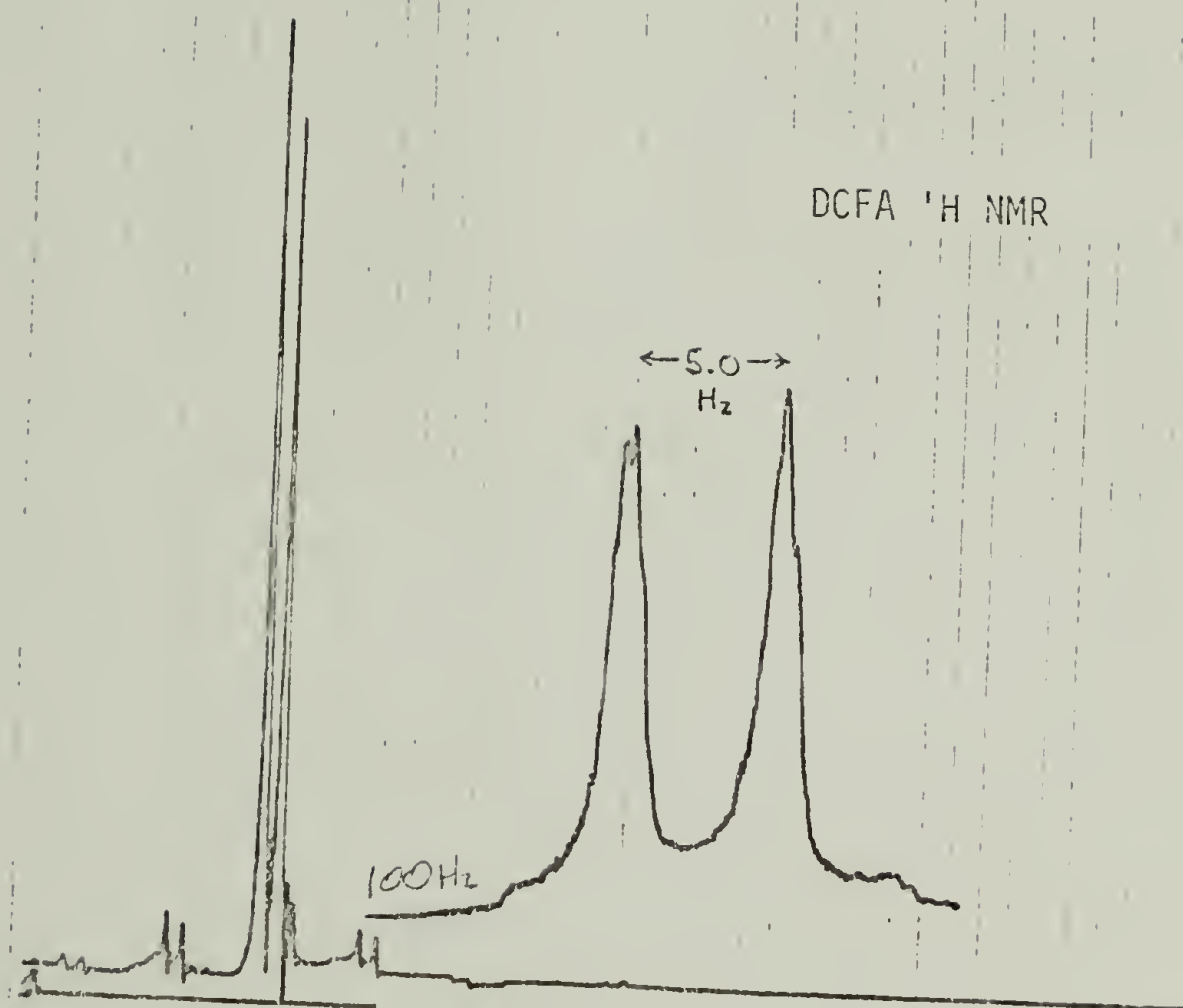


FIGURE 32

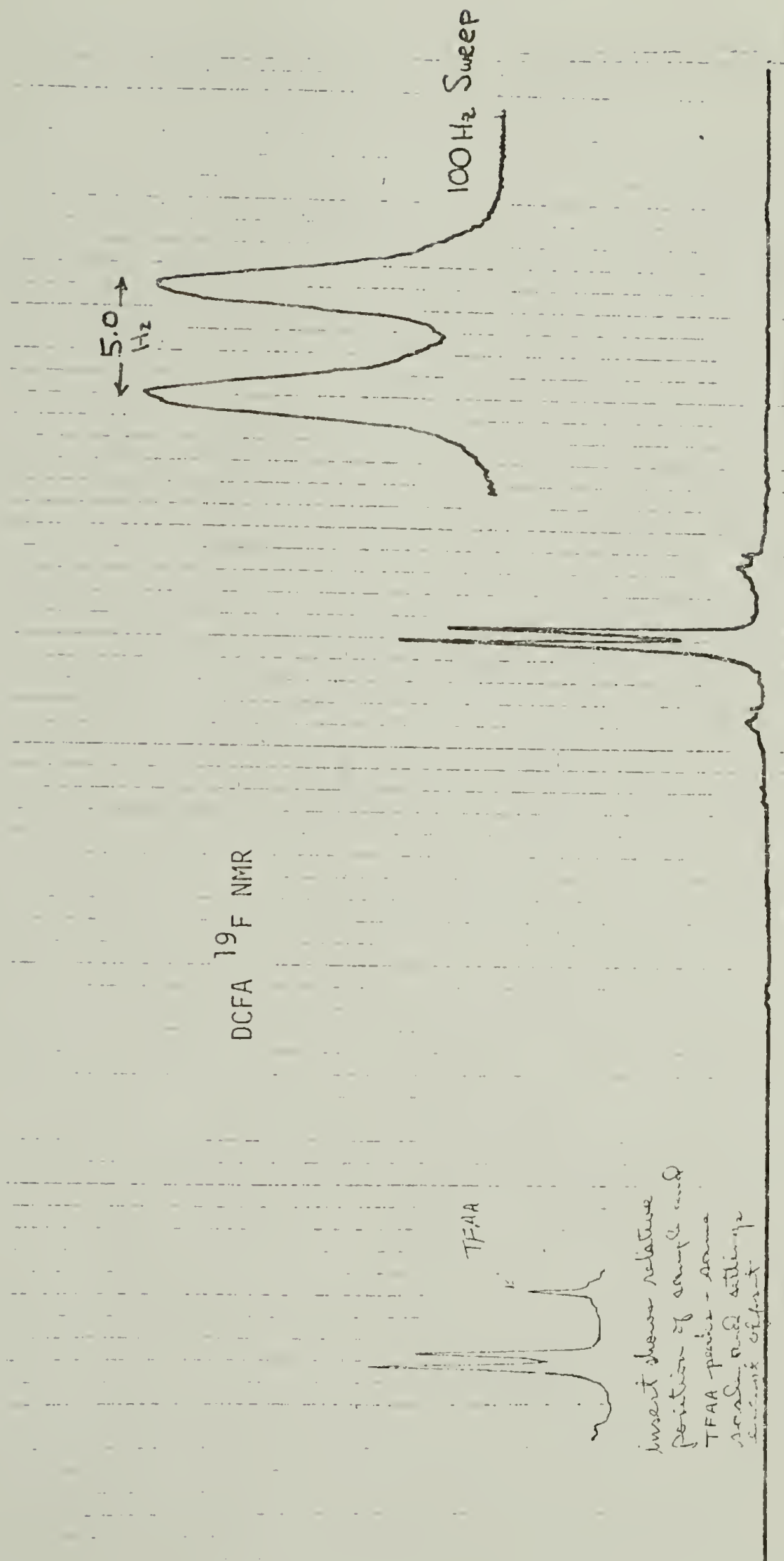


FIGURE 33

60 MHz NMR Spectra
 ClCF_2CHO and Polymer

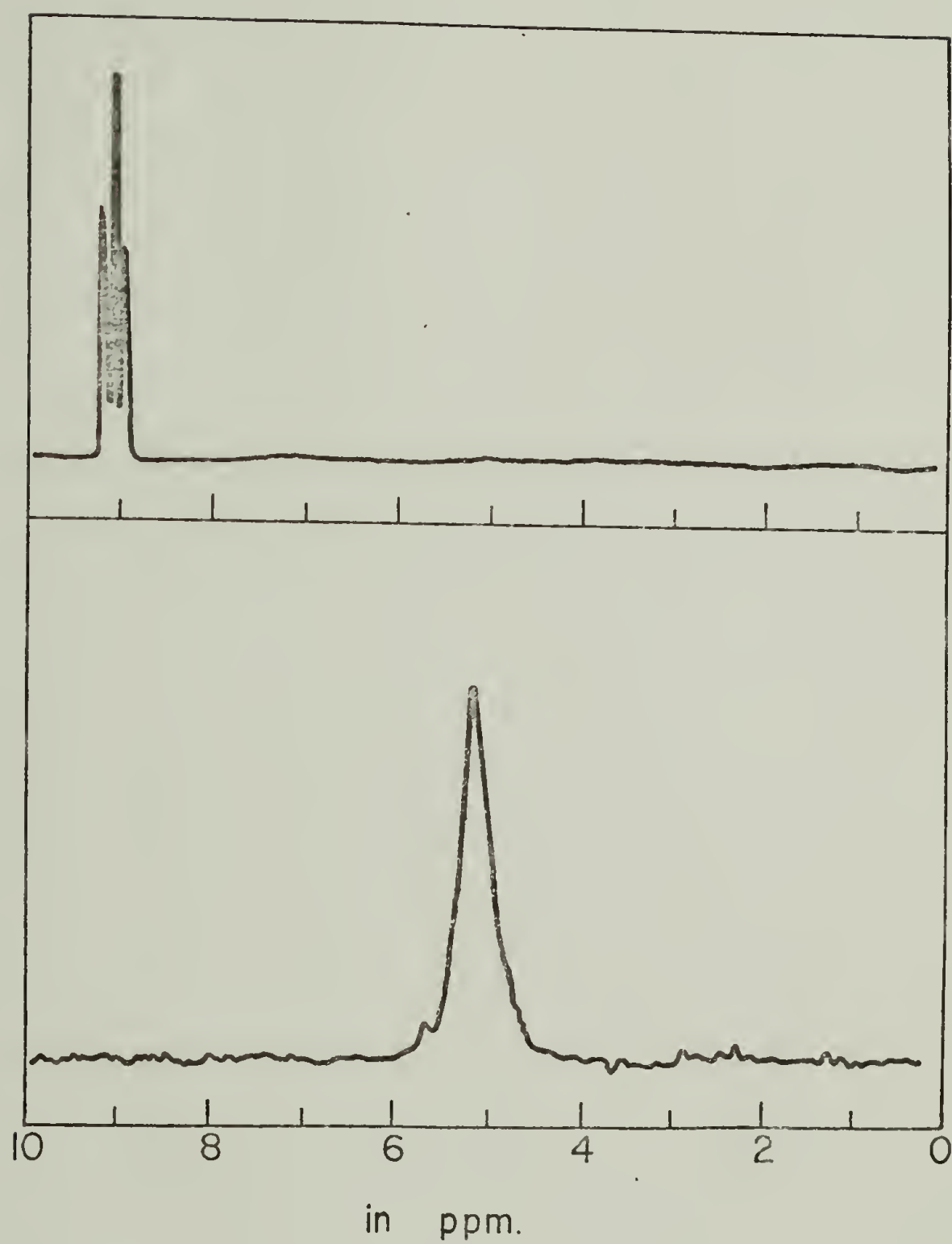


FIGURE 34

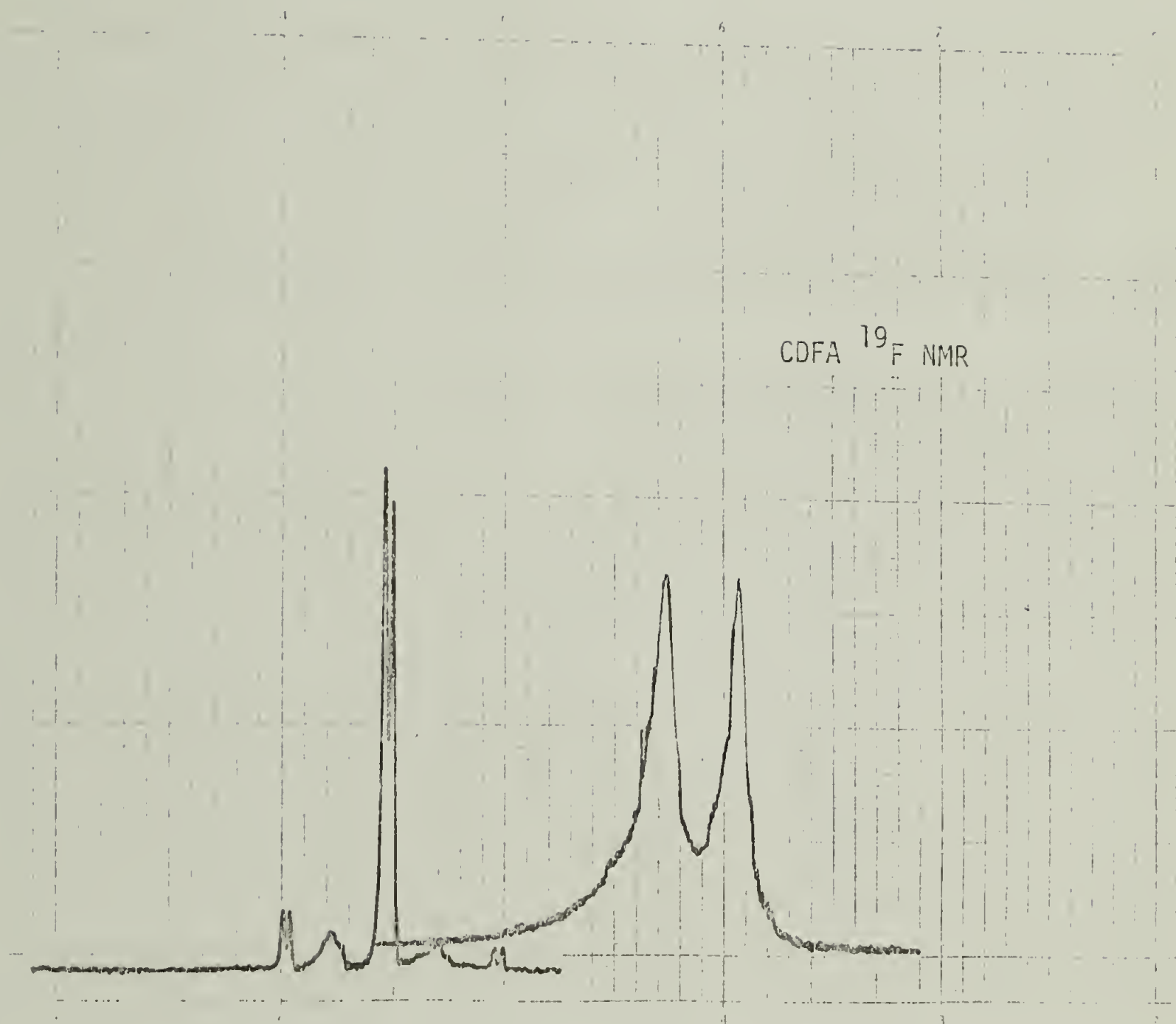


