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Synthesis of polymeric and oligomeric ultraviolet absorbers.

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SYNTHESIS OF POLYMERIC AND OLIGOMERIC
ULTRAVIOLET ABSORBERS

A Dissertation Presented

by

DAVID B. BAILEY

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

DOCTOR OF PHILOSOPHY

April

1975

Major Subject: Polymer Science and Engineering

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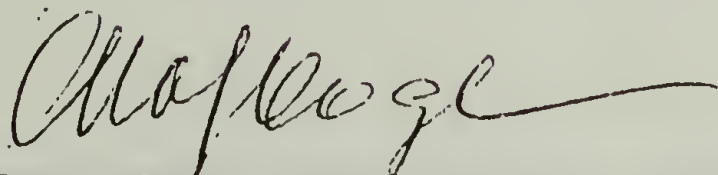
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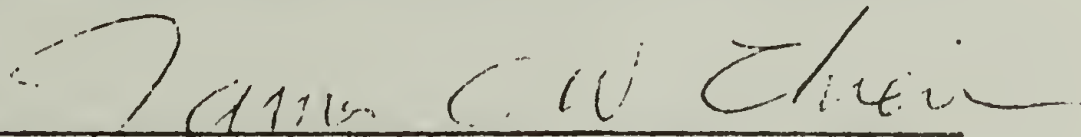
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April 1975

To Carol, Davy, and Tricia

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ABSTRACT

Synthesis of Polymeric and Oligomeric Ultraviolet Stabilizers

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Directed by: Dr. Otto Vogl

Polymeric ultraviolet absorbers were synthesized by the polymerization of vinyl substituted ultraviolet absorbers and by mild polymer modification reactions. Oligomeric ultraviolet absorbers were synthesized by endcapping of oligo(oxyethylenes) varying in molecular weight from 62 to 400.

Methyl salicylate, a commonly used ultraviolet absorber, was substituted in the position para to the phenol group with a vinyl group by a five-step synthesis. The overall yield of methyl 5-vinylsalicylate was 37%. Methyl 5-vinylsalicylate was polymerized and copolymerized with methacrylic acid or acrylic acid in order to obtain polymeric ultraviolet absorbers. Methyl 5-vinylacetylsalicylate was also synthesized and polymerized to yield a high molecular weight polymer.

Polymerizable derivatives of the commonly used ultraviolet stabilizer, 2,4-dihydroxybenzophenone, were synthesized. Both 2,4-dihydroxy-4'-vinylbenzophenone and 2,4-diacetoxy-4'-vinylbenzophenone were prepared; however, both

of these monomers were contaminated with impurities and would require further purification by liquid chromatography.

A polymeric ultraviolet absorber was obtained by a displacement reaction on poly(epichlorohydrin). The reaction of poly(epichlorohydrin) and tetraethylammonium N,N-dimethyl-p-aminobenzoate resulted in a copolymer consisting of 90 mole % glycidyl N,N-dimethyl-p-aminobenzoate and 10% epichlorohydrin repeat units. The reaction conditions were relatively mild as compared to displacement reactions of sodium or potassium salts of carboxylic acid on poly(epichlorohydrin) or poly(3,3-bis(chloromethyl)-oxacyclobutane) which have been reported in the literature.

Poly(epichlorohydrin) was converted to an 83/17 copolymer of epiodohydrin and epichlorohydrin by a displacement reaction with sodium iodide (Finkelstein reaction). It was expected that the copolymer would be a very reactive substrate for polymer modification reactions.

A mild polymer modification reaction was carried out on poly(methacrylic acid) in order to obtain a polymeric ultraviolet absorber. Poly(methacrylic acid) was converted to poly(tetrabutylammonium methacrylate) which was then reacted with 2-hydroxy-4-(1-bromoethoxy)benzophenone. The product was a copolymer of 2-hydroxy-4-(1-methacryloxy)-benzophenone and methacrylic acid.

Oligo(oxyethylenes) were endcapped with ultraviolet

absorbing esters. Oligo(oxyethylene) di-N,N-dimethyl-p-aminobenzoates were prepared by an ester interchange reaction of oligo(oxyethylene) and methyl N,N-dimethyl-p-aminobenzoate. Oligo(oxyethylene) disalicylates were prepared by a displacement reaction of sodium salicylate on the corresponding oligo(oxyethylene) di-p-toluene-sulfonates. The oligo(oxyethylene) di-p-toluenesulfonates had been prepared from oligo(oxyethylene) and p-toluene-sulfonyl chloride.

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C H A P T E R I

INTRODUCTION

Polymeric ultraviolet absorbers may be classified as both functional polymers and as additives for the stabilization of plastics against oxidative photodegradation. Therefore, a brief and general overview of both of these subjects is included in the first two sections of the introduction.

The primary motivation for the preparation of polymeric ultraviolet absorbers has been to decrease the mobility and increase the permanence of stabilizers in plastics. (Ultraviolet absorbers are also referred to as ultraviolet stabilizers.) Information published in the literature concerning the relationship between the mobility of additives in plastics and the molecular weight of the additive is presented in section C. The permanence or reduced mobility of polymeric and oligomeric ultraviolet absorbers is also discussed in section F.

Ultraviolet absorbers with reduced mobility have been classified in this dissertation as either polymeric or oligomeric. The polymeric ultraviolet absorbers are compounds prepared by chain growth or step growth polymerization of monomeric ultraviolet absorbers or by polymer modification reactions. Compounds prepared by dimerization reactions, endcapping of di, tri, and tetra functional compounds, and by the attachment of long aliphatic chains to ultraviolet absorbers are classified as oligomeric ultraviolet absorbers.

A literature review of the synthesis of these materials is presented in sections D and E.

The permanence and compatibility of the high molecular weight ultraviolet absorbers in plastics and their properties in general are discussed in section F.

The research presented in this dissertation includes the preparation of polymeric ultraviolet absorbers by reactions of poly(epichlorohydrin) and, to a lesser extent, reactions on poly(methacrylic acid). Therefore, the last two sections of this introduction are concerned with reactions of poly(epichlorohydrin) and poly(methacrylic acid).

A. General Background of the Synthesis and Utilization of Functional Polymers

This section is intended to give a brief survey of the various kinds of functional polymers that have been reported in the literature. The emphasis is on polymers which contain active groups; however, polymers capable of being converted to active polymers (polymeric substrates) are also discussed.

Active groups have been incorporated into polymer chains by polymerization and copolymerization of compounds containing diol, dicarboxylic acid, vinyl, epoxy, and other polymerizable groups and by polymer modification reactions. The monomer polymerization approach is sometimes limited by the

low yield of final compound that results from a multi-step synthesis and the difficulties in obtaining an adequate amount of monomer with the high degree of purity required for the preparation of a high polymer. Premature polymerization of vinyl and epoxy monomers during synthesis and purification have caused problems. Nevertheless, the monomer polymerization approach is attractive because a broad range of copolymer properties (strength, elasticity, solubility, degree of crosslinking) can be obtained by copolymerization with the appropriate comonomers.

The introduction of active groups into polymers by polymer modification reactions is attractive if the reaction is mild and free of side reactions or if the attachment of a polymerizable functional group to the active compound is not feasible. It would also be necessary to use the polymer reaction approach rather than the monomer polymerization approach if the active group could inhibit radical or ionic polymerization or interfere with step growth polymerization. Side reactions and difficulties encountered in separating polymers from side products, some of which may be attached to the polymer chain, complicate product characterization and limit the utility of polymer reactions.

Functional polymers have been used in solution, as insoluble swollen resins, and in the solid state. For example, many of the polymer modification reactions are carried out

in solution. Some examples of insoluble resins are ion exchange resins, supports for polypeptide synthesis, and polymeric enzymes. Functional polymers in this form have the advantage that they can easily be separated from the reaction medium by filtration or they can be used in a column. Functional polymers used in the solid state include heparinized heart valves.

Ion exchange resins¹⁻⁵ are the most widely utilized type of functional polymer. Most are based on a lightly crosslinked polystyrene resin. Anion exchange resins are prepared by the reduction of nitrated polystyrene or by chloromethylation followed by amination. Cation exchangers are obtained by sulfonation of crosslinked polystyrene. Crosslinked poly(methacrylic acid) and poly(acrylic acid) also serve as weak acid cation exchangers. The resins have been used on a large commercial scale for the exchange of calcium and magnesium for sodium in water (water softening), water deionization, sugar purification by the removal of ionic impurities, isolation of anionic complexes of uranium, purification of glycerol, purification of formaldehyde solutions by removing formic acid, and isolation and purification of antibiotics such as streptomycin. Ion exchange resins are also used on a smaller scale in analytical chemistry for the separation of ions,⁶ separation of amino acids,⁸ and as insoluble catalysts and reagents for hydrolysis, esterifica-

tion, displacement, and various other reactions.⁷ Polymers capable of separating or chelating ions have been prepared by attaching crown ethers and other chelating groups to polymer chains.⁸⁻¹⁵

Electron transfer polymers¹⁶⁻¹⁹ or oxidation-reduction polymers have been developed over the last 25 years. Most of these polymers are based on the quinone-hydroquinone system; however, polymers containing ferrocene, phenothiazine, pyridine, and sulfhydryl groups have also been prepared. Redox polymers have found applications in the conversion of oxygen to hydrogen peroxide, for removal of oxygen from water in boilers, as oxidizing agents in preparative organic chemistry, non-migrating antioxidants in polymers, polymerization inhibitors for vinyl monomers, analogs for oxido-reductase enzymes,²⁰ and a number of other applications.

Enzymes²⁰⁻²³ have been attached to crosslinked reactive polymers which contain carboxylic acid chloride, carboxylic acid anhydride, sulfonyl chloride, isocyanate, carboxylic acid azide, aromatic diazonium salt, and other groups. In general, the activity of the enzyme attached to a synthetic polymer was found to be reduced due to the small pore size of the resin which may have isolated some of the enzymes from the substrate. The conformation of the enzyme could have been altered or the active site could have been blocked when the enzyme was linked to the polymer.

Polymers have been used in medicine as drugs²⁴⁻²⁹ and implants.³⁰⁻³⁵ Pharmaceuticals have been attached to polymers or imbedded in polymer matrices in order to prolong their activity. Slow release of the drug from a polymer or polymer matrix is desirable since the body is not exposed to a large dose over a short period of time, but rather a mild dose over an extended period. In addition, the substituted polymer itself may function as a macromolecular pharmaceutical rather than releasing the drug. Although inertness to body chemistry is a desirable property for many implants, such as poly(tetrafluoroethylene), it is sometimes necessary to attach active groups to the plastic to prevent rejection by the body. For example, synthetic heart valves have been heparinized to prevent blood clotting.³⁵

Bioaffinity chromatography has been accomplished with crosslinked polymers which contained specific active groups capable of complexing with the compounds being separated.^{8,36-43} For example, antigens have been isolated with polymers which contained covalently bound antibodies.

Biologically active synthetic polymers containing purine and pyrimidine groups have been studied.^{44,45} Some showed a hypochromicity when mixed with denatured RNA which indicated that base pairing had occurred. It is possible that the synthetic polymers could interfere with replication, transcription, and translation in living cells.

Polymers with active groups such as imidazole⁴⁶⁻⁴⁹ for ester hydrolysis, pyridine⁵⁰ for catalysis of the reaction of isocyanates with alcohols, and rhodium⁵¹ for hydrogenation of olefins such as cyclohexane have been prepared. Polymeric catalysts have also been made with imidazole groups adjacent to hydroxyl groups to simulate the active site in enzymes such as chymotrypsin. Polymers can enhance the catalysts activity by attracting the substrate to the active site by hydrophobic interactions or electrostatic forces.

Polymers containing the appropriate photoreactive substituents have been designed to degrade, isomerize (photochromic polymers), or crosslink on exposure to light.^{52-55,59}

Stable polymeric radicals have been obtained by incorporating groups such as the triphenylmethane group into polymer chains.^{56,59,60}

Polymeric reagents have been used in acylation reactions⁵⁷ with mixed sulfonic anhydride polymers and in halogenation reactions⁵⁸ with N-bromosuccinimide polymers. In both cases, the polymers were used in the form of an insoluble swollen resin.

The majority of the polymer reactions reported in the literature deal with polymers as substrates (polymer modification reactions⁵⁹⁻⁷⁷). These include crosslinking, degradation, grafting, polypeptide synthesis,^{67,68} mild reactions for the introduction of active groups such as pharmaceuticals

onto polymers,^{62,63} modification of polymers for analytical purposes,⁷⁰ polystyrene reactions,⁶⁹ and reactions on cellulose.⁶⁴

In general, modification reactions on polymers differ from reactions of low molecular weight compounds for reasons of solubility and because of the effects of neighboring groups. As the polymer modification reaction proceeds, the partially substituted polymer could gel or precipitate due to cross-linking or due to an inherent insolubility of the product. The starting polymer may be only partially soluble due to crystallinity. This insolubility may decrease the accessibility of reaction sites on the polymer. Neighboring groups can hinder each others reactivity for steric reasons or can enhance the reactivity of the polymer, as in the base hydrolysis of poly(vinyl acetate). Hydrolysis of an ester linkage surrounded by two hydroxyl groups was found to be faster than an ester adjacent to two ester groups. The effect has been attributed to an increase in the local concentration of hydroxide ion due to an attraction by the free hydroxyl groups. This led to sequences or blocks of hydroxyl and ester groups on the polymer chain as the reaction proceeded. On the other hand, base hydrolysis of poly(methyl acrylate) in water was found to be hindered by neighboring groups. A carboxylate anion on the polymer chain electrostatically repelled a hydroxide ion as it approached an adjacent ester

group. Hydrophobic interactions between poly(vinyl acetate) and dodecylbenzenesulfonic acid catalysts have been shown to enhance the rate of hydrolysis of the polymer. The reaction conversion for reactions between pairs of neighboring groups, as in the formation of poly(vinyl butyral) from poly(vinyl alcohol) and butyraldehyde, are limited due to the isolation of single unreacted groups between reacted groups. Reactions between neighboring groups or effects of neighboring groups on the reactivity of a functional group could be dependent on polymer tacticity.

B. Photooxidative Degradation and Stabilization of Polymers⁷⁸⁻⁸⁷

Plastics used in outdoor applications are exposed to the harmful solar radiation between 290 and 400 nm. Fortunately, the higher energy radiation below 290 nm is prevented from reaching the surface of the earth by the ozone in the outer atmosphere. The intensity of solar radiation at the surface of the earth is a maximum in July and a minimum in January due to changes in the thickness of the ozone layer. The intensity also varies with the time of day, location, and weather conditions.

A chromophore in a polymer chain, such as a carbonyl group, can absorb the ultraviolet radiation and be excited to the singlet state. The excited polymer usually returns unharmed to the electronic ground state dissipating the energy

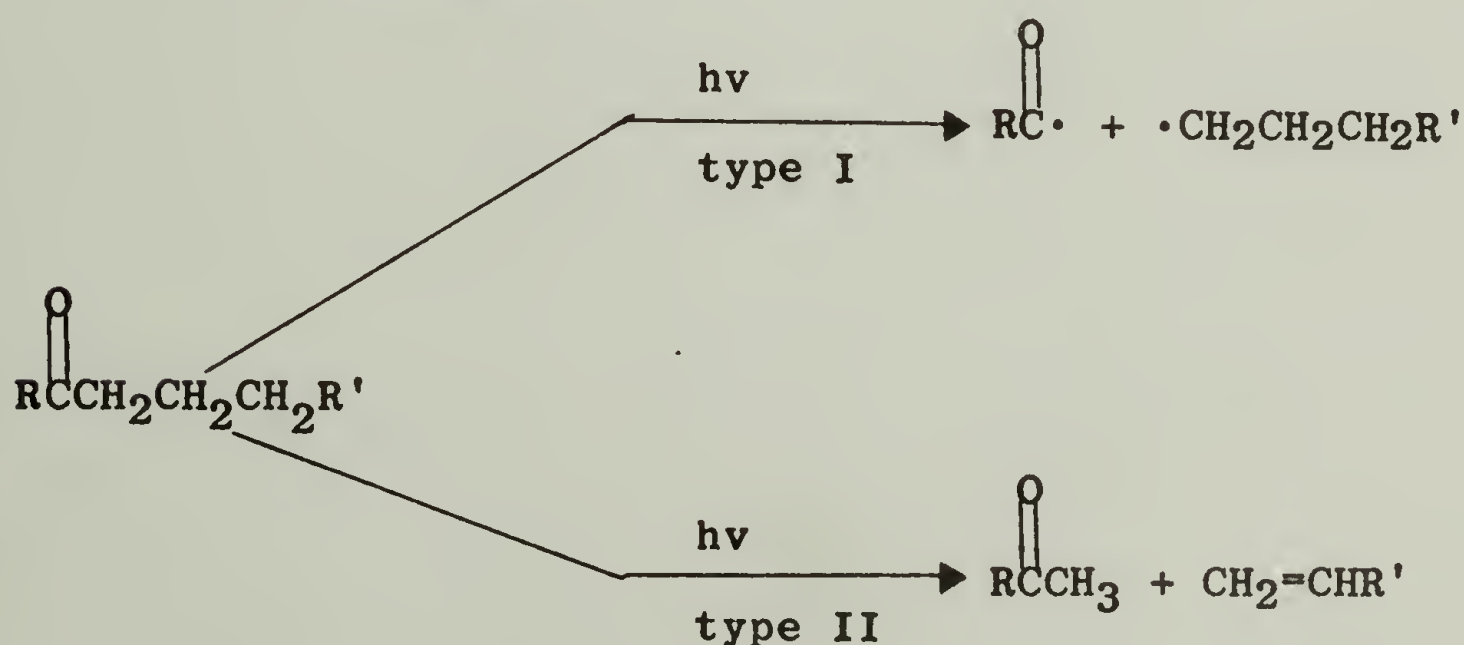
by the following radiative and nonradiative photophysical routes: (1) reemitting the energy from its singlet state at a longer wavelength (fluorescence), (2) intersystem crossing to a triplet state and reemitting the energy at an even longer wavelength (phosphorescence), (3) undergoing a radiationless conversion from the singlet or triplet state to the electronic ground state giving off the energy in the form of heat-excited vibrational states, (However, it is possible that the molecule in its excited vibrational state could undergo a reaction.), (4) transferring the energy to another molecule which could then dissipate it by the above photophysical processes.

The absorbed energy could lead to photochemical reactions and therefore polymer degradation rather than reemitting the energy in the nonharmful form. The number of molecules which degrade per quantum of absorbed energy is quite low (10^{-3} to 10^{-4}) for most polymers.⁷⁹ Polypropylene and polyethylene have higher quantum efficiencies (10^{-1} to 10^{-2}) than most polymers. Although the quantum yields are in general low, plastics are exposed to solar radiation over a period of years and therefore, polymer oxidative photodegradation is a serious problem.

The photochemical reactions which can occur in a polymer on exposure to solar radiation are chain cleavage, cross-linking, and the formation of carbonyl groups, carbon-carbon

double bonds, and other degradation products. Radicals formed as a result of photochemical reactions in polymers can lead to further degradation reactions such as depolymerization, elimination, unzipping, and autooxidation in the presence of oxygen. The observable effects of the reactions are a decrease in tensile strength, embrittlement, discoloration, and ultimately, failure of the plastic. For example, polyethylene may contain a small amount of carbonyl groups in the chain. These groups could have been introduced either through thermal oxidation during high temperature processing or by inadvertant copolymerization with carbon monoxide. When exposed to UV radiation, the carbonyl group could undergo an n to π^* excitation and lead to Norrish type I and II reactions (Figure 1) and consequently, chain cleavage.

FIGURE 1. Norrish Type I and II Reactions of Aliphatic Ketones.

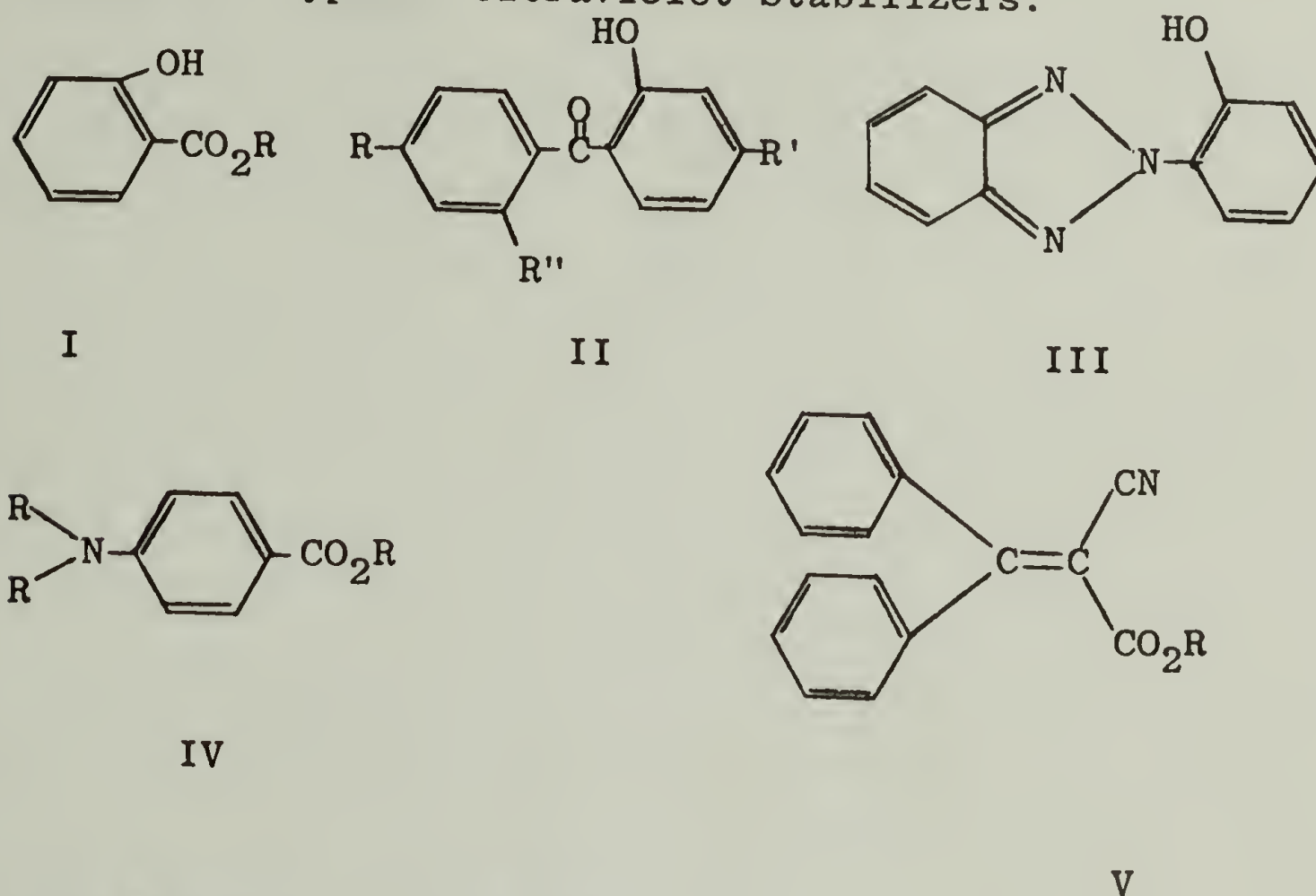


The radicals formed could then initiate autooxidation in the presence of oxygen. Singlet oxygen molecules could be formed by quenching the (n,π^*) triplet state of the carbonyl group formed in the Norrish type II reaction. The excited oxygen molecule could then react with the vinyl group produced in the Norrish type II cleavage to form a hydroperoxide which could lead to further degradation reactions.

Plastics are generally protected from the solar radiation by mixing them with small amounts of compounds, commonly called ultraviolet absorbers, which can absorb most of the harmful radiation and reemit it in a nonharmful form such as heat. The ultraviolet absorber must be effective over a long period of time and must therefore not degrade, volatilize from the plastic, be leached out by solvents, or in any other way be removed from the plastic. The strongest absorption of the additive should be in the wavelength region where the polymer is most sensitive. Furthermore, the additive must be evenly distributed throughout the polymer which requires that it be compatible with the polymer.⁸⁶ UV stabilizers (Figure 2) which have been used not only for plastics but also other applications (polishes, inks, and skin protection) are salicylate esters (I), 2-hydroxybenzophenones (II), 2-hydroxyphenylbenzotriazoles (III), 4-aminobenzoate esters (IV), and α -cyano- β,β -diphenylacrylate esters (V).

Polymers can also be stabilized with excited state quenchers. The polymer in its excited state transfers the energy to the quencher molecule before polymer degradation

FIGURE 2. Typical Ultraviolet Stabilizers.



R, R' = Alkyl R'' = H, OH

occurs and the quencher then disposes of the energy in a nonharmful form. Nickel chelates have been used for this purpose.

Pigments and carbon black are also effective stabilizers; however, they are obviously limited to applications where color is acceptable.

A comparison of stabilizing effectiveness of additives in cellulose acetate butyrate is presented in Table 1.

TABLE 1. Stabilization of Cellulose Acetate Butyrate.
Exposure Time Required to Cause 25% Loss of
Flexural Strength.⁸⁶

Additive ^a	Hr. in Modified Weather-Ometer	Yr. Outdoors in Kingsport, Tenn.
None	200	1
Phenyl salicylate	1,000	5
Resorcinol monobenzoate	1,800	7
2,4-Dihydroxybenzophenone	2,400	8
4(4,-Nitrophenylazo)phenol	> 8,000	—
6,13-Dichloro-3-10-diphenyl- triphenodioxazine	> 22,000	—
Carbon black (channel)	> 30,000	10

^a 1% concn.

C. Mobility of Additives in Polymers

Significant amounts of stabilizers can be lost from plastics due to exudation, volatilization, and solvent extraction during fabrication and end use. The problem is most severe for articles with a high surface area to volume ratio such as fibers and film. For example, perchloroethylene cleaning ("dry cleaning") of polyester and

polyamide fibers stabilized with 2,2'-dihydroxy-4,4'-dimethoxybenzophenone reportedly extracted as much as 20% of the stabilizer from the fibers.⁸⁷

Hawkins⁸⁹ demonstrated that the resistance of antioxidants to 200 hours of aqueous extraction at 60° from films of low density polyethylene increased with an increase in stabilizer molecular weight. The results of his tests are shown in Table 2.

TABLE 2. Aqueous Extraction of Antioxidants from Polyethylene.⁸⁹

Antioxidant (MW) ^a	Induction period for autooxidation hr.		Effectiveness retained, %
	Before Extn.	After Extn.	
Polymeric xylene disulfide	250	230	92%
2,6-Di-tert-butyl-4-methyl- phenol (220)	120	20	14%
N,N'-Diphenyl-p-phenylene- diamine (260)	500	220	44%
4,4'-Thiobis(3-methyl-6-tert- butylphenol) (358)	550	120	21%

^a 0.1% concn.

A number of workers have shown that stabilizer volatilization during high temperature processing and accelerated end use tests decreased with an increase in stabilizer molecular weight.⁸⁷⁻⁹² Newland and Tamblyn⁸⁸ found that compounding phenyl salicylate (MW 214) and polypropylene at 325° for five minutes caused 61% of the stabilizer to volatilize. Only 20% of a higher molecular weight aromatic salicylate (MW 500) and less than 5% of some salicylates with molecular weights from 325 to 450 volatilized during compounding. Hawkins⁸⁹ conducted accelerated end use tests and found that substantial amounts of additive evaporated from low density polyethylene films heated at 105° for two weeks under a flow of nitrogen. As shown in Table 3,

TABLE 3. Evaporation of Antioxidants from Polyethylene.⁸⁹

Antioxidant (MW) ^a	Induction period for autooxidation hr.		Effectiveness retained, %
	Before Evap.	After Evap.	
Polymeric xylene disulfide	151	170	100%
2,6-Di-tert-butyl-4-methyl- phenol (220)	70	15	17%
N,N'-Diphenyl-p-phenylene- diamine (260)	470	70	14%
4,4'-Thiobis(3-methyl-6-tert- butylphenol) (358)	440	40	8%

^a 0.1% concn.

evaporation of low molecular weight stabilizers had occurred, as evidenced by an 83 to 92% decrease in the induction period for autooxidation. The polymeric antioxidant was resistant to volatilization. Lappin⁹¹ studied the stabilization of polypropylene with antioxidants varying in molecular weight from 300 to 800. He concluded that the major structural factor affecting antioxidant potency was molecular weight and that the oven life of the samples was largely determined by the volatility of the antioxidant. Plant and Scott⁹² investigated the stabilization of polypropylene fibers with antioxidants of molecular weights ranging from 200 to 700. The weight loss of stabilizer increased with an increase in temperature from 100-220° and decreased with an increase in stabilizer molecular weight. Consequently, the induction period for autooxidation increased with an increase in stabilizer molecular weight.

Migration of additives in polymers has also been investigated. The diffusion of 2-hydroxy-4-alkoxybenzophenone in polypropylene was shown to decrease as the side chain length increased from methyl to octyl to dodecyl.⁹³ It has also been shown that 2-hydroxy-4-alkoxybenzophenones with long side chains are more compatible with polyethylene and more effective than stabilizers with short side chains. Polyethylene plates containing 1% of 4-dodecyloxy-2-hydroxybenzophenone showed no exudation or surface cracking after five

years, while plates containing 1% of 2-hydroxy-4-methoxybenzophenone showed exudation and cracked after two years of weathering.⁸⁶ Additional information concerning this subject is presented in Table 5.

D. Synthesis of Polymeric Ultraviolet Absorbers

The polymeric ultraviolet absorbers reported in the literature have been prepared by four general routes: (a) by radical chain growth polymerization and copolymerization of commonly used ultraviolet absorbers such as 2-hydroxybenzophenones, 2-hydroxyacetophenones, 2-hydroxyphenylbenzotriazoles, salicylates, and 4-aminobenzoates which contain acrylate, allyl, or other polymerizable functional groups, (b) by step growth polymerization with difunctional 2-hydroxybenzophenones, (c) by polymer modification reactions, and (d) by initiating radical polymerization with a radical initiator molecule attached to an ultraviolet absorber.

1. Chain growth polymerization of substituted ultraviolet absorbers. 2-Hydroxybenzophenones. The attachment of polymerizable functional groups to the 4-hydroxyl group of 2,4-dihydroxybenzophenone and various halogen, alkyl, hydroxy, and alkoxy substituted 2,4-dihydroxybenzophenones has been widely utilized to obtain polymerizable ultraviolet absorbers.

Tocker⁹⁴⁻⁹⁷ prepared 2-hydroxy-4-methacryloxybenzo-

phenone and 2-hydroxy-4-acryloxybenzophenone by the reaction of methacrylyl chloride and acrylyl chloride respectively with 2,4-dihydroxybenzophenone. Polymeric ultraviolet stabilizers were obtained by homopolymerization and copolymerization of the compounds with ethylene, vinylidene chloride, and acrylate esters by using a radical initiator. Ciba Ltd. chemists⁹⁸ copolymerized 2-hydroxy-4-acryloxybenzophenone with acrylates and acrylonitrile. Osawa^{99,100} copolymerized 2-hydroxy-4-acryloxybenzophenone with styrene with radical initiation and homopolymerized 2-hydroxy-4-acryloxybenzophenone with initiation by metallic salts with dioxane hydroperoxide.

Tocker¹⁰¹ prepared 2-hydroxy-2'-methacryloxybenzophenone and copolymerized it with ethylene by radical polymerization.

Fertig¹⁰²⁻¹⁰⁷ converted 2,4-dihydroxybenzophenone to polymerizable ultraviolet stabilizers by reacting the 4-hydroxyl group with glycidyl derivatives of unsaturated compounds. Glycidyl acrylate and glycidyl methacrylate yielded 2-hydroxy-4-(3-acryloxy-2-hydroxypropoxy)benzophenone and the corresponding methacryloxy monomer.^{103,105-107} The compounds were homopolymerized and copolymerized with ethyl methacrylate, styrene, vinylidene chloride-ethyl acrylate, vinylidene chloride-butyl acrylate, vinyl chloride, and vinyl acetate by radical initiation. He pointed out that the phenol group did not inhibit the radical polymerization, probably because it was internally hydrogen bonded to the

carbonyl group. He reacted 2,4-dihydroxybenzophenone with various glycidyl fumarate, maleate, and methacrylate esters. The products could not be homopolymerized but could be emulsion copolymerized with vinyl chloride, vinylidene, ethyl acrylate, vinyl acetate, and styrene.¹⁰² He also reacted 2,4-dihydroxybenzophenone with allyl glycidyl ether and butadiene monoxide to obtain 2-hydroxy-4(3-allyloxy-2-hydroxypropoxy)benzophenone and 2-hydroxy-4(2-hydroxy-3-buten-1-yloxy)benzophenone respectively, which were then used in the preparation of copolymers.^{104,106}

Horton and Brooks¹⁰⁸ esterified 2-hydroxy-4-(2-hydroxyethoxy)benzophenone with acrylic acid and methacrylic acid and obtained 2-hydroxy-4-(2-acryloxyethoxy)benzophenone and the corresponding methacryloxy compound. The compounds were polymerized with radical initiation by azobisisobutyronitrile (AIBN).

Hardy¹⁰⁹ carried out displacement reactions on various alkyl substituted allyl bromides with 2,2',4-trihydroxybenzophenone to obtain a series of allyl ether monomers which could be copolymerized.

Milionis and Arthen¹¹⁰ carried out a displacement reaction on 4-chloromethylstyrene with 2,4-dihydroxybenzophenone to obtain 2-hydroxy-4-(vinylphenyl)methoxybenzophenone. Polymeric ultraviolet stabilizers were obtained by copolymerization with vinyl monomers.

Pinazzi and Fernandez^{111,112} synthesized 2-methoxy-4'-vinylbenzophenone by reacting 2-methoxybenzonitrile with p-styrylmagnesium chloride followed by chromic acid oxidation of the alcohol to a ketone group. They also prepared 2,4-dimethoxy-4'-vinylbenzophenone. The compounds were homopolymerized and copolymerized with styrene by radical initiation to yield high molecular weight products. In these publications, the reactivity ratios for the copolymerizations were reported. They were 1.63 and 2.12 for 2-methoxy-4'-vinylbenzophenone and 2,4-dimethoxy-4'-vinylbenzophenone respectively and 0.28 and 0.41 for styrene respectively. In order to convert the polymers to ultraviolet absorbers, it was necessary to convert the ortho methoxy group to an ortho phenol group. This was accomplished with aluminum trichloride in nitrobenzene.

Tocker^{94,113} prepared 3-allyl-2-hydroxybenzophenone by a Claisen rearrangement of 2-allyloxybenzophenone and copolymerized it with ethylene using a vanadium chloride-butyl lithium initiator system. Tocker reported that the stabilizing monomer partially deactivated the organometallic coordination initiator which made the copolymerization difficult. He concluded that a better method would be to melt mix a homopolyolefin and a copolymer consisting of the olefin and a large concentration of ultraviolet absorbing monomer (3%) prepared by radical initiation.

Luston^{114,115} prepared 2-hydroxy-4-(2,3-epoxypropoxy)-benzophenone from 2,4-dihydroxybenzophenone and epichlorohydrin. The product could be copolymerized with a molar equivalent or excess of dicarboxylic acid anhydrides using tertiary amines or potassium benzoate as initiators. When the epoxide was in excess, undesirable side reactions occurred at the phenol groups. The molecular weights of the polymers were not greater than 1600.

2-Hydroxyacetophenones. Tocker⁹⁴⁻⁹⁶ synthesized 2-hydroxy-4-methacryloxyacetophenone from 2,4-dihydroxyacetophenone and methacrylyl chloride in pyridine. The monomer was polymerized and copolymerized with vinylidene chloride and acrylate or methacrylate esters by radical initiation.

Tocker¹¹³ prepared 3-allyl-2-hydroxyacetophenone by a Claisen rearrangement reaction from 2-allyloxyacetophenone and polymerized and copolymerized it with ethylene using a vanadium chloride-butyl lithium initiator system. As in the polymerization of 3-allyl-2-hydroxybenzophenone with vanadium chloride and butyl lithium (p. 21), 3-allyl-2-hydroxyacetophenone partially deactivated the organometallic coordination initiator.

Tocker¹¹⁶ rearranged 2-methacryloxyacetophenone with sodium methoxide and boiling pyridine to obtain methacryloyl-salicyloylmethane. The product was copolymerized with ethylene.

2-Hydroxyphenylbenzotriazoles. Milionis and Hardy¹¹⁷ carried out a displacement reaction on 4-chloromethylstyrene with 5-hydroxy-2-(2-hydroxyphenyl)benzotriazole to obtain 5-(vinylbenzyloxy)-2-(2-hydroxyphenyl)benzotriazole. The monomers could be copolymerized with styrene, acrylonitrile, and butadiene.

Milionis and Hardy¹¹⁸ prepared a variety of 2-hydroxyphenylbenzotriazoles substituted in either ring with halogen, sulfonamide, nitro, carboxy, alkoxy, and alkyl groups and acryloylamino, methacryloylamino, acryloyloxy, or methacryloyloxy groups. The monomers were copolymerized with styrene-acrylonitrile, butadiene, and acrylate esters using benzoperoxide (BPO) initiation.

Heller¹¹⁹ polymerized approximately twenty 2-hydroxyphenylbenzotriazole compounds substituted with allyloxy, acryloylamino, methacryloylamino vinylsulfonyl, and vinyloxy groups. For example, 2-(2-hydroxy-5-(β -allyloxycarbonyl-ethyl)phenyl)benzotriazole was copolymerized with vinyl chloride.

Salicylate esters. Fertig¹²⁰⁻¹²² prepared 4-acryloxy, 4-methacryloxy, 5-acryloxy, and 5-methacryloxysalicylate esters of phenol by the reaction of phenol 2,4-dihydroxybenzoate and phenyl 2,5-dihydroxybenzoate with methacrylyl chloride and acrylyl chloride. He also chloromethylated phenyl salicylate and then carried out a displacement reaction

on the phenyl 5-chloromethylsalicylate with sodium methacrylate or sodium acrylate to obtain phenyl 5-methacryloxymethylsalicylate. The products were polymerized and copolymerized with vinylidene chloride, vinyl chloride, and vinyl acetate using radical initiators. Fertig demonstrated that the phenol group of the monomer would not affect the copolymerization by polymerizing vinyl acetate in the presence and absence of phenyl salicylate (1.37 wt. %). The intrinsic viscosities of the vinyl acetate polymers were nearly equal.

Tocker^{96,123} obtained polymeric stabilizers by the copolymerization of methyl 4-acryloxysalicylate with vinylidene chloride, acrylates, styrene, ethylene, propylene, vinyl acetate, acrylonitrile, and vinylidene fluoride.

Acrylate derivatives of 4-hydroxysalicylate esters were copolymerized with acrylic esters and acrylonitrile by Ciba Ltd. chemists.⁹⁸

Tocker^{94,113} also prepared 3-allylsalicylate esters by a Claisen rearrangement reaction of 2-allyloxybenzoates and copolymerized them with olefins using a vanadium chloride-butyl lithium catalyst system. As in the polymerization of 3-allyl-2-hydroxybenzophenone with vanadium chloride and butyl lithium (p. 21), 3-allyl-2-hydroxybenzoates partially deactivated the organometallic coordination initiator.

Handy^{124,125} and Rothrock stabilized polymers by blending or coating them with methacrylate, ethylene, and vinyl

acetate copolymers of vinyl salicylate or allyl salicylate.

p-Aminobenzoate esters. Ciba Ltd. chemists⁹⁸ prepared ethyl p-acrylamino benzoate and copolymerized it with conventional acrylic esters, acrylic acid, and acrylonitrile.

Hopff and Lussi¹²⁶⁻¹²⁸ prepared and copolymerized vinyl N,N-dimethyl-p-aminobenzoate.

Skoultchi¹²⁹ and Meier prepared and copolymerized 4-(N,N-diallylamino)benzoic acid and its ethyl esters.

2. Step growth polymerization of difunctional 2-hydroxybenzophenones. A small number of polyesters, polyamides, and polyurethanes containing a 2-hydroxybenzophenone group in the main chain have been reported in the literature. Balaban¹³⁰ synthesized 2-hydroxybenzophenone-4,4'-dicarboxylic acid and polymerized it with ethylene glycol to obtain a light yellow-brown polymer with a molecular weight of 12,000 to 18,000. He prepared polymers from 2-hydroxy-4,4'-bishydroxymethylbenzophenone and 5,5'-dithiovaleric acid, sebacic acid, succinic acid, and 3,3'-thiopropionic acid. Balaban also prepared a polyamide from 2-hydroxy-4-aminobenzophenone-3'-carboxylic acid.

Strobel and Catino¹³¹ prepared over twenty 2,2',4-trihydroxybenzophenones and 2,2',4,4'-tetrahydroxybenzophenones substituted in the 4 and 4' position with dicarboxylic acids such as phthalic, succinic, and maleic acid. Some of the compounds were further substituted on the rings with vinyl,

allyl, halogen, alkoxy, and alkyl groups. Ultraviolet stabilized polyesters were prepared by polymerization of the compounds with diols and dicarboxylic acids.

Coleman¹³² synthesized 2,2'-dihydroxy-4,4'-di(2-hydroxyethoxy)benzophenone which could be used in the synthesis of polyamides and polyisocyanates.

Tocker¹³³ prepared polyesters from 2,2',4,4'-tetrahydroxybenzophenone and sebacoyl chloride.

3. Polymer rearrangement reactions. Pendant group rearrangements. Tocker^{94,134} heated a copolymer of 2-methacryloxyacetophenone and ethylene with potassium hydroxide in pyridine for 15 minutes, which caused the rearrangement of the 2-methacryloxyacetophenone repeat units to form methacryloylsalicyloylmethane repeat units.

Tocker^{94,134} copolymerized p-t-butylphenyl methacrylate (2%) with ethylene (98%). The copolymer was dispersed in nitrobenzene with aluminum trichloride and the mixture was heated at 120° for 20 minutes, which caused the p-t-butylphenyl methacrylate repeat units to Fries rearrange to the ultraviolet stabilizing 4-t-butyl-2-acryloylphenol groups. A graft copolymer of p-t-butylphenyl methacrylate on polyethylene was also prepared.¹³⁴

Okawara¹³⁵ irradiated a film of poly(p-cresyl acrylate) with ultraviolet light, which caused approximately 10% of the repeat units to undergo a photo Fries rearrangement.

The 4-methyl-2-acryloylphenol groups that formed inhibited any further photo Fries rearrangement.

Main chain rearrangements. A great deal of work has been done in studying the Fries rearrangement of ester groups in polyesters based on a bisphenol and dicarboxylic acid to form 2-hydroxybenzophenone groups. Bellus^{136,137} rearranged polyesters of bisphenols and dicarboxylic acids in the melt with a four-fold excess of aluminum trichloride, titanium tetrachloride, or stannic chloride. He also used a boiling nitrobenzene solution with a four-fold excess of aluminum trichloride. The aluminum trichloride reaction in nitrobenzene resulted in rearrangement of some of the ester groups as evidenced by a 1638 cm^{-1} infrared absorption. The rearrangement reaction was accompanied by a sharp decrease in molecular weight after a very short reaction time, crosslinking, and a gradual discoloration of the solution from yellow to black. Evidently, side reactions, such as hydrolysis and interchain Fries rearrangement, led to a decrease of molecular weight and crosslinking respectively. Crosslinking occurred to a lesser extent in the melt rearrangement reactions. The lower mobility of the polymeric acyl ion in the melt was believed to hinder the interchain substitution reaction (crosslinking).

Bellus^{136,137} subjected polyesters of bisphenols and dicarboxylic acids to photo Fries rearrangements in chloroform

solution. The reaction resulted in a decrease in molecular weight and formation of o-hydroxybenzophenone groups which were detected by infrared and ultraviolet spectroscopy. In this case, crosslinking did not occur and the reaction solutions were yellow, not black as in the aluminum trichloride catalyzed rearrangement. It was pointed out that the ultraviolet stabilizing o-hydroxybenzophenone groups which formed retarded further photo Fries rearrangement. Photo Fries rearrangement in the solid state and melt were also demonstrated.

It was shown by Okawara¹³⁵ that a polymer derived from isophthalic acid and bisphenol A could rearrange in solution or in film form on exposure to ultraviolet light. He found that the ultraviolet absorbing 2-hydroxybenzophenone groups which formed inhibited further photo Fries rearrangement.

Maerov¹³⁸ found that a rapid chain scission accompanied the photo Fries rearrangement of a polyester film. Initially, the rate of photolysis was 2.5 times greater than the rate of rearrangement. The rates decreased with increasing rearrangement conversion due to a self-screening effect by the 2-hydroxybenzophenone groups.

Cohen¹³⁹ prepared a series of aromatic polyesters with structural irregularities in order to decrease the crystallinity of the polymers and thereby obtain polyesters with good solubility properties. For example, bisphenol A was modified

by the attachment of a long aliphatic chain at the central carbon atom. Solutions of the polymers could be used to coat plastics with a UV protecting film. He found by attenuated total reflectance infrared spectroscopy that the photo Fries rearrangement took place in a thin skin (0.46 mil) on the surface of the film and that the UV absorbing skin which formed protected the plastic and prevented further rearrangement of polyester in lower layers.

Korshak¹⁴⁰ showed that polyesters of isophthalic acid and phenophthalein had a self-protecting effect due to a photo Fries rearrangement of the ester groups to form 2-hydroxybenzophenone groups. The rearrangement also improved the thermal stability of the polymer. Decomposition of the rearranged polymers, which contained phenol groups, began 40° higher than the unirradiated polyester.

Young¹⁴¹ prepared a polymeric ultraviolet stabilizer by benzoylating a phenolic novolac resin containing 50 mole % unsubstituted ortho position. The polymer would presumably undergo a photo Fries rearrangement on exposure to ultraviolet radiation.

Bellus^{137,142} showed that poly[(2,2'-propane bis(4-phenyl-carbonate))] had a self-stabilizing effect when exposed to ultraviolet radiation. Some of the aromatic carbonate groups rearranged photochemically to phenyl salicylate groups which then further rearranged to 2,2'-dihydroxybenzophenone groups.

Similar results were obtained by Mullen and Searle.¹⁴³

4. Ultraviolet stabilizers attached to radical initiator molecules. Sheppard and MacLeay¹⁴⁴ prepared 4-(4-t-butylazo-4-cyanovaleryloxy)-2-hydroxybenzophenone from 4-(5-butylazo)-4-cyanovaleryl chloride and 2,4-dihydroxybenzophenone. The compound was used as a radical polymerization initiator for styrene polymerization. The polystyrene had a molecular weight of 300,000, and the ultraviolet stabilizing group was, as expected, attached to the polymer.

E. Synthesis of Oligomeric Ultraviolet Stabilizers

Medium molecular weight stabilizers (MW<1,000) have been prepared by endcapping difunctional molecules with ultraviolet stabilizers, by attaching long aliphatic chains to ultraviolet stabilizers, and by condensation of aldehydes or formaldehyde with substituted phenols.

1. 2-Hydroxybenzophenones. Karvas^{145,146} prepared α,ω -bis(3-hydroxy-4-benzoylphenoxy)alkanes by a nucleophilic displacement reaction of 2,4-dihydroxybenzophenone on α,ω -dichloro or dibromoalkanes. They also esterified 2-hydroxy-4-(2-hydroxyethoxy)benzophenone with a series of dicarboxylic acids to obtain, for example, bis 2-(3-hydroxy-4-benzoylphenoxy)ethyl adipate.

Lappin and McConnel¹⁴⁷ esterified 2-hydroxy-4-(2-hydroxyethoxy)benzophenone with a variety of aliphatic and aromatic

di, tri, and tetra carboxylic acids.

Mosse and Cordes¹⁴⁸ carried out a condensation reaction with a two to one mole ratio of 2,4-dihydroxybenzophenone and formaldehyde to obtain an ultraviolet stabilizer with a molecular weight of 440.

Mather¹⁴⁹ carried out a condensation reaction of 2-hydroxy-4-n-octyloxybenzophenone with paraformaldehyde to obtain an ultraviolet stabilizer with a molecular weight of 660.

Tocker^{150,151} synthesized an ultraviolet absorbing oligomer with a molecular weight of 600 by the condensation of 2-hydroxybenzophenone, dodecylphenol, and formaldehyde in formic acid. He also used a variety of halogen and alkyl substituted 2-hydroxybenzophenones and aliphatic and aromatic aldehydes.

2. 2-Hydroxyphenylbenzotriazoles. Balaban¹⁵² prepared a series of 2-(2-hydroxy-5-alkylphenyl)benzotriazoles where alkyl was a C₆ to C₂₄ aliphatic chain.

3. Salicylate esters. Heim and Poe¹⁵³ prepared the disalicylates of ethylene glycol and diethylene glycol. The compounds were used as food preservatives.

Kovoc¹⁵⁴ prepared monomethyl, monoethyl, monopropyl, monoisopropyl, and monobutyl ethers of ethylene glycol and diethylene glycol and esterified them with salicyloyl chloride.

Armitage and Hyson¹⁵⁵ prepared tetraethylene glycol di-

salicylate, 1, 10 decane diol disalicylate, and octadecylsalicylate as ultraviolet stabilizers for polymers.

Schurman¹⁵⁶ prepared sunscreens for skin protection by a sodium hydroxide catalyzed ester interchange reaction of salicylate esters and propylene glycol or glycerol.

4. p-Aminobenzoate esters. Thomas¹⁵⁷ reduced ethylene glycol, 1,3 glyceryl, and 1,4-erythritol di-p-nitrobenzoates to obtain the corresponding p-aminobenzoate esters.

Matter^{158,159} carried out an ester interchange reaction between ethyl-p-hexylaminobenzoate and octaethylene glycol monomethyl ether in order to obtain a local anesthetic.

5. α -Cyano- β,β -diphenylacrylates. Carlson¹⁶⁰ prepared bis(α -cyano- β,β -diphenylacrylates) of ethane, propane, hexane, and decane diols and diethylene glycol by esterification of the diols with cyanoacetic acid followed by a Knoevenagel condensation with benzophenone. A number of halogen derivatives were also prepared.

F. Properties of Polymeric and Oligomeric Ultraviolet Stabilizers

A comparison of the effectiveness of all the polymeric and oligomeric ultraviolet stabilizers on the basis of the data reported in the literature is not possible because the stabilizers were evaluated under different conditions. The amount of stabilizers incorporated into the polymer, type of

polymer, film thickness, weathering conditions, and other variables prevent a detailed comparison. However, several groups conducted studies designed to evaluate the relative effectiveness of low molecular weight, oligomeric, and polymeric stabilizers. On the basis of their results, an attempt can be made to draw conclusions concerning the structure vs. property relationships of polymeric and oligomeric ultraviolet stabilizers as compared to low molecular weight UV stabilizers.

Most of the polymers and oligomers that were reported in the previous section were tested as ultraviolet stabilizers for plastic films. In every case, the stability of the plastic was improved by the addition of approximately 1% of stabilizer. The films were generally subjected to accelerated weathering tests over a period of several weeks and examined for a loss of flexibility, tensile strength, molecular weight, discoloration, surface crazing, or stabilizer exudation. Polyester laminates of some of the stabilized films were examined for delamination.

1. Permanence. Polymeric ultraviolet stabilizers have been shown to be more resistant to solvent extraction, volatilization during high temperature processing, and exudation from plastics than low molecular weight stabilizers. They are also more permanent than many of the oligomeric stabilizers. Therefore, over a long period of time or in the presence of

solvents, polymeric stabilizers appear to be superior to low molecular weight additives.

Luston¹¹⁴ showed that a polymeric stabilizer (MW 1600) prepared from 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone and phthalic anhydride is almost as effective as 2-hydroxy-4-octyloxybenzophenone for polypropylene stabilization. He also showed that the polymeric stabilizer is much more resistant to trichloroethylene extraction than the lower molecular weight stabilizer. A 1 cm.² polypropylene film stabilized with 2-hydroxy-4-octyloxybenzophenone and exposed to ultraviolet light in an oxygen atmosphere at 60° required 250 hours to react with 1 ml.² of oxygen, while polypropylene stabilized with the polymeric ultraviolet stabilizer required 240 hours. After the stabilized films were subjected to one hour of trichloroethylene extraction at 25°, the film containing the polymeric stabilizer was much more resistant to photooxidative degradation than the 2-hydroxy-4-octyloxybenzophenone stabilized film (200 vs. 125 hours).

Fertig¹⁰⁷ also demonstrated the resistance of polymeric stabilizers to solvent extraction. He blended a small amount (0.2%) of 2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)benzophenone with polypropylene at high temperature, which evidently caused the monomer to polymerize since soxhlet extraction with perchloroethylene removed only 3% of the stabilizer and methanol removed only 5%. Extraction of films stabilized

with 2-hydroxy-4-octyloxybenzophenone removed 20% and 70% of stabilizer with perchloroethylene and methanol respectively.

Tocker⁹⁴ demonstrated the superiority of a copolymeric ultraviolet stabilizer of 2-hydroxy-4-methacryloxybenzophenone and ethylene as compared to 4-dodecyloxy-2-hydroxybenzophenone for the stabilization of polyethylene. He found that thin polyethylene film (0.1 mm.) stabilized with 2-hydroxy-4-methacryloxybenzophenone incorporated as a comonomer were much more resistant to weathering than films stabilized by blending in additives. However, with thicker films (0.25 mm.), the 4-dodecyloxy-2-hydroxybenzophenone stabilized polymer performed as well as the copolymer. Evidently, the mobile oligomer could continuously exude to the surface of the thick film and replenish the stabilizer that was lost by evaporation or degradation. The smaller amount of stabilizer within the thin film would be insufficient and therefore, the film was less stable. The results of his experiments are presented in Table 4. The same relationship between film thickness and stabilizing effectiveness was observed by DeCroes and Tamblyn¹⁶¹ in the stabilization of cellulose acetate butyrate with phenyl salicylate.

Tocker⁹⁴ also pointed out that the highest concentration of low molecular weight stabilizer that could be incorporated into crystalline polyolefins was about 1 wt. % due to their limited compatibility. Evidently, the stabilizer would be

TABLE 4. Comparison of the Weathering^a of Polyethylene Films with Chemically Bound and Mechanically Added UV Stabilizers.⁹⁴

Film ^b	Thickness (mm)	Mole % 2-hydroxybenzo-phenone groups in the Polymer	Elongation (%) at Breaking Point	
			Before Weathering	After Weathering
Branched Polyethylene (control)	0.075-0.10	0.00	600	brittle
Ethylene/2-hydroxy-4-methacryloxybenzo-phenone Copolymers	0.07-0.10	0.10	500-600	200
	0.07-0.10	0.60	500-600	480
	0.07-0.10	1.00	500-600	500
	0.25	0.10	500-600	300
	0.25	0.60	500-600	500
Additive System				
Polyethylene with 4-Dodecyloxy-2-hydroxybenzo-phenone	0.075-0.10	0.50	500	20-40
	0.075-0.10	0.10	500	20-40
	0.25	0.10	500	450-500

^a 1,000 hours in an Atlas Weather-Ometer.

^b Containing 0.1 wt. % santowhite crystals.

lost by exudation. On the other hand, the concentration of polymeric ultraviolet stabilizers was only limited by the effect on the physical properties of the polymer (strength, degree of crystallinity, color). Tocker concluded that polymeric ultraviolet stabilizers were superior to low molecular weight additives for the systems he studied.

Tocker⁹⁷ reported that repeated toluene extraction of a copolymer of ethylene and 2-hydroxy-4-methacryloxybenzophenone could not remove any of the ultraviolet stabilizer, and the polymer showed no evidence of exudation. However, a polyethylene film stabilized with 2-hydroxy-4-methacryloxybenzophenone showed exudation on long term exposure.

An ultraviolet stabilizer attached to polystyrene as end groups by polymerization initiation with 4-(4-t-butylazo-4-cyanovaleryloxy)-2-hydroxybenzophenone was reported to be resistant to extraction and evaporation.¹⁴⁴

One hundred hours of ethanol soaking of a polyurethane prepared with diisocyanates and 2,2'-dihydroxy-4,4'-di(2-hydroxyethoxy)benzophenone did not remove any stabilizer.¹³²

Milioni¹¹⁰ found that copolymers of 2-hydroxy-4-(vinylphenyl)methoxybenzophenone and vinyl monomers did not lose ultraviolet stabilizer during molding or by oil extraction.

Tocker¹³³ reported that isotactic polypropylene, stabilized with 2 wt. % of a polyester (MW 1600) prepared from 2,2,4,4'-tetrahydroxybenzophenone and sebacoyl chloride, had no tendency to crack after 1,000 hours of exposure while an unstabilized film cracked after 300 hours exposure. A film containing 2 wt. % of 2-hydroxy-4-dodecyloxybenzophenone cracked after 600 hours, and severe blushing of the stabilizer was reported to have occurred.

Tocker¹⁵⁰ also stabilized a poly(vinylfluoride) film with an oligomer (MW 560) prepared from condensing formaldehyde with 2-hydroxybenzophenone. The film showed no evidence of stabilizer exudation and did not blush after 2,000 hours in a weatherometer.

An oligomeric stabilizer prepared from the condensation of formaldehyde with 2-hydroxy-4-octoxybenzophenone was reportedly resistant to extraction from polypropylene by dry cleaning solvents.

2. Compatibility. In addition to permanence, a second property that is very important for polymeric, oligomeric, or low molecular weight stabilizers is compatibility. A compatible additive would be expected to be evenly distributed throughout the plastic and would therefore be a more effective stabilizer.

The work of Fertig¹⁰⁷ indicated that compatible polymeric ultraviolet stabilizers perform better than incompatible polymers. Polystyrene and a vinylidene chloride-acrylonitrile copolymer were each stabilized with 1% of poly(2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)benzophenone). The stabilizer showed marked incompatibility with both polymers. However, poly(2-hydroxy-4-(3-acryloxy-2-hydroxypropoxy)benzophenone) was compatible with the polystyrene and vinylidene chloride-acrylonitrile copolymer. He also prepared a copolymer of styrene and 2-hydroxy-4-(3-methacryloxy-2-hydroxy)-

benzophenone. After eight hours exposure to ultraviolet light, 65% of an unstabilized vinylidene chloride-acrylonitrile copolymer was insoluble in acetone, 50% of the copolymer stabilized with the incompatible polymeric stabilizer was insoluble, and only 10% of the copolymer stabilized with the compatible polymeric stabilizer was insoluble in acetone.

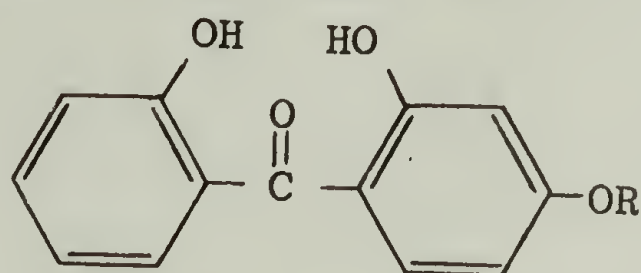
The effect of ultraviolet light on the molecular weight of the polystyrene samples clearly showed the advantage of a compatible, evenly dispersed stabilizer. The percent molecular weight decrease after 160 hours of exposure to UV radiation was 55% for polystyrene without stabilizer, 42% for polystyrene with the incompatible polymeric stabilizer, 23% for polystyrene with the compatible polymeric stabilizer, and 21% for the polystyrene copolymer. Fertig¹⁰⁷ also pointed out that the test conditions were not designed to show the long term advantages of polymeric stabilizers (resistance to volatilization and extraction).

Balaban¹⁵² reported that the stability of polyethylene sheets stabilized with 2-(2-hydroxy-5-alkylphenyl)benzotriazoles improved as the length of the alkyl group increased. The strength of the polymer decreased 30% in 15 months with an octyl substituted stabilizer, 30% in 6 months with a methyl substituted stabilizer, and 30% in 3 weeks in the absence of stabilizer.

The effect of long aliphatic solubilizing groups on

2,2'-dihydroxy-4-alkoxybenzophenone stabilizers in polyethylene is shown in Table 5.¹⁶¹

TABLE 5. Effect of Varying the Alkoxy Group of 2,2'-Dihydroxy-4-alkoxybenzophenones on Polyethylene Stability.¹⁶¹



R—	Concentration (%)	Carbonyl (%)				Retained Elongation ^a (%)	
		Fadeometer		Arizona			
		500 hr.	1000 hr.	2 mos.	4 mos.	2 mos.	4 mos.
CH ₃	0.1	0.22	0.54	0.41	0.6	7	0
C ₂ H ₅	0.1	0.07	0.37	0.25	0.6	20	5
C ₃ H ₁₇	0.1	0.04	0.19	0.08	0.6	44	4
C ₁₂ H ₂₅	0.1	0.04	0.17	0.33	0.6	61	3
No Additive	—	0.30	0.64	0.33	0.6	9	0

^a Arizona

3. General information concerning the properties of polymeric ultraviolet absorbers. Osawa⁹⁹ prepared copolymers of styrene with 0.47, 0.76, and 6.82% of 2-hydroxy-4-acryloxy-

benzophenone respectively. He also blended the same concentration of monomer with polystyrene and prepared test films. He found that on exposure to ultraviolet light over a period of 50 hours, the carbonyl content of the blends and copolymers did not increase as much as the carbonyl content of unstabilized polystyrene, and that the increase was smallest for those polymers with the highest concentration of stabilizer. The copolymer stability was not superior to the stability of the blend. This is not surprising because the test conditions do not show the long term advantage of the more permanent polymeric stabilizer. Assuming that the film was molded at high temperatures, (the conditions were not given) it is likely that the monomer polymerized as in the case of Fertig's¹⁰⁷ experiment (p. 34). Since no mention was made of the compatibility of the additives, it can probably be assumed that the additive, whether it was monomer or polymer, was compatible. If both stabilizers were compatible, a difference in stabilizing effectiveness would not be expected.

Osawa¹⁰⁰ found that the order of effectiveness of a number of stabilizers in polyethylene was 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole > p-octyloxyphenyl salicylate > poly(2-hydroxy-4-methacryloxybenzophenone) = poly(2-hydroxy-4-acryloxybenzophenone) > 2,4-dihydroxybenzophenone. (The additives were mixed with polyethylene and compression molded to 0.35 mm. thick films and placed in a

weatherometer at 65° and 50% relative humidity for 200 hours and tested for residual strength, residual elongation, melt index, carbonyl content, and color difference.) The order of effectiveness appears to contradict the previous comments concerning the overall superior properties of polymeric ultraviolet stabilizers. However, on the basis of the data presented in Table 5, (p. 40) p-octyloxyphenyl salicylate was probably more compatible and more evenly dispersed than the 2,4-dihydroxybenzophenone and the polymeric stabilizers, which would partially account for the superior performance of the salicylate stabilizer. The thickness of the test specimens was greater than 0.25 mm. which, according to the work of Tocker⁹⁴ on polyethylene stabilization, would be too thick to show the advantages of a nonmigrating polymeric stabilizer over a compatible migrating stabilizer such as p-octyloxyphenyl salicylate. In fact, for thick test specimens, it may be advantageous to use a migrating, exuding additive which could replenish the stabilizer lost at the surface of the plastic. It would have been interesting to determine the effect of sample thickness on the order of stabilizer effectiveness and to evaluate the performance of the more compatible 2-hydroxy-4-octyloxybenzophenone.

Tocker⁹⁴ showed that introducing an ultraviolet stabilizing group into a polymer chain can decrease the mechanical properties of the plastic by decreasing the polymer

crystallinity. He concluded that the best approach would be to mix the crystalline homopolyolefin with an olefin-ultra-violet stabilizer copolymer containing a high concentration of stabilizer. By this approach, he found that it was possible to stabilize the polymer with a smaller loss of physical properties as shown in Table 6. Therefore, a dilute

TABLE 6. Properties of Polyethylene Films Prepared from a Copolymer and a Mixture of a Homopolymer and a Copolymer.⁹⁴

	Initial Modulus (1% elongation) Kg./cm. ²	UV Stability ^a hrs. in Atlas Weatherometer
Branched polyethylene	1260	300
Branched polyethylene and 20% E/MBH ^b (97/3 mole ratio total 0.6 mole % MBH)	980	1500
E/MBH ^b copolymer with 0.6 MBH	700	1500

^a Weathering time until elongation drops to half its initial value.

^b Ethylene/2-hydroxy-4-methacryloxybenzophenone copolymers.

copolymer is undesirable since it affects the crystallinity of the polymer and a homopolymer is undesirable since, as Fertig¹⁰⁷ (p. 38-39) showed, it could be incompatible with

the polymer being stabilized.

It may be possible to covalently incorporate ultraviolet stabilizers into polymers without affecting the crystallinity of the polymer by attaching the stabilizers as polymer end groups. This could be accomplished by using a radical polymerization initiator which contains an ultraviolet stabilizing group such as 4-(4-t-butylazo-4-cyanovaleryloxy)-2-hydroxybenzophenone. The amount of stabilizer which could be incorporated in the polymer would be limited by the amount of initiator used in the polymerization.

Copolymerization of monomeric ultraviolet stabilizer enables a broad range of polymeric ultraviolet stabilizer physical properties to be obtained and consequently, the products could be used in a wide variety of applications. As mentioned above, the copolymers could be used as permanent, compatible additives. Heller¹¹⁹ copolymerized allyl substituted 2-hydroxyphenylbenzotriazoles with vinyl chloride to obtain materials useful for the fabrication of plastic bottles which could be used to store ultraviolet sensitive liquids. Skoultchi and Meier¹²⁹ copolymerized 4-(N,N-di-allylamino)benzoic acid and its ethyl ester with a mixture of acrylic acid, hydroxypropyl acrylate, and methyl acrylate in order to obtain an alcohol soluble polymeric ultraviolet stabilizer useful for skin protection. Tocker⁹⁶ prepared a polymeric ultraviolet stabilizer with vinylidene chloride and

long chain acrylates (C_{14} to C_{18}) which could be used as a coating for polyethylene. Cohen¹³⁹ prepared a wide variety of soluble polyesters based on bisphenols and dicarboxylic acids which were used to coat plastics. As described earlier, a thin skin on the surface of the polyester coating photo Fries rearranged on exposure to radiation, and the skin protected the substrate and lower layers of the coating from degradation. As the skin of rearranged polymer was slowly destroyed, the radiation was able to penetrate causing the lower layers of polyester to rearrange. This was described as a "self-healing" process.

4. Conclusions. On the basis of the above information, the following conclusions can be drawn.

(1) UV absorbing groups can be attached to polymers without destroying the stabilizers ability to absorb radiation and dissipate the energy in a nonharmful form.

(2) Polymeric UV stabilizers are less susceptible to solvent extraction, exudation, and evaporation from plastics than low molecular weight stabilizers and most oligomeric stabilizers.

(3) Oligomeric UV stabilizers prepared by the condensation of two benzophenone molecules with formaldehyde are more resistant to exudation and extraction than oligomeric stabilizers prepared with long aliphatic side chains.

(4) Oligomeric UV stabilizers prepared with long side

chains and copolymers containing low percentages of polymerizable UV stabilizers are more compatible with polymers than many low molecular weight stabilizers. Compatible copolymers which contain low percentages of UV stabilizer repeat units are more effective than incompatible polymeric UV stabilizers.

(5) The advantages of using polymeric UV stabilizers for the protection of plastics against oxidative photodegradation are most evident in samples with high surface area to volume ratios which are processed at high temperatures, exposed to solvents, and used or tested over a long period of time. In short term tests, UV stabilizer compatibility is most important for polymer protection.

(6) For thick plastic articles, it may be advantageous to coat the sample with a film of a copolymer containing stabilizer units rather than mixing the copolymeric stabilizer into the plastic. The comonomer should be chosen to give the copolymeric UV stabilizer good adhesion to the plastic substrate.

(7) For thick plastic articles, it may also be advantageous to use a UV stabilizer with a long side chain which can continuously exude from the plastic and replenish the stabilizer lost at the surface.

(8) Copolymers which contain low percentages of UV stabilizer repeat units can affect the physical properties

of the copolymers by decreasing the crystallinity of the copolymers. It is preferable to stabilize highly crystalline homopolymers such as polyethylene with a large amount (20%) of copolymer containing a high concentration (3 mole %) of UV stabilizer repeat units.

(9) A broad range of polymer properties can be obtained by copolymerization of monomeric UV stabilizers with the appropriate comonomers. Consequently, the copolymers may be used in a wide variety of applications.

G. Displacement Reactions on Chloroalkyl Substituted Polyethers

The focus of this section is on modification reactions of poly(epichlorohydrin). Reactions of poly(glycidyl p-toluenesulfonate), poly(3,3-bis(chloromethyl)oxacyclobutane), and chloride endcapped poly(oxyethylene) are also included. Poly(epichlorohydrin) vulcanization (crosslinking) has not been included. Most of the reactions which are described are displacement reactions; however, the degradation reaction of poly(epichlorohydrin) and, to a lesser extent, the degradation of poly(3,3-bis(chloromethyl)oxacyclobutane) are also discussed. Degradation reactions and other side reactions which occur during polymer modification reactions severely limit the utility of this technique for the introduction of active groups into polymers. Reference is made to a report

on graft polymerization on poly(epichlorohydrin). Most of the information in this section was taken from Chemical Abstract references.

The poly(epichlorohydrin) reactions described in this section are classified according to the type of nucleophile used in the displacement reactions. Poly(epichlorohydrin) has been used to alkylate: (1) oxygen-containing nucleophiles such as sodium or potassium salts of carboxylic acids, (2) nitrogen-containing nucleophiles such as sodium azide and aliphatic or aromatic amines, (3) sulfur-containing nucleophiles such as sodium salts of thiols, (4) phosphorous-containing nucleophiles such as tributylphosphine, and (5) carbon-containing nucleophiles such as sodium cyclopentadiene.

The products of these reactions have been used in a broad spectrum of applications which includes photosensitive polymers, anion exchange polymers, flocculating agents, polymeric antioxidants, and polymeric flame retardants.

1. Reactions with oxygen-containing nucleophiles.

Nishikubo¹⁶² studied the effects of reaction conditions (time, temperature, solvents, and catalyst) on the degree of substitution and polymer molecular weight for the displacement reaction of potassium cinnamate on poly(epichlorohydrin). In general, it was possible to incorporate high percentages (>80%) of cinnamate groups into the polymer; however, the degree of polymerization of the product was greatly reduced.

The copolymer of epichlorohydrin and glycidyl cinnamate which was obtained was used as a light sensitive polymer.

Hexamethyl phosphoric acid triamide (HMPA) appeared to be superior to dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF) as a solvent for the displacement reaction. As the data in Table 7 indicates, the highest degrees of esterification at 80 and 100° were for the reactions carried out in HMPA.

TABLE 7. Effect of Solvent and Temperature on the Degree of Esterification (%) of Poly(epichlorohydrin)¹⁶²

Time (hr.)	80° DMF	80° HMPA	100° DMF	100° DMSO	100° HMPA
4	20	25	40	55	65
8	20	35	60	75	80
10	25	40	60	80	85

Pech: 0.1 mole, potassium cinnamate 0.1 mole, methyltriethylammonium iodide, 2 g.

In a separate experiment, Nishikubo¹⁶² found that the degrees of esterification were generally higher for reactions which were catalyzed by methyltriethylammonium iodide. The degrees of esterification with and without the catalyst were 86.3 and 85.8% in DMSO, 62.1 and 53.2% in DMF, and 87.3 and

81.5% in HMPA at 100° for 10 hours.

Polymer degradation occurred as a serious side reaction during the entire course of the displacement reaction under the conditions used by Nishikubo (HMPA, 100°).¹⁶² Nishikubo found that reaction times of greater than 6 hours did not increase the degree of esterification appreciably but did significantly decrease the molecular weight of the polymers. As the data in Table 8 shows, the degree of polymerization

TABLE 8. Effect of Reaction Time on the Degree of Esterification and Number Average Degree of Polymerization of Poly(epichlorohydrin).¹⁶²

Reaction time (hr.)	0	2	6	10	14
Degree of Esterification %	0	71	82.7	83.4	84.7
Number Average Degree of Polymerization	1980	734	521	281	131
% Decrease in Number Average Degree of Polymerization over a 4-hour period	—	—	29%	46%	53%

Pech, 1 mole; Potassium cinnamate, 1 mole; Methyltriethylammonium iodide, 1.5 g.; HMPA, 500 ml.; 100°.

decreased rapidly and at an accelerating rate during the reaction.

Other workers have also converted poly(epichlorohydrin) to a copolymer of epichlorohydrin and glycidyl cinnamate by a displacement reaction with potassium or sodium cinnamate. Fukutomi and Ohotani¹⁶³ obtained an 85% degree of esterification by the reaction of potassium cinnamate with poly(epichlorohydrin) in DMF at 130° for 10 hours. Fukutomi¹⁶⁴ obtained a 56% degree of substitution with sodium cinnamate and benzyltrimethylammonium chloride as catalyst in DMF.

2. Reactions with nitrogen-containing nucleophiles.

Vandenberg¹⁶⁵ and Nishikubo¹⁶⁶ converted an epichlorohydrin-ethyleneoxide copolymer and poly(epichlorohydrin) to light sensitive materials by carrying out a displacement reaction with sodium azide. The reaction of Nishikubo was conducted in HMPA for 10 hours at 60° with methyltriethylammonium-iodide as a catalyst.

Fukutomi¹⁶⁷ prepared photoconducting polymers by reacting pyrrole, carbazole, or indole derivatives with poly(epichlorohydrin) in DMF for 9 hours at 70° in the presence of sodium hydroxide. Carbazole gave a 97% degree of substitution.

Kurengina¹⁶⁸ prepared a water soluble polymer containing α -pyrrolidone rings by reacting poly(epichlorohydrin) with an alkali metal salt of pyrrolidone.

Stramberg¹⁶⁹ heated poly(epichlorohydrin) with dimethylaminoethanol in an ampule at 120° for 4 hours to obtain a

97% conversion to the ammonium salt. The salt was treated with silver oxide for 2 hours to yield a quaternary ammonium base.

Lorensen and Bergman¹⁷⁰ reacted low molecular weight poly(epichlorohydrin) (MW 800-1600) with aliphatic or aromatic amines at 150° for 49 hours. The polymeric salts were then treated with aqueous sodium hydroxide at 30-70° to convert the amine hydrochloride salt to an amine.

A salt prepared from pyridine and poly(epichlorohydrin) was used by Poot¹⁷¹ as an electroconductive polymer in an electrophotographic recording element. Mohrmann¹⁷² treated aqueous solutions of humic acid with the polymeric salt.

Poly(epichlorohydrin) has been quaternized with various trialkylamines. A quaternary ammonium salt of high molecular weight poly(epichlorohydrin) (MW 300,000) and trimethylamine has been used as a flocculating agent.¹⁷³ A product useful for clarifying raw sewerage was prepared by heating low molecular weight poly(epichlorohydrin) and trimethylamine in an autoclave at 100° for 3½ hours.¹⁷⁴ Jursich and Ciesla¹⁷⁵ used the quaternary ammonium salt of triethylamine and poly(epichlorohydrin) as a coating for the preparation of electroconductive paper for electrophotographic recording elements. McDonald¹⁷⁶ used the quaternary ammonium salt of poly(epichlorohydrin) and long chain oxyethylated amines (DP = 1 to 30) to break up oil in water emulsions in oil

fields.

3. Reactions with sulfur-containing nucleophiles. The reaction conditions reported for the preparation of sulfur derivatives of poly(epichlorohydrin) were, in general, milder than the conditions used in the reaction of poly(epichlorohydrin) with oxygen-containing nucleophiles. For example, Breslow¹⁷⁷ treated poly(epichlorohydrin) in DMSO with thiophenol and sodium hydroxide at 60-70° for 2 hours to obtain a product which contained 88% of thiophenol groups. The polymer was stabilized with 1% phenyl- α -naphthylamine during the reaction. Therefore, Breslow was able to obtain a high degree of substitution under reaction conditions (60-70°, 2 hours) which were much milder than the conditions (100°, 10 hours) reported by Nishikubo¹⁶² for the alkylation of potassium cinnamate with poly(epichlorohydrin).

Vandenberg¹⁷⁸ reacted a copolymer of ethylene oxide and epichlorohydrin with sodium thiosulfate.

Marklow¹⁷⁹ converted the chloride groups of poly(epichlorohydrin) to thiol groups by first reacting them with sodium N,N-dimethyldithiocarbamate in refluxing acetone for 22 hours followed by a reaction with potassium hydroxide on a steam bath for 16 hours.

Hickner and Forber¹⁸⁰ treated poly(epichlorohydrin) with 2-mercaptoethanol and sodium hydroxide for 4 hours in refluxing benzene. The polymeric alcohol was further reacted with a urethane prepolymer to obtain a rigid foam.

Vandenberg¹⁸¹ and Willis obtained a water soluble product by the reaction of an epichlorohydrin-ethylene oxide copolymer with thiourea to obtain a polymeric isothiuronium salt.

Tousignant and Houtman¹⁸² converted a low molecular weight poly(epichlorohydrin) (MW 500) to a poly(sulfonic acid) by carrying out a displacement reaction with sodium sulfite for 6 hours in water at 150° in an autoclave. The chlorine free polymeric sulfonate salt was converted to the free poly(sulfonic acid).

Solodkin¹⁸³ substituted poly(epichlorohydrin) with sodium thiocyanate in acetone.

4. Reactions with phosphorous-containing nucleophiles.

Vandenberg¹⁸⁴ obtained polymeric flame retardants by treating poly(epichlorohydrin), poly(epibromohydrin), and an ethylene oxide-epichlorohydrin copolymer with phosphites, phosphonites, or phosphinites.

Redmore^{185,186} quaternized poly(epichlorohydrin) with tributylphosphine.

5. Reactions with carbon-containing nucleophiles.

Minoura¹⁸⁷ attempted to prepare the Grignard reagent of poly(epichlorohydrin); however, he found that the polymeric Grignard reagent quickly reacted with an adjacent chloromethyl group to form a cyclic ether. Poly(epichlorohydrin) was also treated with benzylmagnesium chloride and allyl-

magnesium chloride in refluxing THF. The degree of substitution increased with an increase in the Grignard reagent concentration; however, some chain cleavage and cyclic ether formation occurred as side reactions.

Asai¹⁸⁸ treated poly(epichlorohydrin) (MW 1500) with sodium cyclopentadiene in THF at room temperature for 3 hours.

6. Degradation of poly(epichlorohydrin). Vandenberg¹⁸⁹ studied the mechanism of the base cleavage of poly(epichlorohydrin). He found that chain cleavage occurred much more rapidly with poly(epichlorohydrin) than with other poly(alkylene oxides). In fact, the polymer in dilute toluene solution at -78° was cleaved as readily as butyl lithium was added to the solution. Vandenberg found that the end groups formed in the chain scission reaction consisted of about equimolar amounts of hydroxyl and carbonyl groups with a small amount of acetylene end groups. A chain cleavage reaction also occurred at 65° in DMSO with sodium hydroxide or sodium methoxide base; however, no acetylene groups were formed. Vandenberg believed that the facile cleavage may have been due to complexation of the lithium ion, not only with the main chain ether but also with the chlorine atom.

The major degradation reaction (Figure 3) was believed to be the base abstraction of a main chain proton on the

in DMSO at 110-130° for 3 to 24 hours. In general, the reaction mixtures became dark as the reaction proceeded, and the products were discolored. In many cases, polymer chain scission occurred as a side reaction.

A very high degree of substitution (97%) on poly-(3,3-bis(chloromethyl)oxacyclobutane) was obtained with sodium thiophenolate in 30 minutes at 110-120°. The solution viscosities of the gray polymers were not influenced by reaction times up to 5 hours, which indicated that polymer chain cleavage was not a serious side reaction under these conditions.

Minoura found that sodium phenolate was a less effective nucleophile than sodium thiophenolate. After 2 hours at 120-135°, only a 57% degree of substitution of phenoxide for chloride was obtained.

Minoura also carried out a displacement reaction on poly(3,3-bis(chloromethyl)oxacyclobutane) with sodium cyanide at 120-130° for 3 hours. He found that the brown product had a high degree of substitution (80%); however, the infrared spectrum of the product indicated that a chain scission side reaction accompanied the displacement reaction. The infrared spectrum of the polymer showed an absorption due to a hydroxyl group which was probably formed as a result of a chain cleavage reaction.

The reaction of sodium acetate, which had a low

solubility in DMSO, with poly(3,3-bis(chloromethyl)oxycyclobutane) at 130-140° resulted in brown polymers with 8.7 and 83.6% degrees of substitution after 2 and 24 hours respectively. A large decrease in the solution viscosity of the polymer accompanied the sodium acetate displacement reaction, which indicated that some chain cleavage had occurred. The infrared spectrum of these products also showed hydroxyl end group absorptions.

A sodium methoxide displacement reaction evidently caused polymer degradation and crosslinking since a polymeric gel formed.

Minoura concluded that these poly(3,3-bis(chloromethyl)-oxacyclobutane) displacement reactions were complicated by the instability of DMSO to heat and basic reagents. He pointed out that metallation of DMSO by alkaline compounds and the successive reaction of metallated or decomposed intermediates with the main chain and side chain of the polymer seemed to occur.

9. Displacement reaction on poly(glycidyl p-toluenesulfonate). Khanh¹⁹² carried out a displacement reaction on a polymer analogous to poly(epichlorohydrin). He polymerized (2,3-epoxypropoxy)trimethylsilane with aluminum alkyls, hydrolyzed the polymer to obtain polyglycidol, and then esterified the polymer with p-toluenesulfonyl chloride. A nucleophilic displacement reaction was carried out on the

poly(glycidyl p-toluenesulfonate) with lithium aluminum hydride in ether to obtain poly(propylene oxide). The effect, if any, of the hydride reduction on polymer molecular weight was not discussed. The investigators studied the effect of polymerization catalyst on the optical activity of the poly(propylene oxide).

10. Displacement reactions on chloride endcapped poly(oxyethylene). Booth¹⁹³ converted the hydroxyl end groups of low molecular weight poly(oxyethylene) (MW 1000, 1500, and 3300) to chloride groups by a reaction with thionyl chloride in pyridine. The oligomeric dichlorides were then subjected to a nucleophilic displacement reaction with sodium phenoxide in DMSO at 60° for 6 hours. He reported that no decrease of molecular weight was observed in the preparation of the chloro and phenoxy endcapped polymers.

11. Conclusions. It can be concluded from the work of Vandenberg,¹⁸⁹ Nishikubo,¹⁶² and Minoura^{187,191} that nucleophilic displacement reactions on poly(epichlorohydrin) and poly(3,3-bis(chloromethyl)oxacyclobutane) with strong bases are accompanied by chain cleavage degradation reactions. Also, side reactions leading to discoloration occur at high temperatures (100°) in the presence of bases in DMSO.

H. Reactions of Poly(methacrylic acid) and Poly(acrylic acid)

1. General reactions of poly(methacrylic acid) and poly(acrylic acid). Poly(methacrylic acid) and poly(acrylic acid) have been subjected to a wide variety of modification reactions.⁷⁰ As mentioned earlier, poly(methacrylyl chloride) was used to attach enzymes to polymer chains. Poly(acrylic acid) derivatives have been reduced to obtain a polymer with primary alcohol groups. The poly(allyl alcohol) was further reacted to form poly(allyl acetate), poly(allyl p-toluenesulfonate), and other polymeric esters.¹⁹⁴ Copolymers of ethylene and methacrylic acid have been reacted with alkali metal hydroxides to obtain the unique class of polymers known as ionomers.¹⁹⁵ Poly(methacrylic acid) and poly(acrylic acid) have been esterified with diazomethane and derivatives of diazomethane. For example, an anthracene group was introduced into a polymer by the reaction of poly(methacrylic acid) with 9-diazomethylanthracene.¹⁹⁶ Finally, Ferruti^{61,62} and Ringsdorf⁶³ have developed a number of poly(methacrylate) and poly(acrylate) esters with good leaving groups such as poly(N-methacryloxysuccinimide). These reactive polymers were useful for the introduction of pharmaceutical chemicals onto polymers under mild conditions.

2. Nucleophilic displacement reactions of salts of poly(methacrylic acid) and poly(acrylic acid). Nucleophilic displacement reactions with salts of poly(methacrylic acid) have been studied by Morawetz.¹⁹⁷ He found that the carboxylates in partially ionized poly(methacrylic acid) were 4 to 10 times as reactive with bromoacetamide as those of monomeric dicarboxylic acids. The reactivity of the polymer decreased sharply with a rising degree of ionization of the polymer. The high reactivity was believed to be due to a high concentration of substrate within the polymer coil. He reported that the dependence of the reaction rate of poly(methacrylic acid) with bromoacetamide depended on the degree of ionization of the polymer because the amide was bound to the neighboring carboxyl groups and this bond was stronger when the carboxyls were not ionized.

A facile nucleophilic displacement reaction of poly-(sodium acrylate) with dibutyltin dichloride, triphenyltin chloride, diphenyltin dichloride, diphenylsilicon dichloride, and triphenylsilicon chloride was carried out by Carraher¹⁹⁸ by an interfacial technique. He found that reaction times of 30 seconds were sufficient to complete the reactions.

In our laboratory,¹⁹⁹ displacement reactions were carried out with poly(cinnamic acid). The best technique for the esterification of the polymer was by methylation of the sodium salt of the polymer in water with dimethyl

sulfate.. It was concluded after elemental analysis for sodium and acid titration for sodium carboxylate groups, that at least 99.8% of carboxylate anions had been alkylated.

CHAPTER II

EXPERIMENTAL SECTION

A. Synthesis and Polymerization of Methyl 5-Vinylsalicylate and Methyl 5-Vinylacetylsalicylate

1. Synthesis of methyl salicylate. Methyl salicylate was prepared from salicylic acid, concentrated sulfuric acid, and methanol according to the procedure described by Vogel.²⁰⁰

2. Synthesis of methyl acetylsalicylate. Acetic anhydride (21 ml., 0.22 mole) was added to methyl salicylate (15.2 g., 0.10 mole) in a 50-ml. Erlenmeyer flask. Concentrated sulfuric acid (4 drops) was added as the solution was stirred. The flask was then tightly stoppered and the reaction was allowed to continue at room temperature.

The progress of the reaction was determined by PMR spectroscopy. After 105 minutes, a 2-ml. aliquot was added to a test tube which contained 2 ml. of carbon tetrachloride and 4 ml. of water. The test tube was stoppered and the contents were carefully shaken. The organic layer was separated and then washed twice with a 10% aqueous sodium bicarbonate solution (4 ml.), water (4 ml.), and dried with magnesium sulfate. The PMR spectrum of the solution indicated that the conversion to methyl acetylsalicylate was complete since the phenol peak ($\delta = 10.55$) of methyl

salicylate was absent and the integration of the acetyl protons ($\delta = 2.22$) and methyl ester protons ($\delta = 3.75$) were equal.

After standing for 2 hours at room temperature, the contents of the flask was added to a cold mixture of sodium carbonate (42 g., 0.40 mole) and water (400 ml.) which caused methyl acetylsalicylate to separate as a white solid. The product was filtered with suction, washed with water, air dried on the filter, dried for 16 hours over phosphorous pentoxide in a vacuum desiccator (0.05 mm.), and further dried for 2 hours in the melt at 65° in a vacuum oven (0.4 mm.). The colorless liquid was dissolved in chloroform (50 ml.) and the solution was filtered to remove a small amount of insoluble impurities. After the chloroform was removed by distillation at reduced pressure* in a rotary evaporator, the clear, colorless liquid crystallized to yield 17.8 g. (92% yield) of methyl acetylsalicylate (m.p. $49.5-51^{\circ}$, lit. m.p.²⁰¹ $51-52^{\circ}$). In two other experiments, the yields were both 91%. The infrared spectrum (KBr) showed absorptions at 1755 and 1720 cm^{-1} (C=O stretching). The PMR spectrum (CDCl_3) showed δ : 2.27 (CH_3CO_2 , 3); 3.80 (CO_2CH_3 , 3); 6.95 to 8.05 (aromatic protons, 4).

*See measurements section for the reduced pressure value.

3. Synthesis of methyl 5-acetylsalicylate - Procedure

I - Fries rearrangement. Aluminum trichloride (120 g. \pm 2 g., 0.90 mole) was quickly added to a 1-l. Erlenmeyer flask which contained nitrobenzene (360 ml.) and a magnetic stirring bar. The flask was fitted with a pressure-equalizing dropping funnel which contained a solution of methyl acetylsalicylate (83.5 g., 0.43 mole) in nitrobenzene (240 ml.). The dropping funnel was fitted with a calcium chloride drying tube, and the contents of the flask were cooled for 1 hour by an ice-water bath. The methyl acetylsalicylate solution was then added dropwise over a period of 1 hour to the magnetically stirred aluminum trichloride-nitrobenzene solution. As the reaction proceeded, the color changed from green-yellow to brown. The solution was allowed to warm to room temperature 10 minutes after the addition was completed.

The progress of the Fries reaction was followed by PMR spectroscopy. An aliquot (4 ml.) of the dark solution was added to cold 6N hydrochloric acid (4 ml.) in a test tube. The stoppered test tube was carefully shaken and the lower organic layer was removed. The aqueous phase was washed with carbon tetrachloride (2 ml.), and the combined organic phases were washed four times with 2N hydrochloric acid (6 ml.), twice with water (6 ml.), and the organic phase was dried with magnesium sulfate. The PMR spectrum showed δ : 2.50 (CH_3CO); 3.90 and 3.95 (CO_2CH_3); 10.75 (OH of methyl

salicylate); 11.20 (OH of the methyl 5-acetylsalicylate). (The unreacted methyl acetylsalicylate had evidently hydrolyzed to methyl salicylate during the aqueous washings since the signal due to the acetate protons was absent.) A comparison of the integrated signal intensities of the methyl ester, acetyl, and phenolic protons showed that the reaction conversion was 76% after $4\frac{3}{4}$ hours and 94% after 41 hours. The results are presented in Figure 5 (p. 165).

After 49 hours, the dark solution was slowly added to a mixture of ice (400 g.) and 12N hydrochloric acid (125 ml.) in a 2-l. beaker and the mixture was stirred for 10 minutes. A light green-yellow organic layer was separated in a separatory funnel and the aqueous phase was washed with chloroform (100 ml.). The combined organic phases were washed once with 3N hydrochloric acid (300 ml.) and twice with water (300 ml.). After drying the organic layer with magnesium sulfate, most of the nitrobenzene was removed by distillation in a rotary evaporator at 75° and reduced pressure (0.1 mm.). The remaining nitrobenzene (b.p. 35° , 0.04 mm.) and methyl 5-acetylsalicylate (b.p. $123-125^{\circ}$, 0.7 mm.) were separated by fractional distillation through a Microglass Claisen head fitted with a 10-cm. Vigreux column. On standing at room temperature, the clear, colorless liquid crystallized. The product (64.5 g., 77% yield) had a very faint odor of nitrobenzene and melted at $60-61^{\circ}$ (lit. m.p.²⁰² 55°).

A second reaction was conducted in which methyl acetylsalicylate was added as a solid. A 300-ml. round-bottomed flask, which contained nitrobenzene (80 ml.) and a magnetic stirring bar, was fitted with a three-way connecting tube. The connecting tube had a calcium chloride drying tube fitted to the side arm and a thermometer protruding into the nitrobenzene fitted in the center tube. Aluminum trichloride (26.5 ± 0.5 g., 0.20 mole) was quickly added to the yellow nitrobenzene with stirring and the green solution was cooled to less than 10° by an ice-water bath. Methyl acetylsalicylate (17.4 g., 0.090 mole) was added to the side arm of the connecting tube. The apparatus was then gently tilted and tapped causing the methyl acetylsalicylate to slowly fall over a period of 10 minutes into the aluminum trichloride-nitrobenzene solution. The temperature of the solution during the addition did not exceed 10° . The brown solution was allowed to warm to room temperature 10 minutes after the addition was completed and the reaction was allowed to continue for 51 hours. A 72% yield (12.6 g.) of methyl 5-acetylsalicylate was obtained after a work up and distillation similar to that described above (b.p. 101° , 0.08 mm., m.p. $59-60.5^{\circ}$). A second reaction, which was run on a larger scale, resulted in a 68% yield (35.4 g.) of methyl 5-acetylsalicylate (b.p. 95° , 0.07 mm.). The white solids had a faint odor of nitrobenzene.