FIGURE 35

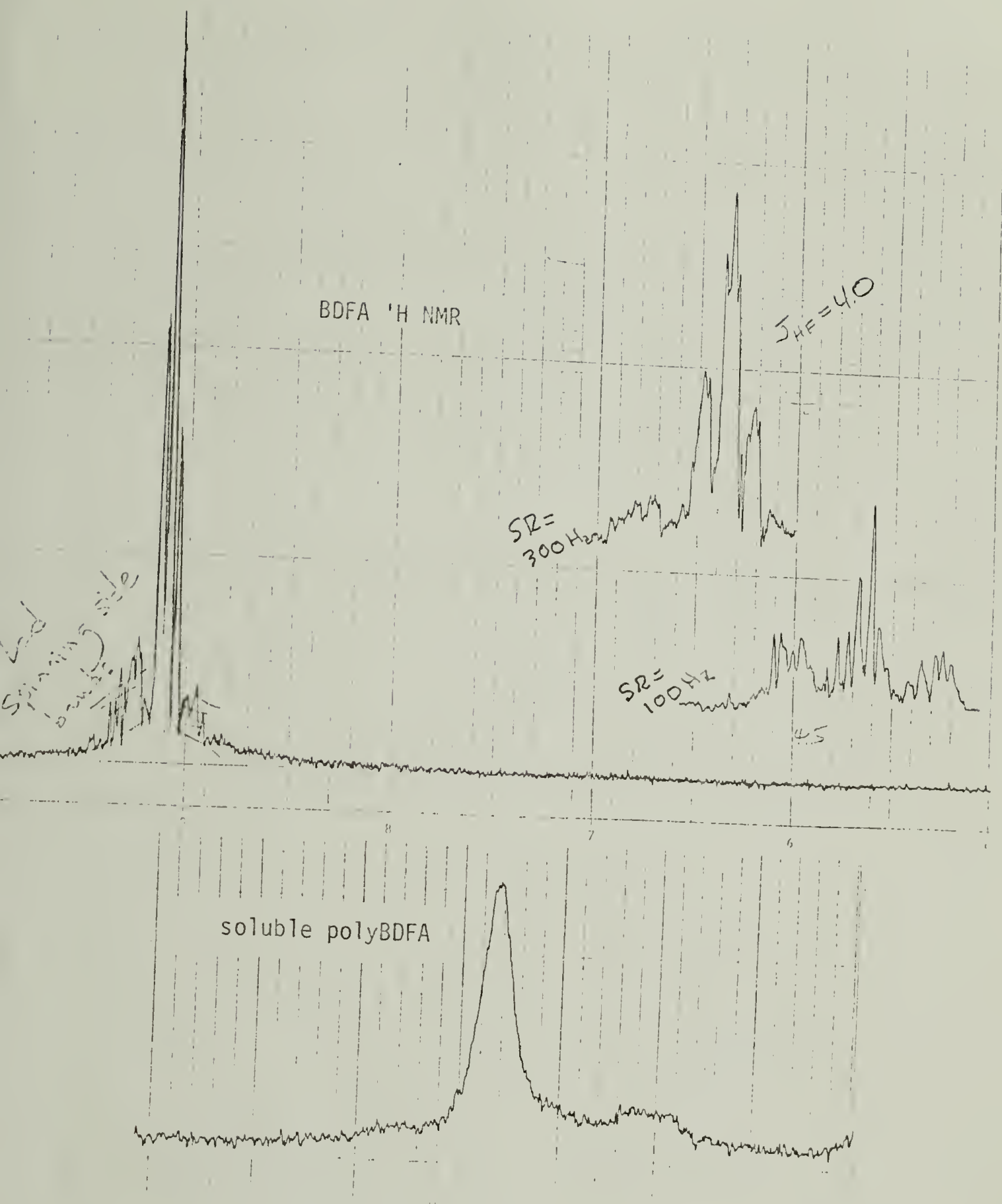


FIGURE 36

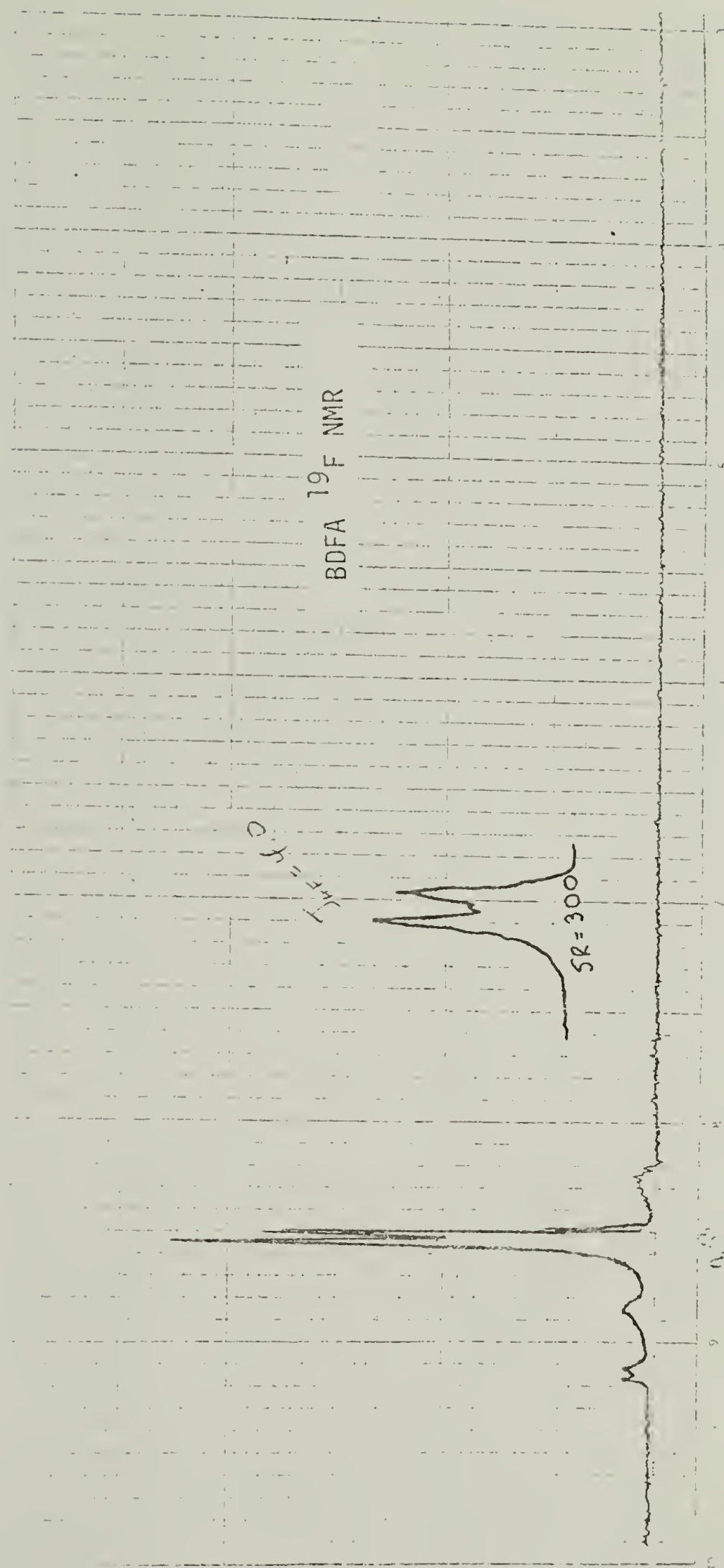


FIGURE 37

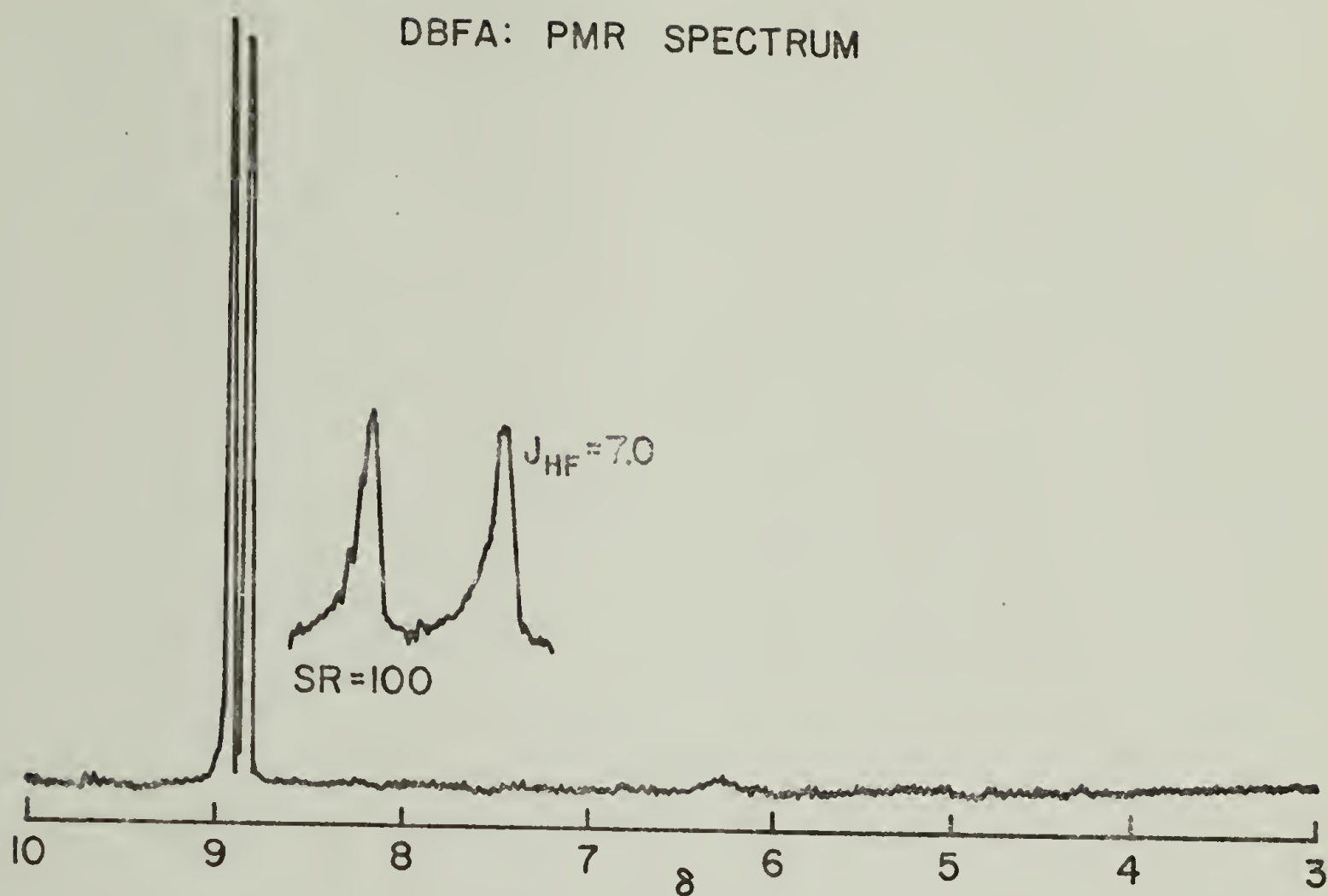


FIGURE 38

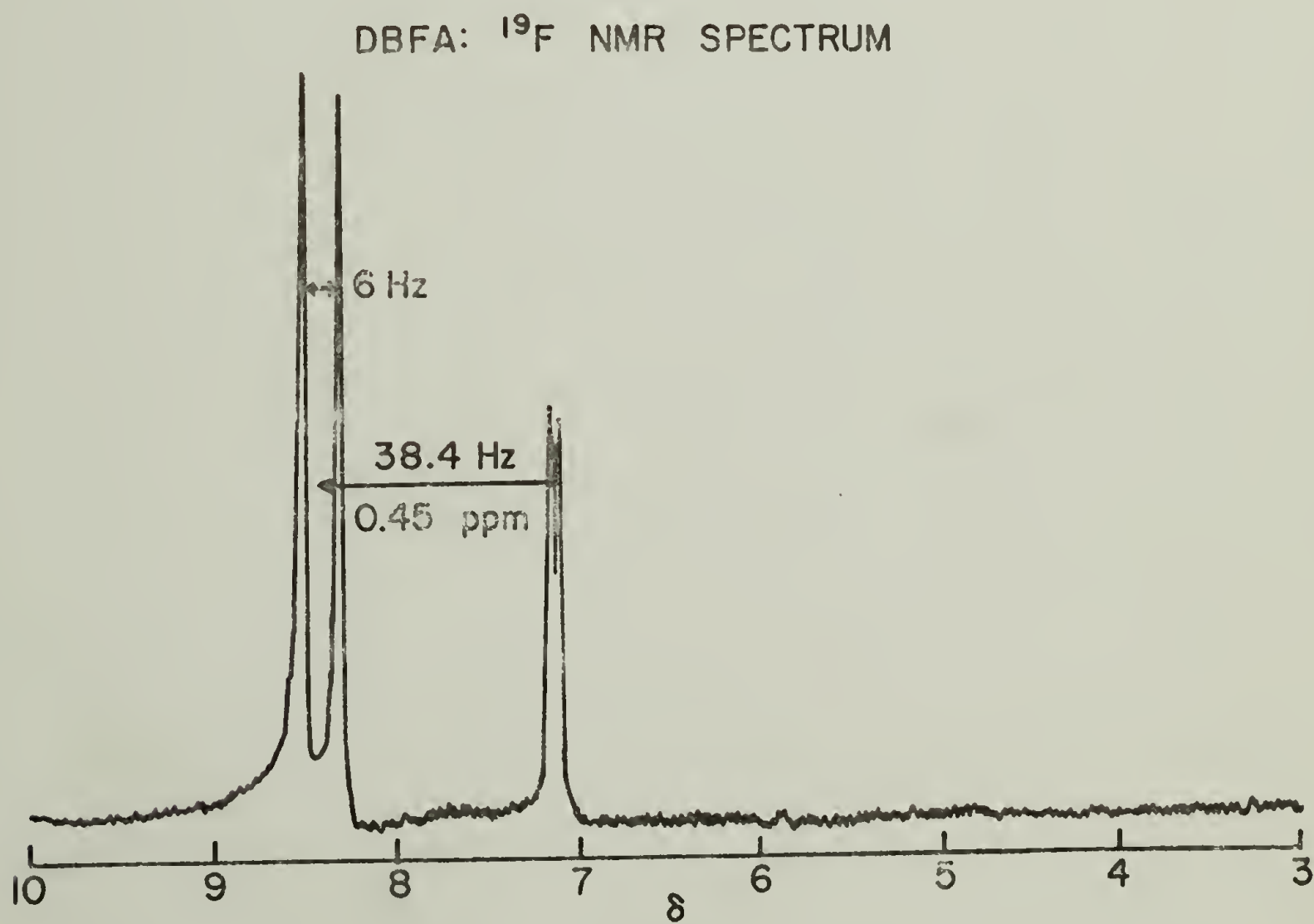


FIGURE 39

NMR Spectrum of Soluble