4. Synthesis of methyl 5-acetylsalicylate - Procedure II - Friedel-Crafts acylation. A 1-l. three-necked round-bottomed flask was charged with nitrobenzene (600 ml.) and fitted with a mechanical stirrer, a pressure-equalizing dropping funnel, and a three-way connecting tube. The connecting tube was equipped with a thermometer protruding through the center tube into the nitrobenzene and a reflux condenser topped with a calcium chloride drying tube in the side arm. Aluminum trichloride (240 g., 1.75 mole) was quickly added which caused a mild exothermic reaction as it formed a green solution. Acetyl chloride (65 ml., 0.9 mole) was added over a period of 15 minutes via the dropping funnel. Methyl salicylate (104 g., 0.68 mole) was added dropwise with stirring over a period of 30 minutes while maintaining the temperature of the solution at 8-12°. Ten minutes after the addition was completed, the solution was allowed to warm to room temperature.

The progress of the acylation of methyl salicylate to methyl 5-acetylsalicylate was determined by PMR spectroscopy. A PMR sample was obtained by the same procedure described in the Fries rearrangement reaction. Two and one-half hours after the methyl salicylate addition was completed, the PMR spectrum showed δ : 2.50 (CH_3CO , 27); 3.98 (CO_2CH_3 , 28); 10.7 (methyl salicylate OH , 1); 11.15 (methyl 5-acetylsalicylate OH , 9) which indicated a greater than 90%

conversion of methyl salicylate to methyl 5-acetylsalicylate. The results are presented in Figure 5 (p. 165).

Three and one-half hours after completing the methyl salicylate addition, the dark solution was added cautiously with stirring to a mixture of ice (1000 g.) and 12N hydrochloric acid (200 ml.) in a 5-l. beaker. The exothermic reaction during the addition melted all of the ice. The lower nitrobenzene layer was separated in a separatory funnel and the aqueous phase was washed with chloroform (200 ml.). The combined organic phases were filtered to remove a small amount of black material and then washed with 1N hydrochloric acid (400 ml.), water (400 ml.), 5% aqueous sodium bicarbonate solution (400 ml.), water (400 ml.), and dried with magnesium sulfate. The reaction was essentially complete according to the PMR spectrum of the solution. After removing most of the solvents by distillation in a rotary evaporator at 65° and reduced pressure (0.1 mm.), the remaining nitrobenzene (b.p. 35°, 0.40 mm.) and methyl 5-acetylsalicylate (b.p. 91-94°, 0.04 mm.) were separated by fractional distillation through a Microglass Claisen head fitted with a 10-cm. Vigreux column. The clear, faintly yellow liquid crystallized on standing. Methyl 5-acetylsalicylate (106.5 g., 81% yield) had a faint odor of nitrobenzene and melted at 58-61°. The PMR spectrum (CDCl₃) was identical to the spectrum of pure methyl 5-acetyl-

salicylate reported below.

5. Preparation and characterization of analytically pure methyl 5-acetylsalicylate. Approximately 2 g. of a mixture of methyl 5-acetylsalicylate and methyl 5-acetylacetylsalicylate, which were obtained from an unsuccessful attempt to acetylate methyl 5-acetylsalicylate, were saponified by heating for 30 minutes in 10% sodium hydroxide (30 ml.) on a steam bath. The solution was acidified and the white solid precipitate was filtered, washed with water, and was crystallized from aqueous ethanol. The compound melted at 208-211° (dec.). The reported melting point for 5-acetylsalicylic acid is 209-210°, and the reported melting point for the ortho isomer, 3-acetylsalicylic acid, is 148-149°. ²⁰³

An analytically pure sample of methyl 5-acetylsalicylate was obtained by esterification of 5-acetylsalicylic acid with methanol and sulfuric acid by the usual procedure.²⁰⁰ After short path distillation, the clear, colorless liquid solidified and melted at 60.5-61.5°. The infrared spectrum (KBr) showed absorptions at 2800 to 3500 cm^{-1} (OH stretching) and 1680 cm^{-1} (C=O stretching). See p. 259. The PMR spectrum (CDCl_3) showed δ : 2.53 (CH_3CO , 3); 3.95 (CO_2CH_3 , 3); 6.87 to 8.40 (aromatic protons, 3); 11.10 (ArOH , 1). See p. 240. Anal. calcd. for $\text{C}_{10}\text{H}_{10}\text{O}_4$: C, 61.85%; H, 5.19%. Found: C, 61.89%; H, 5.09%.

6. * Attempted reduction of methyl 5-acetylsalicylate.

A 50-ml. round-bottomed flask, which contained a mixture of sodium borohydride (0.57 g., 15 mmole) in 100% ethanol, (14 ml.) was cooled by a dry ice-acetone bath. A solution of methyl 5-acetylsalicylate (2.4 g., 12 mmole) in 100% ethanol (7 ml.), which was contained in a pressure-equalizing dropping funnel fitted with a calcium chloride drying tube, was added dropwise over a period of 10 minutes. After the addition was completed, the temperature of the purple mixture was maintained at 5° by an ice-water bath. The mixture had thickened considerably after 25 minutes.

The progress of the reduction was followed by PMR spectroscopy. A 1-ml. aliquot was cautiously added to a test tube containing cold 1N hydrochloric acid (4 ml.) and carbon tetrachloride (2 ml.). The addition caused a gas evolution. The contents were carefully mixed until the bubbling ceased and the test tube was then stoppered and gently shaken. The carbon tetrachloride layer was separated and washed once with 1N hydrochloric acid (4 ml.), twice with water (4 ml.), and dried with magnesium sulfate. The PMR spectrum (CCl_4) showed δ : 1.30 to 1.40 (CH_3CHOH); 2.40 (CH_3CO); 3.95 (CO_2CH_3 of the starting material); 3.90 (CO_2CH_3 of the product); 10.42 (ArOH of the product); 10.97 (ArOH of the starting material); 6.77 to 8.20 (aromatic protons). The signal of the methyl ester protons of methyl

5-acetylsalicylate was used as a reference and assigned the value of 3.95 ppm. The spectra revealed that the reaction conversion was 25% after 25 minutes, 25% after 55 minutes, and 30% after 20 hours. The work up of the 20 hour aliquot did not cause bubbling which indicated that by this time, the sodium borohydride had been destroyed by the ethanol.

The reaction was repeated using DMAc as the solvent. In this case the reaction proceeded in a homogeneous solution and, as before, the color was purple. The progress of the reaction, as determined by PMR spectroscopy, was 10% after 25 minutes, 20% after 2½ hours, 20% after 6 hours, and 30% after 24 hours. The work up of the 24 hour aliquot resulted in a vigorous evolution of gas which indicated that the sodium borohydride had not been destroyed.

7. Synthesis of methyl 5-acetylacetylsalicylate.

Methyl 5-acetylsalicylate (60.6 g., 0.31 mole) was dissolved with gentle heating in acetic anhydride (100 ml., 1.06 mole) in a 250-ml. Erlenmeyer flask. Concentrated sulfuric acid (0.5 ml., 10 mmole) was then added with stirring and the flask was stoppered.

The progress of the reaction was monitored by PMR spectroscopy. The PMR spectrum of the reaction solution showed δ : 2.52 (CH_3CO of the starting material); 2.60 (CH_3CO of the product); 2.34 (CH_3CO_2); 3.90 (CO_2CH_3 of the product); 4.00 (CO_2CH_3 of the starting material). The

acetylation was 50% after 4 hours and complete after 45 hours.

Addition of the contents of the flask to cold water (800 ml.), which contained 3 g. of sodium bicarbonate, caused an oil to precipitate which quickly solidified to clumps of off-white solid. The moist product was ground with a mortar and pestle, and the finely divided solid was stirred with water and filtered to remove the acetic acid. The crude product (65.0 g., 88%) was dried for 16 hours over phosphorous pentoxide in a vacuum desiccator (0.05 mm.). Distillation (b.p. 119-121^o, 0.05 mm.) through a Microglass Claisen head fitted with a 10-cm. Vigreux column yielded 60.2 g. (82%) of a clear, colorless, odorless liquid which solidified on standing (m.p. 66.5-67.5^o). The infrared spectrum (KBr) showed absorptions at 1740, 1715, and 1675 cm.⁻¹ (C=O stretching). See p. 259. The PMR spectrum (CDCl₃) showed δ : 2.33 (CH_3CO , 3); 2.60 (CH_3CO_2 , 3); 3.87 (CO_2CH_3 , 3); 7.12 to 8.60 (aromatic protons, 3). See p. 240. Anal. calcd. for $\text{C}_{12}\text{H}_{12}\text{O}_5$: C, 61.01%; H, 5.12%. Found: C, 60.89%; H, 5.02%.

8. Synthesis of methyl 5-(1-hydroxyethyl)acetylsalicylate. A 250-ml. Erlenmeyer flask was charged with dry ethanol (65 ml.) and fitted with a three-way connecting tube equipped with a calcium chloride drying tube in the side arm and a thermometer protruding into the ethanol through the center tube. The ethanol was cooled to 10^o by an ice-water

bath. Sodium borohydride (2.6 g., 68 mmole) was added and the mixture was shaken for 25 minutes as most (> 95%) of the sodium borohydride dissolved. Methyl 5-acetylsalicylate (21.7 g., 92 mmole) contained in the side arm of the three-way connecting tube was then added over a period of 10 minutes by tilting and gently tapping the apparatus while shaking the flask in an ice-water bath. The temperature climbed to 10-15° during the addition. The reaction was allowed to continue for an additional 15 minutes. The faintly yellow solution, which contained a small amount of insoluble material, was then added to ice (200 g.) in a 1-l. beaker and slowly acidified with cold 4N hydrochloric acid (100 ml.). After the gas evolution subsided, the oil which had separated was extracted from the aqueous mixture with two 50-ml. portions of chloroform. The combined organic phases were washed with 1N hydrochloric acid (50 ml.), water (50 ml.), 5% aqueous sodium bicarbonate solution (50 ml.), water (50 ml.), dried with magnesium sulfate, and filtered. A 97% yield (21.2 g.) of faintly yellow crude methyl 5-(1-hydroxyethyl)acetylsalicylate was obtained after removal of the chloroform by distillation at reduced pressure in a rotary evaporator. The product was distilled (b.p. 134-137°, 0.09 mm.) through a Microglass Claisen head fitted with a 10-cm. Vigreux column to yield 17.4 g. (79%) of a colorless, viscous oil ($n_d^{20} = 1.5227$,

$n_d^{25} = 1.5205$) and 1.45 g. (7%) of a faintly yellow forerun. The reaction was repeated twice and resulted in 94 and 96% yields of crude product. The infrared spectrum (neat) showed absorptions at 3100 to 3700 cm^{-1} (OH stretching), 1765 and 1720 cm^{-1} (C=O stretching). See p. 259. The PMR spectrum (CDCl_3) showed δ : 1.30 to 1.40 (CH_3CHOH , 3); 2.27 (CH_3CO_2 , 3); 3.73 (CO_2CH_3 , 3); 4.55 to 4.90 (CH_3CHOH , 1); 5.35 (CH_3CHOH , 1); 6.87 to 7.90 (aromatic protons, 3). See p. 240. Anal. calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_5$: C, 60.50%; H, 5.92%. Found: C, 60.65%; H, 5.83%.

9. Attempted synthesis of methyl 5-vinylacetylsalicylate. Two 10-ml. Erlenmeyer flasks were each charged with methyl 5-(1-hydroxyethyl)acetylsalicylate (1.0 g., 4.2 mmole) and pyridine (4 ml., 50 mmole) and capped with a rubber septum. While cooling the flasks in a dry ice-acetone bath, thionyl chloride (0.9 ml., 1.5 g., 12.6 mmole) was slowly injected via a syringe. One flask was left at room temperature and the other was heated by an oil bath maintained at 55° . The yellow solutions gradually darkened over a period of 1 to 2 hours. After $2\frac{1}{2}$ hours, a 1-ml. aliquot from the black solution which was heated to 55° was added to a test tube containing 4N hydrochloric acid (4 ml.) and carbon tetrachloride (3 ml.) and shaken. The organic layer was separated and washed once with 1N hydrochloric acid (3 ml.), twice with water (3 ml.), and dried with magnesium sulfate.

The PMR spectrum did not reveal the presence of any vinyl proton signals in the 5 to 6 ppm. range. However, the doublet at 1.3 to 1.4 ppm. (CH_3CHOH) had nearly disappeared while a new doublet appeared at 1.78 to 1.88 ppm. (relative to the acetoxy protons at 2.27 ppm.). The PMR spectrum of the black room temperature reaction after 5 hours gave the same results. No further characterization of the solutions was attempted.

10. Dehydration of methyl 5-(1-hydroxyethyl)acetylsalicylate. A 50-ml. three-necked round-bottomed flask was fitted with a capillary tube which reached the bottom of the flask and was connected to a nitrogen source, a pressure-equalizing dropping funnel, and a vacuum distillation apparatus (10-cm. Vigreux column on a Claisen head, 2 thermometers, condenser, vacuum take-off adapter, and a 50-ml. round-bottomed receiving flask containing a small amount of picric acid). The three-necked flask was charged with freshly fused, finely divided potassium hydrogen sulfate (0.6 g.) and approximately 10 mg. of picric acid (polymerization inhibitor). The system was connected to a vacuum pump and the pressure was adjusted to approximately 0.2 mm. by restricting the nitrogen flow through the capillary tube. A silicone oil bath maintained at 225° was used to heat the flask as the viscous methyl 5-(1-hydroxyethyl)acetylsalicylate (9.8 g., 41 mmole) was added over a period of 35

minutes via the dropping funnel. A clear, colorless liquid, which turned out to be a mixture of methyl 5-vinylsalicylate and methyl 5-vinylacetylsalicylate, distilled (b.p. 120-125°, 0.18-0.20 mm.) as the reaction proceeded. A mist, presumably water, quickly flowed through the system to the cold trap. At the end of the reaction, a small amount of product which remained in the column was distilled by heating the column with a heat gun. The yield of products (7.4 g., 36 mmole) was 88 mole %.

The composition of the reaction product was determined by comparing the integrated signal intensity of the acetoxy protons (2.20 ppm.) and the integrated signal intensity of the phenol proton (10.7 ppm.) to the integrated signal intensity of the methyl ester protons (3.78 and 3.82 ppm.) of the PMR spectrum (CCl_4). The mixture was 63 mole % methyl 5-vinylacetylsalicylate and 37 mole % methyl 5-vinylsalicylate. A second run on a larger scale yielded 88 mole % of a mixture which contained 59 mole % of methyl 5-vinylacetylsalicylate and 41 mole % of methyl 5-vinylsalicylate. When crude methyl 5-(1-hydroxyethyl)acetylsalicylate was used instead of the pure starting material, the yields were 77 and 74 mole % of 63/37 and 44/56 mole ratios of methyl 5-vinylacetylsalicylate to methyl 5-vinylsalicylate.

11. Synthesis of methyl 5-vinylacetylsalicylate. A mixture consisting of 63/37 mole ratio of methyl 5-vinyl-

acetylsalicylate to methyl 5-vinylsalicylate (5.9 g., 29 mmole) was placed in a 50-ml. Erlenmeyer flask and treated with acetic anhydride (15 ml., 160 mmole) and concentrated sulfuric acid (3 drops). The tightly stoppered flask was left at room temperature for 3 hours. The solution was added to an ice-water mixture and the reaction product separated as an oil. The product was dissolved in chloroform and the solution was washed with water followed by repeated washings with 5% aqueous sodium carbonate until the aqueous solution was strongly basic (pH paper). The chloroform solution was washed with water, dried with magnesium sulfate, and filtered. After the chloroform was removed by distillation in a rotary evaporator at reduced pressure, the product was distilled through a Microglass Claisen head fitted with a 10-cm. Vigreux column (b.p. 100-103.5°, 0.12 mm.) to yield 3.0 g. (47%) of a clear, colorless, viscous liquid. Picric acid was used as the polymerization inhibitor. A large amount of material had polymerized in the distillation flask during the distillation. A second preparation resulted in a 40% yield of pure methyl 5-vinylacetylsalicylate after distillation (b.p. 99-101°, 0.07 mm.). (A large forerun (b.p. 91-99°, 0.07 mm., 32%) which contained less than 5 mole % of methyl 5-vinylsalicylate, as determined by PMR spectroscopy, had been removed.) The infrared spectrum (neat) of the methyl 5-vinylacetylsalicylate showed absorptions at

1765 and 1720 cm^{-1} ($\text{C}=\text{O}$ stretching). See p. 260. The PMR spectrum (CDCl_3) showed δ : 2.24 (CH_3CO_2 , 3); 3.78 (CO_2CH_3 , 3); 5.1 to 6.83 and 6.85 to 7.92 (vinyl and aromatic protons, 6). See p. 240. Anal. calcd. for $\text{C}_{12}\text{H}_{12}\text{O}_4$: C, 65.44%; H, 5.49%. Found: C, 65.35%; H, 5.38%.

12. Synthesis of methyl 5-vinylsalicylate. A 125-ml. Erlenmeyer flask was charged with a mixture of methyl 5-vinylacetylsalicylate and methyl 5-vinylsalicylate (63/37 mole ratio, 8.2 g., 41 mmole) and methanol (55 ml.). After sodium methoxide (5.0 g., 91 mmole) was slowly added, the flask was tightly stoppered and the yellow solution was left at room temperature for 1 hour. The sodium methoxide addition caused an exothermic reaction. The yellow solution was added to cold 1N hydrochloric acid (150 ml.) and the product was extracted with chloroform (50 ml.). The aqueous phase was washed again with chloroform (25 ml.) and the combined organic phases were washed with 1N hydrochloric acid (50 ml.), twice with water (50 ml.), once with 10% aqueous sodium bicarbonate solution (50 ml.), water (25 ml.), dried with magnesium sulfate, and filtered. After the chloroform was removed by distillation at reduced pressure in a rotary evaporator, methyl 5-vinylsalicylate was distilled (b.p. 62.5-64.5°, 0.07 mm.) through a Microglass Claisen head fitted with a 10-cm. Vigreux column. The distillation was carried out with the aid of a capillary tube connected to a nitrogen

source and picric acid as a polymerization inhibitor. A silicone oil bath at 160° was used as the heat source to avoid overheating. The yield of clear, colorless methyl 5-vinylsalicylate was 5.8 g. (80%). A second run on a slightly larger scale yielded 4.5 g. (54%, b.p. $66.0-67.0^{\circ}$, 0.16-0.18 mm.) of methyl 5-vinylsalicylate. The infrared spectrum (neat) showed absorptions at 2800 to 3500 cm^{-1} (OH stretching) and 1670 cm^{-1} (C=O stretching). See p. 260. The refractive index was $n_D^{20} = 1.5692$ and $n_D^{25} = 1.5666$. The PMR spectrum (CCl_4) showed δ : 3.87 (CO_2CH_3 , 3); 4.95 to 6.75 and 6.75 to 7.65 (vinyl and aromatic protons, 6); 10.74 (ArOH , 1). See p. 241. Anal. calcd. for $\text{C}_{10}\text{H}_{10}\text{O}_3$: C, 67.40%; H, 5.66%. Found: C, 67.66%; H, 5.72%.

13. Polymerization of methyl 5-vinylacetylsalicylate.

A 25-ml. round-bottomed flask equipped with a reflux condenser topped with a three-way stopcock was charged with benzene (10 ml.), AIBN (19 mg., 0.12 mmole, 0.5 mole %) and methyl 5-vinylacetylsalicylate (5.1 g., 23 mmole). The system was three times evacuated and refilled with nitrogen. The solution was then heated by an oil bath maintained at 65° while a slow flow of nitrogen was introduced into and vented from the flask via the three-way stopcock. A gas bubbler which contained mineral oil was attached to the outlet valve. After 19 hours, the cooled solution was added to ether (150 ml.) which caused a white solid to precipitate.

The polymer (3.8 g., 73% yield) was filtered and dried in a drying pistol over phosphorous pentoxide at 78° and reduced pressure (0.05 mm.) for 16 hours. The polymer was insoluble in 95% ethanol and isopropanol but was soluble in chloroform and THF. It had a glass transition (by DSC) at 106° and began to decompose around 300°. The polymer had an inherent viscosity of 0.32 dl./g. (0.5% DMSO). VPO indicated that the molecular weight of the polymer was not less than 20,000. The infrared spectrum (KBr) showed absorptions at 1765 and 1720 cm^{-1} (C=O stretching). See p. 261. The PMR spectrum (CDCl_3 , 35°) showed δ : 0.7 to 2.7 (CHCH_2 and CH_3CO_2 , 6); 3.5 to 4.0 (CO_2CH_3 , 3); 6.3 to 7.4 (aromatic protons, 3). See p. 241. The UV spectrum (THF) showed an absorption at 285 nm. ($1.48 \times 10^3 \text{ l. mole}^{-1} \text{ cm}^{-1}$). Anal. calcd. for $\text{C}_{12}\text{H}_{12}\text{O}_4$: C, 65.44%; H, 5.49%. Found: C, 65.34%; H, 5.45%.

The polymerization was repeated on a smaller scale by heating methyl 5-vinylacetylsalicylate (1.07 g., 4.8 mmole) with AIBN (30 mg., 0.2 mmole, 4 mole %) in benzene (5.2 ml.) for 16 hours at 65°. The yield of white powder, after drying at reduced pressure (0.2 mm.) in a vacuum oven at 60° for 16 hours, was 0.95 g. (89%). The polymer had a glass transition (by DSC) at 105° and the inherent viscosity of a 0.5% DMSO solution was 0.14 dl./g. The infrared and PMR spectra were identical to the spectra reported above.

Anal. calcd. for $\{ \text{C}_{12}\text{H}_{12}\text{O}_4 \}_n$: C, 65.44%; H, 5.49%.
 Found: C, 64.19%; H, 5.36%.

14. Attempted conversion of poly(methyl 5-vinylacetylsalicylate) to poly(methyl 5-vinylsalicylate). A 100-ml. round-bottomed flask fitted with a reflux condenser and topped with a calcium chloride drying tube was charged with methanol (45 ml.), p-toluenesulfonic acid (37 mg., 0.2 mmole), and poly(methyl 5-vinylacetylsalicylate) (0.43 g., 2.0 mmole). The polymer aggregated to a gel-like mass after 30 minutes of reflux and after 24 hours, it had solidified to a hard material. The lump of product was dissolved in acetone, precipitated with ether, and dried for 16 hours in a vacuum desiccator (0.05 mm.) at room temperature. The product had a glass transition (by DSC) at 122° . The infrared spectrum (KBr) showed absorptions at 1765, 1720, and 1675 cm^{-1} (C=O stretching). See p. 261. The PMR spectrum (CDCl_3) showed δ : 0.7 to 2.5 (CH_2CH and CH_3CO , 42); 3.6 to 4.1 (CO_2CH_3 , 32); 6.3 to 7.4 (aromatic protons, 34); 10.5 (ArOH , 9). See p. 241. According to the PMR spectrum, the conversion of methyl 5-vinylacetylsalicylate repeat units to methyl 5-vinylsalicylate repeat units was estimated to be 78%. The UV spectrum (THF) of the copolymer showed maxima at 315 nm. ($15.2 \text{ l. g}^{-1} \text{ cm}^{-1}$) and 235 nm. ($34.8 \text{ l. g}^{-1} \text{ cm}^{-1}$). The long wavelength absorption at 315 nm. did not have a shoulder at 285 nm.

15. Attempted copolymerization of methyl 5-vinylacetylsalicylate with vinyl acetate. A 15-ml. round-bottomed flask was charged with vinyl acetate (0.51 g., 5.9 mmole, freshly distilled), methyl 5-vinylacetylsalicylate (0.80 g., 3.6 mmole), AIBN (12 mg., 0.07 mmole, 0.74 mole %) and benzene (6 ml.). The polymerization was carried out by the same procedure described above. The yield of polymer was 0.55 g. (42%). It had a glass transition (by DSC) at 107°. The inherent viscosity of a 0.5% DMSO solution was 0.12 dl./g. The infrared (KBr) and PMR (CDCl₃) spectra were identical to those of poly(methyl 5-vinylacetylsalicylate).

16. Polymerization of methyl 5-vinylsalicylate in THF. A 5-ml. round-bottomed flask was charged with methyl 5-vinylsalicylate (0.49 g., 2.7 mmole), THF (3.5 ml.), and AIBN (3.4 mg., 0.021 mmole, 0.8 mole %) and the polymerization was carried out at 61° as described in the polymerization of methyl 5-vinylacetylsalicylate. After 14 hours, the solution was added to ether (50 ml.) which resulted in the precipitation of a white solid and an opaque solution. The suspension was filtered and the product was dried for 16 hours in a vacuum oven at 65° and reduced pressure (0.4 mm.) to give 0.11 g. (22% yield) of product. The polymer was insoluble in 95% ethanol and isopropanol but soluble in chloroform. It had a glass transition (by DSC) at 127°. The infrared spectrum (KBr) showed an absorption at 1675 cm.⁻¹

(C=O stretching). Anal. calcd. for $\{C_{10}H_{10}O_3\}_n$:
 C, 67.40%; H, 5.66%. Found: C, 66.66%; H, 5.93%.

17. Copolymerization of methyl 5-vinylsalicylate with methacrylic acid in THF. A 25-ml. round-bottomed flask was charged with methyl 5-vinylsalicylate (1.0 g., 5.7 mmole, 42 mole %), methacrylic acid (0.67 g., 7.8 mmole, freshly distilled), THF (11 ml.), and AIBN (15 mg., 0.09 mmole, 0.7 mole %). The polymerization was carried out at 61° as described above. After 14 hours, the solution was added to ether (150 ml.) which resulted in the formation of a solid precipitate and an opaque solution. After filtration, the solid was dried for 16 hours at 60° in a vacuum oven (0.4 mm.) to yield 0.50 g. (30% yield) of copolymer. It was soluble in hot 95% ethanol, swelled in hot isopropanol, and was insoluble in deuterated chloroform. The copolymer did not show a glass transition by DSC and the inherent viscosity of a 0.5% DMSO solution was 0.32 dl./g. The infrared spectrum (KBr) showed broad carbonyl absorptions. See p. 262. The PMR spectrum (d-DMSO, R-32) at 135° showed δ : 0.4 to 2.4 ($\underline{CHCH_2}$, $\underline{CH_2C(CH_3)}$, 58); 2.4 to 2.9 (DMSO); 3.7 to 4.1 ($CO_2\underline{CH_3}$, 21); 6.5 to 7.5 (aromatic protons, 19); 9.7 to 10.5 ($ArOH$, 5). See p. 242. Since no internal standard was used, the DMSO signal was assigned a value of 2.5 ppm. According to the PMR spectrum, the copolymer consisted of approximately 46 mole % methyl

5-vinylsalicylate and 54 mole % methacrylic acid, as judged by the relative integrated signal intensity of the methyl ester protons and aromatic protons of the methyl 5-vinylsalicylate repeat units and the main chain protons. The UV spectrum (THF) showed maxima at 316 nm. ($13.4 \text{ l. g.}^{-1} \text{ cm.}^{-1}$) and 237 nm. ($27.6 \text{ l. g.}^{-1} \text{ cm.}^{-1}$). Anal. calcd. for $\text{[C}_{10}\text{H}_{10}\text{O}_3]_{42\%} \text{[C}_4\text{H}_6\text{O}_2]_{58\%}$: C, 62.76%; H, 6.20%. Found: C, 62.78%; H, 6.25%.

The copolymerization was repeated using methyl 5-vinylsalicylate (0.50 g., 2.8 mmole, 17.2 mole %), methacrylic acid (1.16 g., 13.5 mmole), and AIBN (15 mg., 0.091 mmole, 0.6 mole %) in THF (11 ml.). A 44% yield (0.74 g.) of copolymer was obtained. It was soluble in 95% ethanol, swelled in hot isopropanol, and was insoluble in deuterated chloroform. DSC did not show a glass transition and the inherent viscosity of a 0.5% DMSO solution was 0.48 dl./g. The infrared spectrum (KBr) showed broad carbonyl absorptions. See p. 262. The PMR spectrum (d-DMSO, R-32) at 135° showed δ : 0.5 to 2.4 (CHCH_2 and $\text{CH}_2\text{C}(\text{CH})_3$, 73); 2.4 to 2.9 (DMSO); 3.0 to 4.1 (CO_2CH_3 , 10); 6.6 to 7.7 (aromatic protons, 12); 9.8 to 10.4 (ArOH , 2). See p. 242. Since no internal standard was used, the DMSO signal was assigned a value of 2.5 ppm. According to the PMR spectrum, the copolymer consisted of approximately 23 mole % methyl 5-vinylsalicylate and 77 mole % methacrylic acid. The UV

spectrum (THF) showed maxima at 316 nm. ($8.10 \text{ l. g.}^{-1} \text{ cm.}^{-1}$) and 239 nm. ($18.0 \text{ l. g.}^{-1} \text{ cm.}^{-1}$). The UV spectrum in DMSO showed a maximum at 316 nm. ($8.12 \text{ l. g.}^{-1} \text{ cm.}^{-1}$). After the polymer was dried for 30 hours at 100° over phosphorous pentoxide in a drying pistol (0.05 mm.), the elemental analysis was obtained. Anal. calcd. for $\{ \text{C}_{10}\text{H}_{10}\text{O}_3 \}_{14\%} \{ \text{C}_4\text{H}_6\text{O}_2 \}_{86\%}$: C, 58.71%; H, 6.68%. Found: C, 58.74%; H, 6.43%.

18. Bulk polymerization of methyl 5-vinylsalicylate.

A test tube, which had been modified by narrowing its diameter near the open end of the tube, was charged with methyl 5-vinylsalicylate (0.56 g., 3.2 mmole) and AIBN (10.0 mg., 0.06 mmole, 2 mole %). The tube was attached to a vacuum pump and the contents of the tube were frozen in a dry ice-acetone bath as the system was evacuated. The solid was allowed to slowly melt under vacuum and the system was returned to atmospheric pressure with nitrogen gas. The freezing and evacuating procedure was repeated. The tube was sealed at reduced pressure (0.05 mm.) and then heated in an oil bath maintained at 65° . After 20 minutes, the clear, colorless liquid had become viscous and after 90 minutes, an immobile glass was obtained. The tube was opened and the hard solid plug was dissolved in chloroform (10 ml.), filtered, and the solution was poured into hexane (150 ml.) which precipitated the polymer. After filtration, the polymer was dried for 16 hours at 95° at reduced pressure

(0.05 mm.) and weighed (0.46 g., 82% yield). Poly(methyl 5-vinylnsalicylate) had a glass transition (by DSC) of 127-130° and the inherent viscosity of a 0.5% DMSO solution was 0.93 dl./g. The infrared spectrum (KBr) showed an absorption at 1685 cm.⁻¹ (C=O stretching). See p. 261. The PMR spectrum (CDCl₃) showed δ : 0.8 to 2.2 (CHCH_2 , 3); 3.6 to 4.3 (CO_2CH_3 , 3); 6.4 to 7.3 (aromatic protons, 3); 10.2 to 10.6 (ArOH , 1). See p. 241. The UV spectrum (THF) showed maxima at 316 nm. (3.46×10^3 l. mole⁻¹ cm.⁻¹, 19.4 l. g.⁻¹ cm.⁻¹), and 236 nm. (6.83×10^3 l. mole⁻¹ cm.⁻¹, 38.3 l. g.⁻¹ cm.⁻¹). Anal. calcd. for $(\text{C}_{10}\text{H}_{10}\text{O}_3)_n$: C, 67.40%; H, 5.66%. Found: 67.52%; H, 5.80%.

The polymerization was repeated with methyl 5-vinylnsalicylate (0.28 g., 1.6 mmole), AIBN (1.2 mg., 0.007 mmole, 0.4 mole %), and a 24 hour polymerization period. The polymer (0.20 g., 70% yield) had an inherent viscosity (0.5% DMSO solution) of 2.46 dl./g. and a glass transition (by DSC) at 131°. VPO indicated that the molecular weight of the polymer was not less than 20,000. The infrared spectrum was identical to that reported above.

19. Copolymerization of methyl 5-vinylnsalicylate with methacrylic acid. Methyl 5-vinylnsalicylate (1.14 g., 6.40 mmole, 31.7 mole %), methacrylic acid (1.19 g., 13.8 mmole), and AIBN (14.7 mg., 0.09 mmole, 0.5 mole %) were placed in a glass tube and the contents of the tube

were purged with nitrogen. The tube was sealed as described above and then immersed in an oil bath maintained at 60°. After 24 hours, the tube was opened and the solid, sticky polymer was dissolved in DMSO (20 ml.). After filtration, the solution was poured into distilled, deionized water (200 ml.) and a precipitate of finely divided, swollen particles was obtained. The copolymer was filtered and dried for 16 hours over phosphorous pentoxide in a vacuum desiccator (0.05 mm.). The copolymer (1.4 g., 60% yield) was dissolved in 100% ethanol (15 ml.), filtered, and added to ether (350 ml.) which caused the precipitation of a rubbery mass. The product was filtered and dried at reduced pressure (0.05 mm.) at room temperature; the copolymer was brittle and friable. The material (1.3 g., 57% yield) was ground in a mortar and pestle and further dried for 16 hours in a drying pistol over phosphorous pentoxide at 78°. The copolymer was soluble in DMSO and ethanol but insoluble in water, ether, and acetone. DSC did not show a glass transition and the inherent viscosity of a 0.5% DMSO solution was 1.78 dl./g. (The PMR spectrum (d-DMSO, R-32) at 135° showed a quartet at 3.30 to 3.52 ppm., presumably due to ethanol. Therefore, the glassy copolymer was dissolved in DMSO and precipitated with water. The fluffy material was dried at 100° over phosphorous pentoxide and reduced pressure (0.05 mm.) for 24 hours.) The PMR spectrum (d-DMSO, R-32) at 135° showed δ : 0.4 to 2.4

(CHCH_2 , $\text{CH}_2\text{C}(\text{CH}_3)$, 51); 2.4 to 2.7 (DMSO); 3.7 to 4.1 (CO_2CH_3 , 11); 6.6 to 7.5 (aromatic protons, 13); 9.8 to 10.3 (ArOH). See p. 243. Since no internal standard was used, the DMSO signal was assigned a value of 2.5 ppm. According to the PMR spectrum, the copolymer consisted of approximately 34 mole % methyl 5-vinylsalicylate and 66 mole % methacrylic acid, as judged by the relative integrated signal intensity of the methyl ester protons and aromatic protons of methyl 5-vinylsalicylate repeat units and main chain protons. The infrared spectrum (KBr) showed broad carbonyl absorptions. See p. 262. The UV spectrum (DMSO) showed an absorption at 316 nm. ($10.8 \text{ l. g.}^{-1} \text{ cm.}^{-1}$). Anal. calcd. for $\left(\text{C}_{10}\text{H}_{10}\text{O}_3 \right)_{35\%} \left(\text{C}_4\text{H}_6\text{O}_2 \right)_{65\%}$: C, 61.91%; H, 6.30%. Found: C, 61.89%; H, 6.11%.

A second copolymer was made by the same procedure from methyl 5-vinylsalicylate (0.56 g., 3.1 mmole, 16.0 mole %), methacrylic acid (1.39 g., 16.2 mmole), and AIBN (16 mg., 0.10 mmole, 0.5 mole %). The yield of copolymer was 1.0 g. (52%). The copolymer was soluble in DMSO and ethanol but insoluble in water, ether, and acetone. DSC did not show a glass transition and the inherent viscosity of a 0.5% DMSO solution was 1.80 dl./g. (As before, the PMR spectrum showed the presence of ethanol in the copolymer. The brittle copolymer was dissolved in DMSO, precipitated with

water, and the light material was dried at 100° over phosphorous pentoxide and reduced pressure (0.05 mm.) for 24 hours.) The PMR spectrum (d-DMSO, R-32) at 135° showed δ : 0.3 to 2.3 (CHCH_2 , $\text{CH}_2\text{C}(\text{CH}_3)$, 68); 2.3 to 2.7 (DMSO); 3.7 to 4.1 (CO_2CH_3 , 9); 6.6 to 7.5 (aromatic protons, 9); 10.0 to 10.3 (ArOH). See p. 243. Since no internal standard was used, the DMSO signal was assigned a value of 2.5 ppm. According to the PMR spectrum, the copolymer consisted of approximately 20 mole % methyl 5-vinylsalicylate and 80 mole % methacrylic acid. The infrared spectrum (KBr) showed broad carbonyl absorptions. See p. 263. The UV spectrum (DMSO) showed an absorption at 316 nm. ($7.28 \text{ l. g.}^{-1} \text{ cm.}^{-1}$). Anal. calcd. for $\text{C}_{10}\text{H}_{10}\text{O}_3 \rightarrow_{20\%} \text{C}_4\text{H}_6\text{O}_2 \rightarrow_{80\%}$: C, 59.75%; H, 6.56%. Found: C, 56.76%, 55.62%; H, 6.44%, 6.20%.

20. Copolymerization of methyl 5-vinylsalicylate with acrylic acid. Methyl 5-vinylsalicylate (1.03 g., 5.76 mmole, 28.6 mole %) and acrylic acid (1.03 g., 14.4 mmole, freshly distilled) were copolymerized with initiation by AIBN (16.4 mg., 0.10 mmole, 0.5 mole %) by the same procedure described above. The copolymer was precipitated from a DMSO solution with water, from a DMSO solution with ether, and finally from a DMSO solution with water. The product was filtered and dried in a drying pistol at 78° over phosphorous pentoxide at reduced pressure (0.05 mm.) for

24 hours. The yield of fine, light copolymer was 0.9 g. (44%). The copolymer was soluble in DMSO and insoluble in ethanol, water, and ether. DSC did not show a glass transition and the inherent viscosity of a 0.5% DMSO solution was 1.91 dl./g. The PMR spectrum (d-DMSO, R-32) at 135° showed δ : 0.9 to 2.8 (CHCH_2 , DMSO); 3.7 to 4.1 (CO_2CH_3); 6.4 to 7.6 (aromatic protons). See p. 242. The phenol proton could not be detected at 135°, however a broad signal was observed between 10.0 and 10.4 ppm. at 90°. The DMSO signal was used as an internal standard and assigned a value of 2.5 ppm. The copolymer composition could not be estimated from the PMR spectrum due to a poor separation of the signals of the protons of the polymer backbone and the protons of the DMSO. The infrared spectrum (KBr) showed broad carbonyl absorptions. See p. 260. The UV spectrum (DMSO) showed an absorption at 314 nm. ($12.8 \text{ l. g.}^{-1} \text{ cm.}^{-1}$). Anal. calcd. for $\left(\text{C}_{10}\text{H}_{10}\text{O}_3 \right)_{34\%} \left(\text{C}_3\text{H}_4\text{O}_2 \right)_{66\%}$: C, 59.75%; H, 5.63%. Found: C, 59.92%, 59.68%; H, 5.55%, 6.00%.

B. Synthesis of Crude 2,4-Dihydroxy-4'-vinylbenzophenone and Crude 2,4-Diacetoxy-4'-vinylbenzophenone

1. Synthesis of p-ethylacetophenone.²⁰⁴ A 2-1.

three-necked round-bottomed flask, which contained freshly

distilled carbon tetrachloride (640 ml.), was equipped with a mechanical stirrer, a pressure-equalizing dropping funnel, and a reflux condenser topped with a calcium chloride drying tube. Aluminum trichloride (156 ± 2 g., 1.17 mole) was quickly added. Acetyl chloride (92 g., 1.17 mole) was then added via the dropping funnel over a period of 15 minutes to the vigorously stirred mixture while cooling the contents of the flask by an ice-water bath. Ethylbenzene (84.5 g., 0.8 mole) was added dropwise over a period of $1\frac{1}{2}$ hours while the contents of the flask were cooled by the ice-water bath. The brown mixture was stirred an additional $2\frac{1}{2}$ hours at room temperature and then added to a mixture of ice (600 g.) and 12N hydrochloric acid (150 ml.) in a 5-l. beaker. The carbon tetrachloride solution was washed once with 3N hydrochloric acid (400 ml.), twice with water (400 ml.), once with a 5% aqueous sodium carbonate solution (400 ml.), water (400 ml.), dried with magnesium sulfate, and filtered. After removal of the carbon tetrachloride and excess ethylbenzene by distillation in a rotary evaporator at reduced pressure, the product was distilled (b.p. 105° , 7.2 mm.; lit. b.p.²⁰⁴ $116-117^{\circ}$, 13 mm.) to yield 106 g. (90%) of p-ethylacetophenone. The reaction was repeated on a larger scale and also yielded 90% (135 g.). The PMR spectrum (CCl_4) showed δ : 1.10 to 1.36 (CH_2CH_3 , 3); 2.45 and 2.45 to 2.85 (CH_3CO and CH_2CH_3 , 5); 7.1 to 7.8

(aromatic protons, 4) which was in agreement with the published PMR spectrum.²⁰⁵ See p. 244.

2. Synthesis of p-ethylbenzoic acid.²⁰⁶ A 3500-ml. three-necked round-bottomed flask was charged with sodium hydroxide (108 g., 2.7 mole), water (950 ml.), and dioxane (675 ml.) and fitted with a thermometer, a mechanical stirrer, and a pressure-equalizing dropping funnel. The solution was cooled to 5° by an ice-water bath and bromine (179 g., 1.12 mole) was added. p-Ethylacetophenone (50 g., 0.34 mole) was then added via the dropping funnel to the yellow solution over a period of 20 minutes while maintaining the temperature below 13° by ice-bath cooling. The solution, which had become colorless and cloudy shortly after the p-ethylacetophenone addition was completed, was stirred for 40 minutes at 5-10° and then 100 minutes without ice-bath cooling. Bromoform, which separated from the upper aqueous phase, was removed in a separatory funnel. The aqueous phase was washed first with chloroform (20 ml.) and then with hexane (200 ml.). The aqueous solution was acidified with 4N hydrochloric acid which caused an oil to separate. The oil solidified on cooling with ice. The white solid was filtered with suction, washed with water, and dried at reduced pressure (0.4 mm.) in a vacuum oven at 80° for 16 hours. The yield of crude product was 41.2 g. (81%). A second run gave an 82% yield. After

recrystallization from 40% aqueous ethanol (400 ml.), the yield of p-ethylbenzoic acid was 38.5 g., (76%, m.p. 110-112°, lit. m.p.²⁰⁶ 111-112°). The infrared spectrum (KBr) showed an absorption at 1680 cm.⁻¹ (C=O stretching). See p. 263. The PMR spectrum (CDCl₃) showed δ : 1.15 to 1.40 (CH₂CH₃, 3); 2.50 to 2.90 (CH₂CH₃, 2); 7.20 to 8.08 (aromatic protons, 4); 12.1 (CO₂H, 1). See p. 244.

3. Synthesis of 2,4-Dihydroxy-4'-ethylbenzophenone.

A 1-l. three-necked round-bottomed flask was charged with resorcinol (134 g., 1.22 mole), p-ethylbenzoic acid (92.2 g., 0.61 mole), and tetrachloroethane (90 ml.). Resorcinol and p-ethylbenzoic acid had been ground and intimately mixed with a mortar and pestle. The flask was fitted with a mechanical stirrer, a gas inlet tube protruding beneath the surface of the colorless mixture, and a reflux condenser topped with a calcium chloride drying tube. The gas inlet tube was connected to a boron trifluoride gas cylinder. The reaction mixture was rapidly stirred and heated to 80° by an oil bath as boron trifluoride gas was rapidly bubbled into the mixture. After 15 minutes, the mixture had become a deep red solution. The rate of boron trifluoride gas addition was gradually decreased over a period of 2 hours and the dark solution was heated for an additional 2 hours under a flow of nitrogen. The contents of the flask were then added to water

and the mixture was neutralized with sodium bicarbonate. The organic layer was dissolved in ether and washed with a 5% aqueous sodium bicarbonate solution, water, dried with magnesium sulfate, and filtered. A large volume of ether (500 ml.) had to be used to obtain good phase separation. (In a separate experiment, the product had been worked up in chloroform. In this case, the phase separation was slow and incomplete.) Ether and tetrachloroethane were removed by distillation at reduced pressure in a rotary evaporator. Distillation of the red oil (b.p. 195-200°, 0.1 mm.) through a Microglass Claisen head fitted with a 10-cm. Vigreux column gave 129 g. (88%) of a yellow sticky, viscous material. The product was crystallized from 750 ml. of 50% aqueous acetic acid to yield 74 g. (50% yield) of bright yellow crystals of 2,4-dihydroxy-4'-ethylbenzophenone. Additional product (13 g., 9%) was recovered from the mother liquor by adding it to an equal volume of cold water. A second run was carried out on a smaller scale and gave 39 g. (72%) of product. The 2,4-dihydroxy-4'-ethylbenzophenone melted at 111-113°. The infrared spectrum (KBr) showed absorptions at 2800 to 3500 cm^{-1} (OH stretching) and 1620 cm^{-1} (C=O stretching). See p. 263. The PMR spectrum (CDCl_3) showed δ : 1.12 to 1.37 (CH_2CH_3 , 3); 2.48 to 2.88 (CH_2CH_3 , 2); 6.2 to 6.4 and 7.15 to 7.58 (aromatic protons and ArOH , 8); 12.68

(ArOH, 1). See p. 245. The UV spectrum (methanol) showed maxima at 326, 289, and 246 nm. with molar extinction coefficients of 11.4×10^3 , 14.6×10^3 , and 9.40×10^3 l. mole⁻¹ cm.⁻¹ respectively. Anal. calcd. for C₁₅H₁₄O₃ : C, 74.36%; H, 5.82%. Found: C, 74.49%; H, 5.77%.

4. The reaction of N-bromosuccinimide with 2,4-dihydroxy-4'-ethylbenzophenone. A 50-ml. round-bottomed flask was charged with a solution of 2,4-dihydroxy-4'-ethylbenzophenone (2.4 g., 10 mmole) and carbon tetrachloride (13 ml.). N-Bromosuccinimide (1.8 g., 10 mmole) and AIBN (0.02 g.) were then added and the flask was fitted with a reflux condenser topped with a three-way stopcock. The reaction assembly was blanketed with nitrogen and the exit tube was connected to a gas bubbler which contained mineral oil. The mixture was heated to a gentle reflux by an oil bath at 80° for 10 minutes at which time the N-bromosuccinimide had reacted. The PMR spectrum of the carbon tetrachloride solution showed that the expected bromination of the methylene carbon of the ethyl group had not occurred, but rather ring bromination had taken place. See p. 245.

5. Synthesis of 2,4-di(trimethylsilyloxy)-4'-ethylbenzophenone. A 100-ml. round-bottomed flask which contained a magnetic stirring bar, 2,4-dihydroxy-4'-ethylbenzophenone (7.1 g., 29 mmole) and dry pyridine (50 ml.) was fitted with

a pressure-equalizing dropping funnel topped with a calcium chloride drying tube. Chlorotrimethylsilane (8.6 g., 79 mmole, 35% excess) was added via the dropping funnel over a period of 5 minutes while the flask was cooled by an ice-water bath. The contents of the flask were stirred for 10 minutes in the ice-bath, 110 minutes at room temperature, and 3 hours at 50°. The mixture was cooled to 10° and filtered from the pyridine hydrochloride. The yellow solution was concentrated in a rotary evaporator at reduced pressure to yield 10.5 g. (93%) of an orange oil. A light yellow oil (9 g., 80%) was obtained after distillation (b.p. 141-153°, 0.02 mm.) through a Microglass Claisen head fitted with a 10-cm. Vigreux column. The PMR spectrum showed that the integrated signal intensities of the trimethylsilyloxy protons at 0.00 (61) and 0.26 ppm. (74) were not equal. In addition, a small signal due to the ortho phenol proton was present at 12.5 ppm. (1). Redistillation did not improve the purity of the product as judged by the PMR spectrum. The impure product (7.8 g.) was again treated with chlorotrimethylsilane (5 ml.) and pyridine by the above procedure. Distillation (132-136°, 0.01 mm.) yielded 6.5 g. (58%) of a slightly yellow oil. The infrared spectrum (neat) showed absorptions at 2975 cm^{-1} (CH stretching) and 1650 cm^{-1} (C=O stretching). See p. 265. The PMR spectrum (CDCl_3) showed δ : 0.00 and 0.26 ($\text{OSi}(\text{CH}_3)_3$, 18); 1.07 to 1.35

(CH_2CH_3 , 3); 2.50 to 2.85 (CH_2CH_3 , 2); 6.30 to 7.80 (aromatic protons, 7). See p. 246. Addition of a few drops of tetramethylsilane increased the intensity of the signal assigned to 0.00 ppm. Anal. calcd. for $\text{C}_{21}\text{H}_{30}\text{Si}_2\text{O}_3$: C, 65.23%; H, 7.82%. Found: C, 65.50%; H, 7.64%.

A small amount of the product which had been exposed to the atmosphere for 2 months had solidified to a yellow solid and melted at 110.5-113° which corresponds to the melting point of 2,4-dihydroxy-4'-ethylbenzophenone mentioned earlier (111-113°).

6. The attempted reaction of N-bromosuccinimide with 2,4-di(trimethylsilyloxy)-4'-ethylbenzophenone. A 10-ml. round-bottomed flask was charged with a solution of 2,4-di(trimethylsilyloxy)-4'-ethylbenzophenone (1.93 g., 5 mmole) in carbon tetrachloride (7 ml.), N-bromosuccinimide (0.9 g., 5.0 mmole), and AIBN (12 mg.) and fitted with a reflux condenser topped with a three-way stopcock. The reaction assembly was blanketed with nitrogen and the exit tube was connected to a gas bubbler filled with mineral oil. The reaction mixture was heated to a gentle reflux by an oil bath at 80°. After 1½ hours, a reaction had not occurred on the ethyl group as judged by the unreacted NBS and the PMR spectrum of the solution. See p. 246.

7. Bromination of toluene with N-bromosuccinimide.

Another NBS reaction was carried out on toluene (0.5 g.,

5 mmole) by the above procedure with carbon tetrachloride (6 ml.), NBS (0.9 g., 5 mmole), and AIBN (10 mg.). The chemicals were obtained from the same sources as above. Bromination occurred in less than 2 hours according to PMR analysis.

8. Attempted synthesis of 2,4-dimethoxymethoxy-4'-ethylbenzophenone. Synthesis of 2-hydroxy-4-methoxy-methoxy-4'-ethylbenzophenone. A 200-ml. round-bottomed flask was charged with a solution of 2,4-dihydroxy-4'-ethylbenzophenone (10.0 g., 41.1 mmole) in dry methanol (30 ml.) and 14.7 ml. of a freshly prepared solution of sodium methoxide in methanol (3.04N, 44.6 mmole). The mixture was concentrated at reduced pressure in a rotary evaporator which resulted in a yellow solid. The round-bottomed flask was then charged with dry benzene (30 ml.) and a magnetic stirring bar and the flask was fitted with a three-way connecting tube. The connecting tube was fitted with a three-way stopcock in the side arm and a 50-ml. buret topped with a calcium chloride drying tube in the center tube. The system was blanketed with nitrogen. Chloromethyl methyl ether (3.59 g., 3.39 ml., 44.6 mmole) was then added to the mixture from the buret. After 7 hours, the benzene was removed by distillation at reduced pressure in a rotary evaporator and the above procedure was repeated with methanol (30 ml.), sodium methoxide solution

(7.30 ml., 22.2 mmole), benzene (50 ml.), and chloromethyl methyl ether (1.68 ml., 1.78 g., 22.1 mmole). After 7 hours, the benzene was removed by distillation at reduced pressure in a rotary evaporator and methanol (50 ml.) and 3.04N sodium methoxide in methanol (7 ml.) were added. The solution was filtered from the sodium chloride and the methanol was removed by distillation at reduced pressure (0.5 mm.) in a rotary evaporator. The product was dissolved in ether (100 ml.), washed once with water (100 ml.), twice with 10% aqueous sodium hydroxide solution (50 ml.), water (100 ml.), dried with magnesium sulfate, filtered, and the product was short path distilled (b.p. 170-190°, 0.005 mm.) to yield 4 g. of a yellow liquid. The PMR spectrum (CDCl₃) showed that the product was not the expected 2,4-dimethoxymethoxy-4'-ethylbenzophenone, but rather 2-hydroxy-4-methoxymethoxy-4'-ethylbenzophenone. See p. 246, 247. The infrared spectrum is shown on page 264.

9. The reaction of N-bromosuccinimide with 2-hydroxy-4-methoxymethoxy-4'-ethylbenzophenone. A 15-ml. round-bottomed flask was charged with 2-hydroxy-4'-methoxymethoxy-4'-ethylbenzophenone (2.0 g., 7.0 mmole), N-bromosuccinimide (1.25 g., 7.0 mmole), AIBN (10 mg.), carbon tetrachloride (7 ml.), and fitted with a reflux condenser topped with a three-way stopcock. The same procedure described in the previous NBS reactions was used. After 30 minutes of mild

reflux, the PMR spectrum of the carbon tetrachloride solution showed that the reaction had not taken place on the ethyl group since its triplet and quartet were still present, but rather ring bromination had occurred. See p. 246.

10. Synthesis of 2,4-diacetoxy-4'-ethylbenzophenone.

To a 125-ml. Erlenmeyer flask, which contained a solution of 2,4-dihydroxy-4'-ethylbenzophenone (10.5 g., 0.44 mole) in acetic anhydride (50 ml., 0.52 mole), was added concentrated sulfuric acid (5 drops). The flask was stoppered and left at room temperature for 18 hours. The solution was then added to cold water (400 ml.) which caused an oil to separate from solution. The aqueous phase was made basic with sodium carbonate and the product was extracted with chloroform (50 ml.). The aqueous phase was washed twice with chloroform (50 ml.) and the combined organic phases were washed twice with water (100 ml.) and dried with magnesium sulfate. The mixture was filtered and the chloroform was removed by distillation at reduced pressure in a rotary evaporator. The light yellow oil (13.2 g., 94% yield) was distilled (b.p. 175-185°, 0.006 mm. pump pressure) and gave 10.8 g. (77% yield) of 2,4-diacetoxy-4'-ethylbenzophenone. Crude yields of 95% (17.4 g.) and 82% (82 g.) were obtained in two other experiments which were run on a larger scale. The infrared spectrum (neat)

showed absorptions at 1660 and 1770 cm^{-1} ($\text{C}=\text{O}$ stretching). See p. 264. The infrared spectra of the crude products were identical to that of the distilled product. The PMR spectrum (CDCl_3) showed δ : 1.09 to 1.35 (CH_2CH_3 , 3); 1.92 and 2.28 (CH_3CO_2 , 6); 2.52 to 2.90 (CH_2CH_3 , 2); 7.05 to 7.80 (aromatic protons, 7). See p. 245. Anal. calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_5$: C, 69.93%; H, 5.56%. Found: C, 69.70%; H, 5.34%.

11. Synthesis of 2,4-diacetoxy-4'-(1-bromoethyl)-benzophenone. Crude 2,4-diacetoxy-4'-ethylbenzophenone (82 g., 0.20 mole) was dissolved in carbon tetrachloride (285 ml.) in a 1-l. round-bottomed flask fitted with a reflux condenser. N-Bromosuccinimide (47.6 g., 0.27 mole) and AIBN (0.20 g.) were added and the mixture was heated under a nitrogen atmosphere by an oil bath at 85° . After 13 minutes, the reaction became very vigorous and was complete in 10 more minutes. After a total heating period of 50 minutes, the mixture was cooled, filtered, and the carbon tetrachloride was removed by distillation at reduced pressure in a rotary evaporator. The yellow product was twice recrystallized from 500 ml. and 700 ml. respectively of 95% ethanol. The mother liquor of the first recrystallization was yellow. A 75% yield (77 g., m.p. $91-92^\circ$) of white needles was obtained. The infrared spectrum (KBr) of the product showed absorptions at 1745 and 1650 cm^{-1} .

(C=O stretching). See p. 264. The PMR spectrum (CDCl_3) showed δ : 1.05, 2.25 and 1.92 to 2.05 (CH_3CO_2 and CHBrCH_3 , 9); 5.00 to 5.37 (CHBrCH_3 , 0.8); 7.00 to 7.15 and 7.37 to 7.82 (aromatic protons 2 and 5). See p. 245. Anal. calcd. for $\text{C}_{19}\text{H}_{17}\text{O}_5\text{Br}$: C, 56.31%; H, 4.23%. Found: C, 56.25%; H, 4.24%.

Part of the product decomposed to a dark oil when exposed to the atmosphere over a period of several weeks.

12. The reaction of 2,4-diacetoxy-4'-(1-bromoethyl)-benzophenone with potassium hydroxide. Potassium hydroxide (0.7 g., 12 mmole), 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone (0.3 g., 0.7 mmole), ethanol (3 ml.), water (3 ml.), and a drop of nitrobenzene (polymerization inhibitor), which were contained in a 25-ml. beaker, formed a red solution on heating to 75° on a steam bath. After 10 minutes, the supernatant liquid was decanted from a small amount of sludge and the dark solution was acidified with 1N hydrochloric acid which caused an oil to separate. The dark oil was dissolved in chloroform, filtered from a small amount of black material, washed with water, 5% aqueous sodium bicarbonate solution, dried with magnesium sulfate, and filtered. The chloroform was removed by distillation in a rotary evaporator at reduced pressure. The PMR spectrum (CDCl_3) of the residue (0.05 g.) is shown on page 248.

13. The reaction of 2,4-diacetoxy-4'-(1-bromoethyl)-benzophenone with sodium t-butoxide. Sodium hydride (0.22 g., 9.2 mmole) was allowed to react with a solution of t-butanol (5 ml.) and HMPA (4 ml.) which was contained in a 15-ml. round-bottomed flask topped with a calcium chloride drying tube. An orange precipitate formed immediately after 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone (1.2 g., 3.0 mmole) was added to the solution. The mixture was heated by an oil bath at 70° and then added to acetic anhydride (20 ml.) to reacetylate any phenol groups which may have formed. The material did not completely dissolve. After 10 minutes, the mixture was added to water (100 ml.) which caused a brown oil to separate. The oil was dissolved in carbon tetrachloride (20 ml.) and benzene (20 ml.), washed with 5% aqueous potassium bicarbonate, dried with magnesium sulfate, filtered, and the solvents were evaporated at reduced pressure in a rotary evaporator. The PMR spectrum (CDCl_3) of the oil which was obtained is shown on page 248.

14. The reaction of 2,4-diacetoxy-4'-(1-bromoethyl)-benzophenone with lithium chloride. Lithium chloride (0.25 g., 6.0 mmole), which was contained in a 25-ml. round-bottomed flask fitted with a reflux condenser and calcium chloride drying tube, was allowed to react with 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone (0.8 g., 2.0 mmole)

in DMAc (10 ml.) at 100° under nitrogen in the presence of a small amount of nitrobenzene and benzoquinone as polymerization inhibitors. After 36 hours, the dark solution was added to water and the oil which precipitated was dissolved in ether, washed four times with water, dried with magnesium sulfate, and filtered. The ether was evaporated at reduced pressure in a rotary evaporator and the PMR spectrum (CDCl₃) of the product was obtained. See p. 248.

15. The reaction of 2,4-diacetoxy-4'-(1-bromoethyl)-benzophenone with tetraethylammonium chloride. A 25-ml. round-bottomed flask fitted with a reflux condenser was charged with DMF (5 ml.), tetraethylammonium chloride (0.5 g., 3.0 mmole), 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone (0.4 g., 1 mmole) and a small amount of nitrobenzene and benzoquinone as polymerization inhibitors. The solution was heated by an oil bath at 100° under a nitrogen atmosphere for 36 hours. The solution was then added to an ice-water mixture which caused an oil to separate. The supernatant liquid was decanted and the oil was washed twice with water, dissolved in carbon tetrachloride, and dried with magnesium sulfate. The PMR spectrum (CCl₄) of the product is shown on page 248.

16. The reaction of 2,4-diacetoxy-4'-(1-bromoethyl)-benzophenone with pyridine. Three PMR tubes were each charged with one-third of a solution of pyridine (0.60 ml.,

7.4 mmole), 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone (0.30 g., 0.74 mmole), benzoquinone (0.02 g.), and nitrobenzene (one drop). The tubes were heated to 35°, 67°, and 100° respectively and the PMR spectra were measured in order to follow the progress of the reaction. See p. 249.

17. The reaction of 2,4-diacetoxy-4'-(1-bromoethyl)-benzophenone with triethylamine. A 5-ml. round-bottomed flask was charged with 2,4-diacetoxy-4'-(1-bromoethyl)-benzophenone (0.10 g., 0.25 mmole), DMAc (0.5 ml.), triethylamine (0.50 ml., 3.6 mmole), and a small amount of picric acid (polymerization inhibitor). The solution was heated for 90 minutes at 90° under nitrogen and the PMR spectrum of the dark solution was obtained. See p. 249.

In a second experiment, a solution of 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone (5.0 g., 12.3 mmole), triethylamine (17 ml., 120 mmole), and nitromethane (17 ml., b.p. 101°) were heated at reflux for 2 hours. The PMR spectrum of the dark solution was obtained. See p. 249.

18. The reaction of 2,4-diacetoxy-4'-(1-bromoethyl)-benzophenone with tributylamine. Four PMR tubes were each charged with one-quarter of a solution of tributylamine (0.15 ml., 0.12 g., 0.63 mmole), 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone (0.05 g., 0.12 mmole), DMAc (0.15 ml.), and a small amount of picric acid and heated by an oil bath at 140°. At various time intervals, the tubes were removed

from the oil bath, thoroughly cleaned with hexane and acetone, and the PMR spectra were measured to determine the progress of the reaction. See p. 250.

19. Synthesis of crude 2,4-dihydroxy-4'-vinylbenzophenone. A 250-ml. round-bottomed flask was charged with 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone (10.0 g., 25 mmole), tributylamine (40 ml., 170 mmole), nitrobenzene (40 ml.), and heated under nitrogen for 1 hour by an oil bath at 140°. The orange color of the solution did not deepen during the course of the reaction. Most of the liquid (64 ml.) was distilled from the solution at 50° (hot water bath) and reduced pressure (0.1 mm.). The yellow colored crude product was stirred for 1 hour with 3N hydrochloric acid (20 ml.) to remove the excess tributylamine. The product was dissolved in chloroform (20 ml.), washed with 3N hydrochloric acid (20 ml.), water (20 ml.), 5% aqueous sodium bicarbonate solution (20 ml.), water (20 ml.), dried with magnesium sulfate, and filtered. The bright yellow solution was concentrated in a rotary evaporator at 35° and reduced pressure for 2 hours to yield 17.9 g. of crude product.

A mixture of methanol (80 ml.), water (20 ml.), sodium bicarbonate (6.5 g., 77 mmole), and the crude product were heated to a gentle reflux on a steam bath. After 20 minutes, an additional 30 ml. of water were added in an attempt to

dissolve all of the sodium bicarbonate; however, the addition caused a small amount of material to oil out of solution. After an additional 40 minutes of gentle reflux, most of the methanol was removed by distillation in a rotary evaporator at reduced pressure. The product was dissolved in dichloromethane (20 ml.) and washed with water (60 ml.). The yellow aqueous phase was washed with dichloromethane (15 ml.) and the combined organic phases were washed with water, dried with magnesium sulfate, and filtered. The dichloromethane was evaporated in a rotary evaporator at room temperature and reduced pressure to yield 13 g. of crude product, which by PMR spectroscopy consisted of 2,4-dihydroxy-4'-vinylbenzophenone, nitrobenzene, and possibly oligomers or polymers.

In order to separate the product from the nitrobenzene, it was dissolved in ether (30 ml.) and the ether solution was washed with three 25-ml. portions of a 10% aqueous sodium carbonate solution. The combined yellow aqueous phases were washed twice with toluene (100 ml. and 50 ml.), petroleum ether (50 ml.), and acidified with 1N hydrochloric acid. The orange oil which separated was dissolved in dichloromethane (50 ml.), washed with water, dried with magnesium sulfate, filtered, and the solvent was evaporated in a rotary evaporator at reduced pressure and room temperature. The oil (1.4 g., 24% yield) did not have an odor of

nitrobenzene.

In an attempt to separate the 2,4-dihydroxy-4'-vinylbenzophenone from what may have been polymeric impurities, the crude product was treated with 10 ml. of ether. (The ether (50 ml.) had been stirred with alumina (50 g.) for 20 minutes to remove peroxides.) A part of the crude product did not dissolve. The mixture was treated with a small amount of decolorizing charcoal, filtered, and the ether was evaporated at reduced pressure. The product was dried for 16 hours at reduced pressure (0.05 mm.) to yield a yellow sticky solid (0.6 g., 10%) which softened at 50° to a viscous mass. The PMR spectrum (CDCl₃) of the crude 2,4-dihydroxy-4'-vinylbenzophenone is shown on page 250.

20. Synthesis of crude 2,4-diacetoxy-4'-vinylbenzophenone. 2,4-Diacetoxy-4'-(1-bromoethyl)benzophenone (1.0 g., 2.5 mmole), tributylamine (3 ml., 13 mmole), DMAc (5 ml.), and picric acid (0.05 g.) were heated at 150° for 80 minutes in a 25-ml. round-bottomed flask. The cooled solution was added to water and the supernatant liquid was decanted from a brown oil which had precipitated. The oil was stirred with water, the water was decanted, and the oil was dried at reduced pressure and room temperature over phosphorous pentoxide for 16 hours. The crude product (0.73 g., 91% yield) was dissolved in acetic anhydride in a 15-ml. Erlenmeyer flask. The solution was treated with

concentrated sulfuric acid (2 drops); the flask was tightly stoppered and then left at room temperature for 16 hours. The contents of the flask were added to an aqueous sodium bicarbonate solution and the product, which precipitated as an oil, was extracted with ether (25 ml.) in a separatory funnel. The yellow ether solution was filtered from some insoluble material and then washed with water. The organic phase was washed with cold 5% aqueous sodium hydroxide solution, filtered, washed twice with water, once with a saturated aqueous sodium chloride solution, dried with magnesium sulfate, filtered, and concentrated at reduced pressure in a rotary evaporator. The yellow oil was further dried at reduced pressure (0.05 mm.) for 16 hours. The yield of crude product was 0.30 g. (37%). The PMR spectrum is shown on page 250.

C. Synthesis of Poly(epichlorohydrin) Derivatives

1. Synthesis of tetraethylammonium N,N-dimethyl-p-aminobenzoate. A 250-ml. round-bottomed flask was charged with aqueous tetraethylammonium hydroxide (0.75N, 67.6 g., 67.7 ml., 51 mmole) and white N,N-dimethyl-p-aminobenzoic acid (9.6 g., 58 mmole). The mixture was stirred until it was weakly basic to pH paper (pH 8). The excess acid was filtered from the solution and most of the water was removed by distillation at 50° and reduced pressure in a rotary

evaporator. The slightly yellow oil was placed in a vacuum desiccator (0.05 mm.) over phosphorous pentoxide for 24 hours during which time it solidified. The tetraethylammonium N,N-dimethyl-p-aminobenzoate, which contained an unknown amount of water, was dissolved in dichloromethane at room temperature. The addition of ethyl acetate caused the solution to turn cloudy and crystals formed as the cloudy solution was cooled in a dry ice-acetone bath. The solvents were decanted and the product was recrystallized from a mixture of dry ethanol and ethyl acetate. The crystals were dried at reduced pressure (0.05 mm.) and 50° for 2 hours (m.p. 64-67°, sealed capillary) and then at 70° for 18 hours. The hygroscopic white powder (7.1 g., 47% yield) then melted at 117-120°. The elemental analysis and potentiometric titration with perchloric acid in acetic acid showed that the tetraethylammonium N,N-dimethyl-p-aminobenzoate was anhydrous. Anal. calcd. for $C_{17}H_{30}N_2O_2$: C, 69.34%; H, 10.27%; N, 9.52%; 294 g./equiv. Found: C, 68.93%; H, 10.36%; N, 9.58%; 292 g./equiv.

2. Synthesis of tetraethylammonium N,N-dimethyl-p-aminobenzoate hemihydrate. Tetraethylammonium hydroxide (81 ml., 0.75N, 61 mmole) was added to a 250-ml. Erlenmeyer flask which contained an excess of N,N-dimethyl-p-aminobenzoic acid (11.0 g., 0.66 mmole). The mixture was stirred for 30 minutes and the excess acid was filtered from the

solution. The slightly yellow solution was then concentrated to an oil in a rotary evaporator at 50° and reduced pressure. The oil partially solidified on cooling. It completely converted to a white solid on further drying in a vacuum desiccator over phosphorous pentoxide at reduced pressure (0.05 mm.) for 1 week. The PMR spectrum (d-DMSO) showed δ : 1.00 to 1.30 ($\text{N}(\text{CH}_2\text{CH}_3)_4$, 12); 2.85 ($\text{N}(\text{CH}_3)_2$, 6); 3.05 to 3.43 ($\text{N}(\text{CH}_2\text{CH}_3)_4$, 8); 4.10 ($\frac{1}{2}\text{H}_2\text{O}$, 1); 6.50 to 7.70 (aromatic protons, 4). See p. 251. Addition of a small amount of water to the deuterated DMSO solution caused the intensity of the signal at 4.1 ppm. to increase. The signal assignments were made with reference to the N-methyl protons assigned to 2.85 ppm. since TMS was not present in the DMSO. The PMR spectrum (CDCl_3) showed δ : 0.90 to 1.27 ($\text{N}(\text{CH}_2\text{CH}_3)_4$, 12); 2.90 and 2.90 to 3.25 ($\text{N}(\text{CH}_3)_2$ and $\text{N}(\text{CH}_2\text{CH}_3)_4$, 14); 6.50 to 6.65 (aromatic protons, 2); 7.75 to 7.90 (aromatic protons and $\frac{1}{2}\text{H}_2\text{O}$, 3). See p. 251. The salt melted from $73-94^{\circ}$. Anal. calcd. for $\text{C}_{17}\text{H}_{30}\text{N}_2\text{O}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$: C, 67.28%; H, 9.97%; N, 9.23%. Found: C, 66.74%; H, 9.99%; N, 9.03%.

3. Synthesis of tetramethylammonium salicylate monohydrate. Salicylic acid (7.5 g., 55 mmole) was added to tetramethylammonium hydroxide in methanol (2.74N, 25 g., 27.8 ml., 76.2 mmole) in a 100-ml. round-bottomed flask. After half of the methanol had been removed by distillation

in a rotary evaporator at reduced pressure, benzene and ethyl acetate were added to the solution. Further distillation of the solvents at reduced pressure resulted in the precipitation of a solid. The crude product was crystallized three times with a mixture of isopropanol, ethyl acetate, and petroleum ether (b.p. 61-70°) and dried at 90° and reduced pressure (0.05 mm.) for 16 hours. The yield of product was 5.9 g. (47%, m.p. 141-143.5°, sealed capillary). The PMR spectrum (d-DMSO) showed δ : 3.15 ($(\text{CH}_3)_4$ and H_2O , 14); 6.5 to 7.8 (aromatic protons, 4); 16.75 (OH , 1). See p. 251. The elemental analysis and potentiometric titration with perchloric acid in acetic acid showed that the salt was a monohydrate. Anal. calcd. for $\text{C}_{11}\text{H}_{17}\text{NO}_3 \cdot \text{H}_2\text{O}$: N, 6.11%; 229.5 g./equiv. Found: N, 6.34%; 230 g./equiv.

4. Titration with perchloric acid in acetic acid.

Perchloric acid in acetic acid (0.1011N) was prepared exactly according to the published procedure.²⁰⁷ The reagent was stored in an automatic buret which was sealed from the atmosphere with clamped rubber hoses when not in use. Titration of 0.6930 g. and 0.6869 g. of potassium acid phthalate in acetic acid with 33.50 ml. and 33.35 ml. of solution indicated that the reagent was 0.1012N and 0.1009N respectively. The end points for the titrations were detected potentiometrically using a glass and calomel

electrode. All of the hygroscopic salts which were titrated were weighed in dry weighing bottles in a glove bag that had been flushed with nitrogen and exposed to a large dish of calcium chloride.

5. Synthesis of 2-ethoxyethyl chloride.²⁰⁸ A 500-ml. three-necked round-bottomed flask which contained 2-ethoxyethyl alcohol (45 g., 0.50 mole, b.p. 135°), pyridine (48.5 ml., 0.60 mole) and chloroform (50 ml.) was equipped with a mechanical stirrer, reflux condenser topped with a calcium chloride drying tube, and a pressure-equalizing dropping funnel which contained thionyl chloride (59.5 g., 0.60 mole). The flask was cooled with an ice-water bath as the thionyl chloride was added dropwise. After the addition was completed, the mixture was stirred for 2 hours without ice bath cooling and then heated to reflux for 1 hour. The contents of the flask were cooled, washed with dilute hydrochloric acid, water, 10% aqueous sodium carbonate solution, water, dried over potassium carbonate, filtered, and the product was distilled (b.p. 105-108°, lit. b.p.²⁰⁹ 108-109°) to yield 24 g. (44%) of 2-ethoxyethyl chloride.

6. GC analysis of the reaction of tetraethylammonium N,N-dimethyl-p-aminobenzoate with 2-ethoxyethyl chloride. A 10-ml. round-bottomed flask, which was fitted with a reflux condenser and calcium chloride drying tube, was charged with dry DMSO (4.1 ml.), 2-ethoxyethyl chloride

(0.40 g., 3.7 mmole), and tetraethylammonium N,N-dimethyl-p-aminobenzoate (1.10 g., 3.7 mmole). (All transferring operations of the chemicals were done in a dry glove bag.) The progress of the reaction, which was allowed to proceed at room temperature, was monitored by gas chromatography. The GC conditions were: column temperature, 105⁰; detector temperature, 245⁰; injector temperature, 215⁰; helium flow rate, 25 ml./min.; current, 125 milliamps; attenuator, 4 and 16; sample size, 0.20 ul.; chart speed, 5 in./min.; column, 3% SE 30 on Varport 100/120 5 ft. x $\frac{1}{8}$ in. The retention times were 62 seconds for DMSO and 35 seconds for 2-ethoxyethyl chloride. The decrease in the ratio of 2-ethoxyethyl chloride peak area to DMSO peak height was used as a measure of the progress of the reaction. The results are presented in Table 10 and Figure 8. The reaction was carried out a second time with heating by an oil bath maintained at 44⁰. The results of this experiment are presented in Table 11 and Figure 8.

7. PMR analysis of the reaction of tetraethylammonium N,N-dimethyl-p-aminobenzoate dihydrate with butyl chloride.

A solution of butyl chloride (0.043 g., 0.46 mmole) in deuterated DMSO (0.46 ml.) was added to a test tube which contained tetraethylammonium N,N-dimethyl-p-aminobenzoate dihydrate (0.15 g., 0.46 mmole). The test tube was tightly stoppered and shaken until the contents formed a homogeneous

solution (3 minutes). (Other than using tightly stoppered test tubes and carrying out the manipulations quickly, no special precautions were taken to prevent moisture absorption by the reactants.) Two PMR tubes were each charged with one-half of the solution. One was left at room temperature and the other was heated in an oil bath at 54°. The PMR spectra of the solutions were measured (see p. 252) and the ratio of the integrated signal intensity of the triplet, which appeared around 4 ppm. (due to the methylene protons adjacent to the carboxylate group of butyl N,N-dimethyl-p-aminobenzoate), to the integrated signal intensity of the aromatic protons between 6.5 and 7.8 ppm. was used to follow the progress of the reaction. The reaction conversion was 50 and 65% after 4 and 21 hours respectively at room temperature. The conversion of the reaction at 54° was 75 and 100% after 4 and 21 hours respectively. The results are presented in Figure 8.

8. GC analysis of the reaction of tetramethylammonium salicylate monohydrate with 2-ethoxyethyl chloride. Tetramethylammonium salicylate monohydrate (0.53 g., 2.3 mmole) was allowed to react with 2-ethoxyethyl chloride (0.27 g., 2.5 mmole) in DMSO (2.7 ml.) at 44°. The progress of the reaction was followed by measuring the decrease in the ratio of the 2-ethoxyethyl chloride peak area to the DMSO peak height as described above. The GC conditions were the same

as described above. The results are presented in Table 12 and Figure 9.

9. PMR analysis of the reaction of tetramethylammonium salicylate monohydrate with butyl chloride. A solution of butyl chloride (0.077 g., 0.83 mmole) in deuterated DMSO (0.83 ml.) was added to a test tube which contained tetramethylammonium salicylate monohydrate (0.19 g., 0.83 mmole). The progress of the reaction at room temperature and at 54° was followed by the same procedure described above for the reaction of butyl chloride with tetraethylammonium N,N-dimethyl-p-aminobenzoate dihydrate. The PMR spectrum (see p. 252) showed a progressive decrease in the integrated signal intensity of the triplet (3.45 to 3.65 ppm.) of the methylene protons in the one position of butyl chloride and an increase in the integrated signal intensity of the triplet (4.15 to 4.35 ppm.) of butyl salicylate. The reaction conversion was 0 and 5% after 4 and 21 hours respectively at room temperature, and the reaction conversion was 25 and 35% after 4 and 21 hours respectively at 54°. The results are presented in Figure 9.

10. Reaction of tetraethylammonium N,N-dimethyl-p-aminobenzoate dihydrate with poly(epichlorohydrin). Poly(epichlorohydrin) (0.50 g., 5.2 mmole) was dissolved with warming in dry DMSO (4.5 ml.) in a 15-ml. round-bottomed flask which was fitted with a reflux condenser. The

reaction system was blanketed with a flow of nitrogen. Tetraethylammonium N,N-dimethyl-p-aminobenzoate dihydrate (0.167 g., 5.1 mmole) was quickly added to the cloudy solution and the reaction was allowed to proceed at 52° (oil bath heating). During the course of the reaction, a colorless gel separated from the solution. After 24 hours, the solution was decanted from the gel. The gel was repeatedly kneaded with water, dissolved in chloroform, and the solution was vigorously stirred with water to remove the remaining DMSO and ammonium salts. Hexane was added to the chloroform solution which caused a rubbery material to precipitate. The product was dried in a drying pistol over phosphorous pentoxide at 78° and reduced pressure (0.05 mm.) for 24 hours. A hard white copolymer (0.98 g.) was obtained which was not completely soluble in chloroform.

A small amount of copolymer (0.050 g.) was added to DMF (10 ml.) in a 10-ml. volumetric flask and shaken for 5 days while being heated by an oil bath maintained at 70°. The solution was filtered and the concentration was twice determined to be 0.4% by evaporating 1 ml. of solution and weighing. The copolymer (0.050 g.) was also added to 1,2-dichloroethane (10 ml.), left at room temperature for 2 weeks, filtered, diluted with 10 ml. of 1,2-dichloroethane, and the concentration of the solution was twice determined to be 0.165%. The inherent viscosities of the 0.4% DMF

solution and 0.165% 1,2-dichloroethane solution were 0.75 dl./g. and 1.4 dl./g. respectively. The copolymer had a glass transition (by DSC) at 60°. The infrared spectrum of a film prepared by evaporating a chloroform gel on a sodium chloride plate showed an absorption at 1695 cm.⁻¹ (C=O stretching). See p. 267. The PMR spectrum (o-dichlorobenzene, R-32) at 120° showed δ : 2.72 (N(CH₃)₂, 54); 3.4 to 4.1 (CHCH₂O and CH₂Cl, 43); 4.2 to 4.7 (CH₂O₂C-, 19). The relative integrated signal intensities indicated that the degree of substitution was 75%. See p. 253. One ml. of the 1,2-dichloroethane solution (1.65 mg./ml.) was diluted to 250 ml. in a 250-ml. volumetric flask. The UV spectrum of the solution (6.61 x 10⁻³ g./l.) showed maxima at 310 nm. (103 l. g.⁻¹ cm.⁻¹) and 229 nm. (27.0 l. g.⁻¹ cm.⁻¹). Anal. calcd. for $\left(\text{C}_{12}\text{H}_{15}\text{NO}_3 \right)_{75\%} \left(\text{C}_3\text{H}_5\text{ClO} \right)_{25\%}$: C, 61.93%; H, 6.66%; N, 5.56%; Cl, 4.69%. Found: C, 60.35%; H, 6.54%; N, 5.55, 6.04%; Cl, 4.53, 4.65, 4.53%.

11. Reaction of tetraethylammonium N,N-dimethyl-p-aminobenzoate hemihydrate with poly(epichlorohydrin). Poly-(epichlorohydrin) (1.9 g., 21 mmole) was dissolved in DMF (20 ml.) with stirring in a 100-ml. three-necked round-bottomed flask for 16 hours under nitrogen. Tetraethylammonium N,N-dimethyl-p-aminobenzoate hemihydrate (7.6 g., 26 mmole, 25% excess) was quickly added to the cloudy

solution and the reaction was allowed to proceed at 54° (oil bath heating). After 30 hours, the clear, viscous solution was cooled and added to water (200 ml.) which caused a slightly off-white elastomeric material to precipitate. The product was completely dissolved in chloroform (30 ml.) and the solution was stirred for 45 minutes with water (20 ml.). The water was decanted and the copolymer was precipitated by pouring the chloroform solution into ethanol (250 ml.). The copolymer was kneaded with fresh ethanol, dissolved in chloroform (30 ml.), precipitated with ethanol (250 ml.), dissolved in chloroform, filtered through a fine fritted glass filter funnel and again precipitated with ethanol. The product was dried for 2 hours at 50° in a vacuum oven at reduced pressure (0.4 mm.) and further dried in a drying pistol over phosphorous pentoxide at 61° and reduced pressure (0.05 mm.) for 24 hours. The yield of slightly off-white polymer was 3.9 g. Fifty mg. of the copolymer was added to DMF (10 ml.) in a 10-ml. volumetric flask and shaken for 5 days in an oil bath at 70°. The solution was filtered from a trace amount of insoluble material. The copolymer concentration was 0.48%. The inherent viscosities of the 0.48% DMF solution and 0.23% 1,2-dichloroethane solution were 0.60 dl./g. and 0.37 dl./g. respectively. VPO indicated that the molecular weight of the polymer was not less than 20,000. The

copolymer had a glass transition (by DSC) of 63° . The infrared spectrum of a film prepared by evaporating a chloroform solution on a sodium chloride plate showed an absorption at 1695 cm^{-1} ($\text{C}=\text{O}$ stretching). See p. 267. The PMR spectrum at 120° (o-dichlorobenzene, R-32) showed δ : 2.70 ($\text{N}(\text{CH}_3)_2$, 63); 3.4 to 4.1 (CHCH_2O and CH_2Cl , 37); 4.2 to 4.7 ($\text{CH}_2\text{O}_2\text{C}-$, 21) and the integration indicated that the degree of substitution was 90%. See p. 253. The UV spectrum of a dichloroethane solution ($9.18 \times 10^{-3}\text{ g./l.}$) showed maxima at 309 nm. ($104\text{ l. g}^{-1}\text{ cm}^{-1}$) and 229 nm. ($29.8\text{ l. g}^{-1}\text{ cm}^{-1}$). Anal. calcd. for $\{ \text{C}_{12}\text{H}_{15}\text{NO}_3 \}_{90\%}$ $\{ \text{C}_3\text{H}_5\text{ClO} \}_{10\%}$: C, 63.98%; H, 6.77%; N, 6.05%; Cl, 1.70%. Found: C, 61.54%; H, 6.18%; N, 6.43%; Cl, 2.35%. A sample of the copolymer was further dried at 100° and reduced pressure (0.05 mm.) over phosphorous pentoxide for 36 hours. Found: C, 63.56%; H, 6.71%; N, 5.83%; Cl, 1.49%.

12. Reaction of sodium iodide with poly(epichlorohydrin). A 100-ml. round-bottomed flask, which was fitted with a reflux condenser, was charged with poly(epichlorohydrin) (3.6 g., 39 mmole), methyl ethyl ketone (40 ml.), and a magnetic stirring bar. A flow of nitrogen was introduced into the flask and vented via an exit tube which was attached to a gas bubbler. The contents of the flask were stirred and heated to a gentle reflux. After the contents

of the flask had formed a cloudy solution, sodium iodide (6.0 g., 40 mmole) was added via the reflux condenser which caused the colorless, cloudy solution to immediately turn yellow. The mixture was gently refluxed for 48 hours and allowed to stand at room temperature for an additional 48 hours. During the course of the reflux, the viscosity of the solution appeared to decrease. The orange solution was cooled, filtered from insoluble sodium salts, and concentrated in a rotary evaporator at reduced pressure. The slimy orange mass was shaken with a mixture of petroleum ether (100 ml., b.p. 61-70°) and 10% aqueous sodium carbonate solution (100 ml.) to remove soluble impurities. In order to remove the remaining methyl ethyl ketone, the copolymer was repeatedly kneaded with petroleum ether (b.p. 61-71°) and then dried at reduced pressure (0.4 mm.) and 65°. Repeated kneading of the polymer with acetone resulted in a colorless opaque material. The copolymer was dissolved in chloroform and filtered to give a clear, colorless solution (20 ml.) from which the copolymer was precipitated with petroleum ether (250 ml., b.p. 61-71°). The product was dried overnight in a vacuum desiccator (0.05 mm.) over phosphorous pentoxide at room temperature. The copolymer (5.2 g.) was a clear, colorless, tacky elastomer and was soluble in chloroform, methylene chloride, benzene, and o-dichlorobenzene. It was insoluble in alcohols, acetone,

and carbon tetrachloride. The copolymer sank to the bottom of a test tube which contained carbon tetrachloride ($d^{20} = 1.59$) while poly(epichlorohydrin) ($d^{20} = 1.36$) floated at the surface. The product slowly settled to the bottom of a test tube containing 1,2-dibromoethane ($d^{20} = 2.18$). DSC showed a glass transition at 10° . The inherent viscosity of a 0.5% chloroform solution was 0.12 dl./g. VPO indicated that the molecular weight of the polymer was not less than 20,000. The infrared spectrum of a film prepared by evaporating a chloroform solution on a KBr plate showed an absorption at 500 cm.^{-1} (C-I stretching) which was not present in the infrared spectrum of poly(epichlorohydrin). See p. 265, 266. The PMR spectrum (o-dichlorobenzene, R-32) at 110° showed δ : 3.35 (CH_2I); 3.70 (CH_2O); 3.55 (CH_2Cl). See p. 254. The elemental analysis indicated an 83% degree of substitution. Anal. calcd. for $\{ \text{C}_3\text{H}_5\text{ClO} \}$ $\overline{17\% \{ \text{C}_3\text{H}_5\text{IO} \}}_{83\%}$: C, 21.39%; H, 2.99%; total halogen, 5.93 milliequiv./g. Found: C, 21.65%; H, 2.74%; total halogen, 5.97 milliequiv./g.

D. Synthesis of Poly(methacrylic acid) Derivatives

1. Synthesis of poly(tetramethylammonium methacrylate).

A 50-ml. round-bottomed flask was charged with tetramethylammonium hydroxide (6.6 g., 20 mmole), poly(methacrylic acid) (1.3 g., 15 mmole) and methanol (10 ml.). The polymer slowly dissolved over a period of 2 hours. The addition of

DMAc (10 ml.) to the solution caused a precipitate to form which gradually redissolved with stirring. As the methanol was evaporated with warming in a rotary evaporator at reduced pressure, the polymer solution became richer in DMAc which caused the poly(tetramethylammonium methacrylate) to precipitate. The yellow mass, which was obtained after most of the DMAc was evaporated, was also insoluble in DMSO.

2. Synthesis of poly(tetrabutylammonium methacrylate).

A 50-ml. round-bottomed flask was charged with tetrabutylammonium hydroxide (25 ml., 7.8 mmole) and poly(methacrylic acid) (0.645 g., 7.5 mmole). The polymer was allowed to dissolve over a period of 16 hours and formed a slightly yellow solution. Most of the methanol was removed from the polymer by distillation in a rotary evaporator at reduced pressure. In order to remove the remaining methanol and some of the water, the yellow viscous mass was dissolved in DMSO (10 ml.) which was then removed from the polymer by distillation at 55° and reduced pressure over a period of 30 minutes. The poly(tetrabutylammonium methacrylate), which probably contained some water, was a yellow solid.

3. Reaction of poly(tetrabutylammonium methacrylate) with butyl bromide.

A solution of butyl bromide (1.2 g., 8.8 mmole) in DMSO (3 ml.) was added to a yellow solution of poly(tetrabutylammonium methacrylate) (7.5 mmole) in DMSO (6 ml.) which was contained in a 50-ml. round-bottomed flask. The flask was stoppered and within 5 minutes of the

addition, a considerable amount of gel separated from solution. The mixture was magnetically stirred for 16 hours at room temperature and then added to 0.1N hydrochloric acid (100 ml.) which caused the gel to harden to a white mass. Attempts to dissolve the product in hot acetic acid and 2-ethoxyethanol were unsuccessful. (These treatments probably extracted the unreacted butyl bromide from the swollen material. In each case, a large excess of water was added to the mixtures before decanting the liquids from the precipitate. The addition of water to acetic acid resulted in a small amount of precipitate.) The product was dissolved in acetone (20 ml.) with heating and was precipitated with water (250 ml.). The white material was dried at reduced pressure (0.05 mm.) in a drying pistol over phosphorous pentoxide at room temperature for 90 minutes and then at 78° for 16 hours. The yield of white product was 0.82 g. (76% based on a 100% degree of esterification). The infrared spectrum (KBr) (see p. 268) was identical to the published spectrum of poly(butyl methacrylate).²¹⁰ Anal. calcd. for $\{C_8H_{14}O_2\}_n$: C, 67.57%; H, 9.92%; N, 0%; Br, 0%. Found: C, 67.75%; H, 10.04%; N, 0.63%; Br, 0.05%.

4. Synthesis of 2-hydroxy-4-(2-bromoethoxy)benzophenone.²¹¹ A 250-ml. round-bottomed flask, which was fitted with a reflux condenser, was charged with 2,4-dihydroxybenzophenone (21.4 g., 0.10 mole), water (80 ml.),

ethanol (80 ml.), dibromoethane (26.4 g., 0.14 mole), and sodium hydroxide (4 g., 0.10 mole) and was heated to reflux for 18 hours. The two phase mixture formed a red solution after 20 minutes. Within 18 hours, a second liquid phase formed which solidified on cooling to room temperature. The orange solid was crystallized from 95% ethanol (100 ml.) to yield 13.3 g. (42%) of off-white needles. The 2-hydroxy-4-(2-bromoethoxy)benzophenone was recrystallized from 95% ethanol (60 ml.) to yield 10 g. (31%) of off-white needles which melted at 97-98° (lit. m.p.²¹¹ 87-88° and 97-98°). The infrared spectrum (KBr) showed an absorption at 1620 cm.⁻¹ (C=O stretching). See p. 269. The PMR spectrum (CDCl₃) showed δ : 3.45 to 3.65 (CH_2Br , 2); 4.17 to 4.37 (OCH_2 , 2); 6.25 to 6.43 and 7.35 to 7.75 (aromatic protons, 2 and 6); 12.63 (ArOH , 1). See p. 244. The UV spectrum (THF) showed maxima at 326, 286, and 242 nm. with molar extinction coefficients of 9.69×10^3 , 15.8×10^3 and 10.9×10^3 l. mole⁻¹ cm.⁻¹.