Poly— FCCl_2CHO

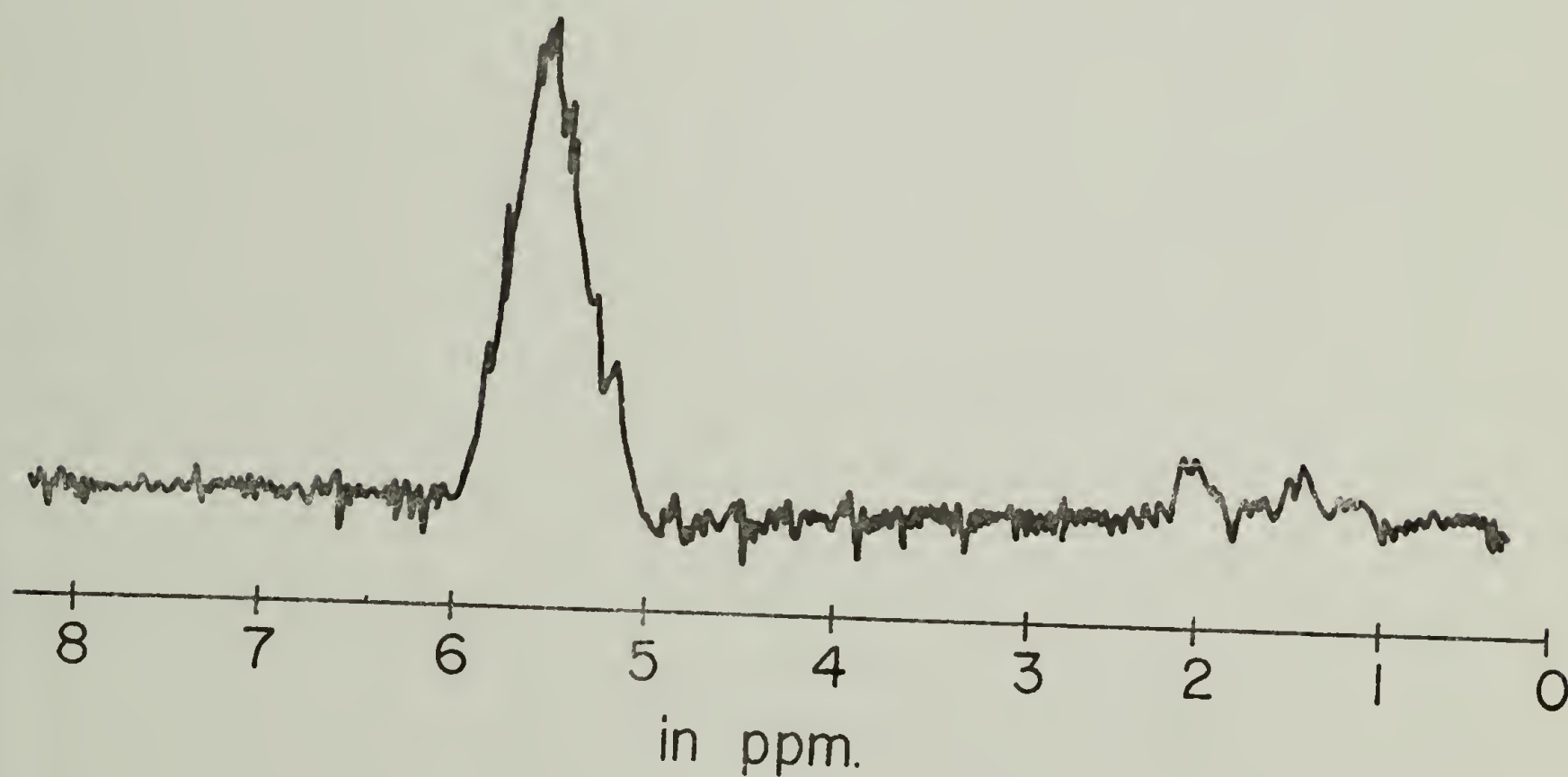


FIGURE 40

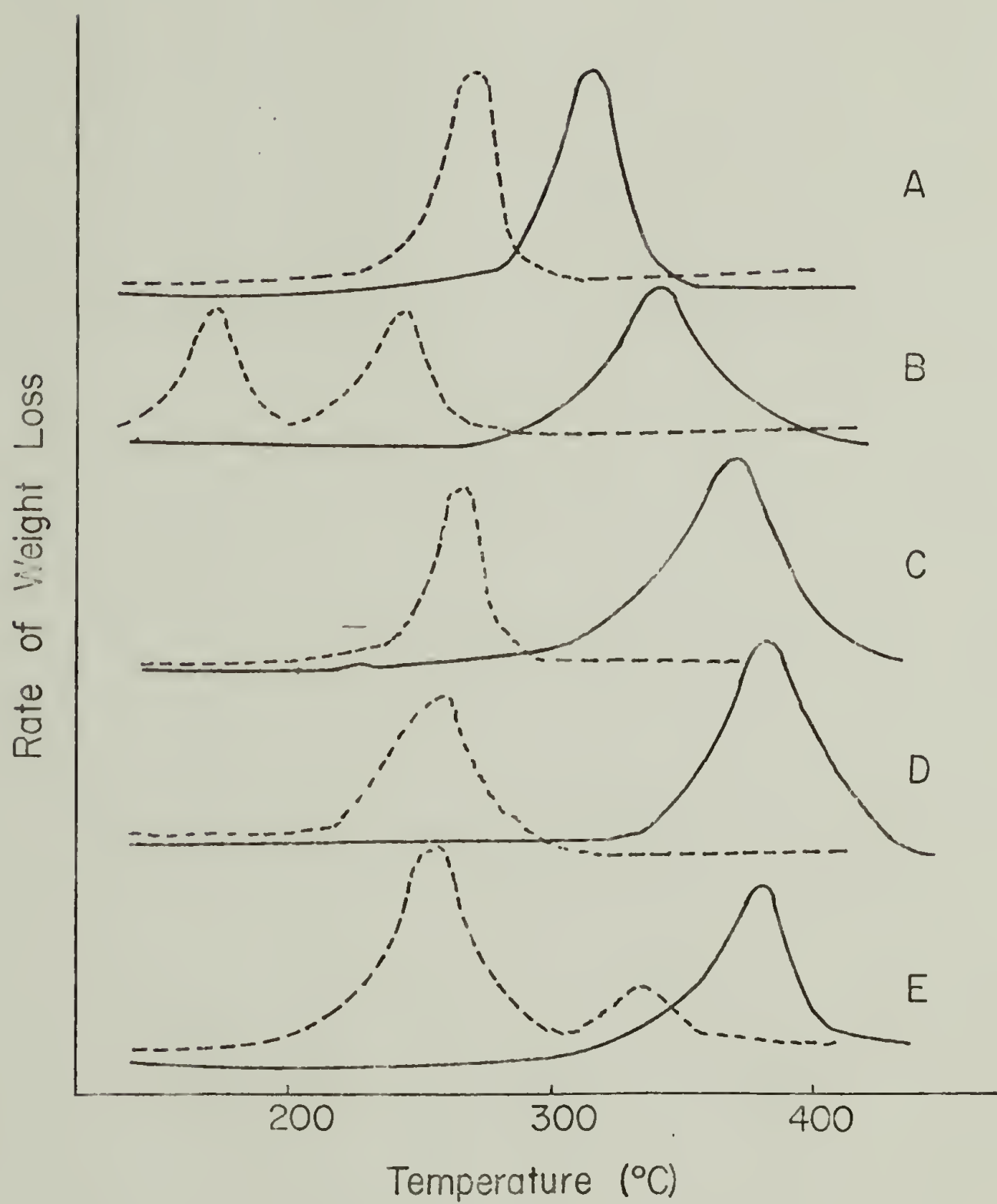
DTG Curves of Poly- FCCl_2CHO 

FIGURE 41

DTG Curves of
Poly- FCCl_2CHO with Ph_3P

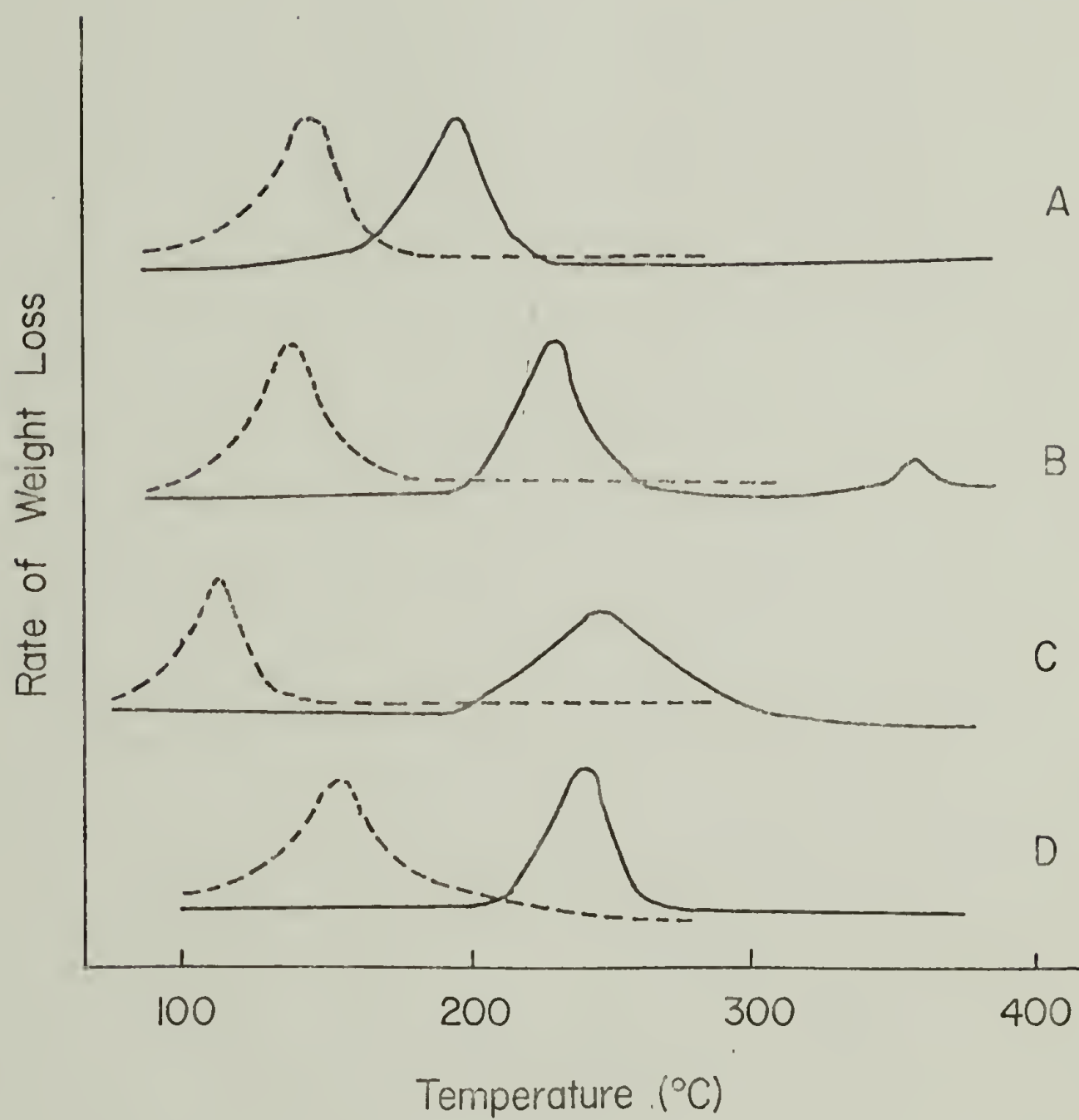


FIGURE 42

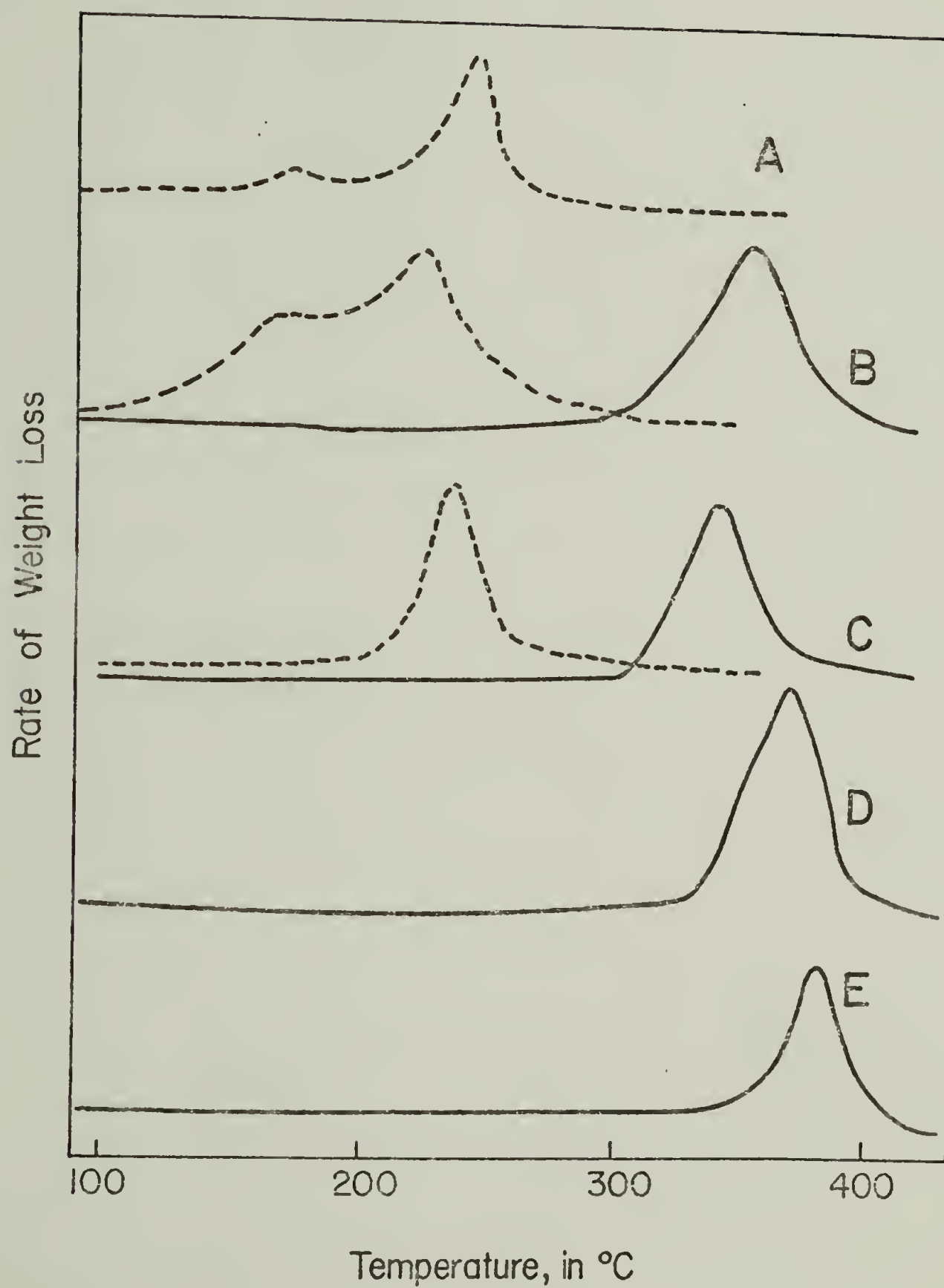
DTG Curves of Poly — ClCF_2CHO 

FIGURE 43

DTG Curves of Poly — ClCF_2CHO
 Ph_3P Initiator

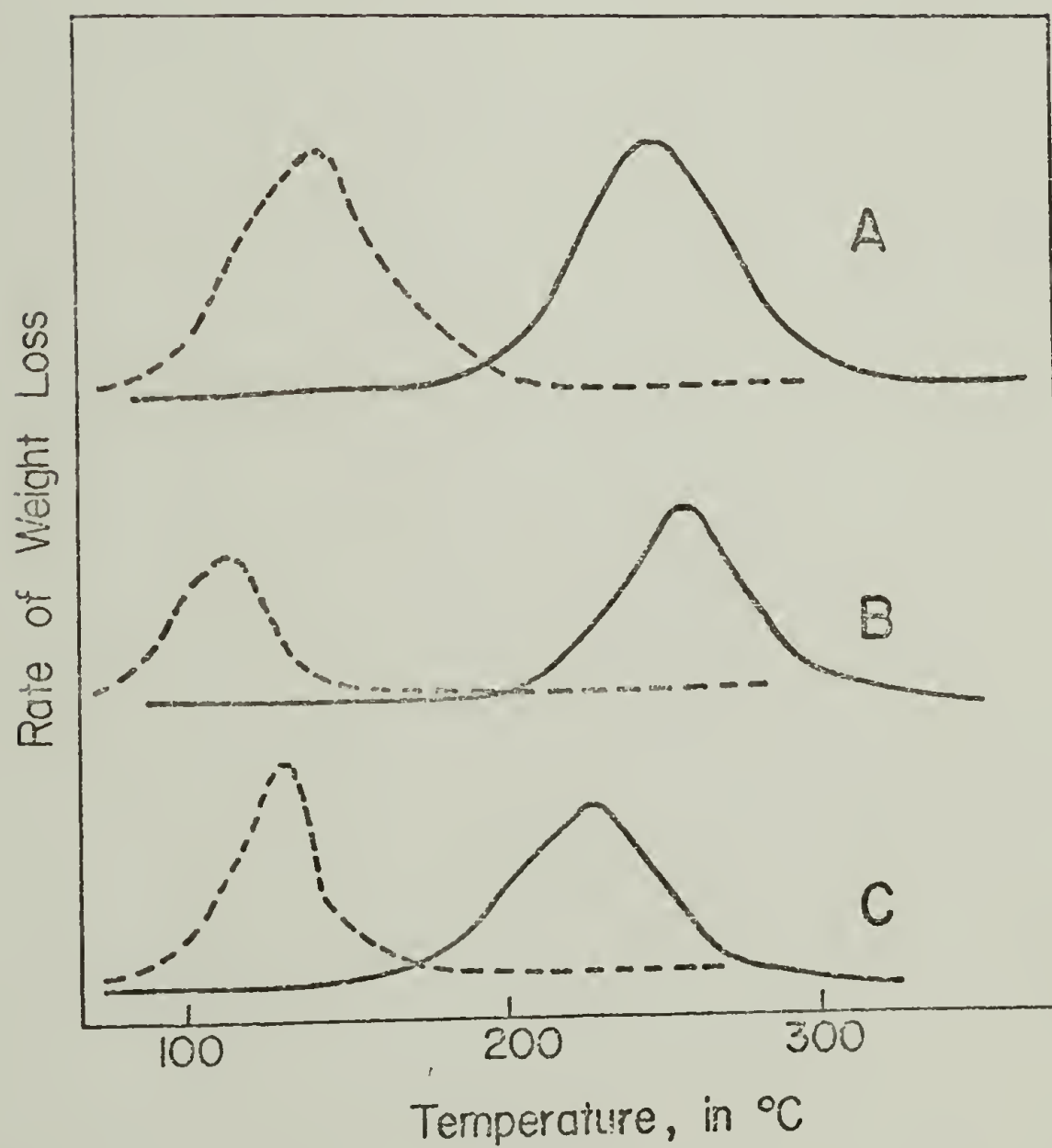


FIGURE 44

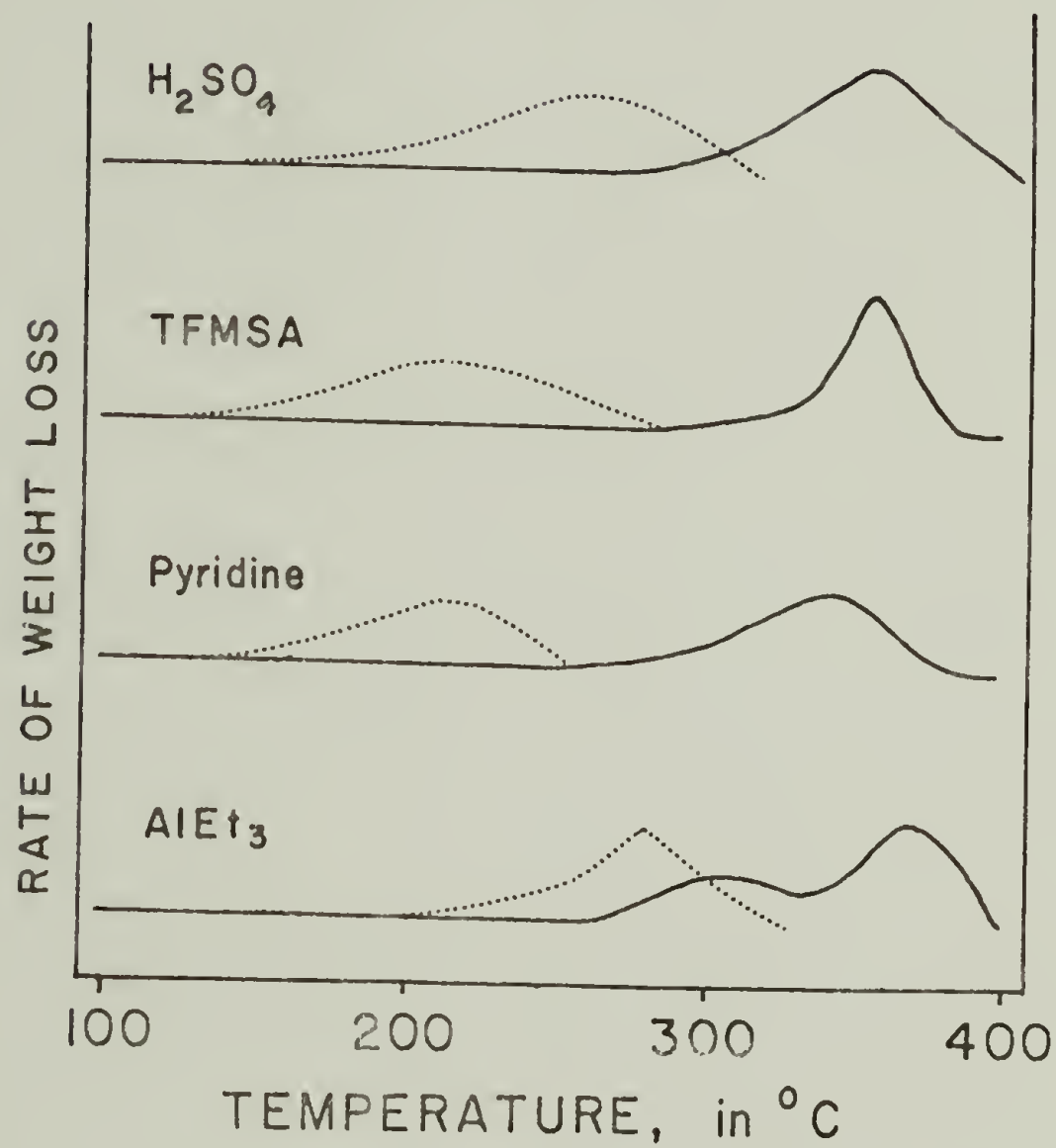
DTG CURVES OF POLY- CBr_2FCHO 