5. Reaction of poly(tetrabutylammonium methacrylate) with 2-hydroxy-4-(2-bromoethoxy)benzophenone. Poly(methacrylic acid) (0.67 g., 7.8 mmole) was allowed to react with tetrabutylammonium hydroxide (26 ml., 8.1 mmole, 10% in methanol) in a 50-ml. round-bottomed flask. The poly(tetrabutylammonium methacrylate) was isolated according to the previously described procedure. The polymer was dissolved in DMSO (0.6 ml.) which resulted in a gold colored

solution. A yellow solution of 2-hydroxy-4-(2-bromoethoxy)-benzophenone (0.70 g., 2.18 mmole, 28 mole %) in DMSO (4 ml.) was added to the polymer solution. The solution was stirred at room temperature for 24 hours and then added to 100 ml. of a 0.15N hydrochloric acid solution which caused a finely divided white polymer to precipitate. The product was filtered on a fritted glass funnel with suction, rinsed with water, and then dried at reduced pressure (0.05 mm.) in a vacuum desiccator over phosphorous pentoxide for 16 hours. The copolymer was then left in benzene for 2 weeks to extract any benzene soluble impurities. The product was filtered and dried in a drying pistol over phosphorous pentoxide at reduced pressure (0.05 mm.) at 78°. The yield of fluffy off-white powder was 1.02 g. (calculated 1.14 g.). The elemental analysis indicated that the product was contaminated with a bromine containing impurity. (Anal. found: C, 60.1%; H, 6.25%; Br, 2.59%.) The copolymer was dissolved in DMSO (10 ml.) and precipitated with ether (100 ml.). The copolymer was redissolved in DMSO (10 ml.) and the orange solution was treated with 1.5 ml. of 1N hydrochloric acid which caused the color to change to yellow. After 10 minutes of stirring, the product was precipitated with water (100 ml.). The copolymer was again dried and then treated with refluxing ether for 24 hours, filtered, and dried as usual in the drying pistol. The copolymer had an inherent viscosity

(0.5% DMSO solution) of 0.5 dl./g. and did not show a glass transition by DSC. The infrared spectrum (KBr) showed a broad peak at 1700 cm^{-1} ($\text{C}=\text{O}$ stretching) and a broad peak at 1615 cm^{-1} (see p. 269) which was not present in the poly(methacrylic acid) infrared spectrum but was present in the 2-hydroxy-4-(2-bromoethoxy)benzophenone infrared spectrum. The PMR spectrum (d-DMSO, R-32) at 135° showed δ : 0.7 to 2.4 ($\text{CH}_2\text{C}(\text{CH}_3)$, 51); 2.4 to 2.6 (DMSO); 4.1 to 4.5 ($\text{OCH}_2\text{CH}_2\text{O}_2\text{C}$, 12); 6.4 to 6.8 and 7.2 to 7.9 (aromatic protons, 5 and 16). See p. 243. A signal was not present between 10 and 20 ppm.; however, at 90° a signal was observed at 11.7 to 12.1 ppm. The DMSO signal (2.5 ppm.) was used as an internal standard. Integration of the PMR spectrum indicated that the degree of substitution was approximately 27 mole %. The UV spectrum (THF) showed maxima at 327, 287, and 243 nm. with extinction coefficients of 16.5, 26.1, and $18.3\text{ l. g}^{-1}\text{ cm}^{-1}$ respectively. Anal. calcd. for $\left(\text{C}_4\text{H}_6\text{O}_2\right)_{73\%}\left(\text{C}_{19}\text{H}_{18}\text{O}_5\right)_{27\%}$: C, 64.05%; H, 6.17%; Br, 0%; N, 0%. Found: C, 60.83%; H, 5.31%; Br, 0.0%; N, 0.18%.

E. Synthesis of Oligo(oxyethylene) Di-N,N-dimethyl-p-aminobenzoates

1. Synthesis of N,N-dimethyl-p-aminobenzoyl chloride.²¹² N,N-dimethyl-p-aminobenzoic acid (20.1 g., 0.12 mole) was added to a 125-ml. Erlenmeyer flask which

contained a solution of potassium hydroxide (7.3 g., 0.13 mole) in 40 ml. of water. The solution, which contained a small amount of insoluble material, was stirred for 30 minutes and then filtered into an 800-ml. beaker. The solution was concentrated by boiling off water until a precipitate formed. After the mixture had cooled to room temperature, acetone (600 ml.) was added to complete the precipitation of potassium N,N-dimethyl-p-aminobenzoate. The potassium salt was filtered with suction, added to a 250-ml. three-necked round-bottomed flask, and dried by heating at 60° and reduced pressure (1.5 mm.) for 3 hours to yield 23.1 g. (94%, 0.11 mole) of potassium N,N-dimethyl-p-aminobenzoate. Dry benzene (90 ml.) was added to the three-necked round-bottomed flask which was then fitted with a mechanical stirrer, a reflux condenser topped with a calcium chloride drying tube, and a pressure-equalizing dropping funnel which contained oxalyl chloride (12 ml., 0.14 mole) in dry benzene (25 ml.). The contents of the flask were cooled by an ice-water bath while the oxalyl chloride was added dropwise with stirring. The mixture turned orange after a small amount of the oxalyl chloride had been added. After the addition was completed, the contents of the flask were stirred at room temperature for 16 hours, heated to reflux for 40 minutes, and the hot mixture was then filtered into a 250-ml. Erlenmeyer flask. N,N-Dimethyl-p-aminobenzoyl chloride (14.8 g., 71%)

crystallized as the solution slowly cooled. The mother liquor was concentrated at reduced pressure (25 mm.) to yield an additional 1.4 g. (6.5%) of product. The acid chloride was recrystallized from dry benzene (100 ml.) and gave 11.3 g. (54%) of N,N-dimethyl-p-aminobenzoyl chloride. (m.p. 145-147°, lit. m.p.²¹² 147-148°).

2. Synthesis of ethylene glycol di-N,N-dimethyl-p-aminobenzoate - Procedure I. A 200-ml. round-bottomed flask was charged with ethylene glycol (2.8 g., 0.045 mole), dry pyridine (40 ml.), N,N-dimethyl-p-aminobenzoyl chloride (20 g., 0.11 mole), and a magnetic stirring bar. The flask was fitted with a reflux condenser topped with a calcium chloride drying tube and the mixture was refluxed for 75 minutes. The contents of the flask were allowed to cool to room temperature and were then added to an aqueous 5% sodium carbonate solution (600 ml.) and were stirred for 30 minutes to dissolve the unreacted N,N-dimethyl-p-amino-benzoic acid. The product was filtered with suction, dried in a vacuum oven at 60° and reduced pressure (50 mm.), and recrystallized from toluene (400 ml.). The off-white solid (14 g., 87%) was recrystallized from 2-ethoxyethanol (300 ml.) with decolorizing charcoal to yield 7.5 g. (47%, m.p. 202-208°) of yellow crystals of ethylene glycol di-N,N-dimethyl-p-aminobenzoate.

3. Synthesis of ethylene glycol di-N,N-dimethyl-p-aminobenzoate - Procedure II. A 200-ml. round-bottomed

flask was charged with ethylene di-p-toluenesulfonate (14.4 g., 0.039 mole), potassium N,N-dimethyl-p-aminobenzoate (28.6 g., 0.14 mole), and DMAc (50 ml.). The salt did not appear to be very soluble in the solvent. The flask was fitted with a reflux condenser topped with a three-way stopcock for the introduction and venting of a stream of nitrogen. The mixture was heated for 4 hours by an oil bath at 90°. The contents of the flask were cooled and added to water to precipitate the product (8.0 g., 58%). Ethylene di-N,N-dimethyl-p-aminobenzoate was recrystallized from toluene to yield 6.9 g. (49%, m.p. 202-210°).

4. Synthesis of ethylene glycol di-N,N-dimethyl-p-aminobenzoate - Procedure III. A 100-ml. round-bottomed flask was charged with dibromoethane (5.2 g., 0.027 mole), DMAc (35 ml.), potassium N,N-dimethyl-p-aminobenzoate (11.5 g., 0.057 mole), and a magnetic stirring bar. The flask was fitted with a reflux condenser topped with a calcium chloride drying tube and the contents of the flask were heated for 6 hours by an oil bath at 94°. The salt did not appear to be very soluble in the DMAc. The contents of the flask were cooled and added to cold water (800 ml.) to precipitate the ethylene glycol di-N,N-dimethyl-p-aminobenzoate. The product was crystallized from benzene (300 ml.) to yield 5.0 g. (52%, m.p. 195-200°).

Three more crystallizations from benzene (200 ml.), a mixture of methyl benzoate (60 ml.) and ethanol (30 ml.), and benzene (110 ml.) respectively resulted in a low yield (2.1 g., 22%) of pure ethylene glycol di-N,N-dimethyl-p-aminobenzoate (m.p. 212-213°). The infrared spectrum (KBr) showed absorptions at 1690 cm^{-1} (C=O stretching) and 1610 cm^{-1} (aromatic). See p. 270. (The UV and PMR spectra were not obtained since the compound was not soluble in methanol or deuterated chloroform.) Anal. calcd. for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$: C, 67.39%; H, 6.79%; N, 7.86%. Found: C, 67.33%; H, 7.00%; N, 7.65%.

5. Synthesis of methyl N,N-dimethyl-p-aminobenzoate.

A 1-l. round-bottomed flask equipped with a reflux condenser was charged with methanol (300 ml., 7.3 mole), N,N-dimethyl-p-aminobenzoic acid (100 g., 0.6 mole) and a few boiling chips. Concentrated sulfuric acid (55 ml., 1.0 mole) was then slowly added to the flask with cooling and shaking. The deep red solution was refluxed for 2 hours, cooled, and added slowly with stirring to a 5% aqueous sodium carbonate solution (1.5 l.) which caused methyl N,N-dimethyl-p-aminobenzoate to precipitate. The product was filtered with suction and crystallized three times from 80% aqueous methanol (900 ml.) to yield 71.3 g. (66%) of white methyl N,N-dimethyl-p-aminobenzoate (m.p. 100-102°, lit. m.p.²¹³ 101-102°). The infrared spectrum (KBr) showed absorptions at

1695 cm^{-1} (C=O stretching), and 1610 cm^{-1} (aromatic). See p. 267. The PMR spectrum (CDCl_3) showed δ : 3.00 ($\text{N}(\text{CH}_3)_2$, 6); 3.82 (CO_2CH_3 , 3); 6.53 to 6.68 and 7.84 to 7.99 (aromatic protons, 4). See p. 255. The UV spectrum (methanol) showed maxima at 310 and 228 nm. with extinction coefficients of 27.5×10^3 and $7.46 \times 10^3 \text{ l. mole}^{-1} \text{ cm}^{-1}$ respectively.

6. Synthesis of ethylene glycol di-N,N-dimethyl-p-aminobenzoate by an ester interchange reaction - Procedure IV.

A 200-ml. three-necked round-bottomed flask was charged with methyl N,N-dimethyl-p-aminobenzoate (23.2 g., 0.13 mole), ethylene glycol (2.5 g., 0.045 mole), dry benzene (40 ml.), sodium methoxide (0.2 g.), and a magnetic stirring bar. The flask was fitted with a stopper, gas inlet tube, and a modified soxhlet extractor²¹⁴ which contained 30 g. of dry "Linde" type 3A molecular sieves and dry benzene. The apparatus was fitted with a calcium chloride drying tube and the contents of the flask were heated to reflux with stirring under a flow of nitrogen. The methanol that was formed was absorbed from the benzene by the molecular sieves as the benzene refluxed. As the reaction proceeded, white ethylene glycol di-N,N-dimethyl-p-aminobenzoate precipitated. After $3\frac{1}{2}$ hours of reflux, the contents of the flask were cooled and added with stirring to water (50 ml.) to remove the base catalyst. The product was filtered with

suction, washed with water, acetone, and dried at 50° for 4 hours at reduced pressure (50 mm.) to yield impure ethylene glycol di-N,N-dimethyl-p-aminobenzoate (13.3 g., 83%, m.p. 197-205°). The product was recrystallized once from toluene (400 ml.) and once from methyl benzoate to yield 9.9 g. (62%, m.p. 212-214.5°) of ethylene glycol di-N,N-dimethyl-p-aminobenzoate.

7. Synthesis of diethylene glycol di-N,N-dimethyl-p-aminobenzoate. A 200-ml. three-necked round-bottomed flask was charged with methyl N,N-dimethyl-p-aminobenzoate (21.5 g., 0.12 mole), diethylene glycol (4.8 g., 0.045 mole), dry benzene (40 ml.), and sodium methoxide (0.2 g.). The flask was fitted with a stopper, gas inlet tube, and a modified soxhlet extractor which contained benzene and 30 g. of "Linde" type 5A molecular sieves. The apparatus was fitted with a calcium chloride drying tube and the contents of the flask were heated to reflux with stirring under a flow of nitrogen. Some of the product precipitated as the reaction proceeded. After 3 hours of reflux, the contents of the flask were cooled, diluted with benzene (50 ml.) to completely dissolve the product, and washed with water (50 ml.) to remove the base catalyst. The benzene solution was dried with magnesium sulfate, filtered, and the diethylene glycol di-N,N-dimethyl-p-aminobenzoate was precipitated by the addition of hexane. The product (15.6 g., 87%) was dissolved in dichloromethane and the yellow

solution was decolorized by passing it through a 10-ml. column of alumina in a 50-ml. buret. Recrystallization was carried out from dichloromethane-hexane to yield diethylene glycol di-N,N-dimethyl-p-aminobenzoate (14.1 g., 79%, m.p. 129-130°). The infrared spectrum (KBr) showed absorptions at 1700 cm^{-1} (C=O stretching) and 1605 cm^{-1} (aromatic). See p. 270. The PMR spectrum (CDCl_3) showed δ : 2.95 ($(\text{CH}_3)_2\text{N}$, 12); 3.75 to 3.92 ($\text{O}(\text{CH}_2\text{CH}_2)_2$, 4); 4.35 to 4.50 (CO_2CH_2 , 4); 6.50 to 6.65 and 7.80 to 7.95 (aromatic protons, 8). See p. 255. The ultraviolet spectrum (methanol) showed maxima at 310 and 228 nm. with molar extinction coefficients of 53.8×10^3 and 14.7×10^3 $\text{l. mole}^{-1} \text{ cm}^{-1}$ respectively. Anal. calcd. for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_5$: C, 65.98%; H, 7.05%; N, 7.00%. Found: C, 65.98%; H, 6.76%; N, 6.97%.

8. Synthesis of triethylene glycol di-N,N-dimethyl-p-aminobenzoate. Methyl N,N-dimethyl-p-aminobenzoate (22.2 g., 0.12 mole), triethylene glycol (6.8 g., 0.045 mole) and sodium methoxide (0.2 g.) in benzene (40 ml.) were allowed to react for 3 hours in the presence of molecular sieves as described above. At the end of the reaction, benzene (50 ml.) was added to the cooled solution which was then washed with water (50 ml.) to remove the base catalyst. The solution was dried with magnesium sulfate and hexane was added to precipitate 17.6 g. (88% yield) of impure

triethylene glycol di-N,N-dimethyl-p-aminobenzoate. The product was dissolved in dichloromethane and the yellow solution was decolorized by passing it through a 10-ml. column of alumina in a 50-ml. buret. The product was recrystallized from a dichloromethane-hexane mixture to yield 10.7 g. (51%, m.p. 94.5-96.5°). The infrared spectrum (KBr) showed absorptions at 1690 cm^{-1} (C=O stretching) and 1610 cm^{-1} (aromatic). See p. 270. The PMR spectrum (CDCl_3) showed δ : 3.0 ($\text{N}(\text{CH}_3)_2$, 12); 3.70 to 3.86 ($\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$, 8); 4.33 to 4.50 (CO_2CH_2 , 4); 6.50 to 6.65 and 7.83 to 7.98 (aromatic protons, 8). See p. 255. The UV spectrum (methanol) showed maxima at 310 and 228 nm. with molar extinction coefficients of 56.8×10^3 and $14.8 \times 10^3 \text{ l. mole}^{-1} \text{ cm}^{-1}$ respectively. Anal. calcd. for $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_6$: N, 6.30%. Found: N, 6.58%.

9. Synthesis of tetraethylene glycol di-N,N-dimethyl-p-aminobenzoate. Methyl N,N-dimethyl-p-aminobenzoate (21.5 g., 0.12 mole), tetraethylene glycol (8.8 g., 0.045 mole), and sodium methoxide (0.2 g.) in benzene (40 ml.) were allowed to react for 3 hours in the presence of molecular sieves as described above. After the reaction was complete, benzene (50 ml.) was added to the cooled mixture to form a solution. The solution was then washed with water, dried with magnesium sulfate, and filtered. The product oiled out when the benzene solution was added to hexane (1 l.). The supernatant liquid was decanted,

the oil was dissolved in benzene (75 ml.), and was again precipitated with hexane (900 ml.). The oil was dissolved in dichloromethane (50 ml.) and passed through a 16-ml. column of neutral alumina which resulted in a colorless solution. The product oiled out when the solution was added to hexane and the oil solidified on standing to yield 13.1 g. (60%) of tetraethylene glycol di-N,N-dimethyl-p-aminobenzoate. The product could be crystallized by dissolving 1 g. in 50 ml. of warm ether and cooling the solution to -20° (m.p. $70.5-71^{\circ}$). The infrared spectrum showed absorptions at 1685 cm^{-1} (C=O stretching) and 1605 cm^{-1} (aromatic). See p. 271. The PMR spectrum (CDCl_3) showed δ : 2.98 ($\text{N}(\text{CH}_3)_2$, 12); 3.62 to 3.82 ($\text{O}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O})_2$, 12); 4.30 to 4.48 (CO_2CH_2 , 4); 6.50 to 6.65 and 7.80 to 7.95 (aromatic protons, 8). See p. 255. The UV spectrum (methanol) showed maxima at 310 and 228 nm. with molar extinction coefficients of 56.3×10^3 and $14.2 \times 10^3\text{ l. mole}^{-1}\text{ cm}^{-1}$ respectively. Anal. calcd. for $\text{C}_{26}\text{H}_{36}\text{N}_2\text{O}_7$: N, 5.74%. Found: N, 5.82%.

10. Synthesis of poly(oxyethylene) (\bar{M}_n 300) di-N,N-dimethyl-p-aminobenzoate. A 200-ml. three-necked round-bottomed flask was charged with methyl N,N-dimethyl-p-aminobenzoate (21.5 g., 0.12 mole), poly(oxyethylene) (13.5 g., 0.045 mole), and dry benzene (45 ml.). Thirty g. of dry "Linde" type 5A molecular sieves were added to the modified soxhlet extractor and the solution was refluxed for

30 minutes under nitrogen to remove water that may have been present in the poly(oxyethylene). After the solution had cooled, sodium methoxide (0.2 g.) was added and the mixture was refluxed for 3 hours. After the reaction was complete, the contents of the flask were cooled and added to benzene (50 ml.). The organic layer was washed with water (50 ml.), 5% aqueous sodium bicarbonate solution (50 ml.), water (50 ml.), dried with magnesium sulfate, and filtered. The benzene solution was added to hexane (850 ml.) which caused an oil to precipitate. The precipitation from benzene with hexane was repeated and the slightly yellow oil was decolorized by passing a dichloromethane (50 ml.) solution through a 16-ml. column of neutral alumina in a 50-ml. buret. The solvent was removed at reduced pressure (0.2 mm.) and 50° for 6 hours to yield 16.9 g. of product (63%). The infrared spectrum (neat) showed absorptions at 1705 cm^{-1} (C=O stretching) and 1605 cm^{-1} (aromatic). See p. 271. The PMR spectrum (CDCl_3) showed δ : 2.94 ($\text{N}(\text{CH}_3)$, 12); 3.55 to 3.80 $\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2$, 20 ; 4.30 to 4.45 (CO_2CH_2 , 4); 6.45 to 6.62 and 7.83 to 7.95 (aromatic protons, 8). See p. 256. The number average molecular weight (by VPO, CHCl_3) was 574. The UV spectrum of the product showed maxima at 310 and 228 nm. with molar extinction coefficients of 53.4×10^3 and 14.4×10^3 l. mole $^{-1}$ cm^{-1} respectively. The nitrogen analysis was calculated assuming the

product had an average molecular weight of 574. Anal. calcd. N, 4.88%. Found: N, 4.91%.

11. Synthesis of poly(oxyethylene) (\bar{M}_n 400) di-N,N-dimethyl-p-aminobenzoate. The procedure for the preparation of the diester was the same as the procedure used to prepare poly(oxyethylene) (\bar{M}_n 300) di-N,N-dimethyl-p-aminobenzoate. The yield of product was 23.1 g. (74%) of a clear, colorless oil. The infrared spectrum (neat) showed absorptions at 1695 cm^{-1} (C=O stretching) and 1605 cm^{-1} (aromatic). See p. 271. The PMR spectrum (CDCl_3) showed δ : 2.97 ($\text{N}(\text{CH}_3)_2$, 12); 3.62 to 3.88 $\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_2\text{CH}_2$, 28 ; 4.32 to 4.50 (CO_2CH_2 , 4); 6.53 to 6.60 and 7.80 to 7.94 (aromatic protons, 8). See p. 256. The number average molecular weight (by VPO) was 666. The UV spectrum of the product showed maxima at 310 and 228 nm. with molar extinction coefficients of 55.6×10^3 and $15.2 \times 10^3\text{ l. mole}^{-1}\text{ cm}^{-1}$ respectively. The nitrogen analysis was calculated assuming the product had an average molecular weight of 666. Anal. calcd.: N, 4.20%. Found: 4.48%.

F. Synthesis of Oligo(oxyethylene) Disalicylates from Oligo(oxyethylene) Di-p-toluenesulfonates

1. Synthesis of ethylene glycol di-p-toluenesulfonate.

A tightly stoppered 125-ml. Erlenmeyer flask, which contained ethylene glycol (4.5 g., 0.072 mole) and dry pyridine

(70 ml.), was cooled to 5° in an ice-water bath. p-Toluenesulfonyl chloride (34 g., 0.18 mole) was added, the flask was stoppered, and the mixture was shaken in the ice-water bath. Pyridine hydrochloride began to precipitate minutes after the p-toluenesulfonyl chloride had dissolved. The flask was left in a refrigerator at 5° for 42 hours. The mixture was then added to an ice-water mixture with stirring which caused ethylene glycol di-p-toluenesulfonate to precipitate. The aqueous mixture was acidified with cold 4N hydrochloric acid and the product was filtered, washed with water, and dried in a vacuum desiccator (0.05 mm.). It was recrystallized from dichloromethane, (after decolorization with charcoal) by cooling in a dry ice-acetone bath to yield 16.9 g. (64%) of ethylene glycol di-p-toluenesulfonate (m.p. 124-127°; lit. m.p.²¹⁵ 126-127°).

2. Synthesis of ethylene glycol disalicylate -

Procedure I. A 200-ml. round-bottomed flask was charged with DMAc (50 ml.), sodium salicylate (30.5 g., 0.19 mole), and ethylene glycol di-p-toluenesulfonate (16.9 g., 0.046 mole). The flask was fitted with a reflux condenser topped with a calcium chloride drying tube and the magnetically stirred mixture was heated by an oil bath at 78°. In a few minutes, the reactants dissolved to form a clear, yellow solution and after 30 minutes, sodium p-toluenesulfonate started to precipitate. After 12 hours, the

mixture was cooled and added to water with stirring which caused the ethylene disalicylate to separate as an oil. The product was dissolved in ether (100 ml.); the ethereal solution was washed with water, dried with magnesium sulfate, filtered, and the ether was evaporated at reduced pressure (25 mm.) to yield 13.3 g. (96%) of crude ester. The ethylene glycol disalicylate was recrystallized from methanol to yield 10.6 g. (76%) of needles (m.p. 78.5-79.5°, lit. m.p. 78.5°²¹⁶ and 84°¹⁵³). The infrared spectrum (KBr) showed an absorption at 1665 cm.⁻¹ (C=O stretching). See p. 272. The PMR spectrum (CDCl₃) showed δ : 4.57 (CO₂CH₂, 4); 6.63 to 7.85 (aromatic protons, 8); 10.55 (OH, 2). See p. 257. The UV spectrum (methanol) showed maxima at 306 and 238 nm. with molar extinction coefficients of 8.76×10^3 and 18.3×10^3 l. mole⁻¹ cm.⁻¹ respectively. Anal. calcd. for C₁₆H₁₄O₄: C, 63.57%; H, 4.67%. Found: C, 63.70%; H, 4.74%. Acetone was also used as a solvent for the reaction of ethylene di-p-toluenesulfonate with sodium salicylate; however, the yield of product was lower than in the DMAc reaction.

3. Synthesis of ethylene glycol disalicylate -

Procedure II. A 250-ml. round-bottomed flask was charged with dibromoethane (5.6 g., 0.03 mole), sodium salicylate (14.4 g., 0.09 mole), and DMAc (25 ml.). The flask was fitted with a reflux condenser and a calcium chloride

drying tube and was heated by an oil bath at 90° with magnetic stirring. Within a few minutes, a clear solution formed and after 30 minutes, a precipitate started to form. The mixture was allowed to cool to room temperature after $5\frac{1}{2}$ hours of heating and was then added to water (250 ml.). A yellow oil separated which was dissolved in ether (100 ml.); the ethereal solution was washed with water (100 ml.), dried with magnesium sulfate, filtered, and the solution was concentrated at reduced pressure (25 mm.). A white solid was obtained, which was recrystallized from aqueous methanol, to yield 7.1 g. (79%) of ethylene disalicylate (m.p. $84.5-86^{\circ}$, lit. m.p. 78.5° ²¹⁶ and 84° ¹⁵³). DMSO and methyl ethyl ketone were also used as solvents for the reaction of dibromoethane sodium salicylate; however, the yields were not as high with these solvents as with DMAc.

4. Synthesis of diethylene glycol di-p-toluene-sulfonate. A tightly stoppered 125-ml. Erlenmeyer flask, which contained diethylene glycol (5.1 g., 0.048 mole) and dry pyridine, (35 ml.) was cooled to 5° in an ice-water bath. Purified p-toluenesulfonyl chloride (21 g., 0.11 mole) was added, the flask was stoppered, and the mixture shaken in an ice-water bath to form a solution. Pyridine hydrochloride began to precipitate minutes after the p-toluenesulfonyl chloride dissolved. The flask was shaken for an

additional 15 minutes and then kept at 5° for 11 hours. The contents of the flask were added to an ice-water mixture with stirring which caused the diethylene glycol di-p-toluenesulfonate to precipitate. The aqueous mixture was acidified with 3N hydrochloric acid and the product was extracted with methylene chloride (100 ml.). The methylene chloride solution was washed with 1N hydrochloric acid (75 ml.), cold water (75 ml.), cold aqueous 5% sodium carbonate solution (75 ml.), cold water (75 ml.), dried with potassium bicarbonate and sodium sulfate, and filtered. The ditosylate was recrystallized from a methylene chloride-hexane solution to yield 16.6 g. (83%, m.p. 88-89°, lit. m.p.²¹⁷ 88-89°). The PMR spectrum (CDCl₃) showed δ : 2.41 (CH₃, 6); 3.48 to 3.64 (CH₂OCH₂, 4); 4.00 to 4.18 (SO₃CH₂, 4); 7.25 to 7.39 and 7.68 to 7.81 (aromatic protons, 8). See p. 257.

5. Synthesis of diethylene glycol disalicylate. A 200-ml. round-bottomed flask was charged with DMAc (50 ml.), sodium salicylate (25.6 g., 0.16 mole), and diethylene glycol di-p-toluenesulfonate (16.6 g., 0.04 mole). The flask was fitted with a reflux condenser and calcium chloride drying tube and the mixture was heated with magnetic stirring by an oil bath at 75°. In a few minutes, the reactants dissolved and after 45 minutes, sodium p-toluenesulfonate started to precipitate.

The progress of the reaction was followed by comparing

the PMR integrated signal intensities of the aromatic methyl group of the tosylate (2.48 ppm.) and the aromatic hydroxyl group of the salicylate (10.48 ppm.). One-half ml. of reaction mixture was added to a test tube which contained water (1 ml.) and carbon tetrachloride (1 ml.). The test tube was stoppered and shaken for $\frac{1}{2}$ minute. The aqueous layer was separated and the organic layer was washed twice with aqueous 5% sodium bicarbonate solution (1 ml.), once with water (1 ml.), dried with magnesium sulfate, and filtered. The PMR spectrum of the clear, colorless solution revealed that the conversion of tosylate groups to salicylate groups was 73% after $2\frac{1}{4}$ hours, 86% after $2\frac{3}{4}$ hours, and 93% after $3\frac{1}{4}$ hours. The results are presented in Figure 13.

After $4\frac{1}{2}$ hours, the reaction mixture was cooled and added to water with stirring. A yellow oil separated which was dissolved in dichloromethane (100 ml.); the dichloromethane solution was washed twice with a 5% aqueous sodium bicarbonate solution (75 ml.), once with water (75 ml.), dilute hydrochloric acid (75 ml.), water (75 ml.), dried with magnesium sulfate, and filtered. The clear, colorless solution was added to cold hexane to precipitate the product. Diethylene glycol disalicylate was recrystallized from a solution of ether (40 ml.) and hexane (50 ml.) to yield 9.2 g. (67%, m.p. $67.5-68.5^{\circ}$, lit. m.p.¹⁵³ 68°).

(One g. of the product could also be recrystallized from a mixture of 6 ml. of toluene and 6 ml. of petroleum ether.) The infrared spectrum (KBr) showed an absorption at 1670 cm^{-1} (C=O stretching). See p. 272. The PMR spectrum (CDCl_3) showed δ : 3.85 to 4.00 ($\text{O}(\text{CH}_2\text{CH}_2)_2$, 4); 4.45 to 4.60 (CO_2CH_2 , 4); 6.75 to 7.95 (aromatic protons, 8); 10.6 (OH , 2). See p. 257. The UV spectrum (methanol) showed maxima at 306 and 238 nm. with molar extinction coefficients of 8.56×10^3 and $18.0 \times 10^3\text{ l. mole}^{-1}\text{ cm}^{-1}$. Anal. calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_5$: C, 62.42%; H, 5.24%. Found: C, 62.59%; H, 5.39%.

6. Synthesis of triethylene glycol di-p-toluenesulfonate. The diethylene glycol di-p-toluenesulfonate procedure was followed to prepare triethylene glycol di-p-toluenesulfonate. The product was recrystallized from a dichloromethane (50 ml.) - hexane (110 ml.) solution to yield 25 g. (77%, m.p. $80.5\text{--}81.5^\circ$, lit. m.p.²¹⁸ $81\text{--}82^\circ$) of product.

7. Synthesis of triethylene glycol disalicylate. The same procedure used in converting diethylene glycol di-p-toluenesulfonate to diethylene glycol disalicylate was used to convert triethylene glycol di-p-toluenesulfonate to triethylene glycol disalicylate. After 4 hours of heating at 75° , the reaction mixture was cooled and added to water with stirring which caused the triethylene glycol disalicylate to separate as an oil. The oil was dissolved in

dichloromethane (100 ml.) and the dichloromethane solution was washed twice with an aqueous 5% sodium bicarbonate solution (75 ml.), once with water (75 ml.), dilute hydrochloric acid (75 ml.), water (75 ml.), dried with magnesium sulfate, and filtered. The yellow dichloromethane solution was passed through a 15-ml. column of alumina in a 50-ml. buret and the solvent was evaporated at reduced pressure (0.2 mm.) to yield 9.8 g. (90%) of a slightly yellow oil. The oil was dissolved in ether, and hexane was added until the solution turned cloudy. The solution was clarified by the addition of a small amount of ether and placed in a dry ice-acetone bath to precipitate the product. After 45 minutes, the supernatant liquid was decanted and the precipitation procedure was repeated. The white solid product was dried in a vacuum desiccator at reduced pressure (0.05 mm.). The yield of triethylene glycol disalicylate was 6.0 g. (55%, m.p. 46.5-49°).

8. Acid catalyzed esterification of triethylene glycol with salicylic acid. A 250-ml. round-bottomed flask equipped with a Dean Stark trap and a reflux condenser topped with a calcium chloride drying tube was charged with triethylene glycol (7.5 g., 0.05 mole), salicylic acid (27 g., 0.20 mole), p-toluenesulfonic acid (0.5 g.), and toluene (70 ml.) and the solution was heated to reflux. After 24, 48, 72, and 96 hours; 55%, 75%, 90%, and 100% of the calculated 1.8 ml. of water were collected

in the trap. The dark solution was cooled, filtered, and treated with hexane which caused a small amount of a dark oil to precipitate. The nearly colorless solution was decanted and concentrated in a rotary evaporator at reduced pressure to yield an off-white solid. The product was dissolved in dichloromethane (50 ml.), the solution was washed with a 5% aqueous sodium bicarbonate solution, twice with water, once with 1N hydrochloric acid, water, dried with magnesium sulfate, and filtered. The solution was concentrated in a rotary evaporator at reduced pressure to yield 12.8 g. (65%) of a solid. The product was twice recrystallized from an ether-petroleum ether solution to yield 4.5 g. (23%) of triethylene glycol disalicylate (m.p. 47.5-49°). The infrared spectrum (KBr) showed an absorption at 1675 cm^{-1} (C=O stretching). See p. 272. The PMR spectrum showed δ : 3.65 to 3.85 ($\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$, 8); 4.33 to 4.48 (CO_2CH_2 , 4); 6.63 to 7.88 (aromatic protons, 8); 10.65 (ArOH , 2). See p. 257. The UV spectrum (methanol) showed maxima at 305 and 238 nm. with molar extinction coefficients of 8.80×10^3 and $18.6 \times 10^3 \text{ l. mole}^{-1} \text{ cm}^{-1}$ respectively. Anal. calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_8$: C, 61.53%; H, 5.68%. Found: C, 61.74%; H, 5.59%.

9. Synthesis of tetraethylene glycol di-p-toluenesulfonate. The procedure used to prepare tetraethylene glycol di-p-toluenesulfonate was the same procedure used in the preparation of diethylene glycol di-p-toluenesulfonate;

however, the purification procedure was changed because in this case, the product was an oil. Tetraethylene glycol di-p-toluenesulfonate in dichloromethane was washed as described above. The yellow solution was then dried with magnesium sulfate and passed through a 10-ml. column of neutral alumina in a 50-ml. buret in order to decolorize the solution. The solution was then added to a large excess of hexane and kept at 0° to precipitate a nearly colorless oil. The supernatant liquid was decanted, the oil was dissolved in dichloromethane, the solution was transferred to a 200-ml. round-bottomed flask, and the solvent was evaporated at room temperature and reduced pressure (0.2 mm.). The yield was 78% (21.5 g.) of a slightly yellow oil. The product was reported to be a highly viscous syrup.²¹⁸

10. Synthesis of tetraethylene glycol disalicylate.

The conversion of tetraethylene glycol di-p-toluenesulfonate (10.8 g., 0.022 mole) to tetraethylene glycol disalicylate was carried out at 75° in DMAc (25 ml.) with sodium salicylate (13.7 g., 0.085 mole). The reaction was also carried out at 65°.

The progress of the reactions was followed by PMR spectroscopy as described in the reaction of diethylene glycol di-p-toluenesulfonate with sodium salicylate. The results are presented in Figure 13.

The total yield of impure tetraethylene glycol disalicylate after 6 hours at 75° or 20 hours at 65° was 9.4 g. (81%). The product was dissolved in ether and the solution was passed through a 15-ml. column of alumina. The oil was twice precipitated from a warm ether-hexane solution by cooling the solution to -78°. The supernatant liquid was decanted and the oil was dried at reduced pressure (0.2 mm.) to yield a slightly yellow oil (6.0 g., 64%). Anal. calcd. for $C_{22}H_{26}O_5$: C, 60.82%; H, 6.03%. Found: C, 60.40%; H, 5.89%.

Tetraethylene glycol disalicylate has been reported in the literature as a colorless viscous oil (b.p. 195°, 1 mm.).¹⁵⁵

G. Measurements

Infrared spectra were recorded on a Perkin-Elmer 727 spectrophotometer. Solid samples were generally measured as KBr pellets and liquid samples were measured as a smear between sodium chloride plates. The infrared spectra of some of the polymers were measured as films cast onto a sodium chloride or potassium bromide plate from a chloroform or dichloromethane solution. Peak assignments were made relative to a polystyrene standard. The smallest division of the infrared chart paper was 20 $cm.^{-1}$; therefore, peak assignments were made to the nearest 5 $cm.^{-1}$.

Most of the PMR spectra were measured on a 60 MHz R-24 Hitachi Perkin Elmer spectrometer. Solutions were generally 10% to 15% in deuterated chloroform or carbon tetrachloride. Some polymer spectra were recorded at elevated temperatures in deuterated DMSO on a 90 MHz R-32 Perkin Elmer spectrometer.

Ultraviolet spectra were recorded on a Beckman MVI spectrophotometer in the double beam servo mode. The maximum absorbance and corresponding wavelength were determined by dialing in the wavelength and recording the absorbance value presented on the digital display. The UV solutions were prepared with a minimum of 0.250 mg. \pm 0.002 mg. of sample weighed on a piece of aluminum foil on a Mettler micro balance.

The thermal properties of the polymers were determined on a Perkin Elmer DSC-1B Differential Scanning Calorimeter at a scan rate of 20°/min. The instrument was calibrated against benzoic acid (m.p. 122°) and salicylic acid (m.p. 159°). For low temperature scans, the instrument was calibrated against cyclohexane (m.p. 5°) and nitrotoluene (m.p. 52°). The melting points of low molecular weight compounds were measured on a Mel-Temp capillary melting point apparatus which had been calibrated against nitrotoluene (m.p. 52°), catechol (m.p. 105°), and salicylic acid (m.p. 159°).

Inherent viscosities of the polymers were determined at 25° in DMSO, DMF, or dichloroethane solutions with an Ostwald-Fenske capillary viscometer. Solution and solvent efflux times were generally greater than 100 seconds and the average value of five runs was used in the calculation of the inherent viscosity.

Number average molecular weights were determined at 35° in chloroform solution with a Perkin Elmer Model 115 Molecular Weight Apparatus (Vapor Pressure Osmometer). Benzil (mw = 210.2) was used as the standard.

The removal of solvents at reduced pressure on a rotary evaporator was carried out at approximately 1-2 mm.

Gas chromatographic separations were carried out with a Varian model 1400 gas chromatograph.

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

H. Chemicals

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

1. Reagents.

Acetic Anhydride (E)	Lithium Chloride (F)
Acetyl Chloride (E)	Methacrylic Acid (E)
Acrylic Acid (E)	Molecular Sieves (MCB)
Aluminum Trichloride (F)	Oxalyl Chloride (A)
Azobisisobutyronitrile (E)	Perchloric Acid (F)
Benzoquinone (E)	Picric Acid (E)
Boron Trifluoride (MT)	Poly(epichlorohydrin) (H)
Bromine (F)	Poly(methacrylic Acid (P)
Bromobutane (E)	Poly(oxyethylene) (300) (U,B)
N-Bromosuccinimide (E)	Poly(oxyethylene) (400) (U,B)
t-Butanol (E)	Potassium Hydrogen Phthalate (Acidi- (F) metric Standard)
Chloromethyl Methyl Ether (A)	Potassium Hydrogen Sulfate (M)
Chlorotrimethylsilane (E)	Pyridine (E)
1,2-Dibromoethane (E)	Resorcinol (MCB)
Diethylene Glycol (A)	Salicylic Acid (E)
2,4-Dihydroxybenzophenone (G)	Sodium Borohydride(F)
Ethylbenzene (E)	Sodium Hydride (V)
Ethylene Glycol (B)	Sodium Iodide (F)
2-Ethoxyethanol (E)	
Lithium Aluminum Hydride (V)	

Sodium Methoxide (F)

Sodium Salicylate (A)

Tetrabutylammonium
Hydroxide (E)Tetraethylammonium
Chloride (E)Tetraethylammonium
Hydroxide (E)

Tetraethylene Glycol (E)

Tetramethylammonium
Hydroxide (A)

Thionyl Chloride (E)

Toluene (M)

p-Toluenesulfonic Acid (E)

p-Toluenesulfonyl
Chloride (E)

Tributylamine (E)

Triethylamine (E)

Triethylene Glycol (E)

Triphenylphosphite (E)

2. Solvents.

Acetic Acid (F)

Carbon Tetrachloride (F)

Carbon Tetrachloride
(Spectrograde) (F)

Chloroform (Spectrograde) (F)

Deuterated Chloroform (A)

Deuterated Dimethyl-
sulfoxide (A)

o-Dichlorobenzene (A)

N,N-Dimethylacetamide (A)

N,N-Dimethylformamide (A)

Dimethylsulfoxide (A)

Dioxane (M)

Hexamethyl Phosphoric
Acid Triamide (E)Methanol
(Spectrograde) (B,F)

Methyl Benzoate (E)

Methylene Chloride (F)

Methyl Ethyl Ketone (E)

Nitromethane (E)

Tetrachloroethane (E)

Tetrahydrofuran (A)

3. Sources.

A = Aldrich

B = Baker

E = Eastman

F = Fisher Scientific Co.

G = G.A.F.	MT = Matheson Gas Products
H = Hercules	P = Polysciences
M = Mallinckrodt	U = Union Carbide
MCB = Matheson, Coleman & Bell	V = Ventron

I. Purification of Solvents and Reagents

All of the distillations were done with a 30-cm. Vigreux column. The reduced pressure distillations were carried out with a 30-cm. Vigreux column fitted to a Claisen head. The pressure was stabilized with a manostat and the contents of the flask were magnetically stirred.

t-Butanol was dried over 3A molecular sieves.

Carbon tetrachloride was fractionally distilled. A large forerun (10%) was discarded.²¹⁹

Dimethylsulfoxide²²⁰ was distilled from calcium hydride at reduced pressure (b.p. 60°, 8 mm.) and stored over molecular sieves.

N,N-Dimethylformamide²²¹ was dried with magnesium sulfate, filtered, distilled (b.p. 78-80°, 40 mm.), and stored over molecular sieves.

N,N-Dimethylacetamide²²² (1 l.) was stirred with barium oxide (10 g.) for 2 days, distilled (b.p. 55-58°, 11 mm.), and stored over molecular sieves.

Ethanol²²³ was reacted with sodium followed by diethyl succinate and distilled.

Methanol²²⁴ was dried by distillation from calcium hydride.

Methyl ethyl ketone was distilled from phosphorous pentoxide.

Tetrahydrofuran²²⁵ was distilled from lithium aluminum hydride.

Acrylic acid (obtained with p-methoxyphenol as stabilizer) was distilled (b.p. 60°, 45 mm.). A large amount of monomer polymerized in the distillation flask.

Azobisisobutyronitrile¹⁹⁹ was recrystallized three times from dry methanol (10 g. AIBN in 50 ml. methanol at 35°, then cooled to 0°, yield 7.5 g.) and dried at 0.1 mm. for 16 hours at room temperature.

N-Bromosuccinimide²²⁶ (10 g.) was added to water (100 ml.) at 80°. The solution was quickly filtered and cooled in an ice-water bath. The white crystals were filtered, washed with water, air dried on the filter, and further dried at 60° in a vacuum oven (0.4 mm.) for 16 hours. The white plates were ground with a mortar and pestle before being used.

Ethylbenzene²²⁷ was repeatedly washed with concentrated sulfuric acid until the washings were nearly colorless. It was then further washed with water, 5% aqueous sodium bicarbonate solution, dried with magnesium sulfate, filtered, and distilled from sodium (b.p. 134-136°).

Lithium chloride was dried in an oven at 160° for 3 hours and cooled in a desiccator over phosphorous pentoxide.

Methacrylic acid was distilled at reduced pressure (b.p. 63°, 12 mm.).

Molecular sieves (30 g., 5A) were dried by heating to 180° for 24 hours under a flow of nitrogen in a glass column wrapped with heating tape.

Pyridine²²⁸ was distilled from sodium hydroxide pellets.

Sodium iodide was dried in an oven at 160° for 48 hours.

Sodium salicylate was recrystallized from aqueous ethanol.

p-Toluenesulfonyl chloride²²⁹ (72 g.) was dissolved in chloroform (80 ml.). Petroleum ether (700 ml., b.p. 30-60°) was added which caused a precipitate to form. The mixture was stirred with decolorizing charcoal and filtered with filter aid. The clear solution was concentrated on a steam bath to 200 ml. and allowed to slowly cool to room temperature. The p-toluenesulfonyl chloride was quickly filtered with suction and dried for 16 hours in a vacuum desiccator under reduced pressure (0.05 mm.). The recovery of p-toluenesulfonyl chloride was 51 g. (71%).

Vinyl acetate was distilled (b.p. 72-73°).

N,N-dimethyl-p-aminobenzoic acid was received as a

tan powder. Recrystallizations from aqueous ethanol yielded only golden brown needles. Therefore, the acid was converted to methyl N,N-dimethyl-p-aminobenzoate (p. 132) and recrystallized three times from 80% aqueous methanol, which resulted in a good yield of white crystals. The ester was saponified by the general procedure described by Vogel.²³⁰ Methyl N,N-dimethyl-p-aminobenzoate was dissolved in a 15% sodium hydroxide solution by heating at 90° for 30 minutes. After cooling, the solution was acidified with dilute hydrochloric acid which caused the N,N-dimethyl-p-amino-benzoic acid to precipitate. Two recrystallizations from 60% aqueous ethanol gave white needles of N,N-dimethyl-p-aminobenzoic acid (m.p. 245-247°, lit. m.p.²¹³ 242-243°). The overall yields were generally greater than 80%.

J. Characterization of Reagents

Poly(epichlorohydrin) (Herculon H Elastomer) was soluble in chloroform, benzene, DMSO, DMF, MEK, and acetone and insoluble in carbon tetrachloride and alcohols. The density was reported to be 1.36.²³¹ The polymer had a glass transition (by DSC) at -17°. The inherent viscosity of a 0.5% DMF solution was 1.52 dl./g. and VPO indicated that the molecular weight was not less than 20,000. The infrared spectrum of a film prepared by evaporating a chloroform solution on a sodium chloride plate is shown

on p. 265, 266. The PMR spectrum (o-dichlorobenzene) at 110° showed δ : 3.58 (CH_2Cl); 3.67 (CHCH O). See p. 254. Anal. calcd. for $\{ \text{C}_3\text{H}_5\text{ClO} \}_n$: C, 38.94%; H, 5.45%; Cl, 38.32%. Found: C, 39.71%; H, 5.78%; Cl, 38.41%.

Poly(methacrylic acid) had an inherent viscosity (0.5% DMSO solution) of 0.68 dl./g. The infrared spectrum (KBr) was identical to the published spectrum.²³² See p. 268. The PMR spectrum (d-DMSO) at 90° showed δ : 0.5 to 2.3 ($\text{CH}_2\text{C}(\text{CH}_3)$); 2.3 to 2.6 (DMSO). A very broad and low signal was present between 7 and 12 ppm. which was presumably due to the acid proton.

Tetramethylammonium hydroxide (20% in methanol, 10.0 ml., 8.99 g., diluted to 40 ml. with water) was titrated potentiometrically with 1.00N hydrochloric acid (Fischer). End points were present at 27.40 ml. (pH = 8.9) and 27.75 ml. (pH = 4.6) which indicated that the solution was 2.74N in tetramethylammonium hydroxide (25% wt./vol., 27.8% wt./wt.) and that a small amount of a weaker base, possibly trimethylamine (0.04N), was present.

Tetraethylammonium hydroxide (10% in water, 10.0 ml., 9.98 g., diluted to 50 ml. with water) was titrated potentiometrically with 0.250N hydrochloric acid (Fischer). End points were present at 30.02 ml. (pH = 8.4) and 30.45 ml. (pH = 4.8) which indicated that the solution was 0.75N in tetraethylammonium hydroxide (11% wt./vol.) and that a small amount of a weaker base, possibly triethylamine

(0.01N), was present.

Tetrabutylammonium hydroxide (10% in methanol, 10.0 ml., 8.10 g., diluted to 40 ml. with water) was titrated potentiometrically with 0.100N hydrochloric acid (Fischer). End points were present at 31.1 ml. (pH = 8.9) and 32.6 ml. (pH = 4.3) which indicated that the base solution was 0.311N in tetrabutylammonium hydroxide (8.1% wt./vol., 10% wt./wt.) and that a small amount of a weaker base, possibly tributylamine (0.02N), was present.

C H A P T E R I I I

RESULTS AND DISCUSSION

A. Objectives

The objective of this work was to attach commonly used ultraviolet absorbers (ultraviolet stabilizers) to polymers and oligomers. These compounds would be less mobile than the corresponding low molecular weight ultraviolet absorbers, and would, therefore, have a greater permanence and effectiveness in the protection of materials (either skin or plastics) from the harmful effects of solar radiation.

It was planned to synthesize these compounds by two routes. The first was to prepare ultraviolet absorbers containing polymerizable functional groups such as a vinyl group. This approach was attractive because copolymerization of the monomer with the appropriate comonomers would allow the synthesis of copolymers with a wide range of properties. For example, an alcohol soluble polymeric ultraviolet absorber (useful for skin protection) could be prepared by copolymerization with comonomers, such as methacrylic acid, which would provide the alcohol soluble portion of the macromolecule.

The second method for the introduction of ultraviolet absorbing groups into polymer chains was by polymer modification reactions. Successful polymer modification reactions could be versatile in that other active groups, besides UV

stabilizers, could be attached to a polymer by the same reaction. These reactions would have to be mild to avoid undesirable side reactions and to obtain pure products. Therefore, it would be possible in future research to use the same mild polymer reaction to prepare polymeric pharmaceuticals and other types of active or functional polymers.

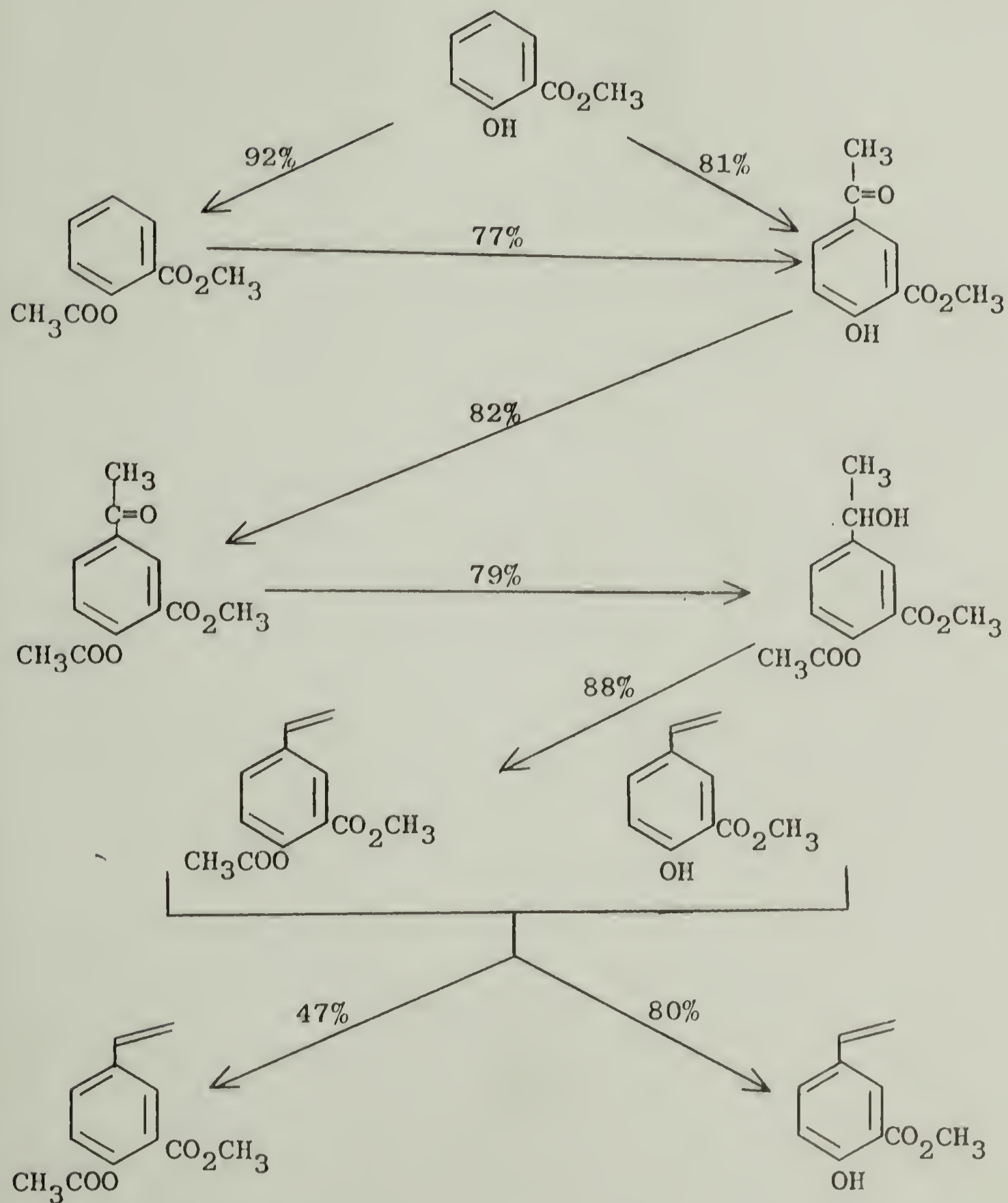
In order to study the esterification reaction of oligo(oxyethylenes) and to prepare UV stabilizers of relatively low molecular weight, a number of oligo(oxyethylenes) were endcapped with ultraviolet stabilizers.

B. Preparation and Properties of Polymers of Methyl 5-Vinylsalicylate and Methyl 5-Vinylacetylsalicylate

1. Introduction. The synthesis of methyl 5-vinylsalicylate and methyl 5-vinylacetylsalicylate is shown in Figure 4. Methyl 5-vinylsalicylate was prepared from methyl salicylate by a 5-step synthesis in an overall yield of 37%. Methyl 5-vinylacetylsalicylate was also prepared by a 5-step synthesis, the first four steps of which were the same as in the methyl 5-vinylsalicylate synthesis, in an overall yield of 18%.

Methyl salicylate was first acetylated with acetyl chloride at room temperature. Under these reaction conditions, the acetylation occurred in the position para to the

FIGURE 4. Synthesis of Methyl 5-Vinylsalicylate and Methyl 5-Vinylacetylsalicylate.



hydroxyl group. Methyl 5-acetylsalicylate could also be obtained by a Fries rearrangement reaction of methyl acetylsalicylate. Both procedures resulted in only the para isomer, methyl 5-acetylsalicylate, and none of the ortho isomer, methyl 3-acetylsalicylate. The phenol group of methyl 5-acetylsalicylate was then acetylated with acetic anhydride to give methyl 5-acetylacetylsalicylate. Sodium borohydride reduction in ethanol of the ketone group of methyl 5-acetylacetylsalicylate gave good yields of methyl 5-(1-hydroxyethyl)acetylsalicylate. The 1-hydroxyethyl group of methyl 5-(1-hydroxyethyl)acetylsalicylate was then dehydrated to a vinyl group by distilling the compound from potassium hydrogen sulfate at 225° and reduced pressure. A mixture of methyl 5-vinylacetylsalicylate and methyl 5-vinylsalicylate was obtained. The mixture could be converted to pure methyl 5-vinylacetylsalicylate by acetylation with acetic anhydride or could be hydrolyzed to pure methyl 5-vinylsalicylate with sodium methoxide in methanol.

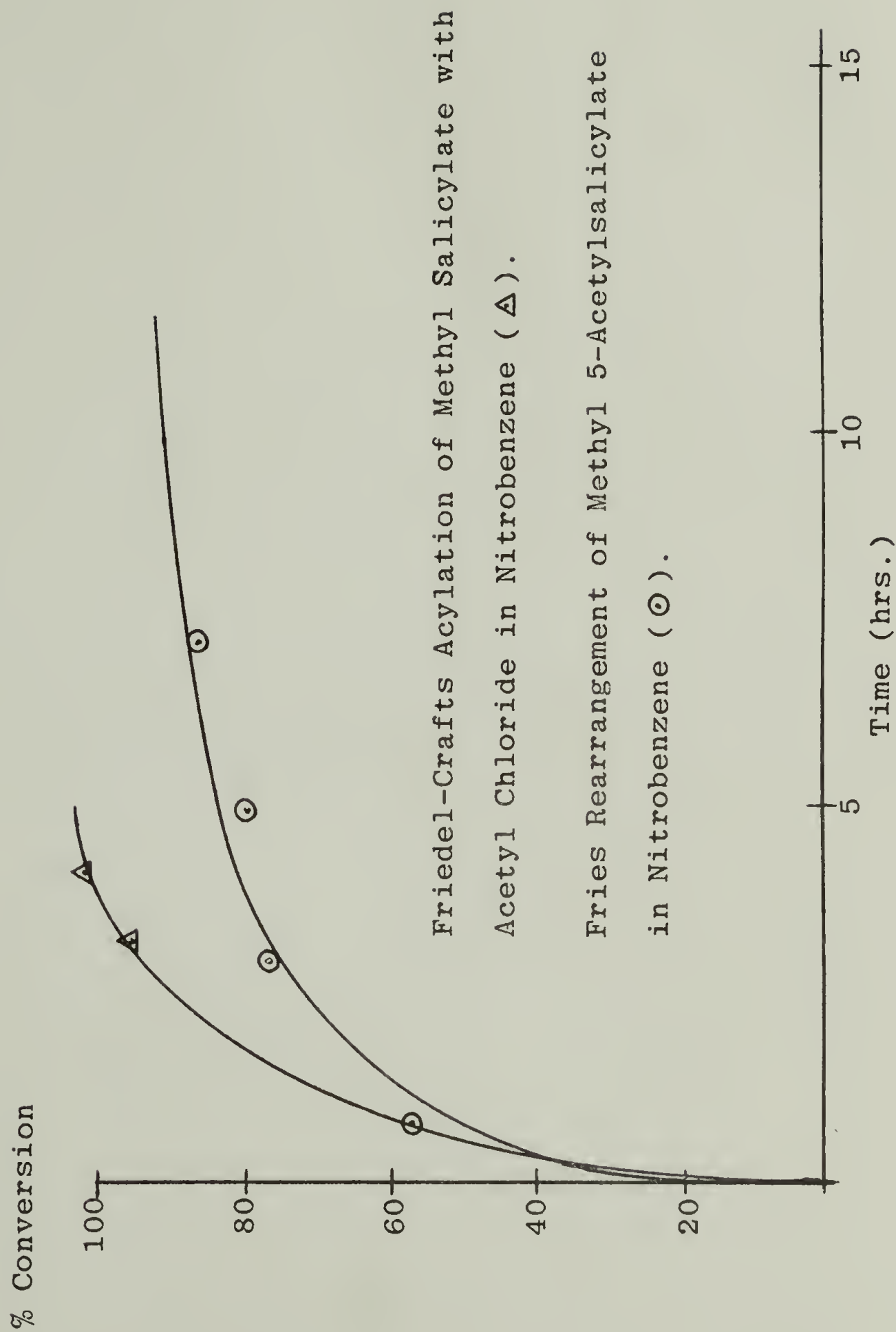
Poly(methyl 5-vinylacetylsalicylate) with a molecular weight of greater than 20,000 could be obtained in 73% yield by radical polymerization of methyl 5-vinylacetylsalicylate in benzene with AIBN. Only a homopolymer of methyl 5-vinylacetylsalicylate was obtained in an attempted copolymerization of methyl 5-vinylacetylsalicylate and vinyl acetate.

Methyl 5-vinylsalicylate could be homopolymerized and

copolymerized with methacrylic acid or acrylic acid in bulk with AIBN. (The copolymers of methyl 5-vinylsalicylate and methacrylic acid were soluble in ethanol.) Polymerization and copolymerization of methyl 5-vinylsalicylate with methacrylic acid with AIBN in THF solution gave polymers in low yields which had low inherent viscosities.

2. Synthesis of methyl 5-vinylsalicylate and methyl 5-vinylacetylsalicylate. Methyl salicylate was acetylated in the position para to the phenol group by the Perrier modification of the Friedel-Crafts acylation reaction and the Fries rearrangement of methyl acetylsalicylate. The one-step Friedel-Crafts acylation was faster, simpler, and gave a higher yield of methyl 5-acetylsalicylate from methyl salicylate than the Fries rearrangement reaction (81% vs. 70%). The latter route required two steps; first, the conversion of methyl salicylate to methyl acetylsalicylate with acetic anhydride (92% yield) and second, the Fries rearrangement reaction (77% yield). In each case, the progress of the reaction was followed by PMR spectroscopy by measuring the ratio of the integrated signal intensity of the acetyl protons of the reaction product to the integrated signal intensity of the methyl ester protons of the starting material and reaction product. As shown in Figure 5, the Friedel-Crafts reaction required approximately one-fifth of the time of the Fries rearrangement reaction to reach 85%

FIGURE 5. Synthesis of Methyl 5-Acetylsalicylate by a Friedel-Crafts Acylation and a Fries Rearrangement Reaction.



conversion.

The Friedel-Crafts acylation and the Fries rearrangement reactions gave pure products in terms of isomer distribution. The reactions were carried out at room temperature or below to suppress formation of the ortho isomer, methyl 3-acetylsalicylate. The PMR spectra of the products of the reactions and of the aliquots that were taken and analyzed by PMR spectroscopy during the course of the reactions showed one signal in the 9 to 20 ppm. range and one signal in the 0 to 4 ppm. range. This indicated that none of the ortho isomer, methyl 3-acetylsalicylate, was present. It had been expected that if a mixture of the two isomers had been present, the PMR spectra would have shown two signals for the two phenol protons in the 9 to 20 ppm. range and two signals for the methyl protons of the two acetyl groups in the 0 to 4 ppm. range.

The single isomer which formed was shown to be the para isomer, methyl 5-acetylsalicylate, and not the ortho isomer, methyl 3-acetylsalicylate, by saponification of the product. The product of the saponification reaction had a melting point (208-211°) which agreed with the literature melting point²⁰³ (209-210°) for 5-acetylsalicylic acid. The ortho isomer, 3-acetylsalicylic acid, which was reportedly prepared by a high temperature (130°) acetylation of salicylic acid, melted at 148-149°.203

Analysis by PMR spectroscopy showed that the product was methyl 5-acetylsalicylate and not methyl 3-acetylsalicylate. The PMR spectrum, which is consistent with that expected for methyl 5-acetylsalicylate, is shown on page 240. The doublet located at 7 ppm. (H_A) has a coupling constant of about 8 cps., which indicates coupling by protons positioned ortho to each other on a benzene ring. Since the doublet is not split further, this proton is not in a meta position relative to another proton on the ring. Therefore, the signal at 7 ppm. can be assigned to the proton (H_A) situated ortho to the phenol group. The signal located near 8 ppm. (H_B) also has a coupling constant of 9 cps. and is therefore in an ortho position relative to the proton (H_A) at 7 ppm. H_B is located further downfield than H_A due to the deshielding effect of the acetyl carbonyl group. The proton (H_B) at 8 ppm. is also coupled to the proton at 8.4 ppm. (H_C) with a coupling constant of 3 cps., which indicates that the two protons are positioned meta to each other on the ring. The H_C proton is the most deshielded proton since it is positioned between two carbonyl groups.

The next step in the reaction sequence was the acetylation of methyl 5-acetylsalicylate with acetic anhydride and a small amount of sulfuric acid (1 mole %) to form methyl 5-acetylacetylsalicylate. The acetylation, which

was followed by PMR spectroscopy, was slower than the acetylation of methyl salicylate. The conversion of methyl salicylate to methyl acetylsalicylate was 100% after 2 hours, while the conversion of methyl 5-acetylsalicylate to methyl 5-acetylacetylsalicylate was only 50% after 4 hours. This is probably because the carbonyl group in the 5-position of methyl 5-acetylsalicylate decreased the nucleophilicity of the phenol oxygen atom relative to the nucleophilicity of the phenol oxygen atom of methyl salicylate by resonance and an electron-withdrawing inductive effect.

The phenol group of methyl 5-acetylsalicylate was acetylated in order to avoid two potential problems. Firstly, it was believed that the phenol group might inhibit the radical polymerization of methyl 5-vinylsalicylate and the molecule would therefore eventually have to be acetylated to form methyl 5-vinylacetylsalicylate. In fact, it was later learned that methyl 5-vinylsalicylate could be successfully polymerized with AIBN as initiator. Secondly, a low conversion was obtained in the sodium borohydride reduction of methyl 5-acetylsalicylate to methyl 5-(1-hydroxyethyl)salicylate. It was believed that the low conversion was due to the formation of a phenoxyborohydride anion from methyl 5-acetylsalicylate and sodium borohydride. Acetylation of the phenol would prevent the formation of the phenoxyborohydride anion. This problem is further discussed

below.

The ketone group of methyl 5-acetylacetylsalicylate was selectively reduced in 25 minutes by sodium borohydride in cold ethanol to form methyl 5-(1-hydroxyethyl)acetylsalicylate. The ester groups were not reduced because sodium borohydride, unlike lithium aluminum hydride, does not readily reduce ester groups.²³³

The use of chloroform or dichloromethane rather than carbon tetrachloride as solvents for the work up of methyl 5-(1-hydroxyethyl)acetylsalicylate gave much better yields of crude product (79% vs. 52%). The PMR spectra of the solutions showed that the chloroform and dichloromethane washings dissolved not only the product, but also extracted ethanol from the aqueous phase during workup. The carbon tetrachloride did not extract the ethanol. Therefore, a sizable fraction of the methyl 5-(1-hydroxyethyl)acetylsalicylate remained in the aqueous ethanol phase. Subsequent ether washings of the aqueous ethanol phase extracted another 26% of crude methyl 5-(1-hydroxyethyl)acetylsalicylate.

Several attempts were made to reduce methyl 5-acetylsalicylate to methyl 5-(1-hydroxyethyl)salicylate with sodium borohydride in ethanol and in DMAc. In each case, the reaction conversion quickly reached a value of about 25% and did not increase any further. This conversion was

approximately equal to the molar fraction of excess sodium borohydride over methyl 5-acetylsalicylate. The phenoxyborohydride anion, which formed by the reaction of the phenol group of methyl 5-acetylsalicylate with sodium borohydride, could have decreased the reactivity of the remaining three hydride groups by an electron-withdrawing inductive effect of the phenoxy group. Therefore, only the excess sodium borohydride reduced the ketone group. It is also possible that the phenoxyborohydride anion increased the electron density at the carbonyl carbon atom and reduced its reactivity. It is known that groups which decrease the positive charge at the carbonyl carbon, decrease the reactivity of the carbonyl group with metal hydrides.²³³ A 2:1 mole ratio of sodium borohydride to methyl 5-acetylsalicylate may have given a successful reduction of the ketone to form methyl 5-(1-hydroxyethyl)salicylate. However, in view of the fact that methyl 5-acetylsalicylate could very easily be acetylated and then reduced to give good yields of methyl 5-(1-hydroxyethyl)acetylsalicylate, the investigation of the methyl 5-acetylsalicylate reduction was terminated.

The (1-hydroxyethyl) group of methyl 5-(1-hydroxyethyl)acetylsalicylate was dehydrated to a vinyl group by heating with potassium hydrogen sulfate at 225°. The product could be distilled from the reaction flask as it

formed by adjusting the pressure of the system to about 0.2 mm. Evidently, some of the acetyl groups were hydrolyzed during the course of the reaction since the dehydration product was a mixture of methyl 5-vinylsalicylate and methyl 5-vinylacetylsalicylate (as determined by PMR spectroscopy).

The high temperature dehydration of (1-hydroxyethyl)-benzene compounds with potassium hydrogen sulfate has been frequently used to form styrene derivatives.²³⁴ In general, the dehydration is carried out at approximately 220-230° and the styrene derivative is distilled as it forms by adjusting the pressure of the system. The styrene derivative usually distills about 20° below the (1-hydroxyethyl)benzene compound which enables a good separation of product from starting material to be obtained. The mixture of methyl 5-vinylacetylsalicylate and methyl 5-vinylsalicylate, which was obtained by the dehydration of methyl 5-(1-hydroxyethyl)-acetylsalicylate, was not contaminated with any of the higher boiling methyl 5-(1-hydroxyethyl)acetylsalicylate (as determined by PMR spectroscopy).

The dehydration of methyl 5-(1-hydroxyethyl)acetylsalicylate to methyl 5-vinylacetylsalicylate was unsuccessfully attempted with thionyl chloride in pyridine at room temperature and at 55°. Thionyl chloride and pyridine have been reported as dehydration agents.²³⁵ The 5 to 6 ppm. range of

the PMR spectra of aliquots taken from the black reaction mixtures after $2\frac{1}{2}$ hours did not show any evidence of a compound which might have had vinyl protons. However, the doublet which was originally at 1.3 to 1.4 ppm. (CH_3CHOH) had nearly disappeared and a new doublet had appeared at 1.8 to 1.9 ppm., which may have been due to methyl protons of a 1-chloroethyl group (CH_3CHCl) of methyl 5-(1-chloroethyl)acetylsalicylate. In view of the fact that the potassium hydrogen sulfate dehydration of methyl 5-(1-hydroxyethyl)acetylsalicylate gave a high yield of a mixture of methyl 5-vinylacetylsalicylate and methyl 5-vinylsalicylate, no attempts were made to further investigate the thionyl chloride-pyridine dehydration reaction, and no attempts were made to isolate the methyl 5-(1-chloroethyl)acetylsalicylate if, in fact, it had formed.

The final step in the reaction sequence was to convert the mixture of methyl 5-vinylacetylsalicylate and methyl 5-vinylsalicylate to either methyl 5-vinylacetylsalicylate or methyl 5-vinylsalicylate. The mixture could easily be converted to pure methyl 5-vinylacetylsalicylate by acetylation with acetic anhydride. The mixture could be hydrolyzed to methyl 5-vinylsalicylate with sodium methoxide and methanol. The reaction did not hydrolyze the methyl ester group since a reaction of sodium methoxide with that group would have regenerated a methyl ester. Reaction of sodium

methoxide at the acetate group would be expected to form a phenoxide ion and methyl acetate. Therefore, it was possible to selectively saponify the acetate group in the presence of the methyl ester group. Sodium hydroxide saponification was not used because it would be expected to saponify both ester groups and convert the mixture of monomers to 5-vinylsalicylic acid.

Methyl 5-vinylacetylsalicylate and methyl 5-vinylsalicylate were each purified by distillation. A large fraction of methyl 5-vinylacetylsalicylate (b.p. 100-103.5°, 0.12 mm.) polymerized in the distillation flask during distillation with picric acid as a polymerization inhibitor. Methyl 5-vinylsalicylate, on the other hand, could be distilled (b.p. 66-67°, 0.16-0.18 mm.) with very little loss of monomer due to polymerization by using picric acid as the polymerization inhibitor. Picric acid has been reported as an effective inhibitor of styrene polymerization.²³⁶

The purity of the methyl 5-vinylsalicylate could not be determined by GC since a sharp peak with a retention time on the order of minutes could not be obtained. A single sharp peak with a retention time of 30 seconds at a column temperature of 215° could be obtained; however, lowering the column temperature or the helium flow rate in order to extend the retention time of the peak caused the peak to broaden considerably. Nevertheless, the carbon and hydrogen analysis of

methyl 5-vinylsalicylate and methyl 5-vinylacetylsalicylate were within 0.3% of the theoretical values.

3. Preparation of polymers of methyl 5-vinylsalicylate and methyl 5-vinylacetylsalicylate. A 73% yield of poly-(methyl 5-vinylacetylsalicylate) with a molecular weight of greater than 20,000 was prepared by polymerization of methyl 5-vinylacetylsalicylate in benzene with AIBN.

Methyl 5-vinylacetylsalicylate could not be successfully copolymerized with vinyl acetate, probably for the same reason that a copolymer of styrene and vinyl acetate containing a substantial amount of vinyl acetate cannot be prepared. It is likely that during the course of the polymerization, the growing polymer radical preferentially added to the styrene like methyl 5-vinylacetylsalicylate monomer to form a resonance stabilized radical rather than adding to the vinyl acetate monomer. The polymer which was obtained contained very few, if any, vinyl acetate groups. The infrared and PMR spectra of the polymer were identical to those of poly(methyl 5-vinylacetylsalicylate). The attempt was made to copolymerize methyl 5-vinylacetylsalicylate with vinyl acetate because it was expected that the copolymer could be converted to an alcohol soluble copolymer of methyl 5-vinylsalicylate and vinyl alcohol by an ester interchange reaction with methanol.

Poly(methyl 5-vinylacetylsalicylate) was converted to a

78/22 copolymer of methyl 5-vinylsalicylate and methyl 5-vinylacetylsalicylate by an acid catalyzed ester interchange reaction in methanol. During the course of the reaction in refluxing methanol, the initially swollen poly(methyl 5-vinylacetylsalicylate) changed to a hard, insoluble material. The composition of the copolymer of methyl 5-vinylsalicylate (78%) and methyl 5-vinylacetylsalicylate (22%) was determined by comparing the PMR integrated signal intensities (see p. 241). The infrared spectrum (see p. 261) of the copolymer showed carbonyl absorptions (1765, 1720, and 1675 cm^{-1}) characteristic of poly(methyl 5-vinylsalicylate) repeat units (1675 cm^{-1}) and poly(methyl 5-vinylacetylsalicylate) repeat units (1765 and 1720 cm^{-1}). It is possible that a quantitative conversion of poly(methyl 5-vinylacetylsalicylate) to poly(methyl 5-vinylsalicylate) could have been obtained by using a cosolvent with the methanol which could have kept the polymer either in solution or in a swollen state during the course of the ester interchange reaction. However, since it was later found that methyl 5-vinylsalicylate could be polymerized directly with radical initiators, no further attempts were made to increase the conversion of this ester interchange reaction.

Methyl 5-vinylsalicylate was polymerized in bulk with AIBN without noticable polymerization inhibition or cross-linking by its phenol group. An 82% yield of poly(methyl

5-vinylsalicylate), which was completely soluble in chloroform and had a molecular weight of greater than 20,000, was obtained. Copolymerization of methyl 5-vinylsalicylate with methacrylic acid and acrylic acid in bulk with AIBN gave copolymers which were soluble in DMSO. The hydrogen of the phenol group of methyl 5-vinylsalicylate or poly(methyl 5-vinylsalicylate) could have been abstracted by the growing polymer radical during the polymerization. The phenoxy radical could have been stable (polymerization inhibition) or the phenoxy radical could have reinitiated polymerization (chain transfer to monomer or polymer) which would have led to chain branching and crosslinking. Neither crosslinking nor polymerization inhibition occurred. In a similar case, Fertig¹⁰⁷ reported that the phenol group of 2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)benzophenone did not inhibit the polymerization of the monomer. As explained by Fertig, this was probably because the phenol group was internally hydrogen bonded to the carbonyl group.

Methyl 5-vinylsalicylate solution polymerization and copolymerization with methacrylic acid in THF with AIBN as the initiator was less successful than the polymerizations in bulk. The polymers were obtained in low yields (20 to 40%) and had low inherent viscosities as compared to the polymers prepared by bulk polymerization. The polymerizations were not in sealed tubes, as was the case with the

bulk polymerizations, but rather in round-bottomed flasks under a continuous flow of nitrogen gas. (It is much more likely under these conditions, as compared to the sealed tube polymerizations, that oxygen could enter the system and inhibit the polymerization.) Hydrogen atoms on the α -carbon atoms of ethers are susceptible to radical abstractions.²³⁷ Therefore, the solvent, THF, could have acted as a chain transfer agent and weak poison during the radical polymerization and decreased the molecular weight and yield of poly(methyl 5-vinylsalicylate) and copolymers.

The texture and purity of the copolymers of methacrylic acid and methyl 5-vinylsalicylate were influenced by the solvents used for the precipitation of the polymers from solution. Precipitation of the copolymers of methyl 5-vinylsalicylate and methacrylic acid prepared by bulk polymerization from an ethanol solution with ether resulted in lumps of hard, brittle material. According to the PMR spectra, the materials had entrapped ethanol which could not be removed by heating in vacuo. At approximately 230° during the DSC scan of the copolymers, the samples expanded to form a solid foam which indicated that the copolymers had enclosed pockets of air, ethanol, or gasses produced as a result of polymer degradation and dehydration. Copolymers of methyl 5-vinylsalicylate and methacrylic acid, which were prepared in THF and precipitated with ether, were fine, light

powders and did not appear to expand on heating during the DSC scan. The brittle copolymers prepared by copolymerization in bulk could be precipitated from a DMSO solution with water to yield fine powders.

4. Characterization and properties of polymers of methyl 5-vinylsalicylate and methyl 5-vinylacetylsalicylate.

A comparison of the thermal properties of poly(methyl 5-vinylsalicylate) and poly(methyl 5-vinylacetylsalicylate) shows the influence of the phenol group on the glass transition. The glass transition of poly(methyl 5-vinylsalicylate) ($127-130^{\circ}$) was about 23° higher than that of poly(methyl 5-vinylacetylsalicylate) (106°). The glass transition of the 22/78 copolymer (122°) of methyl 5-vinylacetylsalicylate and methyl 5-vinylsalicylate was between those of the two homopolymers. The higher glass transition of poly(methyl 5-vinylsalicylate) was probably due to interchain interactions arising from hydrogen bonding by the phenol groups. The effect of the phenol group on the glass transition of poly(methyl 5-vinylsalicylate) is analogous to the effect of interchain hydrogen bonding by hydroxyl groups on the glass transition of poly(vinyl alcohol). Poly(vinyl alcohol) ($T_g = 85^{\circ}$) has a higher glass transition than poly(vinyl acetate) ($T_g = 29^{\circ}$), poly(vinyl methyl ether) ($T_g = -20$ to -10°), and poly(vinyl ethyl ether) ($T_g = -25^{\circ}$).²³⁸

The composition of the copolymers of methyl 5-vinyl-salicylate and methacrylic acid were determined by elemental analysis and the following equation:

$$\%C = 100 \cdot \frac{(C-Sal)x + (C-maa)y}{(MW-Sal)x + (MW-maa)y}$$

Where C-Sal = amount of carbon in the methyl 5-vinyl-salicylate repeat unit (120.10).

C-maa = amount of carbon in the methacrylic acid repeat unit (48.04).

MW-Sal = molecular weight of the salicylate repeat unit (178.18).

MW-maa = molecular weight of the methacrylic acid repeat unit (86.09).

x = mole fraction of methyl 5-vinylsalicylate repeat units.

y = mole fraction of methacrylic acid repeat units.

For example, a copolymer of methyl 5-vinylsalicylate and methacrylic acid analyzed for 61.89% carbon.

$$61.89 = 100 \frac{(120.10)x + (48.04)y}{(178.18)x + (86.09)y}$$

$$(110.28)x + (53.28)y = (120.10)x + (48.04)y$$

$$(5.24)y = (9.82)x$$

$$y/x = 1.87$$

$$\frac{y/x}{y/x + 1} = \frac{y}{y + x} = y = \frac{1.87}{2.87} = 0.652$$

Therefore, the copolymer consisted of 65.2 mole % methacrylic acid repeat units and 34.8% methyl 5-vinylsalicylate repeat units. The carbon analysis is reliable to within $\pm 0.3\%$ ($61.89 \pm 0.3\%$). The copolymer composition calculated for the values of 61.50% carbon and 62.19% carbon were 67.5% and 62.8% methacrylic acid repeat units respectively. Therefore, the copolymer composition was $65 \pm 3\%$ methacrylic acid.

The percent hydrogen in the copolymer (6.30%), which was calculated by a similar equation, was within 0.3% of the 6.11% that was found by elemental analysis.

$$\%H = 100 \frac{(10.08)(0.35) + (6.05)(0.65)}{(178.18)(0.35) + (86.09)(0.65)}$$

The approximate composition of the copolymer could also be calculated from its PMR spectrum with the following equation:

$$\frac{(\text{Sal})}{(\text{Chain})} = \frac{6 \cdot x}{3 \cdot x + 5 \cdot y}$$

Where Sal = integrated signal intensity of the methyl ester protons and aromatic protons of the methyl 5-vinylsalicylate repeat units.

Chain = integrated signal intensity of the protons attached to the main chain carbon atoms and the methacrylic acid methyl protons between 0.5 and 2.5 ppm.

For example, the integrated signal intensity of the aromatic protons and methyl ester protons in the PMR spectrum (see p. 243) of the above copolymer were 13 and 11 respectively. The integrated signal intensity of the main chain protons and methyl protons of methacrylic acid between 0.4 and 2.4 ppm. was 51.

$$\frac{24}{51} = \frac{6 \cdot x}{3 \cdot x + 5 \cdot y}$$

$$y/x = 2.0$$

$$\frac{y/x}{y/x + 1} = \frac{y}{y + x} = y = \frac{2}{3} = 0.67$$

Therefore, the copolymer consisted of 67% methacrylic acid repeat units and 33% methyl 5-vinylsalicylate repeat units.

This value is approximate due to the poor peak separation of the solvent (d-DMSO) used for the copolymers in the PMR scans and the main chain protons of the copolymer. Nevertheless, 67% is very close to the 65% determined by elemental analysis.

The methacrylic acid repeat units of the copolymers of methyl 5-vinylsalicylate and methacrylic acid affected the chemical shifts of the aromatic protons in the PMR spectra of the copolymers. The aromatic protons in the PMR spectrum of poly(methyl 5-vinylsalicylate) show one broad signal centered near 6.8 ppm. (See p. 241.) The copolymers show three broad signals near 6.8, 7.1, and 7.4 ppm. of roughly equal intensity. (See p. 242, 243.) Two of the aromatic protons on the methyl 5-vinylsalicylate repeat units had evidently been deshielded by the carbonyl groups of neighboring methacrylic acid repeat units.

The molar extinction coefficient of the methyl 5-vinylsalicylate repeat units of the poly(methyl 5-vinylsalicylate) and of the copolymers of methacrylic acid and methyl 5-vinylsalicylate appeared to be dependent on copolymer composition and on polymer molecular weight. The results of the UV measurements of the polymers are presented in Table 9. On the basis of the data, a few conclusions can be drawn. Firstly, the polymers with the higher weight percent of methyl 5-vinylsalicylate repeat units had the higher extinction coefficients ($\text{l. g.}^{-1} \text{ cm.}^{-1}$). An exception to this

TABLE 9. Properties of Poly(methyl 5-vinylsalicylate) and Its Copolymers.

<u>Polymer</u>	<u>Mole% MeSala in Feed</u>	<u>Mole% MeSala^a in the Copolymer (wt.%)</u>		<u>Inherent^c Viscosity</u>
		<u>By Elemental Analysis</u>	<u>By PMR</u>	
1	100	100	—	0.93
2	42	42 (60)	46	0.32
3	17	14 (25)	23	0.48
4	32	35 (53)	34	1.78
5	16	—	20(34)	1.80
6 ^b	29	34 (56)	—	1.91

^a Methyl 5-vinylsalicylate

^b Copolymer of methyl 5-vinylsalicylate and acrylic acid

^c dl./g. 0.5% DMSO solution

TABLE 9. Continued

<u>95% Ethanol Solubility</u>	<u>Extinction Coefficient (l.g.⁻¹cm.⁻¹)</u>	<u>Molar Extinction Coefficient (λ max), Solvent</u>
No	38.3 19.4	6.83 x 10 ³ (236) 3.46 x 10 ³ (316) THF
Hot	27.6 13.4	8.2 x 10 ³ (237) 4.0 x 10 ³ (316) THF
Yes	18.0 8.10 8.12	13 x 10 ³ (239) 5.8 x 10 ³ (316) THF 5.8 x 10 ³ (316) DMSO
Yes	10.8	3.6 x 10 ³ (316) DMSO
Yes	7.28	3.8 x 10 ³ (316) DMSO
No	12.8	4.1 x 10 ³ (314) DMSO

statement is copolymer 3 which had a lower weight percent of methyl 5-vinylsalicylate than copolymer 5 (25 vs. 34 wt. %), but had a higher extinction coefficient (8.1 vs. 7.3 l. g.⁻¹ cm.⁻¹). Secondly, a comparison of polymers 1, 2, and 3 shows that the molar extinction coefficient of the methyl 5-vinylsalicylate repeat unit increased as the amount of methyl 5-vinylsalicylate repeat unit in the chain decreased. This pattern does not seem to be the case with the higher molecular weight copolymers 4, 5, and 6. Finally, a comparison of the low molecular weight copolymers 2 and 3 to the higher molecular weight copolymers 4 and 5 shows that the molar extinction coefficient of the methyl 5-vinylsalicylate repeat unit increased as the copolymer molecular weight decreased.

Three points can be made as the amount of methyl 5-vinylsalicylate in the copolymer decreased or as the molecular weight of the copolymer decreased. Firstly, a high concentration of methacrylic acid in the copolymer increased the probability that methyl 5-vinylsalicylate repeat units were adjacent to one or two methacrylic acid repeat units. Secondly, the disparity in concentration of UV absorber in the solvated polymer coil and overall concentration of UV absorber in solution decreased as the polymer chain was diluted with methacrylic acid repeat units. Since the volume occupied by a polymer in solution is several

hundred times the volume of the matter which actually makes up the polymer,²³⁹ the concentration of methyl 5-vinylsalicylate groups within the coil of the homopolymer was probably on the order of 2 g./l. or roughly 10^{-2} M. The overall solution concentration used in the UV measurement was approximately 10^{-4} M. (A greater than 10^{-4} molar concentration of poly(methyl 5-vinylsalicylate) in THF was not used because the absorbance of the polymer solution would be greater than 1.2. It is generally recommended that the absorbance (A) of a UV measurement be maintained between 0.6 and 1.2.) Thirdly, a decrease in the molecular weight of the copolymer of methacrylic acid and methyl 5-vinylsalicylate or the homopolymeric UV absorber would have more evenly distributed the UV absorber throughout the solution and decreased the disparity in overall solution concentration of UV absorber and concentration of UV absorber in the solvated polymer coil. It is possible that these factors, neighboring groups in the copolymer chain and high local concentration of UV absorber, could have affected the values obtained for the methyl 5-vinylsalicylate repeat unit molar extinction coefficients.

A number of experiments could be carried out to further investigate the effect of copolymer composition and molecular weight on the molar extinction coefficient of the methyl 5-vinylsalicylate repeat unit. Clearly, more

information is needed before any final conclusions could be drawn. It would be necessary to determine the effect, if any, of molecular weight on the molar extinction coefficient of poly(methyl 5-vinylsalicylate). A series of low to high molecular weight methyl 5-vinylsalicylate polymers could be obtained by fractionation of the polymer by gel permeation chromatography and by polymerization of methyl (5-vinylsalicylate) in the presence of various concentrations of chain transfer agents. Furthermore, the extinction coefficient of the model compound, methyl 5-ethylsalicylate, could be determined. In addition, in order to rule out the possibility that the phenol group of methyl 5-vinylsalicylate interfered with the radical polymerization, it would be necessary to quantitatively convert poly(methyl 5-vinylacetylsalicylate) to poly(methyl 5-vinylsalicylate) by an ester interchange reaction and compare its extinction coefficient to that of poly(methyl 5-vinylsalicylate) prepared by radical polymerization of methyl 5-vinylsalicylate. In fact, the molar extinction coefficient of the methyl 5-vinylsalicylate repeat units of the 78/22 copolymer of methyl 5-vinylsalicylate and methyl 5-vinylacetylsalicylate prepared by an ester interchange reaction of methanol with poly(methyl 5-vinylacetylsalicylate) was $3.6 \times 10^3 \text{ l. mole}^{-1} \text{ cm.}^{-1}$. This value was slightly higher than the molar extinction coefficient

($3.46 \times 10^3 \text{ l. mole}^{-1} \text{ cm.}^{-1}$) of the poly(methyl 5-vinylsalicylate) prepared by radical polymerization of methyl 5-vinylsalicylate. Thirdly, a series of copolymers of methyl 5-vinylsalicylate and methacrylic acid or other comonomers varying in copolymer composition could be prepared and the effect, if any, of the copolymer composition on the molar extinction coefficients of the methyl 5-vinylsalicylate repeat units could be studied.

Other workers have reported a dependence of absorbance on copolymer composition. Gallo and Russo²⁴⁰ found that the optical density at 269.5 nm. of copolymers of styrene and methyl methacrylate did not increase linearly as the styrene content in the copolymers increased. They tentatively concluded that the non-linearity was due to different absorption coefficients of styrene units isolated between methyl methacrylate repeat units and those of two adjacent styrene repeat units. The optical densities of the styrene copolymers were less than the optical densities of the styrene homopolymers. Also, the copolymer composition which corresponded to the maximum hypochromism depended on the dielectric constant of the solvent used in the measurement. They pointed out that there was no effect of molecular weight on the absorbance values.

The techniques used to isolate and purify the copolymers of methacrylic acid and methyl 5-vinylsalicylate apparently

fractionated the products on the basis of copolymer composition. For example, the amount of methyl 5-vinylsalicylate in copolymers 4, 5, and 6 was greater than the amount of methyl 5-vinylsalicylate in the polymerization feed. (Table 9.) Evidently, purification of the copolymers by precipitation from ethanol or DMSO solution with water did not precipitate those copolymers which were rich in methacrylic acid or acrylic acid repeat units. Copolymers 2 and 3 were isolated by precipitation from a THF solution with ether. In these cases, the mole percent of methyl 5-vinylsalicylate in the copolymer was either equal to or slightly less than the mole percent of methyl 5-vinylsalicylate in the polymerization feed.

The alcohol solubility, which is a desirable property for these polymeric UV absorbers since they are being tested as sunscreens for skin protection, was determined. The copolymers with 53 weight % or less of methyl 5-vinylsalicylate groups were soluble in 95% ethanol. The copolymer containing 60 weight % of the methyl 5-vinylsalicylate was soluble in hot 95% ethanol. The copolymer of acrylic acid and methyl 5-vinylsalicylate (56 wt. %) was insoluble in alcohol.

5. Potential applications and future work. The primary reason for preparing these polymers was to obtain alcohol soluble polymeric ultraviolet absorbers for skin

protection. There also exists the possibility that the polymers and copolymers discussed above or poly(5-vinylsalicylic acid) or poly(5-vinylacetylsalicylic acid) could function as polymeric drugs. These polymers would be of the nonhydrolyzable type. This is in contrast to the acetylsalicylate ester of starch which reportedly functions by a slow release of acetylsalicylic acid to the body.²⁴¹

The polymers could also be useful as chelating resins as was originally proposed by Dr. Dabkowski at the University of Massachusetts.