FIGURE 45

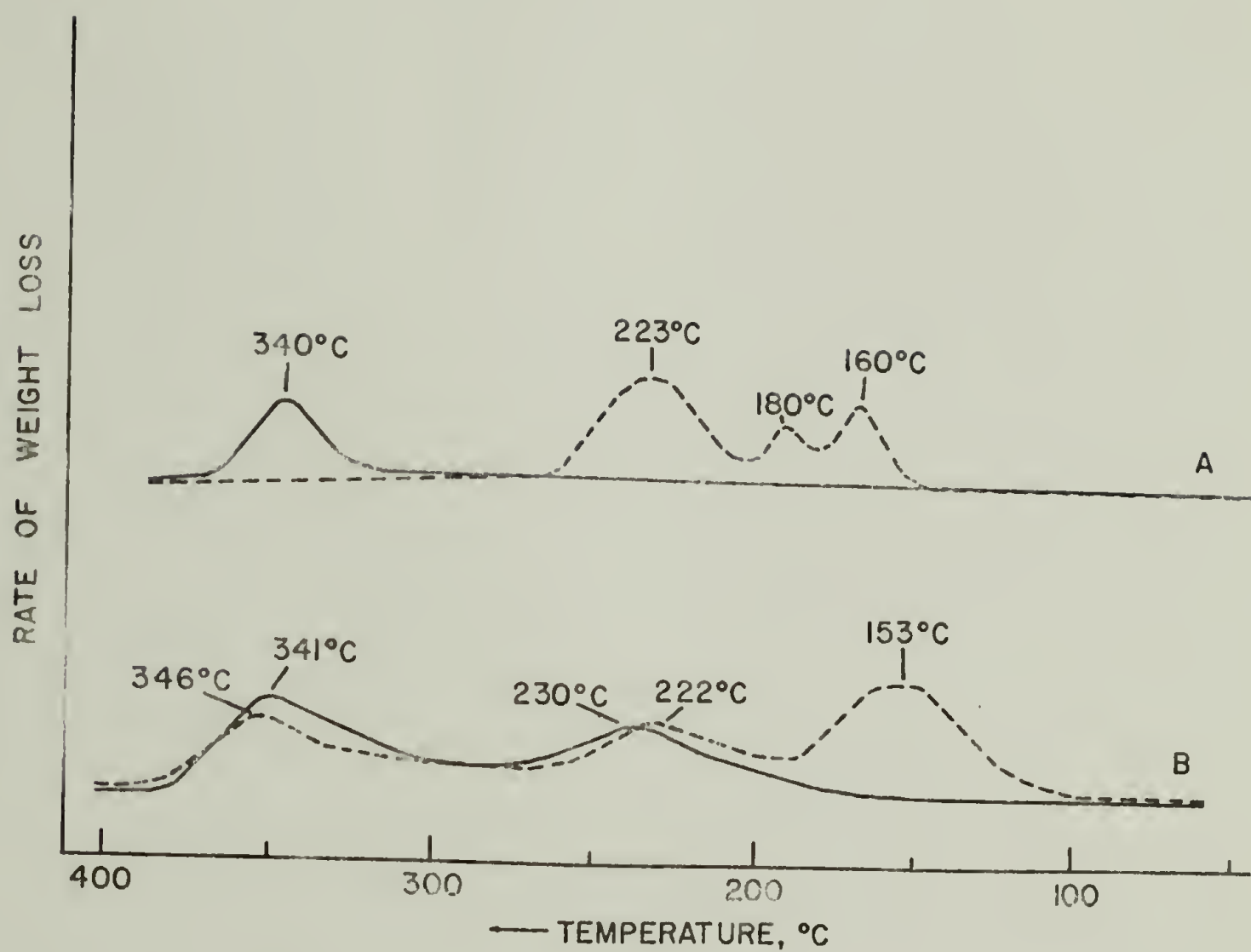


FIGURE 46

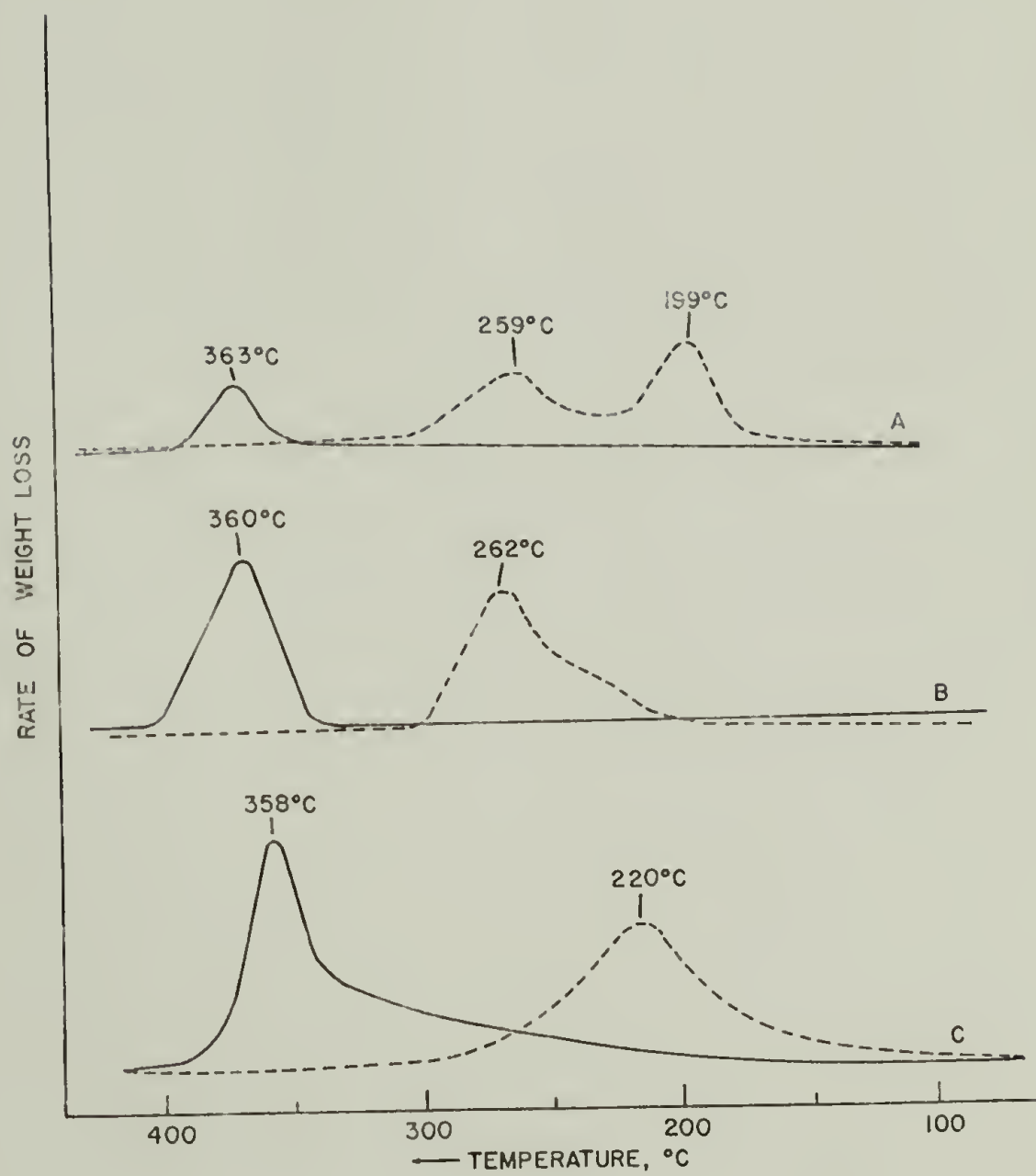


FIGURE 47

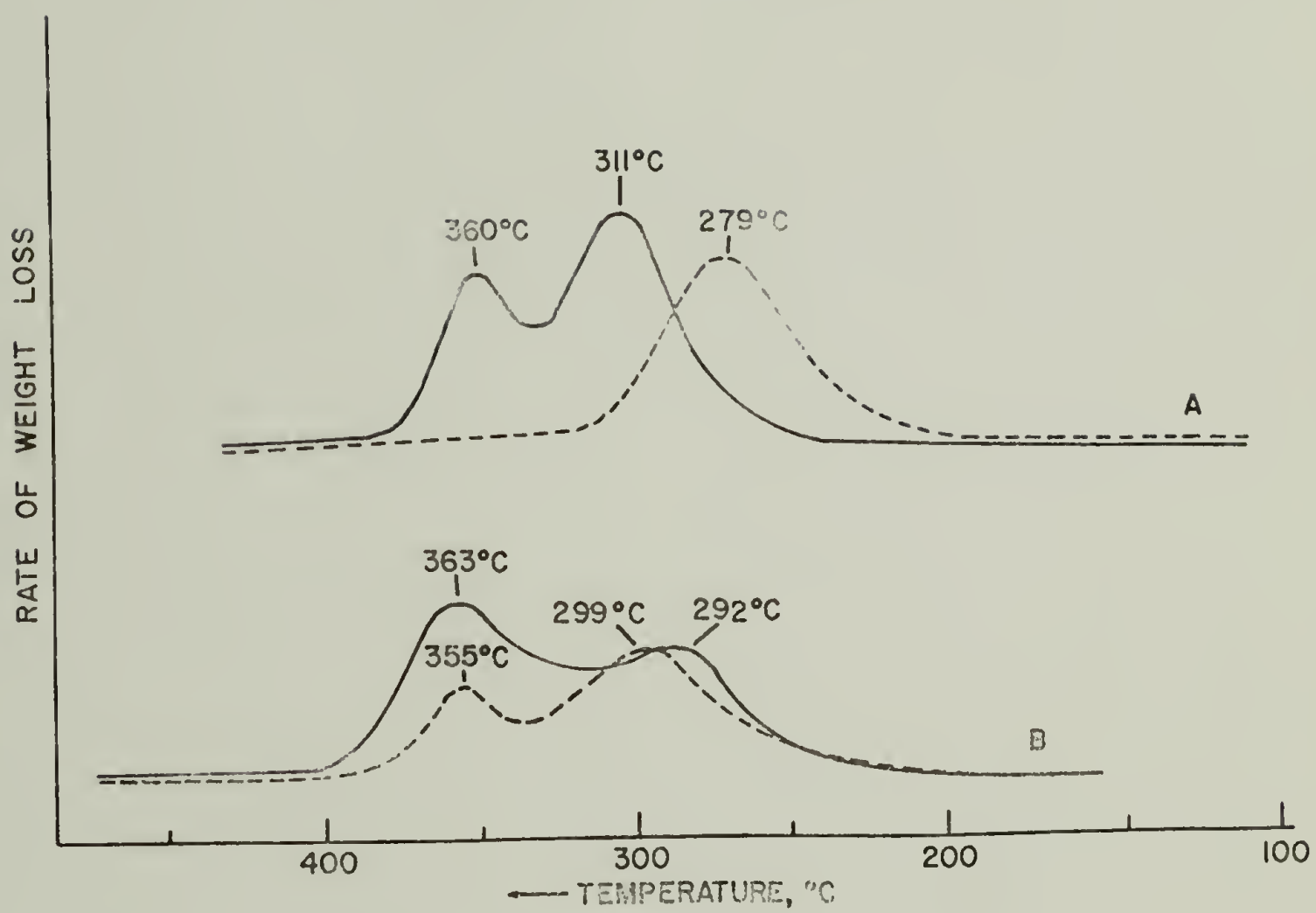


FIGURE 48

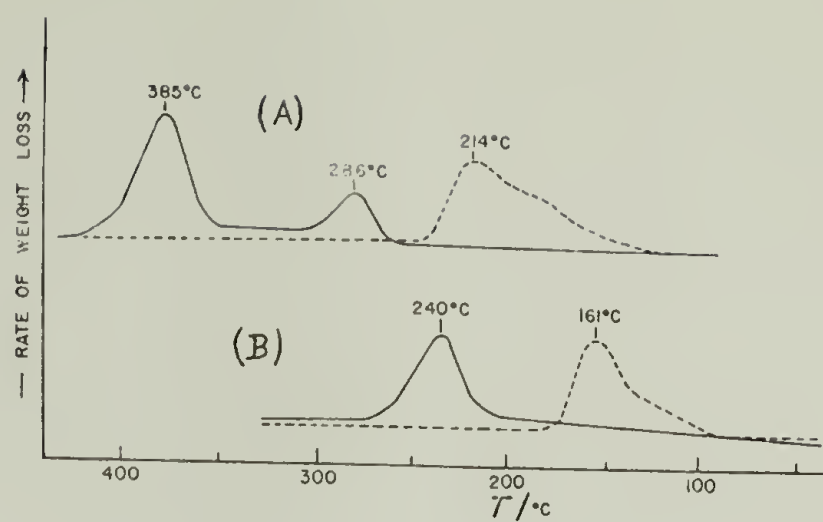


FIGURE 49

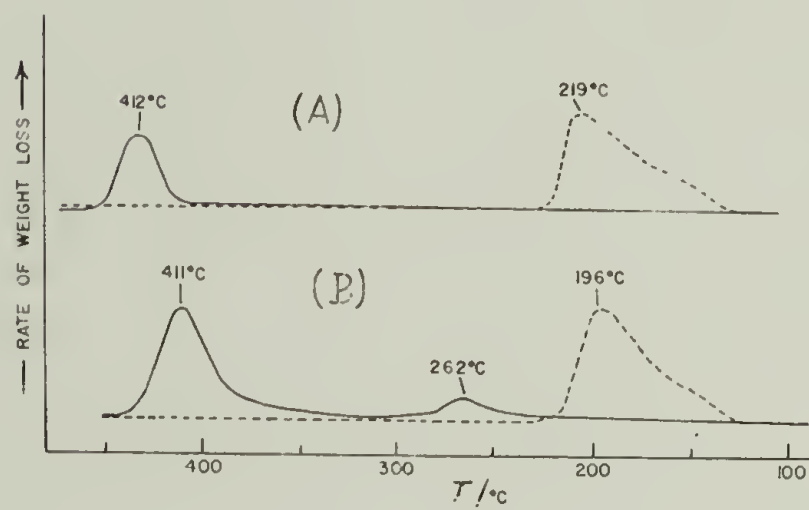


FIGURE 50

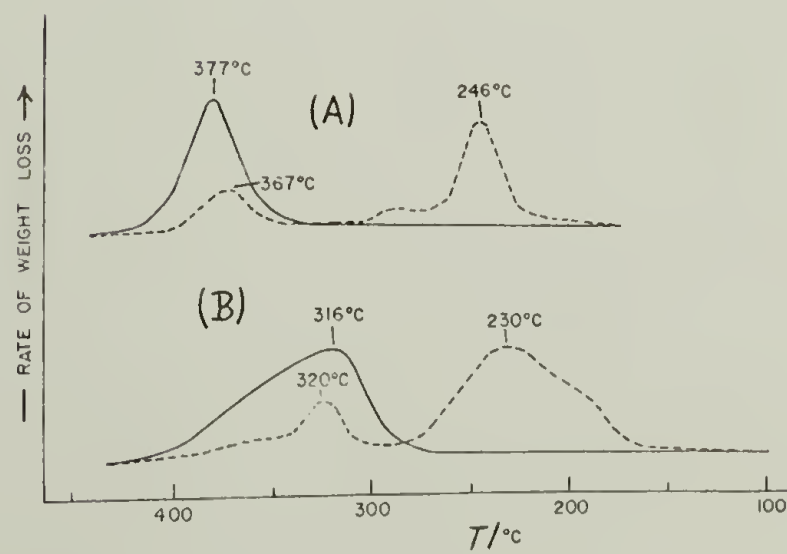


FIGURE 51

PHOTOOXIDATION APPERATUS

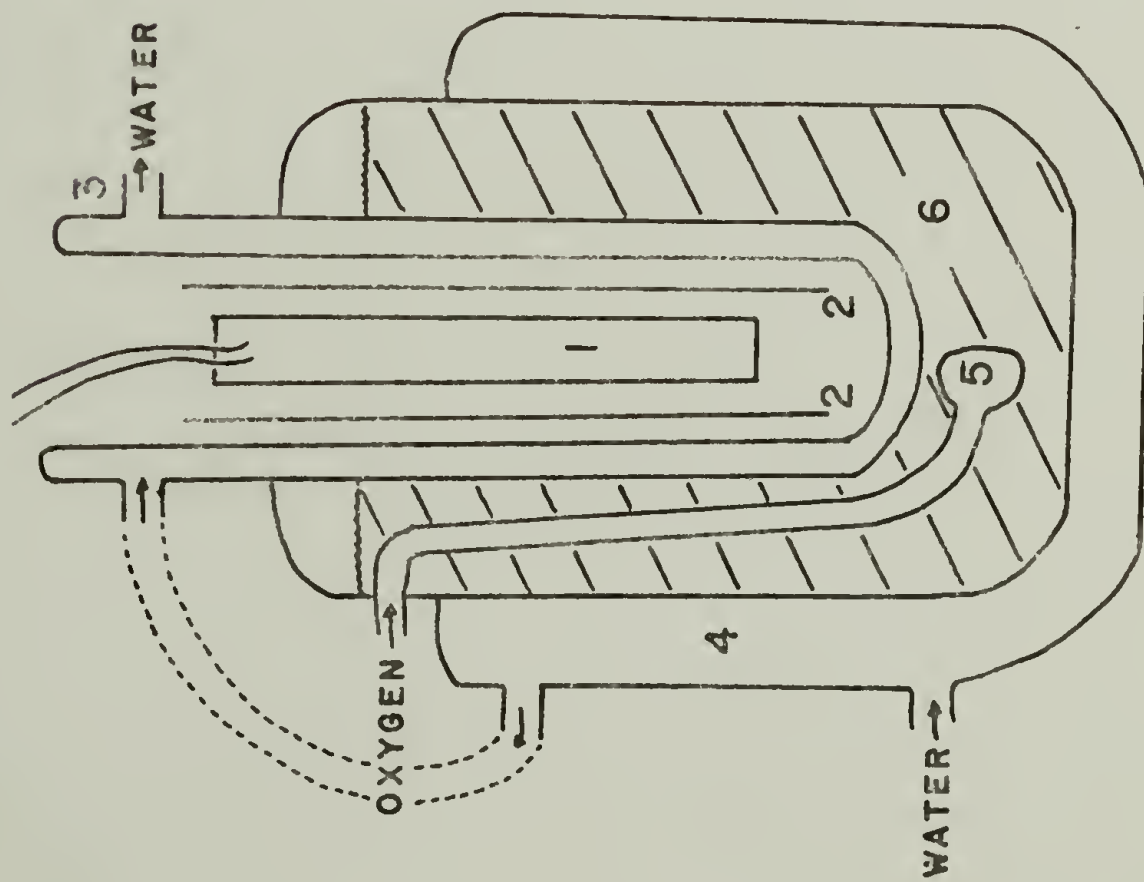


FIGURE 52

PHOTOOXIDATION OF TCE

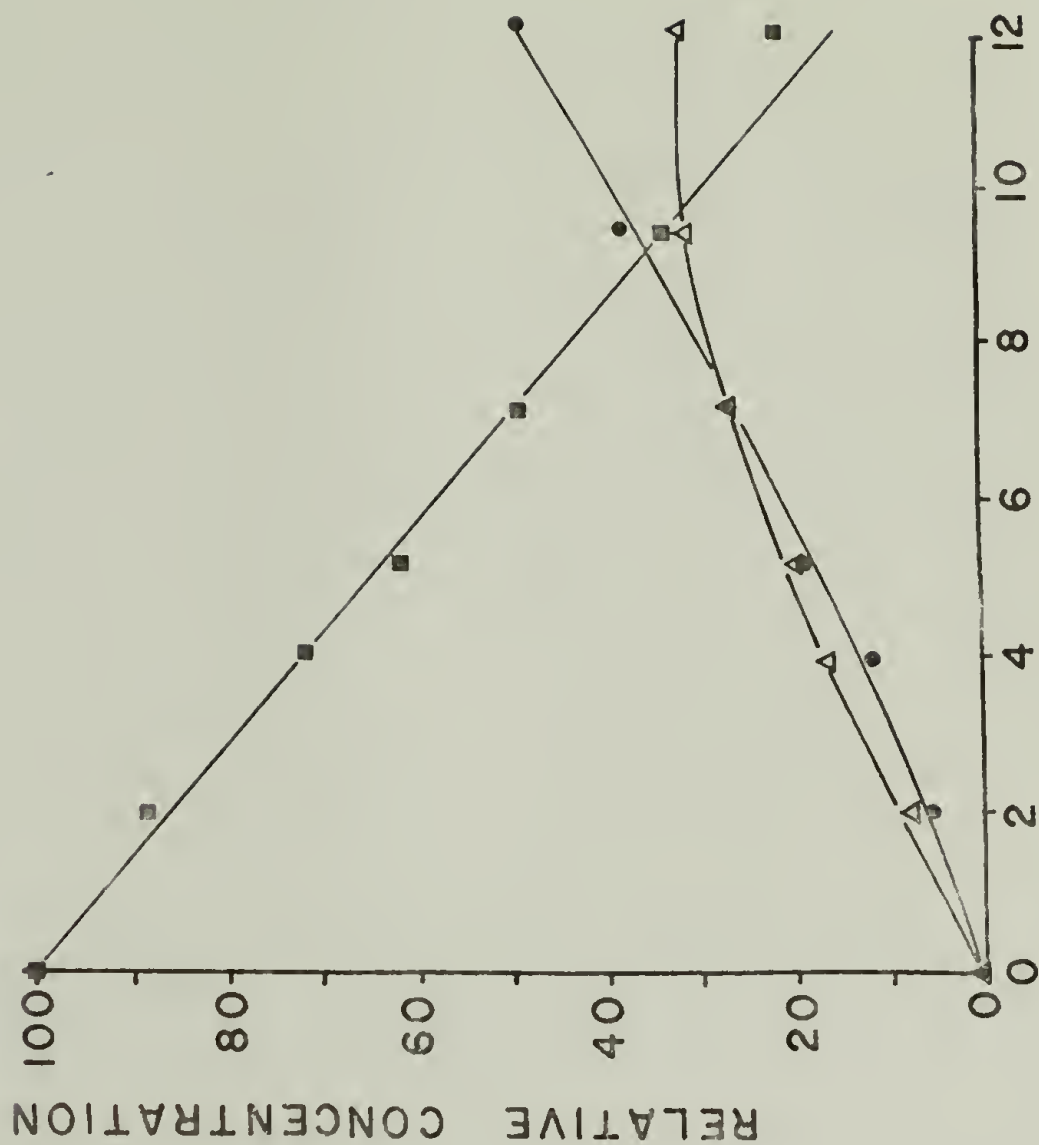


FIGURE 53