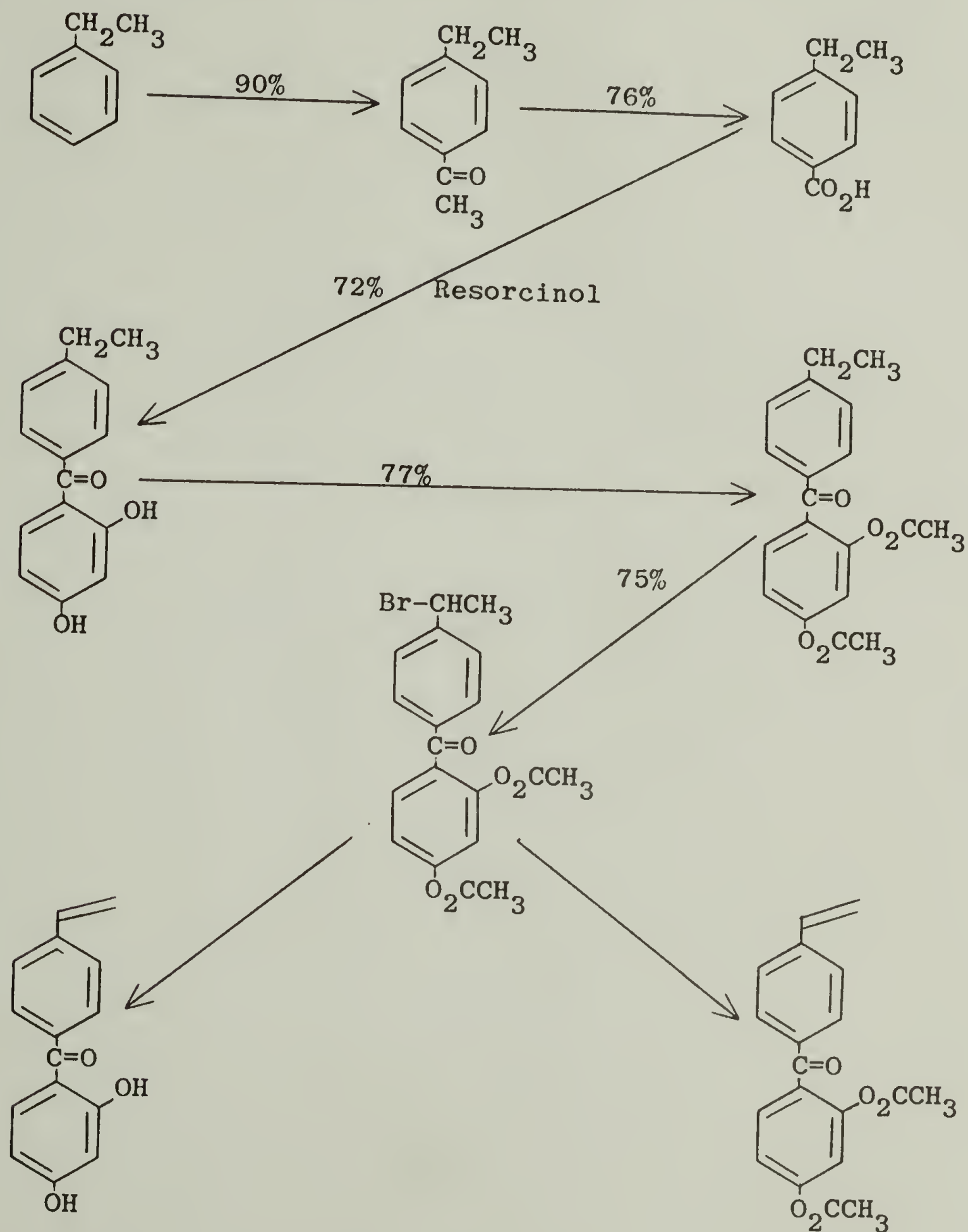
C. Synthesis of Crude 2,4-Dihydroxy-4'-vinylbenzophenone and Crude 2,4-Diacetoxy-4'-vinylbenzophenone

1. Introduction. This work began during a four month period of research by this writer at the laboratory of Professor Pinazzi at the Cité Universitaire du Mans, Le Mans, France. Prof. Pinazzi and Dr. Fernandez had previously synthesized 2,4-dimethoxy-4'-vinylbenzophenone and 2-methoxy-4'-vinylbenzophenone.^{111,112} They found that it was difficult to convert both of the methoxy groups of poly-(2,4-dimethoxy-4'-vinylbenzophenone) to phenol groups. Therefore, it was decided to prepare and polymerize 2,4-dihydroxy-4'-vinylbenzophenone. In the event that the phenol groups of 2,4-dihydroxy-4'-vinylbenzophenone inhibited or

interfered with the polymerization of the monomer, it was planned to block the phenol groups with protecting groups such as trimethylsilyloxy, methoxymethoxy, or acetoxy groups and then remove them after the polymerization.

The synthesis of crude 2,4-dihydroxy-4'-vinylbenzophenone and 2,4-diacetoxy-4'-vinylbenzophenone was carried out as described in Figure 6. An overall yield of 49% was obtained for the synthesis of the previously unreported 2,4-dihydroxy-4'-ethylbenzophenone from ethylbenzene by a three-step synthesis. The procedure for the acylation of ethylbenzene with acetyl chloride to form 4-ethylacetophenone²⁰⁴ and the sodium hypobromite oxidation of 4-ethylacetophenone to form 4-ethylbenzoic acid²⁰⁶ had been described previously in the literature. 2,4-Dihydroxy-4'-ethylacetophenone was prepared by acylating resorcinol with 4-ethylbenzoic acid and boron trifluoride. The phenol groups of 2,4-dihydroxy-4'-ethylbenzophenone were then converted to acetoxy groups with acetic anhydride to form 2,4-diacetoxy-4'-ethylbenzophenone. The ethyl group of 2,4-diacetoxy-4'-ethylbenzophenone was converted to a 1-bromoethyl group by bromination with N-bromosuccinimide (NBS) and was then converted to a vinyl group by an elimination reaction with tributylamine. The acetoxy groups of crude 2,4-diacetoxy-4'-vinylbenzophenone were hydrolyzed to phenol groups by saponification with sodium bicarbonate in aqueous

FIGURE 6. Synthesis of Crude 2,4-Diacetoxy-4'-vinylbenzophenone and 2,4-Dihydroxy-4'-vinylbenzophenone.



methanol to yield 2,4-dihydroxy-4'-vinylbenzophenone.

2,4-Dihydroxy-4'-ethylbenzophenone had to be converted to 2,4-diacetoxy-4'-ethylbenzophenone before carrying out the side chain bromination with NBS to avoid side reactions. The PMR spectrum of the crude product of the reaction of NBS with 2,4-dihydroxy-4'-ethylbenzophenone indicated that bromination had taken place on the phenol containing ring and not on the ethyl group. Ring bromination also predominated over side chain bromination in the reaction of NBS with 2-hydroxy-4-methoxymethoxy-4'-ethylbenzophenone. Neither ring bromination nor side chain bromination took place in the reaction of NBS with 2,4-di(trimethylsilyloxy)-4'-ethylbenzophenone.

2. Synthesis of 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone. 4-Ethylacetophenone (free of 2-ethylacetophenone or 2,4-diethylacetophenone) was obtained by a low temperature (5-25°) acetylation of ethylbenzene with acetyl chloride by the Perrier modification of the Friedel-Crafts reaction. The Perrier modification, in which the acetyl chloride and aluminum trichloride were first allowed to react and the ethylbenzene was added last, was recommended by Pearson²⁴² to avoid alkyl position isomerization and disproportionation and consequently formation of 2,4-diethylacetophenone. The PMR spectrum (see p. 244) of the product, 4-ethylacetophenone, showed that neither 2,4-diethylacetophenone nor

2-ethylacetophenone were present. The integrated signal intensities and coupling constant (8 cps.) for the aromatic signals indicated that a pair of protons were positioned ortho to another pair of protons. The pair of protons (H_B) at 7.75 ppm. were shifted further downfield than the pair of protons (H_A) at 7.15 ppm. due to deshielding by the carbonyl group.

The next step in the reaction sequence was the oxidation of 4-ethylacetophenone with sodium hydroxide and bromine (sodium hypobromite) to form 4-ethylbenzoic acid. The PMR spectrum and melting point of the product were consistent with those of 4-ethylbenzoic acid. Therefore, the oxidation of p-ethylacetophenone was not complicated by a side reaction to form terephthalic acid. This had been reported to be the product of the sodium hypochlorite oxidation of p-ethylacetophenone.²⁴³

Bright yellow crystals of 2,4-dihydroxy-4'-ethylbenzophenone were obtained by the acylation of resorcinol with 4-ethylbenzoic acid and boron trifluoride. The crude red product was first distilled and then recrystallized from aqueous acetic acid to yield the bright yellow crystals.

The UV spectrum of the 2,4-dihydroxy-4'-ethylbenzophenone and the PMR spectrum of a derivative of 2,4-dihydroxy-4'-ethylbenzophenone (2-hydroxy-4-methoxymethoxy-4'-ethylbenzophenone) showed that the product was the 2,4

isomer and not 2,6-dihydroxy-4'-ethylbenzophenone. The UV spectrum of the product had three absorptions (246, 289, and 326 nm.) which are characteristic of 2,4-dihydroxybenzophenones (245-255, 280-290, 335-345 nm.).²⁴⁴ The spectrum was not similar to the UV spectrum of 2,6-dihydroxybenzophenone which has only two absorptions (250 and 280 nm.).²⁴⁴ The PMR spectrum of 2-hydroxy-4-methoxymethoxy-4'-ethylbenzophenone (see p. 247) showed clear, sharp signals, which was not the case with the PMR spectrum of 2,4-dihydroxy-4'-ethylbenzophenone. (The synthesis of 2-hydroxy-4-methoxymethoxy-4'-ethylbenzophenone from 2,4-dihydroxy-4'-ethylbenzophenone and chloromethyl methyl ether is discussed below.) The H_A proton (6.5 ppm.) was coupled to the H_E proton (7.55 ppm.) with the appropriate coupling constant (8 cps.) for protons situated ortho to each other on an aromatic ring. H_A was also coupled to H_B (6.7 ppm.) with a coupling constant of 2 to 3 cps., which indicated that these two protons were positioned meta to each other. The pair of H_C protons (7.3 ppm.) were coupled to the pair of ortho H_D protons (7.6 ppm.) with the appropriate coupling constant (8 cps.) for protons positioned ortho to each other on an aromatic ring. The H_E and H_D protons were shifted furthest downfield due to deshielding by the carbonyl group.

2,4-Dihydroxy-4'-ethylbenzophenone was easily converted

to 2,4-diacetoxy-4'-ethylbenzophenone with acetic anhydride in the presence of a small amount of sulfuric acid. After distillation, the yield of 2,4-diacetoxy-4'-ethylbenzophenone was 77%.

In order to convert the ethyl group of 2,4-diacetoxy-4'-ethylbenzophenone to a vinyl group, it was first necessary to convert it to a 1-bromoethyl group. This was accomplished by the reaction of 2,4-diacetoxy-4'-ethylbenzophenone with N-bromosuccinimide. The PMR spectrum (see p. 245) of the product of the reaction showed that the ethyl group of 2,4-diacetoxy-4'-ethylbenzophenone had been converted to a 1-bromoethyl group. The triplet of the methyl protons (1.09 - 1.35 ppm.) in the ethyl group had changed to the expected doublet for the methyl protons (1.92 - 2.05 ppm.) of the 1-bromoethyl group of 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone. The integrated signal intensity of the quartet of the methine protons (5.00 - 5.37 ppm.) of the 1-bromoethyl group was one-half the integrated signal intensity of the methylene protons (2.52 - 2.90 ppm.) of the ethyl group.

3. Conversion of the 1-bromoethyl group of 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone to a vinyl group.

Potassium hydroxide, sodium t-butoxide, pyridine, triethylamine, lithium chloride, tetraethylammonium chloride, and tributylamine were used as reagents in an attempt to carry

out a dehydrobromination reaction with 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone to form 2,4-diacetoxy-4'-vinylbenzophenone or 2,4-dihydroxy-4'-vinylbenzophenone. The progress or products of these reactions were examined by PMR spectroscopy. It was expected that the signals of the vinyl protons of the product would be similar in appearance to those of methyl 5-vinylsalicylate, methyl 5-vinylacetylsalicylate, and other styrene derivatives and would be in the 5 to 6 ppm. range.

Tributylamine was investigated as a reagent for the dehydrobromination of 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone to form 2,4-diacetoxy-4'-vinylbenzophenone. It was found by PMR spectroscopy (see p. 250) that 60 minutes at 140° with tributylamine in DMAc was sufficient to complete the elimination reaction. After 60 minutes, the quartet of the starting material near 5 ppm. had disappeared and characteristic signals of vinyl protons had developed in the 5 to 6 ppm. range. After 90 minutes at 140° in DMAc with picric acid as a polymerization inhibitor or in nitrobenzene, the orange color of the solutions did not darken. This is in contrast to dehydrobromination reactions which were carried out with potassium hydroxide, potassium t-butoxide, triethylamine, and pyridine which gave dark solutions.

The dehydrobromination reaction was repeated on a small

scale with tributylamine and 2,4-diacetoxy-4'-(1-bromoethyl)-benzophenone (1 g.) at 150° for 1½ hours in DMAc with picric acid as the polymerization inhibitor. After the elimination reaction, the crude product was treated with acetic anhydride and a small amount of sulfuric acid to reacetylate any phenol groups that may have formed. The product was dissolved in ether and the solution was filtered from ether insoluble impurities. The PMR spectrum (see p. 250) of the crude product, which was isolated in a low yield (37%), showed signals due to vinyl protons of 2,4-diacetoxy-4'-vinylbenzophenone in the 5 to 6 ppm. range. However, signals due to impurities were also evident in the 1 to 2 ppm. range of the PMR spectrum. These impurities would have to be separated from the 2,4-diacetoxy-4'-vinylbenzophenone by liquid chromatography.

A dehydrobromination reaction was carried out on a larger scale with 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone (10 g.) and tributylamine at 140° for 60 minutes with nitrobenzene as both the solvent and polymerization inhibitor. The product was then saponified with sodium carbonate in aqueous methanol to form 2,4-dihydroxy-4'-vinylbenzophenone. It was not possible to remove all of the nitrobenzene by distillation at reduced pressure and it was therefore necessary to isolate the crude 2,4-dihydroxy-4'-vinylbenzophenone by extraction with an aqueous sodium carbonate solution. The

crude 2,4-dihydroxy-4'-vinylbenzophenone was then dissolved in ether to separate it from what was believed to be ether insoluble polymeric impurities. The PMR spectrum (see p. 250) of the product, which was isolated in a very low yield (10%), showed signals due to vinyl protons in the 5 to 6 ppm. range and a signal due to the ortho phenol proton at 12.6 ppm. Signals due to impurities were evident in the 1 to 2 ppm. range of the PMR spectrum. The 2,4-dihydroxy-4'-vinylbenzophenone would have to be further purified by liquid chromatography.

The dehydrobromination of the 1-bromoethyl group of 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone was attempted with strong bases such as potassium hydroxide and sodium t-butoxide. These reactions resulted in low yields of dark, impure products and a sizable amount of insoluble dark gels. The PMR spectra (see p. 248) of the soluble portion of these products showed broad signals. It was possible to obtain a very low yield of a crude product, which may have contained 2,4-dihydroxy-4'-vinylbenzophenone, by a potassium hydroxide dehydrobromination reaction. The PMR spectrum (see p. 248) showed signals in the 5 to 6 ppm. range characteristic of vinyl protons. Signals due to a large amount of nitrobenzene impurity are present in the 7.5 to 8.5 ppm. range.

A dehydrobromination reaction was unsuccessfully attempted with 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone

in pyridine at 35, 67, and 100°. After 25 hours at 35°, 25 minutes at 67°, and 20 minutes at 100°, the quartet of starting material at 5.0 to 5.4 ppm. ($-\text{CHBrCH}_3$) in the PMR spectra had disappeared and the solution had become very dark. After 72 hours at each of these temperatures, there was no evidence of vinyl protons in the 5 to 6 ppm. range (see p. 249) of the PMR spectra.

The dehydrobromination reaction was attempted with triethylamine and 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone in DMAc at 90°. The PMR spectrum of the dark solution did not show signals due to vinyl protons in the 5 to 6 ppm. range after $\frac{1}{2}$ and $1\frac{1}{2}$ hours. (See p. 249.) After 2 hours and 4 hours at 100° in nitrobenzene with triethylamine, the PMR spectra showed small broad signals in the 5 to 6 ppm. range that may have been due to vinyl protons. (See p. 249.)

Dehydrobromination reactions were attempted with lithium chloride²⁴⁵ and tetraethylammonium chloride²⁴⁶ respectively in DMF. Lithium chloride has been reported in the literature as useful for effecting dehydrobrominations in the presence of base sensitive groups such as acetates.²⁴⁵ After 36 hours at 100°, the PMR spectra (see p. 248) of the products of both reactions showed signals in the 5 to 6 ppm. range which may have been due to vinyl protons of 2,4-diacetoxy-4'-vinylbenzophenone. However,

the quartet of the starting material, 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone, was also present near 5 ppm. in the PMR spectrum. The integrated signal intensities of both reactions indicated that the conversion of 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone to 2,4-diacetoxy-4'-vinylbenzophenone had reached approximately 50%.

In conclusion, it was possible to obtain crude 2,4-dihydroxy-4'-vinylbenzophenone and 2,4-diacetoxy-4'-vinylbenzophenone by a dehydrobromination reaction of 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone with tributylamine in nitrobenzene or DMAc with picric acid as a polymerization inhibitor. The color of the solution of the dehydrobromination reaction with tributylamine was orange and not dark, as was the case with other strong bases such as potassium hydroxide, pyridine, triethylamine, and sodium t-butoxide. In spite of the polymerization inhibitors, a large amount of product was lost as ether insoluble impurities which may have been polymers and oligomers. The remaining impurities present in the crude 2,4-dihydroxy-4'-vinylbenzophenone and 2,4-diacetoxy-4'-vinylbenzophenone may have been dimers and trimers of the monomers. The 2,4-dihydroxy-4'-vinylbenzophenone and 2,4-diacetoxy-4'-vinylbenzophenone would have to be further purified by liquid chromatography.

4. Reactions of NBS with 2,4-dihydroxy-4'-ethylbenzophenone and its derivatives. An unsuccessful attempt was made to brominate the ethyl group of 2,4-dihydroxy-4'-ethylbenzophenone. The radical side chain bromination did not take place, but rather an aromatic substitution reaction on the phenol containing ring occurred. The PMR spectrum (see p. 245) of the crude product showed that three phenol proton signals were present in the 12.5 to 13.3 ppm. range and the integrated signal intensity of the aromatic protons had decreased from 7 to 6. The PMR spectrum also indicated that the ethyl group was unaffected by the reaction since its quartet and triplet were still present. No attempts were made to isolate or further characterize the product of the reaction.

An attempted side chain bromination of 2-hydroxy-4-methoxymethoxy-4'-ethylbenzophenone with NBS resulted in bromination of the aromatic ring and formation of a mixture of isomers as determined by PMR spectroscopy. The PMR spectrum (see p. 246) of the reaction solution showed four different phenol proton signals in the 12.3 to 13 ppm. range and four different methoxy proton signals in the 3.3 to 3.6 ppm. range. The integrated signal intensity for the aromatic protons between 6 and 7 ppm. was equivalent to 1.2 protons rather than 2 protons, which indicated that the ring had probably been brominated. The PMR spectrum also showed

that the ethyl group had not been converted to a 1-bromoethyl group since the quartet and triplet were still present. No attempts were made to isolate the product of the reaction.

An attempt had been made to synthesize 2,4-dimethoxymethoxy-4'-ethylbenzophenone. It was expected that the methoxymethoxy group would have been an effective base stable protecting group²⁴⁷ for the anticipated dehydrobromination of 2,4-dimethoxymethoxy-4'-(1-bromoethyl)benzophenone. However, the PMR spectrum (see p. 246) of the product, which was isolated after the reaction of 2,4-dihydroxy-4'-ethylbenzophenone and chloromethyl methyl ether, showed that it was 2-hydroxy-4-methoxymethoxy-4'-ethylbenzophenone and not the expected 2,4-dimethoxymethoxy-4'-ethylbenzophenone.

Bromination of the aromatic ring of 2,4-dihydroxy-4'-ethylbenzophenone and 2-hydroxy-4-methoxymethoxy-4'-ethylbenzophenone took precedence over the radical side chain bromination of the ethyl group with NBS. Evidently, the resonance donating phenol and phenyl ether groups activated the aromatic ring to aromatic electrophilic substitution. The phenol groups may have also inhibited the radical side chain bromination. Aromatic bromination with NBS is not unusual. For example, the reaction of NBS with resorcinol, 4-hydroxybenzoic acid, and 1,3-dimethoxybenzene reportedly gave 2,4,6 tribromoresorcinol, 3,5 dibromo-4-hydroxybenzoic

acid, and 4-bromo 1,3-dimethoxybenzene respectively.²⁴⁸ Chapman²⁴⁹ pointed out that impurities present in NBS enables it to affect bromination of aromatic rings.

As described earlier, 2,4-diacetoxy-4'-ethylbenzophenone was successfully brominated on the side chain with NBS to yield 2,4-diacetoxy-4'-(1-bromoethyl)benzophenone. Evidently, acetylating the phenol groups decreased their resonance donating ability and/or sterically hindered substitution on the aromatic ring since side chain bromination occurred rather than ring bromination.

Side chain bromination was unsuccessfully attempted on 2,4-di(trimethylsilyloxy)-4'-ethylbenzophenone with NBS. It could be seen from the PMR spectrum (see p. 246) of the reaction solution that the appearance of the signals of the ethyl protons had not changed. A signal was not present in the 5 to 6 ppm. range, which was expected for the 1-bromoethyl group (CHBrCH_3) of the product, and the aromatic protons between 6.2 and 6.5 ppm. were unchanged after one hour of reaction, which indicated that ring bromination had not occurred. It is possible that for some reason the NBS was unreactive. However, it was shown by carrying out a bromination reaction on toluene that the same NBS, AIBN, and CCl_4 were reactive. It had been expected that the base stable trimethylsilyloxy protecting groups could sterically hinder bromination of the aromatic ring and could be left

on the molecule during the subsequent dehydrobromination reaction of 2,4-di(trimethylsilyloxy)-4'-(1-bromoethyl)-benzophenone and radical polymerization of 2,4-di(trimethylsilyloxy)-4'-vinylbenzophenone. The protecting groups could then have been easily removed under slightly acidic conditions in the presence of water.²⁵⁰

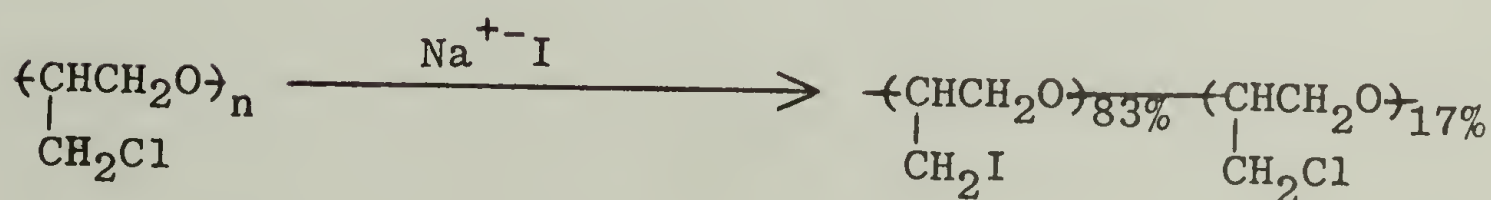
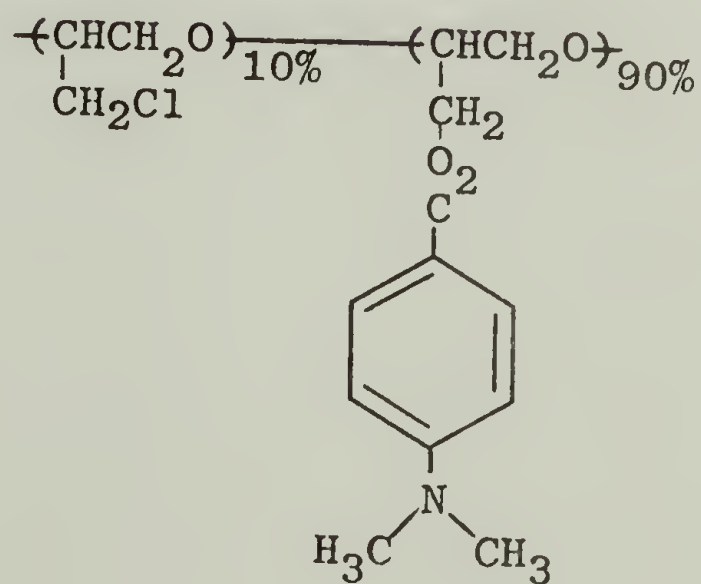
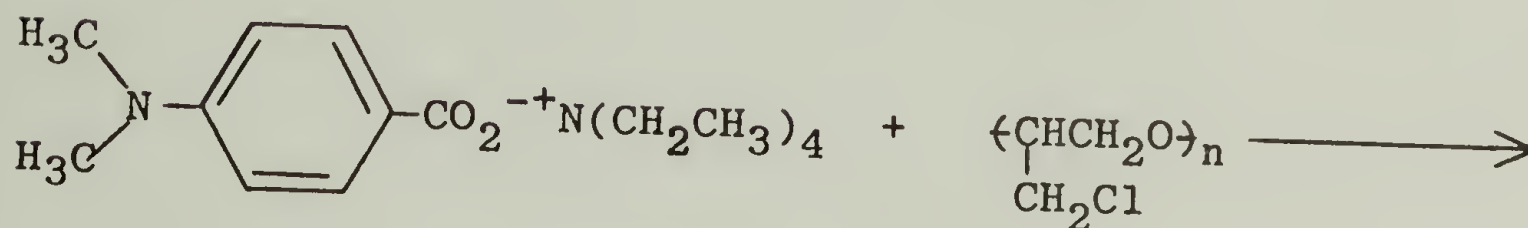
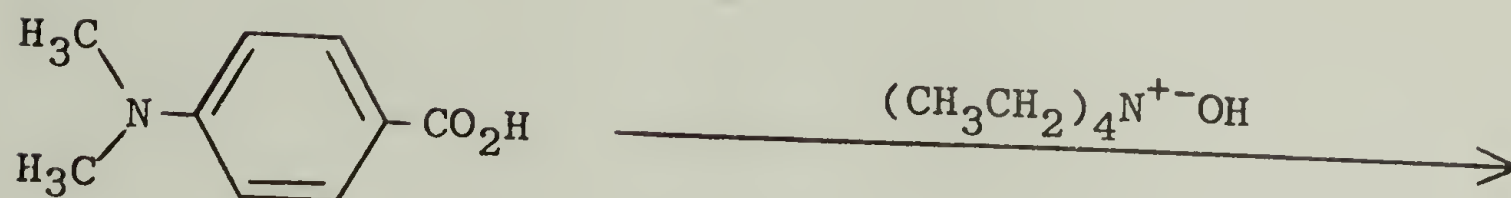
D. Poly(epichlorohydrin) Reactions

1. Introduction. Figure 7 summarizes the poly(epichlorohydrin) reactions that are discussed in this section.

Mild modification reactions on poly(epichlorohydrin) would be desirable in order to avoid side reactions, such as degradation, and subsequent polymer purification problems. As pointed out in the introduction, the alkylation of sodium or potassium salts of carboxylic acids with poly(epichlorohydrin)¹⁶² or poly(3,3-bis(chloromethyl)oxacyclobutane)¹⁹¹ at greater than 100° was reportedly accompanied by serious degradation reactions. Therefore, it was decided to utilize the much more reactive tetraalkylammonium salts of carboxylic acids rather than sodium or potassium salts for displacement reactions on poly(epichlorohydrin).

Wagenknecht²⁵¹ showed in a recent publication that tetraalkylammonium carboxylate salts, unlike sodium or potassium carboxylate salts, were very reactive with alkyl halides in polar aprotic solvents and could be used to form

FIGURE 7. Synthesis of Poly(epichlorohydrin) Derivatives.



esters under "mild" conditions. For example, the reaction of butyl chloride with tetraethylammonium acetate, which contained a few moles of water per mole of salt, reached 50% conversion in 6 hours at room temperature in DMF. The same reaction with butyl bromide reportedly reached 90% conversion in 30 minutes at room temperature. On the other hand, the reaction of butyl bromide with potassium acetate in DMF or DMSO reportedly required 2 hours at 90-100° to obtain a high yield of butyl acetate.²⁵²

In order to model the reaction of tetraalkylammonium carboxylate salts with poly(epichlorohydrin), the conversion vs. time data for the reaction of tetraethylammonium N,N-dimethyl-p-aminobenzoate and tetramethylammonium salicylate monohydrate with butyl chloride and 2-ethoxyethyl chloride at room temperature, 44°, and 54° were obtained. The reaction of tetraethylammonium N,N-dimethyl-p-aminobenzoate with 2-ethoxyethyl chloride reached 50% conversion in 7 hours at room temperature, which was similar to the data reported by Wagenknecht²⁵¹ for the reaction of tetraethylammonium acetate with butyl chloride. Tetramethylammonium salicylate monohydrate was much less reactive (15% conversion, 23 hours, 44°), probably because of hydrogen bonding by the ortho phenol group to the carboxylate anion.

A displacement reaction of tetraethylammonium

N,N-dimethyl-p-aminobenzoate dihydrate on poly(epichlorohydrin) was carried out at 55° for 30 hours to obtain a copolymeric UV absorber consisting of 90% glycidyl N,N-dimethyl-p-aminobenzoate repeat units and 10% epichlorohydrin repeat units. The reaction conditions for this high conversion displacement reaction were much milder than the reported displacement reactions of sodium or potassium cinnamate on poly(epichlorohydrin), which were generally carried out at 100° for 5 to 10 hours.¹⁶²

The UV spectra and thermal properties of the copolymers of epichlorohydrin and glycidyl N,N-dimethyl-p-aminobenzoate were measured.

An 83/17 copolymer of epiodohydrin and epichlorohydrin was prepared by a displacement reaction of sodium iodide on poly(epichlorohydrin). Subsequent displacement reactions were not carried out on the copolymer; however, it was believed that this copolymer would be much more reactive than poly(epichlorohydrin) with tetraalkylammonium carboxylates and could be used to attach UV absorbers or other compounds to the polymer under very mild conditions.

2. Model compound studies. The reaction of tetraethylammonium N,N-dimethyl-p-aminobenzoate and tetramethylammonium salicylate monohydrate with butyl chloride and 2-ethoxyethyl chloride. Tetraethylammonium N,N-dimethyl-p-aminobenzoate was prepared from tetraethylammonium hydroxide

and N,N-dimethyl-p-aminobenzoic acid. The salt initially melted at 64-67°; after heating at 70° in vacuo for 18 hours, the melting point of the salt increased to 117-120°. Elemental analysis and the number of grams per equivalent of salt, as determined by titration with perchloric acid in acetic acid, showed that the tetraethylammonium N,N-dimethyl-p-aminobenzoate (m.p. 117-120°) was anhydrous.

The anhydrous tetraethylammonium N,N-dimethyl-p-aminobenzoate became hydrated with 2 moles of water during 9 months of storage, as determined by PMR spectroscopy in deuterated DMSO. (See p. 251.) The hygroscopic salt had been stored in a screw-cap bottle which was left in a can containing calcium chloride. The can had been covered with a plastic cap. The PMR spectrum of the deuterated DMSO showed a very small peak at 3.25 due to water which could not account for the water (3.54 ppm.) found in the PMR spectrum of the salt. The tetraethylammonium N,N-dimethyl-p-aminobenzoate dihydrate melted at 67-71°

Tetraethylammonium N,N-dimethyl-p-aminobenzoate, which contained approximately 0.5 mole of water as determined by PMR spectroscopy (see p. 251), was also prepared. In this case, the salt was dried at reduced pressure (0.05 mm.) over phosphorous pentoxide at room temperature for 1 week rather than at elevated temperatures. The salt melted from 73 to 94° which was between the melting points of the dihydrate

(67-71°) and the anhydrous tetraethylammonium N,N-dimethyl-p-aminobenzoate (117-120°).

Tetramethylammonium salicylate monohydrate was prepared from salicylic acid and tetramethylammonium hydroxide. Extensive heating at reduced pressure (90°, 0.05 mm., 16 hours) could not remove the mole of water.

The presence of the small amounts of water in the above salts was not considered to be a serious problem.

Wagenknecht²⁵¹ reported that tetraethylammonium acetate, which was hydrated with a few moles of water, reacted rapidly with butyl bromide. However, he also pointed out that the rates of the displacement reactions were somewhat sensitive to the amounts of water present.

The reaction of tetraethylammonium N,N-dimethyl-p-aminobenzoate with 2-ethoxyethyl chloride in DMSO was followed by gas chromatography in order to verify the results of Wagenknecht and to determine conversion vs. time data for the reaction at elevated temperatures. The results of the experiments, which are presented in Tables 10 and 11 and Figure 8, show that the reaction is slow at room temperature but almost complete after 22 hours at 44°.

The displacement reaction of tetraethylammonium N,N-dimethyl-p-aminobenzoate dihydrate with butyl chloride at room temperature and at 54° was followed by PMR spectroscopy (see p. 252). At room temperature, the reaction conversion

was 50% and 65% after 4 hours and 21 hours respectively; at 54°, the reaction conversion was 75% and 100% after 4 hours and 21 hours respectively. The 2 moles of water in the tetraethylammonium N,N-dimethyl-p-aminobenzoate dihydrate did not appear to seriously hinder the reactivity of the N,N-dimethyl-p-aminobenzoate anion.

The displacement reactions of tetramethylammonium salicylate monohydrate with 2-ethoxyethyl chloride and butyl chloride were followed by GC and PMR (see p. 252) respectively and the results are presented in Table 12 and Figure 9. The displacement reactions were very slow as compared to the reaction of tetraethylammonium N,N-dimethyl-p-aminobenzoate with 2-ethoxyethyl chloride and butyl chloride. This was probably because the ortho phenol group hydrogen bonded to the carboxylate anion and decreased its reactivity.

The above model compound studies only approximated the reaction of the tetraalkylammonium salts of carboxylic acids with poly(epichlorohydrin). Nevertheless, it can certainly be stated that these reactions resulted in high conversions under much milder conditions than the reactions of sodium or potassium carboxylates with alkyl chlorides. Therefore, it was expected that displacement reactions on poly(epichlorohydrin) could be carried out under milder conditions (55°, 30 hours, DMF) than was reported for the reaction of

TABLE 10. GC Analysis of the Reaction of Tetraethylammonium
N,N-Dimethyl-p-aminobenzoate with 2-Ethoxyethyl
Chloride at Room Temperature.

<u>Time (hrs.)</u>	<u>Ratio^a (mm.)</u>	<u>Average Ratio (mm.)</u>	<u>Reaction Conversion</u>
0	5.3	6.0 ± 0.4	0%
	6.4		
	6.5		
	5.8		
3.8	3.8	3.7 ± 0.2	38%
	3.5		
	3.9		
7.4	2.8	3.0 ± 0.2	50%
	2.9		
	3.0		
	3.5		
26	1.5	1.4 ± 0.1	77%
	1.3		
	1.5		
50	1.0	1.0	83%

^a Ratio of 2-ethoxyethyl chloride peak area to DMSO peak height.

TABLE 11. GC Analysis of the Reaction of Tetraethylammonium
N,N-Dimethyl-p-aminobenzoate with 2-Ethoxyethyl
Chloride at 44°.

<u>Time (hrs.)</u>	<u>Ratio^a (mm.)</u>	<u>Average Ratio (mm.)</u>	<u>Reaction Conversion</u>
0	7.6	7.1 ± 0.3	0%
	7.2		
	7.0		
	6.6		
0.8	5.5	5.1 ± 0.4	28%
	5.2		
	4.5		
2.8	3.0	2.9 ± 0.1	59%
	2.7		
	3.0		
21.5	0.40	0.38 ± 0.02	94%
	0.40		
	0.35		

^a Ratio of 2-ethoxyethyl chloride peak area to DMSO peak height.

TABLE 12. GC Analysis of the Reaction of Tetramethylammonium Salicylate Monohydrate with 2-Ethoxyethyl Chloride at 44°.

<u>Time (hrs.)</u>	<u>Ratio^a (mm.)</u>	<u>Average Ratio (mm.)</u>	<u>Reaction Conversion</u>
0	9.1	8.6 ± 0.4	0%
	8.0		
	8.8		
0.9	8.7	8.2 ± 0.5	5%
	8.6		
	8.0		
	7.4		
23	7.2	7.4 ± 0.2	15%
	7.7		

^a Ratio of 2-ethoxyethyl chloride peak area to DMSO peak height.

FIGURE 8. Alkylation of Tetraethylammonium N,N-Dimethyl-p-aminobenzoate with Butyl Chloride and 2-Ethoxyethyl Chloride in DMSO.

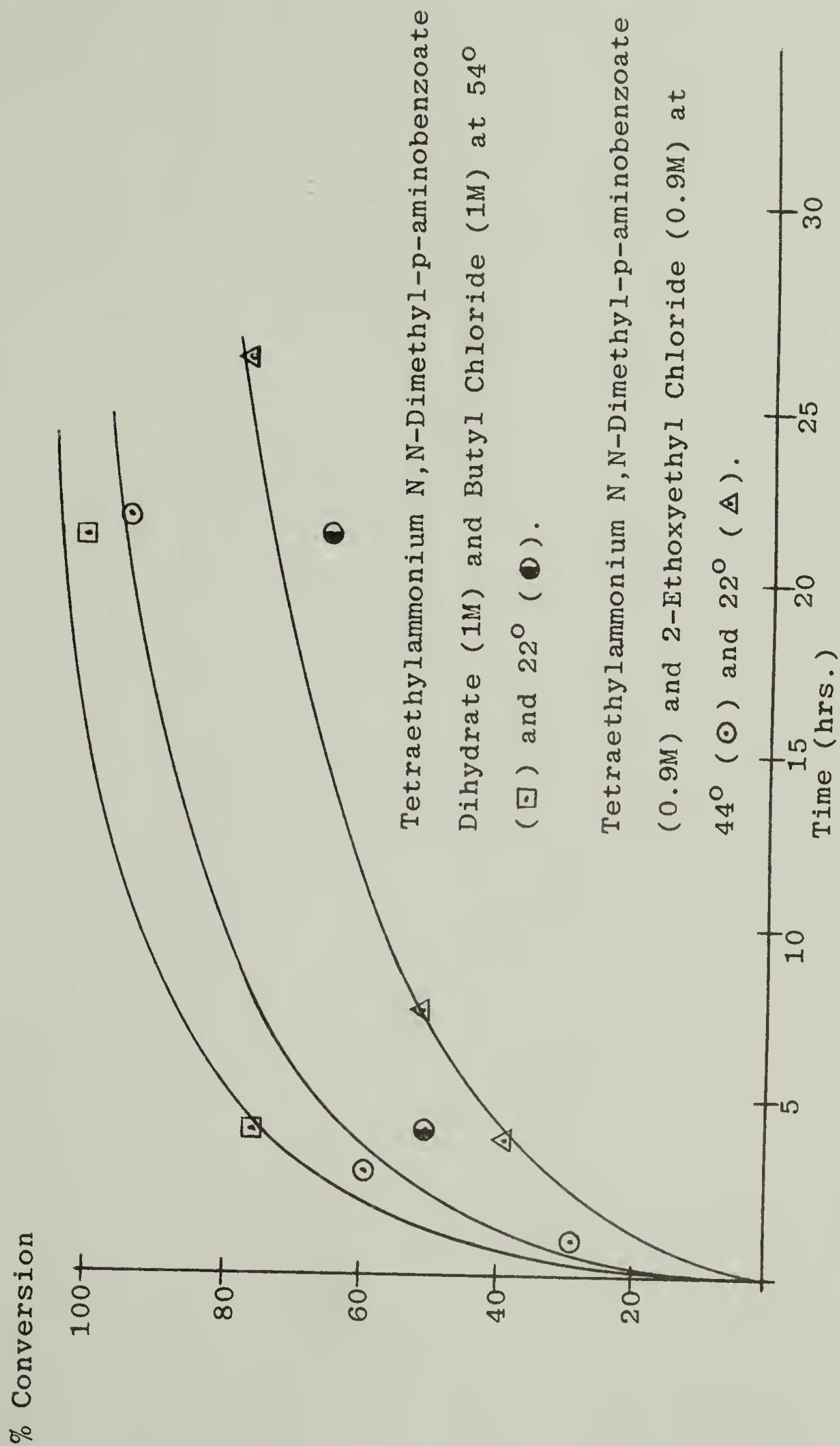
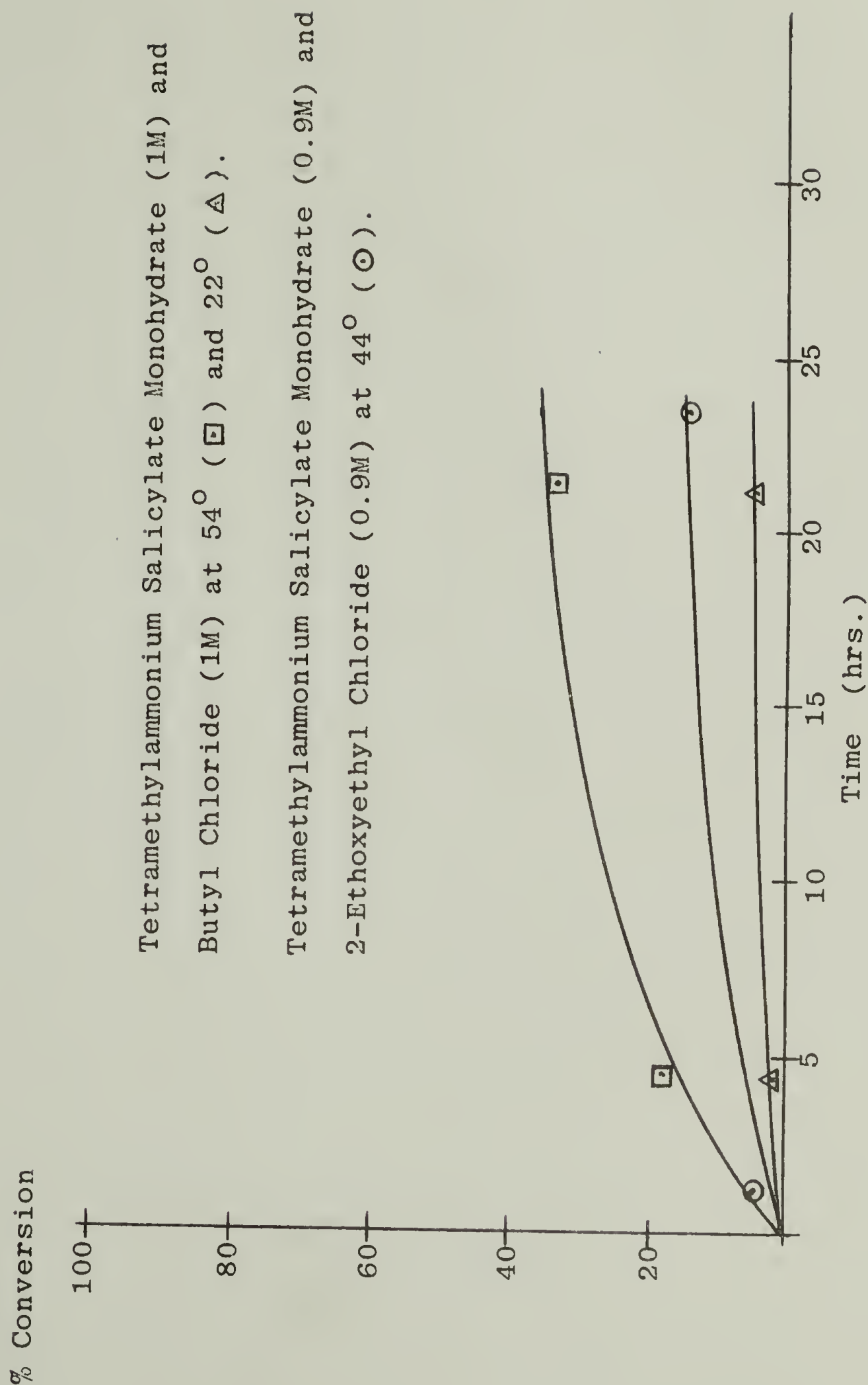


FIGURE 9. Alkylation of Tetramethylammonium Salicylate Monohydrate with Butyl Chloride and 2-Ethoxyethyl Chloride in DMSO.



sodium or potassium salts of carboxylic acids on poly(epichlorohydrin) and poly(3,3-bis(chloromethyl)oxacyclobutane) (100-130°, 10 hours, in DMSO, DMF, and HMPA).

3. The alkylation of tetraethylammonium N,N-dimethyl-p-aminobenzoate hemihydrate and dihydrate with poly(epichlorohydrin). A displacement reaction on poly(epichlorohydrin) was carried out with tetraethylammonium N,N-dimethyl-p-aminobenzoate hemihydrate in DMF at 55° for 30 hours. The product was completely soluble in chloroform and slightly discolored. The product was not soluble in DMSO; therefore, DMF was a superior solvent for this reaction.

The copolymer consisted of 90% glycidyl N,N-dimethyl-p-aminobenzoate repeat units and 10% epichlorohydrin repeat units as determined by PMR spectroscopy (see p. 253) with the following equation:

$$\frac{A}{B} = \frac{8x}{3x + 5y}$$

Where A = intensity of the methylene protons adjacent to the carboxylate group at 4.2 to 4.7 ppm. (21) plus the intensity of the N,N-dimethyl-amino protons at 2.7 ppm. (63).

B = intensity of the protons attached to the main chain carbon atoms and the methylene

protons adjacent to the chloride group at 3.4 to 4.1 (37).

x = mole fraction of glycidyl N,N-dimethyl-p-aminobenzoate repeat units.

y = mole fraction of epichlorohydrin repeat units.

$$\text{degree of substitution} = x = \frac{x/y}{x/y + 1}$$

The elemental analysis of the copolymer was calculated with the following equations:

$$\%C = 100 \frac{(144.12)x + (36.03)y}{(221.25)x + (92.53)y}$$

$$\%H = 100 \frac{(15.12)x + (5.04)y}{(221.25)x + (92.53)y}$$

$$\%N = 100 \frac{(14.01)x}{(221.25)x + (92.53)y}$$

$$\%Cl = 100 \frac{(35.46)y}{(221.25)x + (92.53)y}$$

The reaction of tetraethylammonium N,N-dimethyl-p-aminobenzoate dihydrate with poly(epichlorohydrin) in DMSO at 52° for 24 hours yielded a colorless polymer in which

75% (by PMR spectroscopy and elemental analysis) of the epichlorohydrin repeat units had been converted to glycidyl N,N-dimethyl-p-aminobenzoate repeat units.

Drying of the copolymers of glycidyl N,N-dimethyl-p-aminobenzoate and epichlorohydrin at elevated temperatures affected their solubility. The 75/25 copolymer was completely soluble in chloroform after the displacement reaction, but after the copolymer was dried at 78° for 24 hours in vacuo, it was no longer completely soluble in chloroform. The copolymer readily swelled to form a large number of small gel particles. Only 80% of the copolymer dissolved in DMF. It is possible that a crosslinking reaction occurred by quaternization of the N,N-dimethylamino groups of the glycidyl N,N-dimethyl-p-aminobenzoate repeat units with chloroalkyl groups of the epichlorohydrin repeat units during the drying at 78°. It was not possible to detect the ammonium salts, if they were present, by IR spectroscopy since quaternary ammonium salts do not have characteristic absorptions in the infrared.²⁵³ The 90/10 copolymer of glycidyl N,N-dimethyl-p-aminobenzoate and epichlorohydrin was soluble in chloroform after drying at 61° for 24 hours.