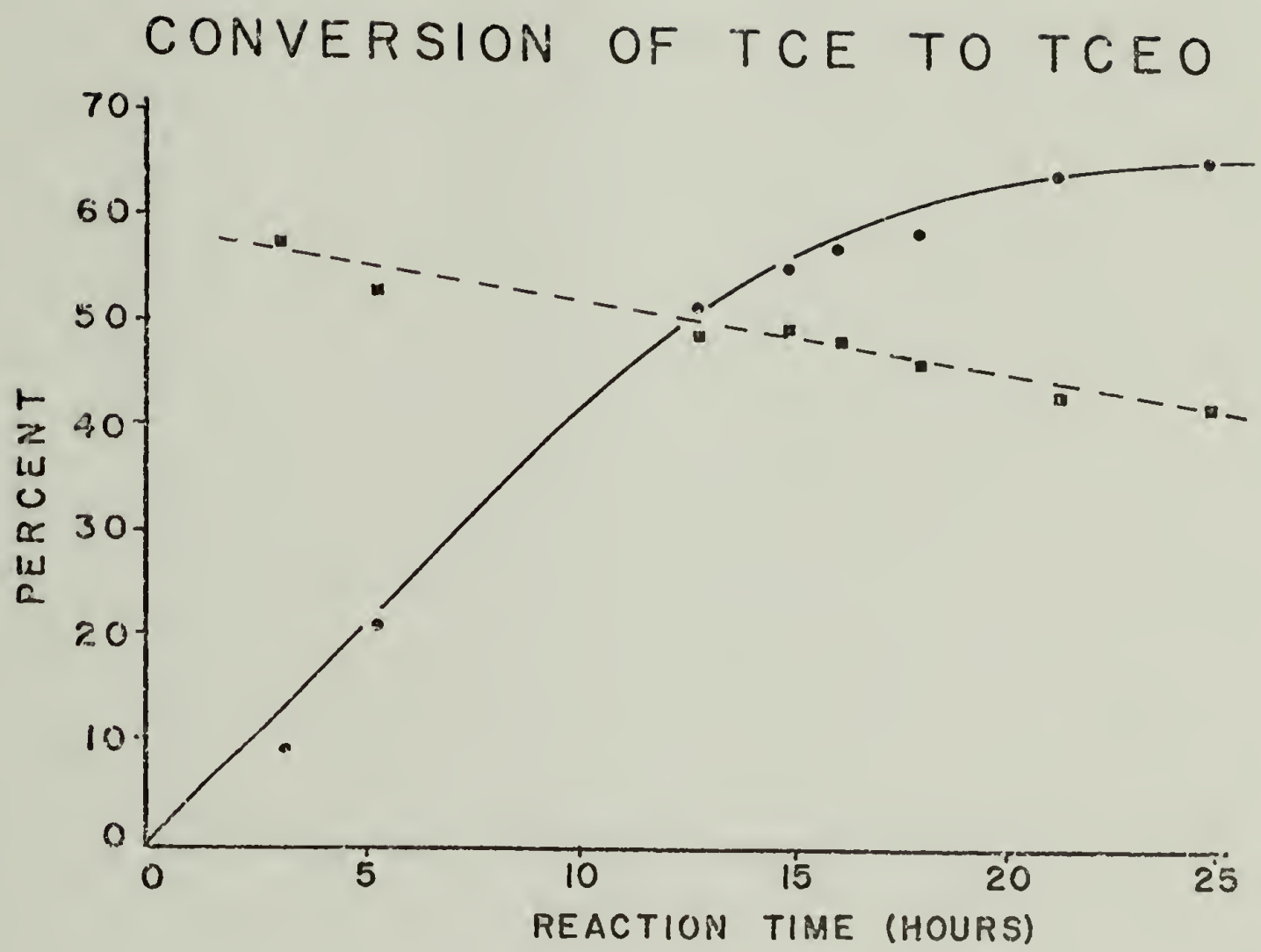


FIGURE 54

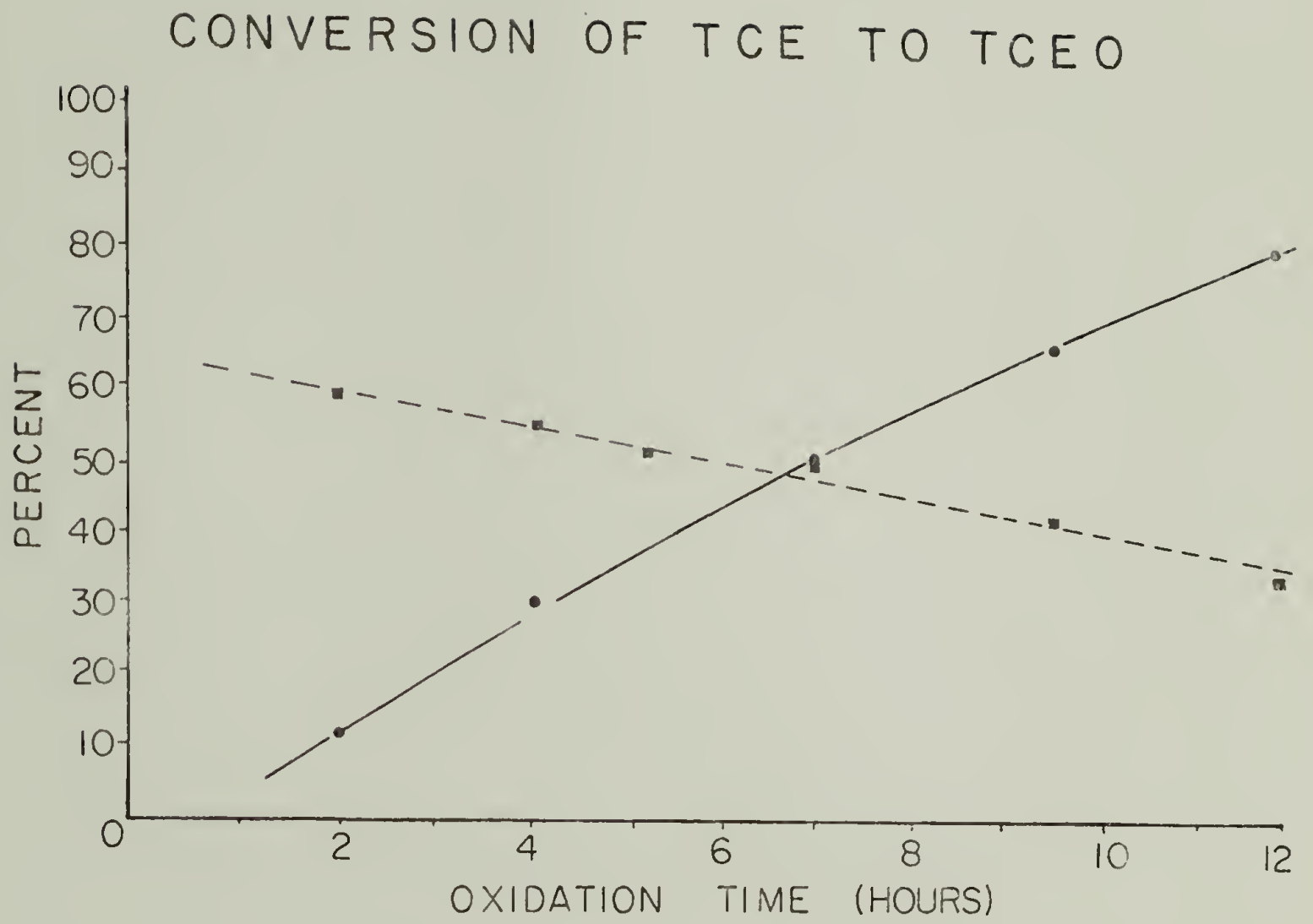


FIGURE 55

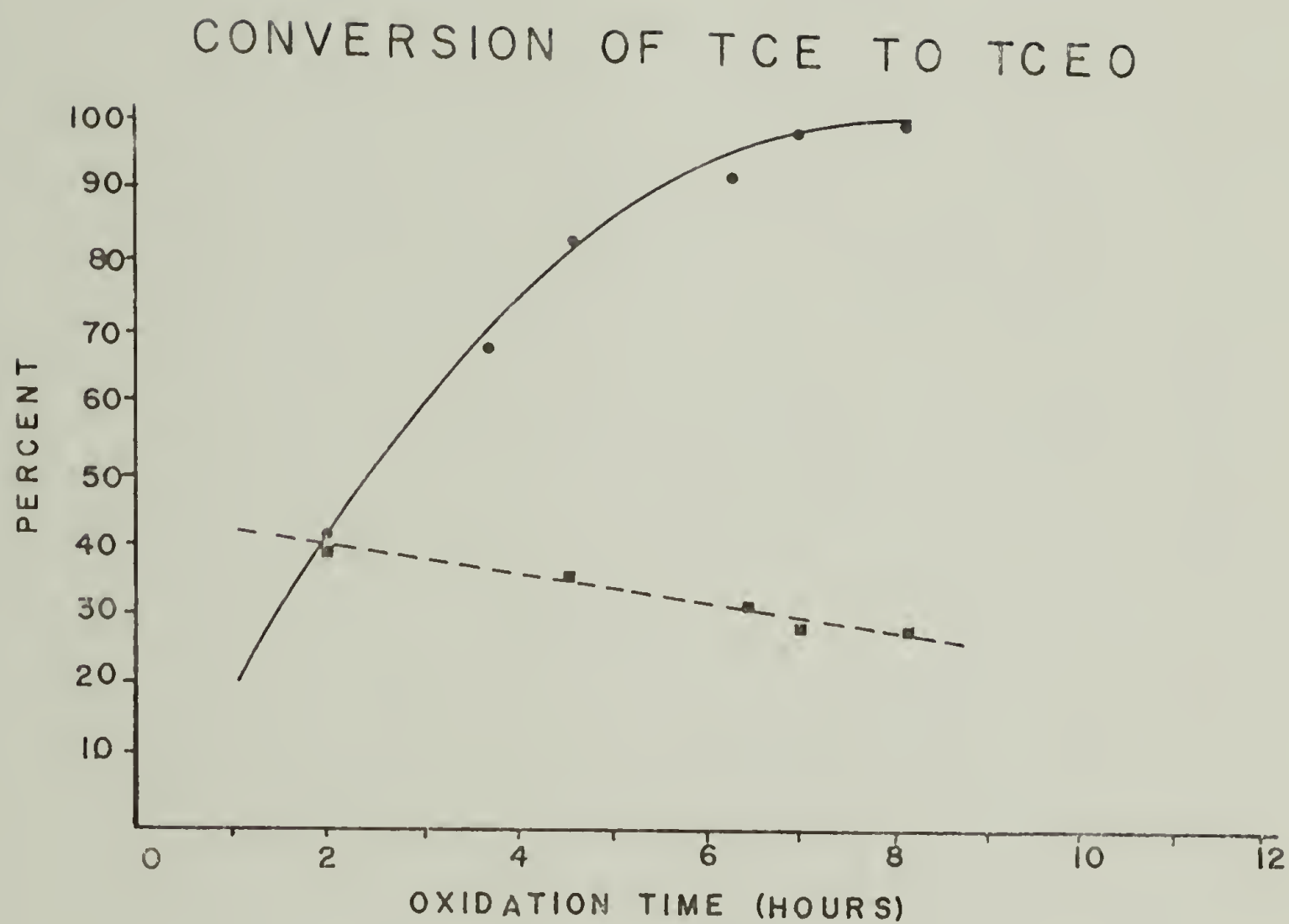


FIGURE 56

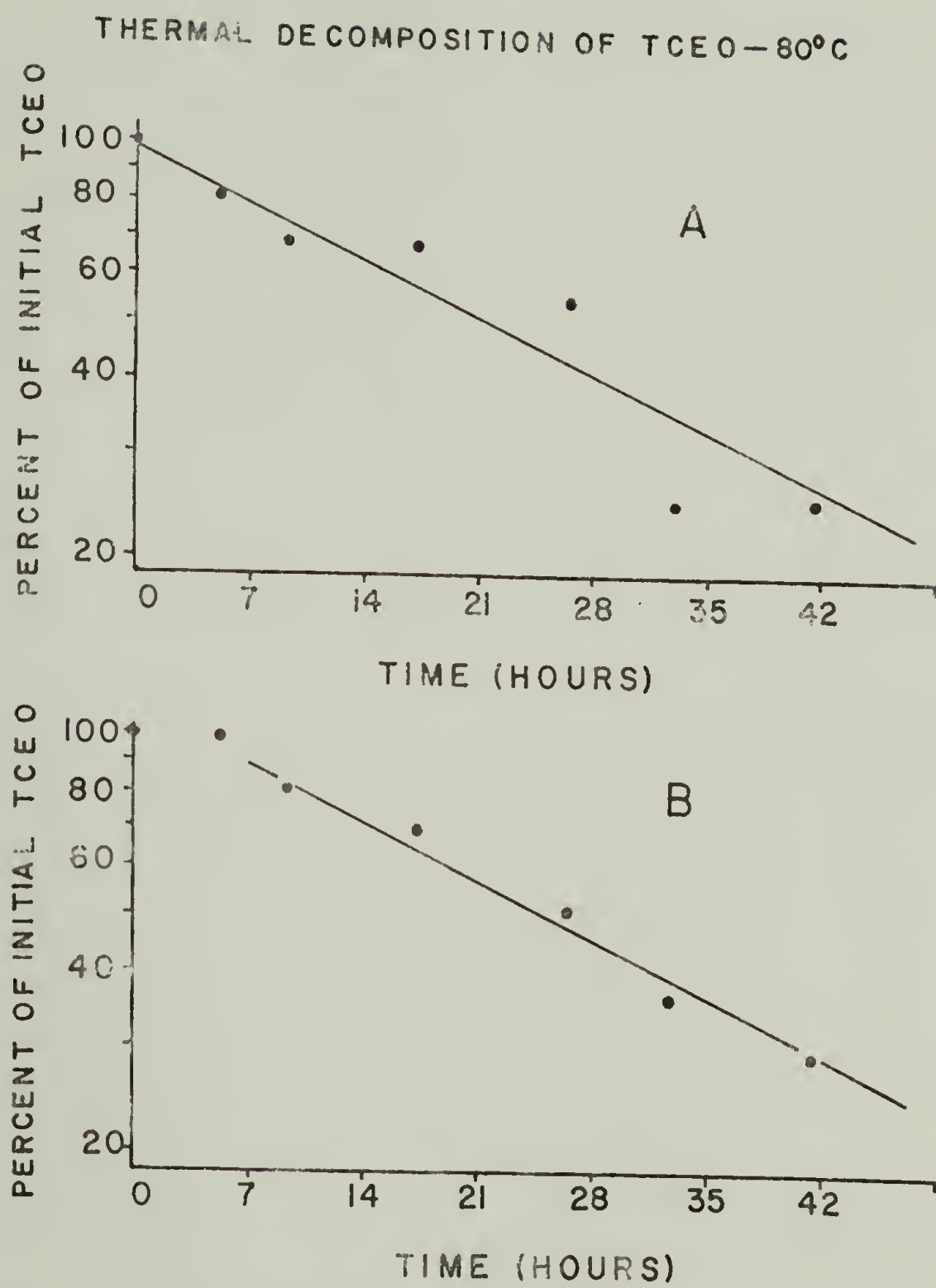


FIGURE 57

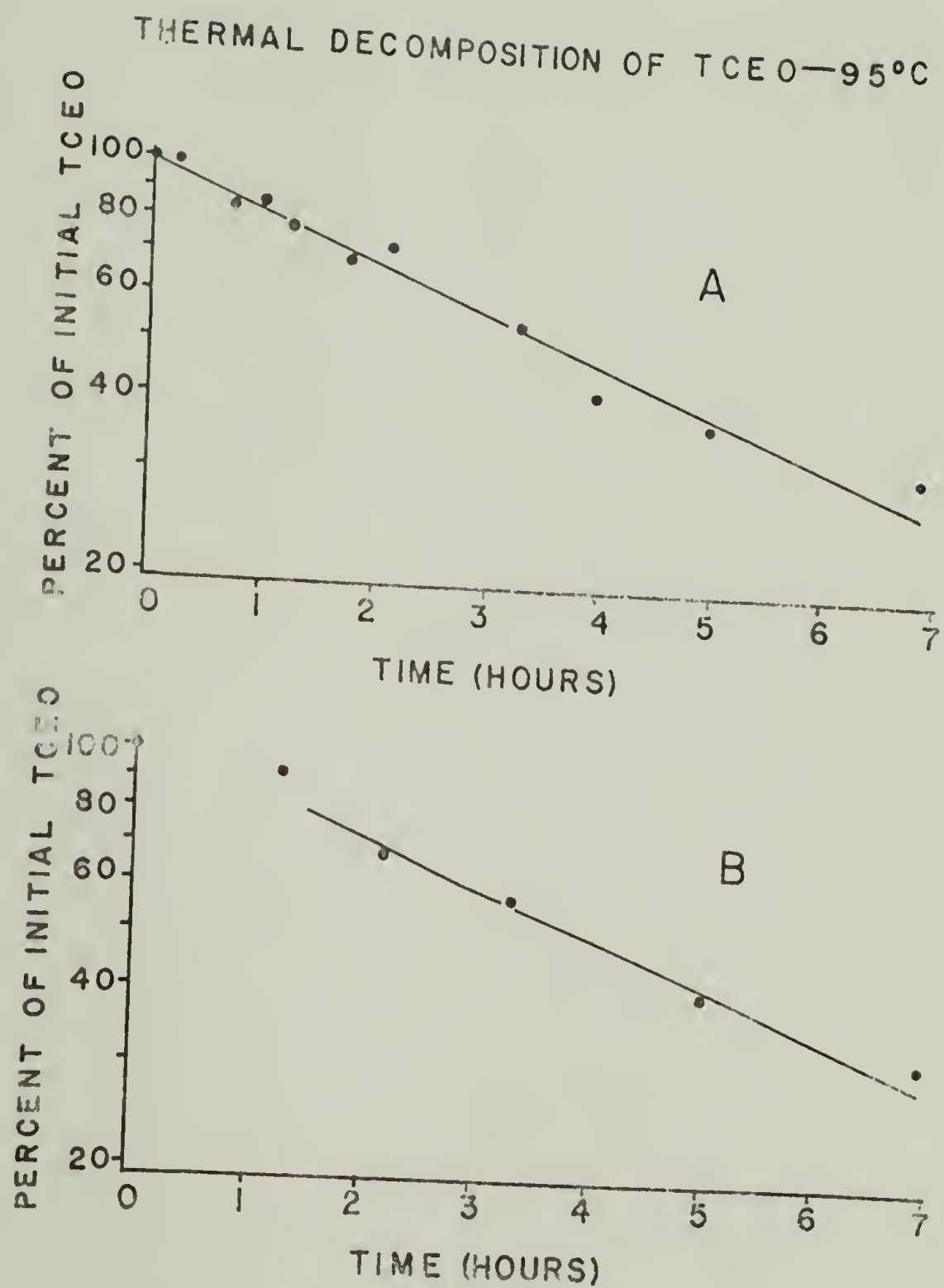


FIGURE 58

THERMAL DECOMPOSITION OF TCEO-110°C

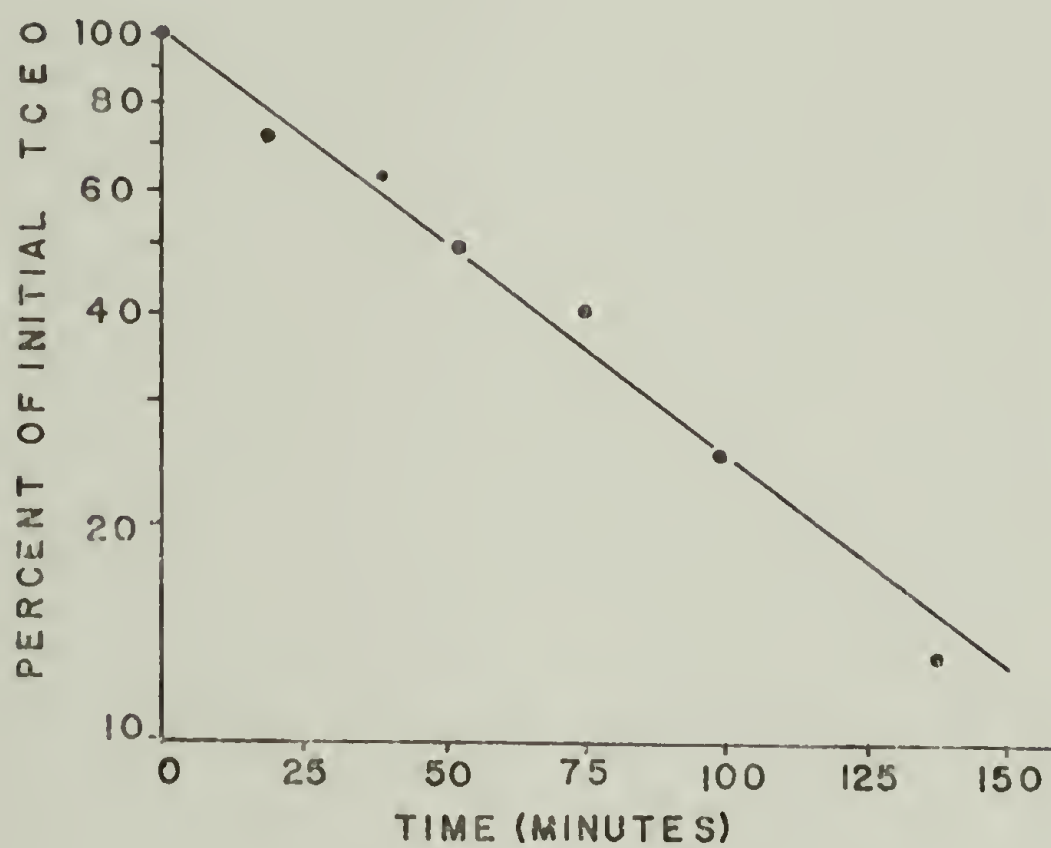


FIGURE 59

ARRHENIUS PLOT
THERMAL DECOMPOSITION - TCEO

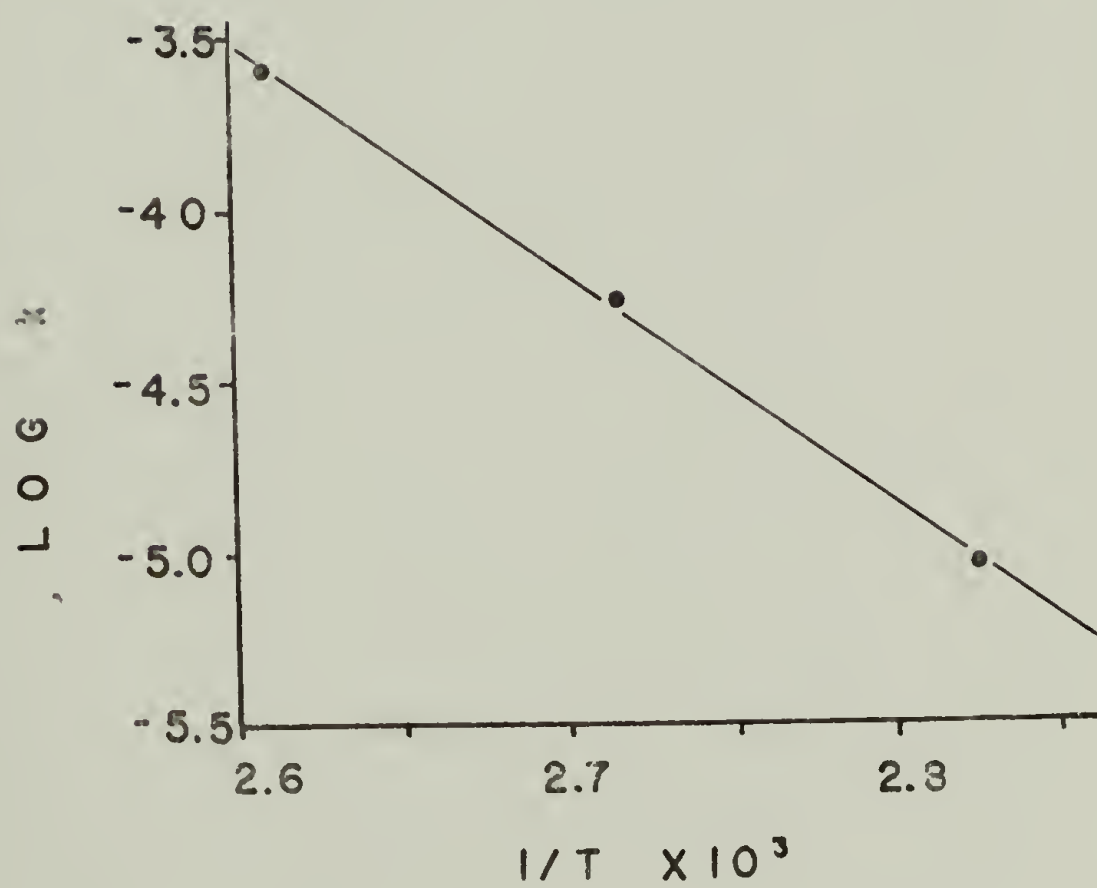


FIGURE 60

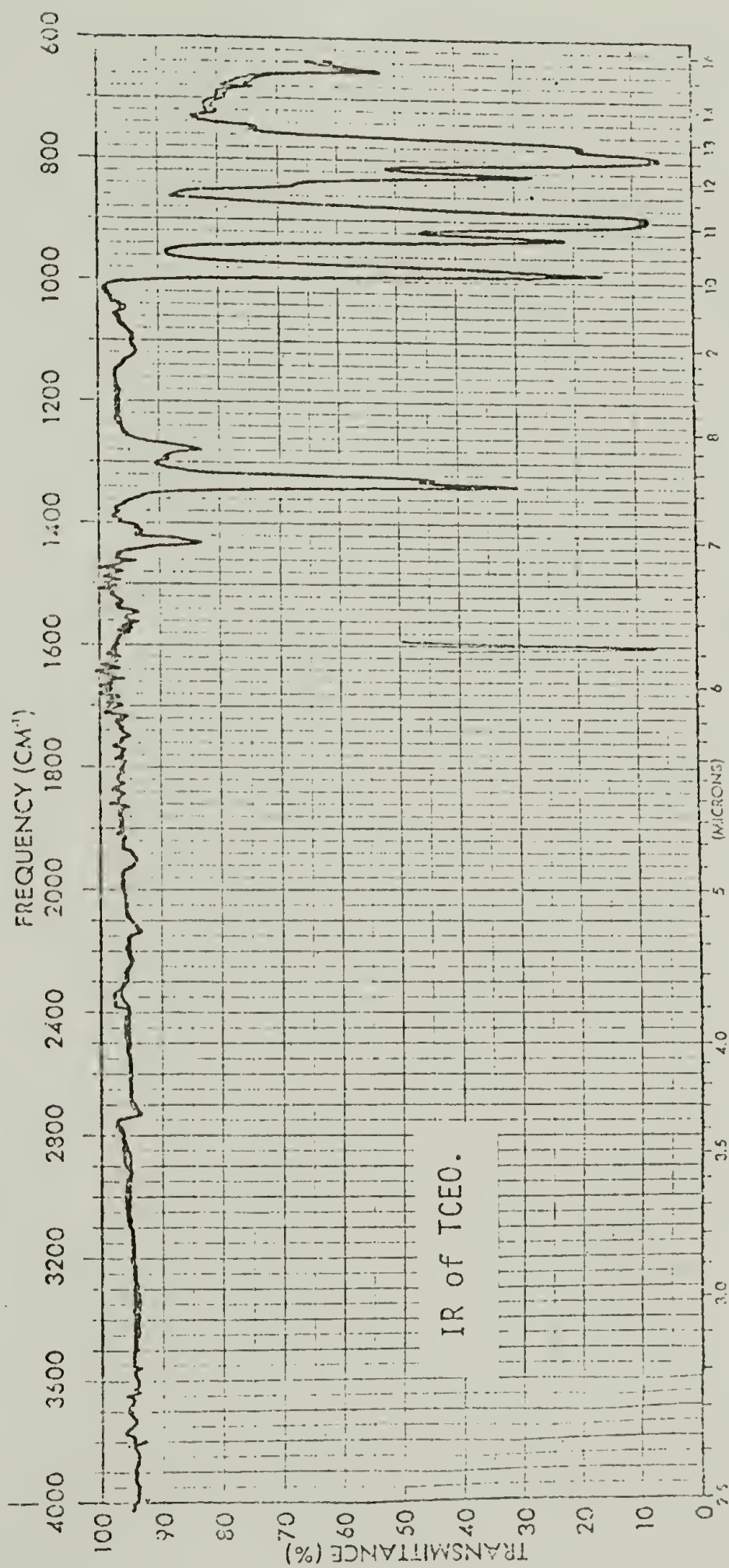


FIGURE 61