The infrared spectra (see p. 267) and absence of significant discoloration of the 90/10 and 75/25 copolymers of glycidyl N,N-dimethyl-p-aminobenzoate and epichlorohydrin

indicated that serious degradation side reactions had not occurred during the course of the displacement reactions. A chain scission side reaction leading to the formation of hydroxyl end groups had evidently not occurred since the infrared spectra of the copolymers did not show absorptions in the 3100 to 3500 cm^{-1} region. Minoura¹⁸⁷ reported that the displacement reaction of sodium acetate on poly(3,3-bis(chloromethyl)oxacyclobutane) at 130° was accompanied by a chain scission side reaction which led to the formation of hydroxyl end groups. Minoura also reported that the product of the reaction was brown.

The copolymers of glycidyl N,N-dimethyl-p-aminobenzoate and epichlorohydrin had much higher glass transitions than poly(epichlorohydrin) ($T_g = -17^\circ$). The 90/10 copolymer had a slightly higher glass transition (63° vs. 60°) than the 75/25 copolymer.

The UV spectra of the 90/10 and 75/25 copolymers of glycidyl N,N-dimethyl-p-aminobenzoate and epichlorohydrin showed absorptions at 309 to 310 nm. and 229 nm. which were characteristic of N,N-dimethyl-p-aminobenzoate ester groups. The 90/10 copolymer had a slightly higher extinction coefficient (104 $\text{l. g}^{-1} \text{ cm}^{-1}$, 309 nm.) than the 75/25 copolymer (103 $\text{l. g}^{-1} \text{ cm}^{-1}$, 310 nm.). As shown in Table 13, the molar extinction coefficients calculated for the glycidyl N,N-dimethyl-p-aminobenzoate repeat units were

TABLE 13. Ultraviolet Absorption Properties of N,N-Dimethyl-p-aminobenzoate Esters in 1,2-Dichloroethane.

<u>Compound</u>	<u>Extinction Coefficient</u>	<u>Molar Extinction Coefficient of the UV Absorbing Group (Wavelength nm)</u>
Methyl N,N-dimethyl-p-aminobenzoate	26.3×10^3 ^c	26.3×10^3 (310)
	7.31×10^3	7.31×10^3 (228)
Diethylene Glycol di-N,N-dimethyl-p-aminobenzoate ^a	53.8×10^3 ^c	26.9×10^3 (310)
	14.7×10^3	7.35×10^3 (229)
90/10 Copolymer ^b	104 ^d	24×10^3 (309)
	29.8	6.9×10^3 (229)
75/25 Copolymer ^b	103 ^d	26×10^3 (310)
	27.0	6.8×10^3 (229)

^a in methanol

^b Copolymer of glycidyl N,N-dimethyl-p-aminobenzoate and epichlorohydrin.

^c $1. \text{ mole}^{-1} \text{ cm.}^{-1}$,

^d $1. \text{ g.}^{-1} \text{ cm.}^{-1}$

both somewhat lower than the molar extinction coefficients of methyl N,N-dimethyl-p-aminobenzoate or diethylene glycol di-N,N-dimethyl-p-aminobenzoate.

In conclusion, the reaction of poly(epichlorohydrin)

in DMF with tetraethylammonium N,N-dimethyl-p-aminobenzoate, which was hydrated with a small amount of water, gave a product with a high degree of substitution (90 mole %, 96 wt. %). Unlike the esters of poly(3,3-bis(chloromethyl)-oxacyclobutane) prepared by Minoura,¹⁸⁷ the copolymers of glycidyl N,N-dimethyl-p-aminobenzoate and epichlorohydrin were not brown, but nearly colorless, and the infrared spectra did not show hydroxyl end groups which could have formed by chain scission side reactions. The effect of reaction time and temperature on molecular weight of the copolymers was not investigated.

4. Reaction of poly(epichlorohydrin) with sodium iodide. It is known that alkyl bromides react much more rapidly than alkyl chlorides at room temperature with tetraalkylammonium salts of carboxylic acids.²⁵¹ It is also known that iodides are much better leaving groups in nucleophilic displacement reactions than either chloride or bromide. Therefore, it was expected that poly(epiodohydrin) would be a much more reactive polymeric substrate than poly(epichlorohydrin).

The preparation of poly(epiodohydrin) was attempted by a 48 hour Finkelstein reaction of sodium iodide on poly(epichlorohydrin) in refluxing methyl ethyl ketone. The product of the Finkelstein reaction consisted of 83% epiodohydrin repeat units and 17% epichlorohydrin repeat

units as determined by elemental analysis with the following equations:

$$\%C = 100 \cdot \frac{(36.03)y + 36.03(x)}{(92.53)y + 183.98(x)}$$

and

$$\frac{\text{milliequiv. halogen}}{\text{g.}} = \left(\frac{Y_w}{92.53} + \frac{X_w}{183.98} \right) 1000$$

$$\text{and} \quad \frac{X_w}{Y_w} \cdot \frac{92.53}{183.98} = \frac{x}{y}$$

$$\text{degree of substitution} = x = \frac{x/y}{x/y + 1}$$

Where x = mole fraction of epiodohydrin repeat units.

y = mole fraction of epichlorohydrin repeat units.

X_w = weight fraction of epiodohydrin repeat units.

Y_w = weight fraction of epichlorohydrin repeat units.

The colorless, tacky copolymer of epiodohydrin and epichlorohydrin was further characterized by PMR and IR spectroscopy, DSC, VPO, solution viscosity, and density measurements. The PMR spectrum of the product, as compared

to the PMR spectrum (see p. 254) of poly(epichlorohydrin), showed that the signal at 3.58 ppm. (CH_2Cl) had decreased and a new signal had appeared at 3.35 ppm. (CH_2I). The poor peak separation prevented a calculation of copolymer composition from the integrated signal intensity. The infrared spectrum of the copolymer of epiodohydrin and epichlorohydrin did not show absorptions due to carbonyl or hydroxyl groups which could have formed due to polymer degradation reactions. The copolymer did show an absorption at 500 cm^{-1} (C-I stretching)²⁵⁴ which was not present in the poly(epichlorohydrin) infrared spectrum (see p. 265, 266). The inherent viscosity of the copolymer was much lower than that of poly(epichlorohydrin). Nevertheless, the molecular weight of the product (by VPO) was greater than 20,000. The density of the 83/17 copolymer was greater than 2 g./ml. The density of poly(epichlorohydrin) was reported to be 1.36 g./ml.²³¹ (The higher density is not surprising since alkyl iodides have greater densities than their corresponding alkyl chlorides. For example, the densities of iodobutane and chlorobutane are 1.61 and 0.89 respectively.) The glass transition of the 83/17 copolymer was 27° higher than that of poly(epichlorohydrin) (10° vs. -17°).

5. Potential applications and future work. In order to prepare an alcohol soluble polymeric ultraviolet absorber

from poly(epichlorohydrin), it would be necessary to further substitute the polymer with tetraalkylammonium salts of carboxylic acids which contain alcohol groups or other solubilizing groups. For example, a displacement reaction could be carried out on the sodium salt of bromoacetic acid with the monosodium salts of ethylene glycol, diethylene glycol, or triethylene glycol. A displacement reaction could then be carried out on poly(epichlorohydrin) or poly(epiiodohydrin) with the tetraalkylammonium salts of these carboxylic acids and tetraethylammonium N,N-dimethyl-p-aminobenzoate to yield what could be an alcohol soluble polymeric ultraviolet absorber.

Other compounds besides ultraviolet absorbers, which contain the appropriate functionality and a carboxylic acid group, could be attached to poly(epichlorohydrin) or a copolymer of epichlorohydrin and epiiodohydrin. It is expected that the epiiodohydrin repeat units of the copolymer of epiiodohydrin and epichlorohydrin would be very reactive with tetraalkylammonium salts of carboxylic acids. It may be possible to obtain a high degree of substitution on the polymer in a matter of minutes at room temperature in polar aprotic solvents.

It would be interesting to determine the effect of catalysts such as tetraalkylammonium iodides or tetraalkylammonium bromides on the reaction of tetraalkylammonium

carboxylates with poly(epichlorohydrin). The effects of reaction time and catalysts, such as tetramethylammonium iodide, on the degree of substitution and polymer molecular weight in the conversion of poly(epichlorohydrin) to poly(epiiodohydrin) could also be studied.

The displacement reactions discussed above could be applied to poly(3,3-bis(chloromethyl)oxacyclobutane) or copolymers of ethyleneoxide and epichlorohydrin.

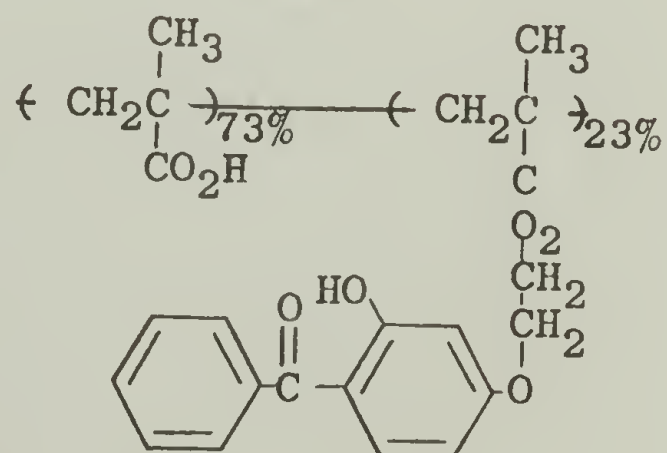
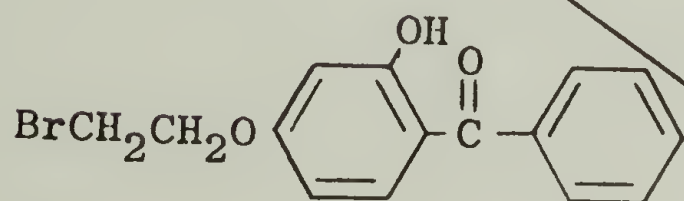
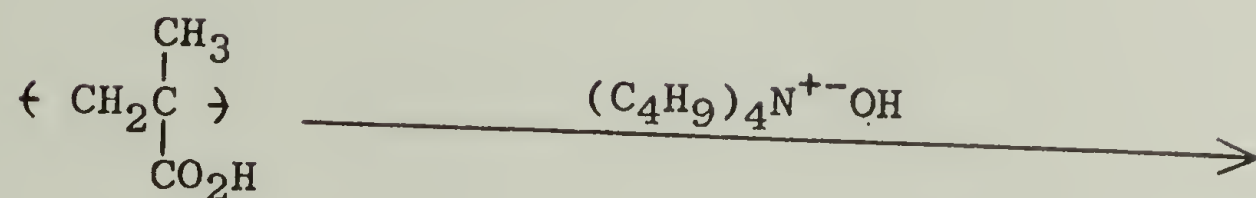
An alternate approach for preparing glycidyl esters is the reaction of poly(glycidol) with acid chlorides. This reaction is limited if the compound which contains the carboxylic acid group also contains a hydroxyl group. Therefore, displacement reactions on poly(epihalohydrins) would be particularly useful for preparing polymeric esters of carboxylic acids which also contain alcohol groups.

E. Displacement Reactions of Poly(tetrabutylammonium methacrylate)

1. Introduction. The reactions discussed in this section are presented in Figure 10.

The mild reaction of tetraalkylammonium salts of carboxylic acids with alkyl bromides (90% conversion, room temperature, 30 minutes) was used in the preparation of esters of poly(methacrylic acid). The advantage of this reaction, as in the poly(epichlorohydrin) reaction, is that

FIGURE 10. Synthesis of Poly(methacrylic acid) Derivatives.



compounds, such as 4-(2-bromoethoxy)-2-hydroxybenzophenone, which contain a primary alkyl bromide group could be selectively esterified in the presence of alcohol or phenol groups. This might not be possible in the esterification of poly(methacrylyl chloride) and 4-(2-hydroxyethoxy)-2-hydroxybenzophenone.

Poly(tetrabutylammonium methacrylate) was alkylated with butyl bromide. The poly(butyl methacrylate) contained very few, if any, unreacted methacrylic acid repeat units as determined by elemental analysis and infrared spectroscopy.

Poly(tetrabutylammonium methacrylate) was partially alkylated with 4-(2-bromoethoxy)-2-hydroxybenzophenone to yield a 73/27 copolymer of methacrylic acid and 2-hydroxy-4-(2-methacryloxyethoxy)benzophenone. The composition of the copolymer was determined by PMR spectroscopy.

2. Alkylation of poly(tetrabutylammonium methacrylate) with butyl bromide and 4-(2-bromoethoxy)-2-hydroxybenzophenone. Poly(tetrabutylammonium methacrylate) was prepared from tetrabutylammonium hydroxide and poly(methacrylic acid). Since the polymeric salt was soluble in DMSO, this solvent was used for the displacement reactions. Poly(tetramethylammonium methacrylate), which was prepared from tetramethylammonium hydroxide and poly(methacrylic acid), was insoluble in DMAc or DMSO, but soluble in methanol. This limits the

utility of this polymeric salt as a reagent. Polar aprotic solvents, such as DMSO or DMAc, do not hydrogen bond to nucleophiles and are therefore superior to protic solvents for displacement reactions. Protic solvents, such as methanol, do hydrogen bond and thereby hinder the reactivity of the nucleophile.²⁵⁵

The feasibility of the polymeric displacement reaction was tested by carrying out a reaction on butyl bromide with poly(tetrabutylammonium methacrylate) at room temperature for 24 hours. (The polymeric salt probably contained some water; however, tetraethylammonium acetate, which reportedly reacted very rapidly with butyl bromide (90%, 30 min., room temperature) was also hydrated with a few moles of water.²⁵¹ Therefore, no attempts were made to dehydrate the polymeric salt.) The infrared spectrum (see p. 268) of the product was identical to the published infrared spectrum of poly-(butyl methacrylate).²¹⁰ The elemental analysis indicated that the degree of substitution was very high; however, elemental analysis also revealed that a small amount of nitrogen and bromine containing impurities were present in the polymer. Nevertheless, it was possible to obtain a high degree of substitution with poly(tetrabutylammonium methacrylate) under very mild conditions.

A copolymer of methacrylic acid and 2-hydroxy-4-(2-methacryloxyethoxy)benzophenone was prepared by the reaction

of poly(tetrabutylammonium methacrylate) with 28 mole % of 4-(2-bromoethoxy)-2-hydroxybenzophenone at room temperature for 24 hours. The infrared spectrum of the product showed a peak at 1600 cm^{-1} which indicated that the 2-hydroxybenzophenone group had been incorporated into the polymer. The 1600 cm^{-1} peak was not present in poly(methacrylic acid) but was present in 4-(2-bromoethoxy)-2-hydroxybenzophenone. See p. 269. The copolymer consisted of 27 mole % 2-hydroxy-4-(2-methacryloxyethoxy)benzophenone and 73% methacrylic acid as determined by PMR spectroscopy (see p. 243) with the following equation:

$$\frac{\text{UV}}{\text{backbone}} = \frac{12x}{5x + 5y}$$

$$x = \frac{x/y}{x/y + 1} = 0.27$$

Where UV = integrated signal intensity of the aromatic protons and the methylene protons of the UV absorbing repeat units (33).

backbone = integrated signal intensity of the protons attached to the main chain carbon atoms and the methyl protons (51).

x = mole fraction of 2-hydroxy-4-(2-methacryloxyethoxy)benzophenone repeat units.

y = mole fraction of methacrylic acid repeat units.

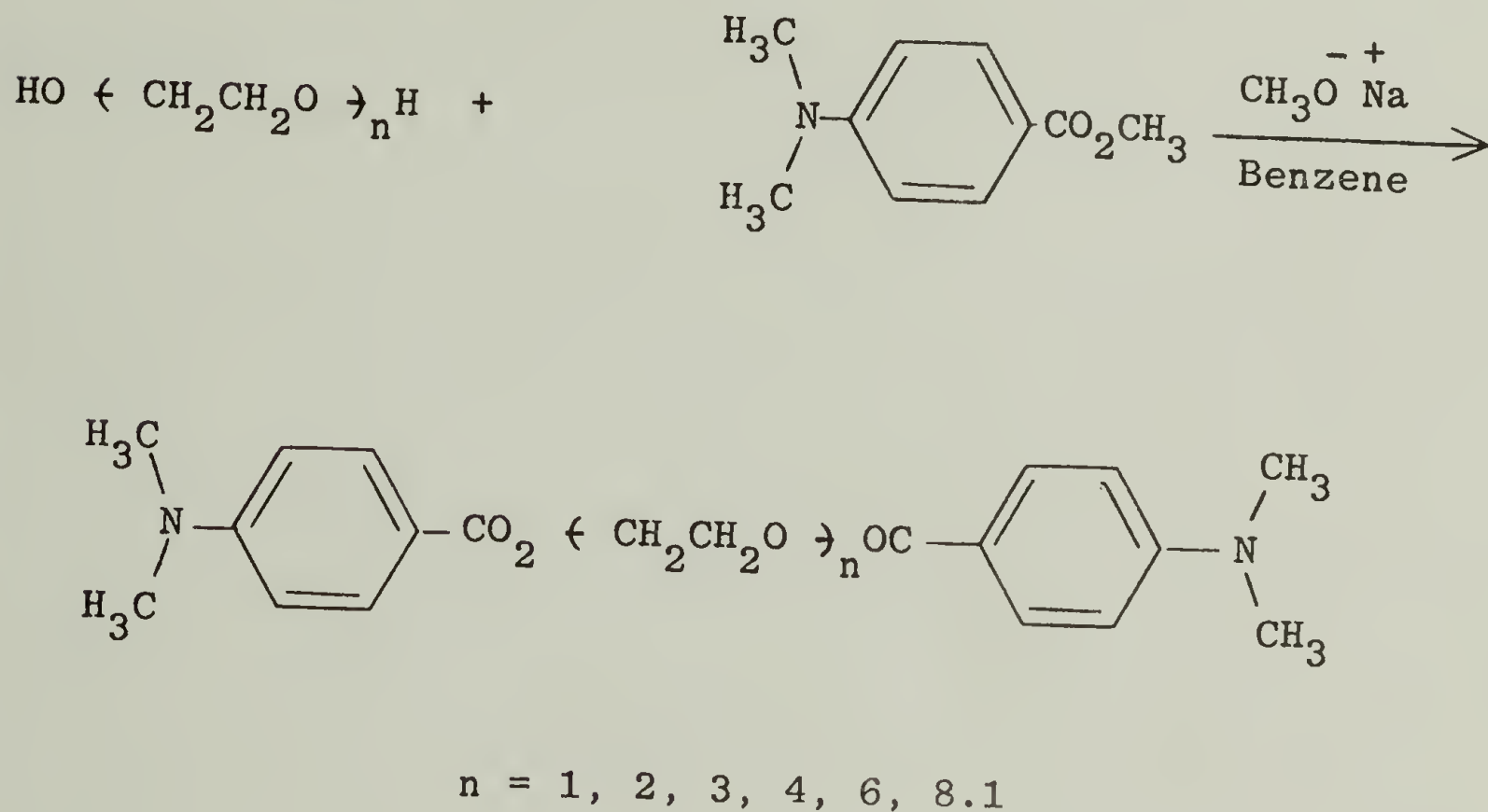
The ultraviolet spectrum of the product showed the characteristic absorptions of the 2-hydroxybenzophenone group²⁴⁴ at 327, 287, and 243 nm. Since the copolymer was 27 mole % (58 weight %) 2-hydroxy-4-(2-methacryloxyethoxy)benzophenone repeat units, the molar extinction coefficients of the UV absorbing repeat units were 9.3×10^3 , 15×10^3 , and 10×10^3 l. mole⁻¹ cm.⁻¹ at 327, 287, and 243 nm. respectively. These values are slightly lower than the molar extinction coefficients of 4-(2-bromoethoxy)-2-hydroxybenzophenone which were 9.69×10^3 , 15.8×10^3 , and 10.9×10^3 l. mole⁻¹ cm.⁻¹ at 326, 286, and 242 nm. respectively.

Attempts to purify the product to a point where the carbon and hydrogen analysis agreed with the values which were calculated were not successful.

F. Synthesis of Diesters of Oligo(oxyethylenes)

1. Oligo(oxyethylene) di-N,N-dimethyl-p-aminobenzoates.

FIGURE 11. Synthesis of Oligo(oxyethylene) Di-N,N-dimethyl-p-aminobenzoates.



Oligo(oxyethylenes) varying in molecular weight from 62 to 400 were endcapped with N,N-dimethyl-p-aminobenzoate ester groups by a 3 hour, sodium methoxide catalyzed, ester interchange reaction of the oligo(oxyethylene) with methyl N,N-dimethyl-p-aminobenzoate in refluxing benzene. The method of Roelofsen²¹⁴ was used to remove the methanol from the reaction medium as it formed and thereby shift the equilibrium to obtain a high reaction conversion. As the

methanol formed, it was continuously distilled with the benzene into a soxhlet extractor which contained molecular sieves. The sieves absorbed the methanol from the benzene and the methanol free benzene then returned to the reaction flask. The soxhlet extractor chamber, which contained the molecular sieves, was modified by fitting it with a water cooling jacket. It was pointed out by Roelofsen that adsorption of methanol by sieves, except 3A sieves, is stronger at lower temperatures.

Another possible method to remove the methanol as it formed and thereby shift the equilibrium would have been to distill the benzene and methanol from the reaction mixture. The reaction equilibrium could also have been shifted by using a large excess of oligo(oxyethylene). However, since the diester was the desired product, it was necessary to use an excess of methyl N,N-dimethyl-p-amino-benzoate.

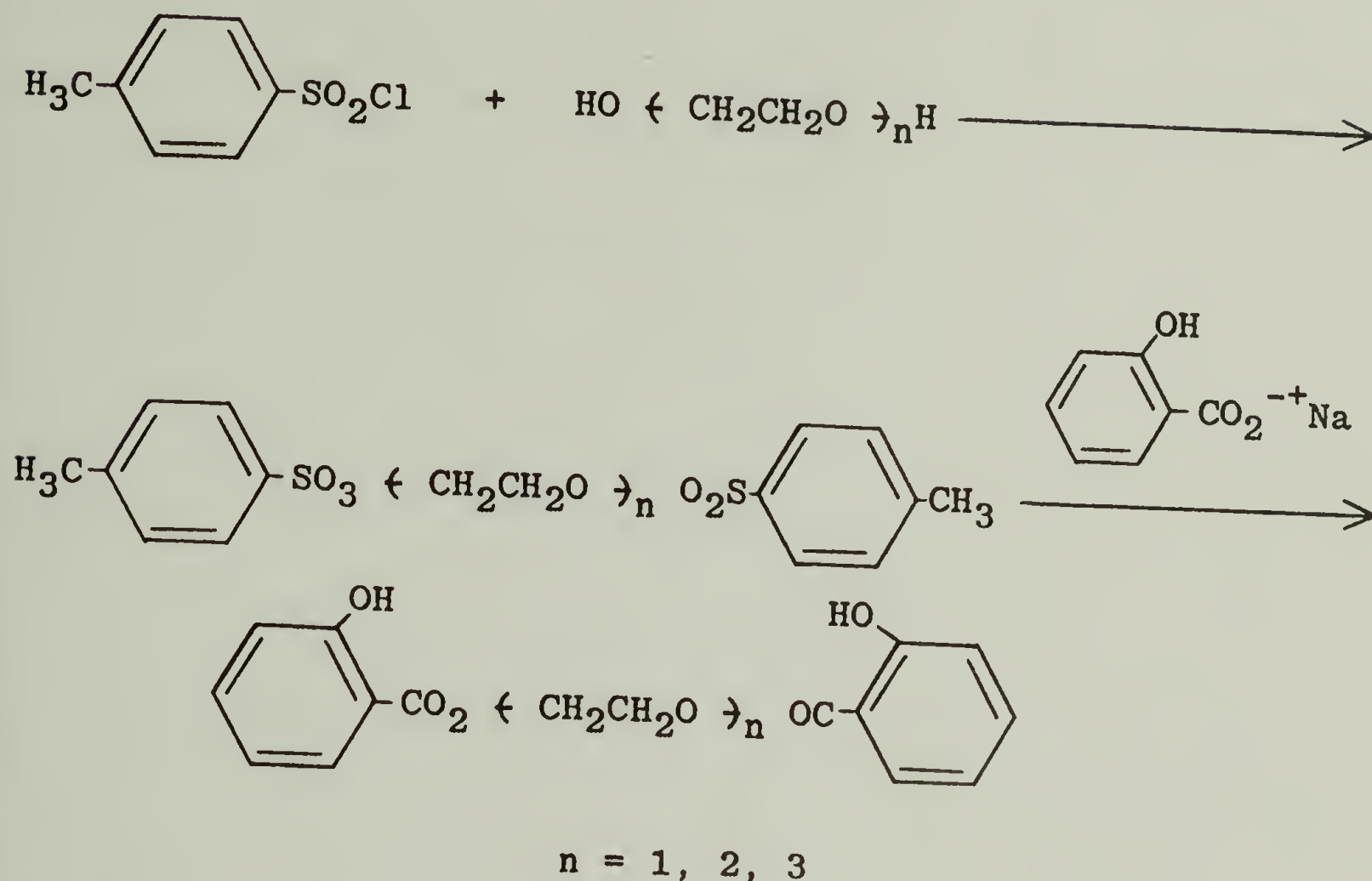
The infrared, PMR, and UV spectra of the diethylene glycol, triethylene glycol, tetraethylene glycol, poly(oxyethylene) (MW 300), and poly(oxyethylene) (MW 400) di-N,N-dimethyl-p-aminobenzoates were all similar. The infrared spectrum of poly(oxyethylene) (MW 400) di-N,N-dimethyl-p-aminobenzoate showed the presence of a small amount of water. The UV data are presented in Table 14. All of the diesters, except ethylene glycol di-N,N-

dimethyl-p-aminobenzoate, were soluble in 95% ethanol.

A number of procedures had been considered for the preparation of oligo(oxyethylene) di-N,N-dimethyl-p-aminobenzoates. A displacement reaction of potassium N,N-dimethyl-p-aminobenzoate on ethylene dibromide or ethylene di-p-toluenesulfonate, the esterification of ethylene glycol with N,N-dimethyl-p-aminobenzoic acid, and the esterification of ethylene glycol in pyridine with N,N-dimethyl-p-aminobenzoyl chloride were all investigated. It was believed that the most convenient procedure for the preparation of di-N,N-dimethyl-p-aminobenzoates of oligo(oxyethylenes) was by an ester interchange reaction with methyl N,N-dimethyl-p-aminobenzoate. The methyl ester was much easier to prepare, purify, and handle than N,N-dimethyl-p-aminobenzoyl chloride. The displacement reactions with potassium N,N-dimethyl-p-aminobenzoate required the prior preparation of oligo(oxyethylene) dibromides or di-p-toluenesulfonates. The ester interchange reaction, on the other hand, could be carried out directly on the oligo(oxyethylenes). Esterification of the diols with excess N,N-dimethyl-p-aminobenzoic acid was not feasible due to the insolubility of the acid in benzene and toluene.

2. Oligo(oxyethylene) disalicylates.

FIGURE 12. Synthesis of Oligo(oxyethylene) Disalicylates.



The disalicylates of ethylene glycol, diethylene glycol, triethylene glycol, and tetraethylene glycol were prepared by a sodium salicylate displacement reaction on the corresponding di-*p*-toluenesulfonates in DMAc for 4.5 hours at 75° or 20 hours at 65°. The progress of some of the displacement reactions were monitored by PMR spectroscopy. The decrease in the integrated signal intensity of the methyl protons at 2.48 ppm. of the *p*-toluenesulfonate group and the increase in the integrated signal intensity of the phenol proton at 10.48 ppm. of the

salicylate group was followed. The results are presented in Figure 13.

The infrared, PMR, and UV spectra of the ethylene glycol, diethylene glycol, and triethylene glycol disalicylates were all similar. The UV data are presented in Table 14.

A second procedure investigated for the preparation of disalicylates was the direct esterification of triethylene glycol with salicylic acid and p-toluenesulfonic acid as the catalyst in refluxing toluene. This technique was less satisfactory since it required approximately 4 days to reach a high conversion. The displacement reaction required only 4 to 5 hours at 75°.

FIGURE 13. Alkylation of Sodium Salicylate with Oligo(oxyethylene)
Di-p-toluenesulfonates.

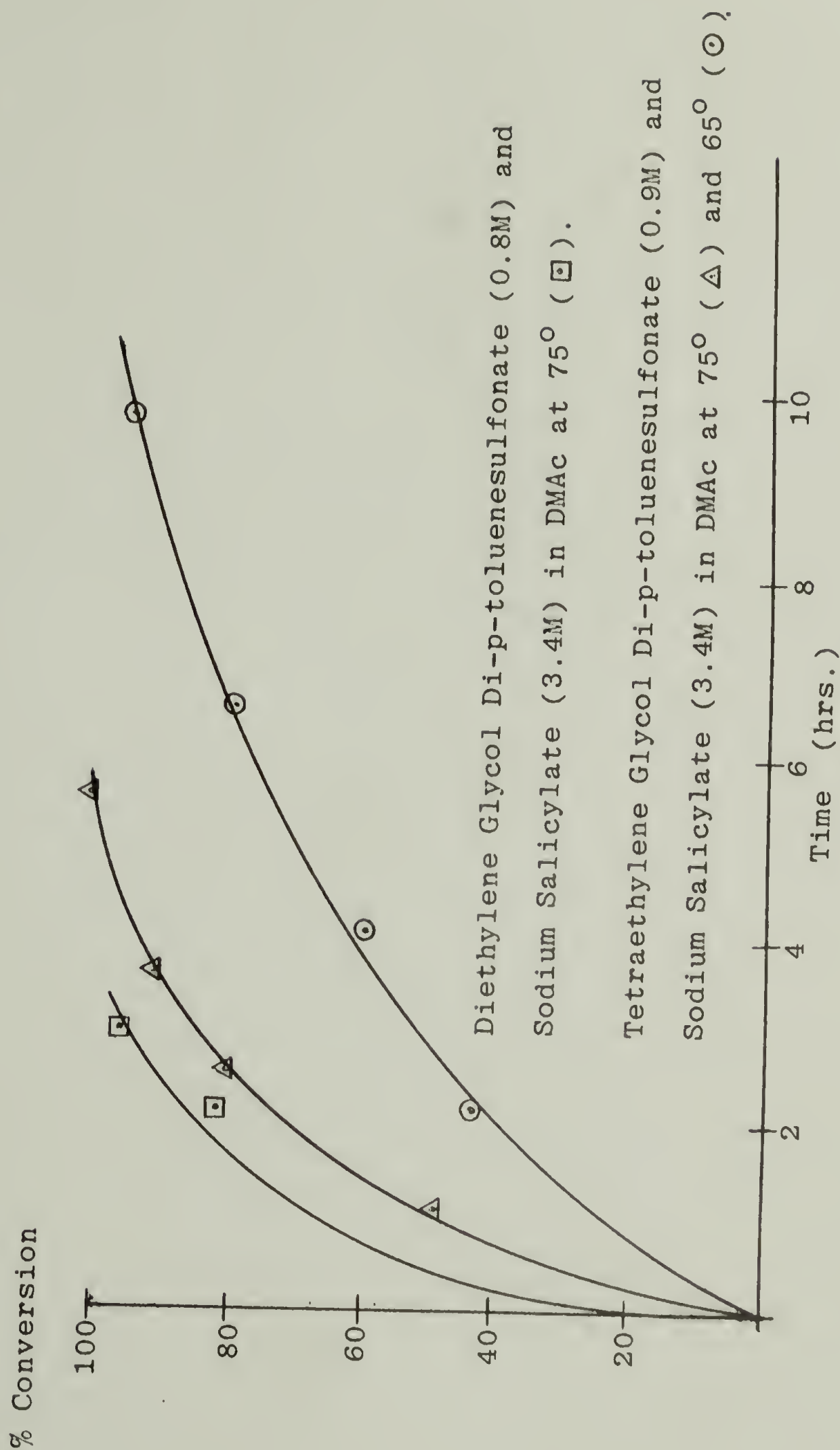
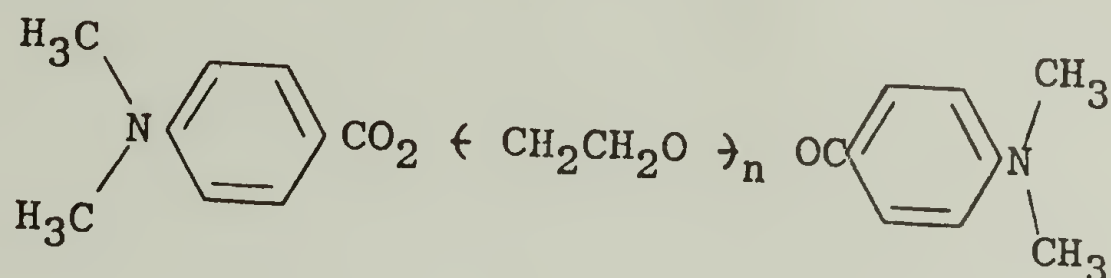
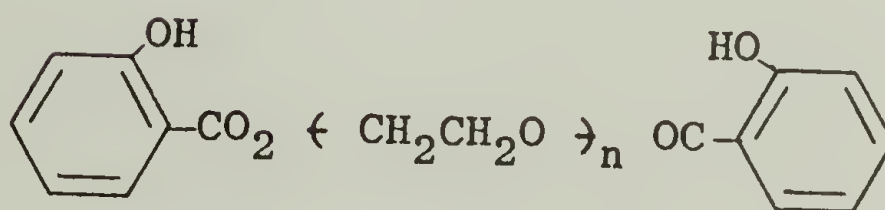


TABLE 14. Ultraviolet Absorption Properties of Oligo-(oxyethylene) Di-N,N-dimethyl-p-aminobenzoates and Disalicylates.



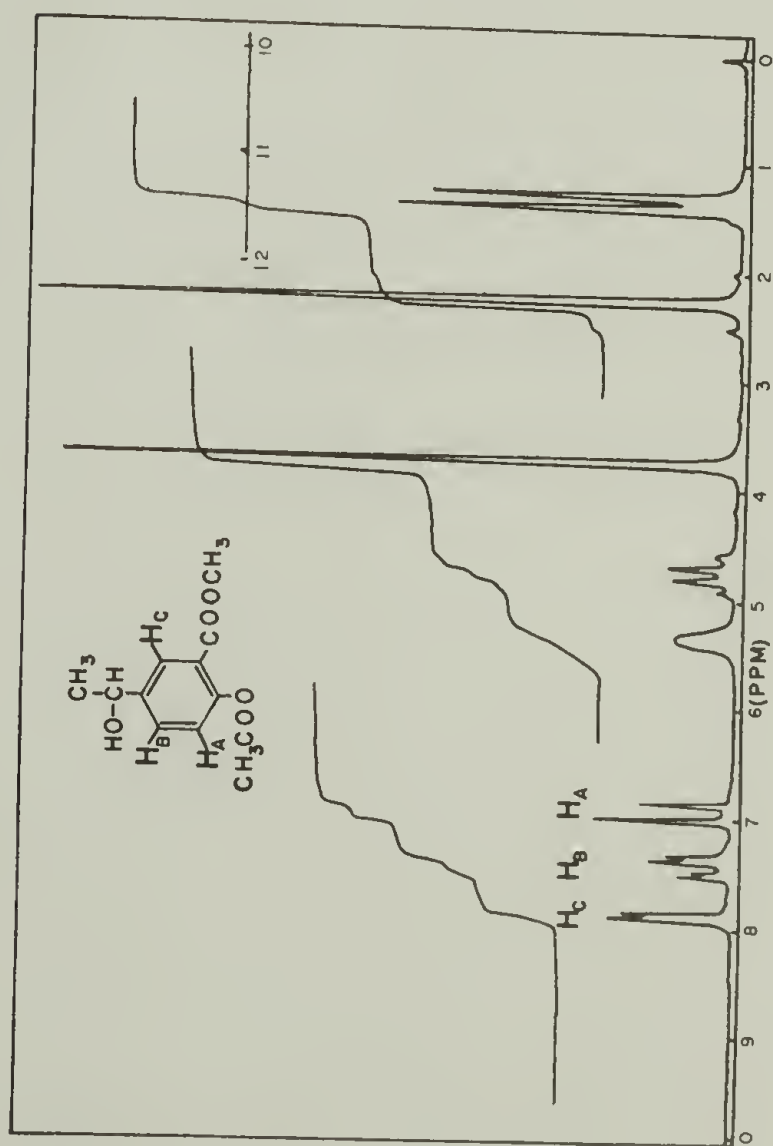
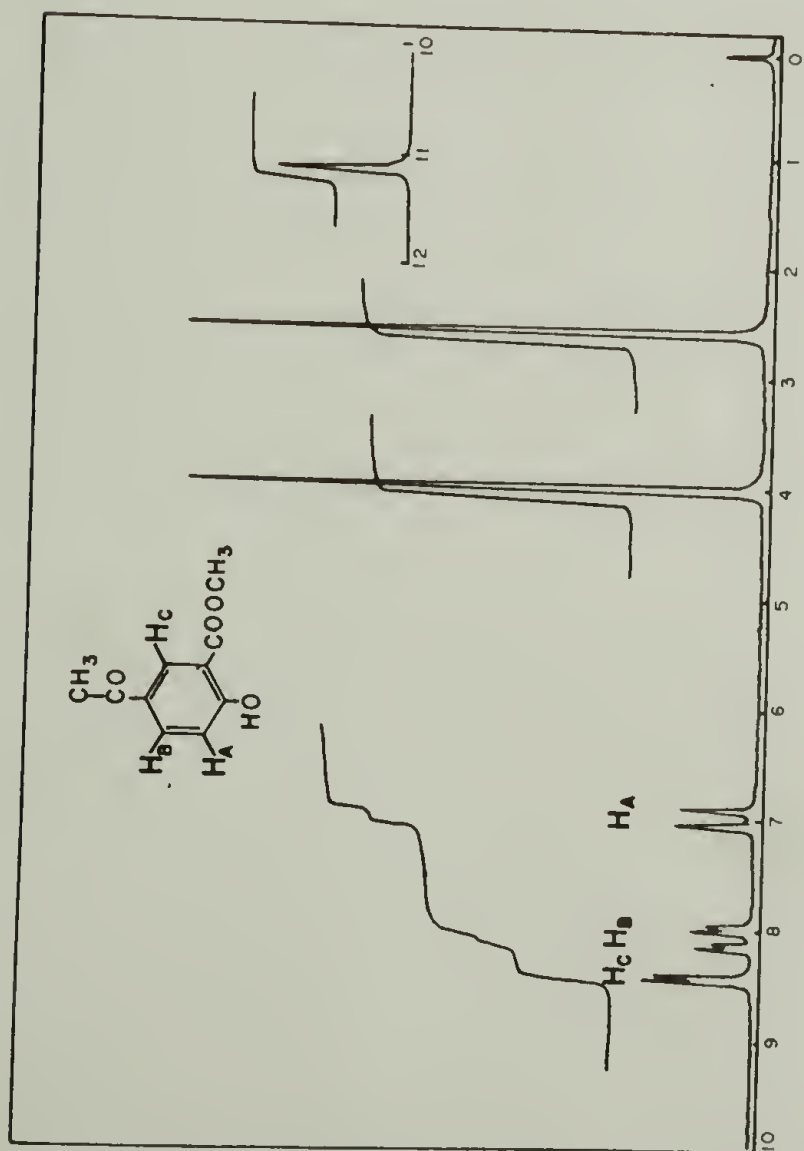
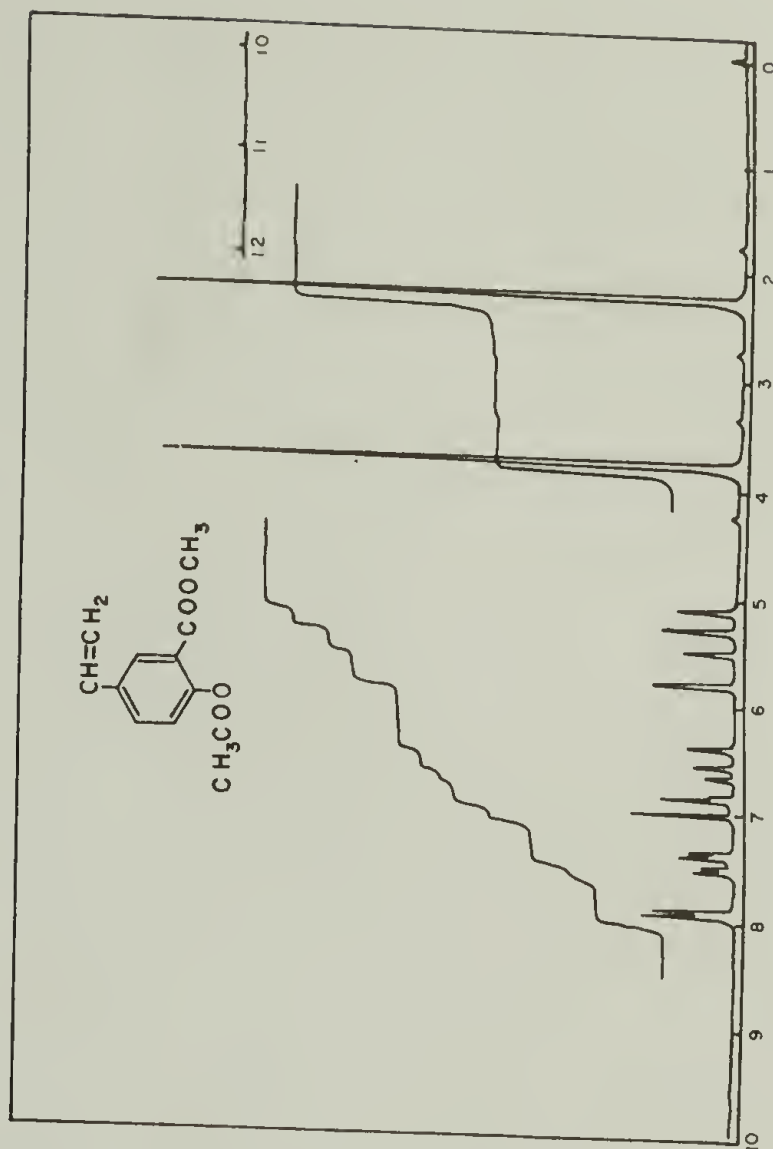
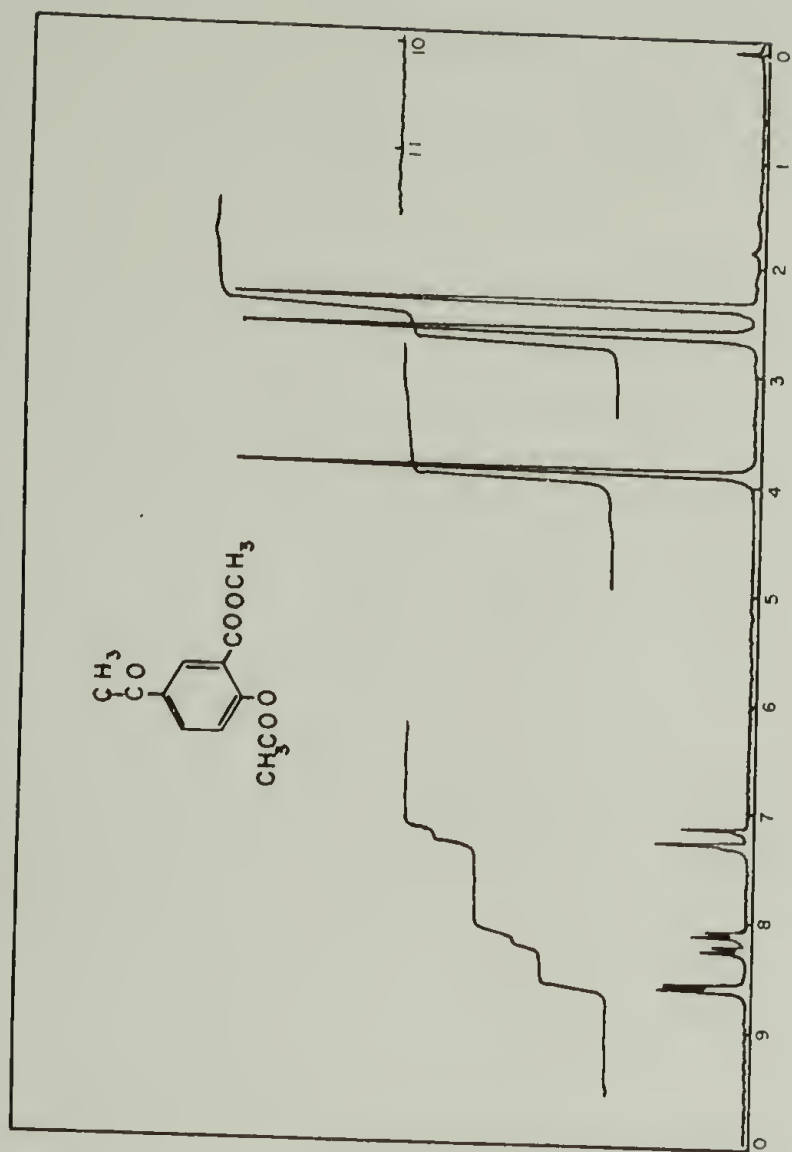
<u>n</u>	<u>E(1. mole⁻¹ cm.⁻¹)</u>	<u>λ(nm.)</u>
2	14.7 x 10 ³ 53.8 x 10 ³	229 310
3	14.8 x 10 ³ 56.8 x 10 ³	229 310
4	14.2 x 10 ³ 56.3 x 10 ³	229 310
$\bar{M}_n = 574$	14.4 x 10 ³ 53.4 x 10 ³	229 310
$\bar{M}_n = 666$	15.2 x 10 ³ 55.6 x 10 ³	229 310

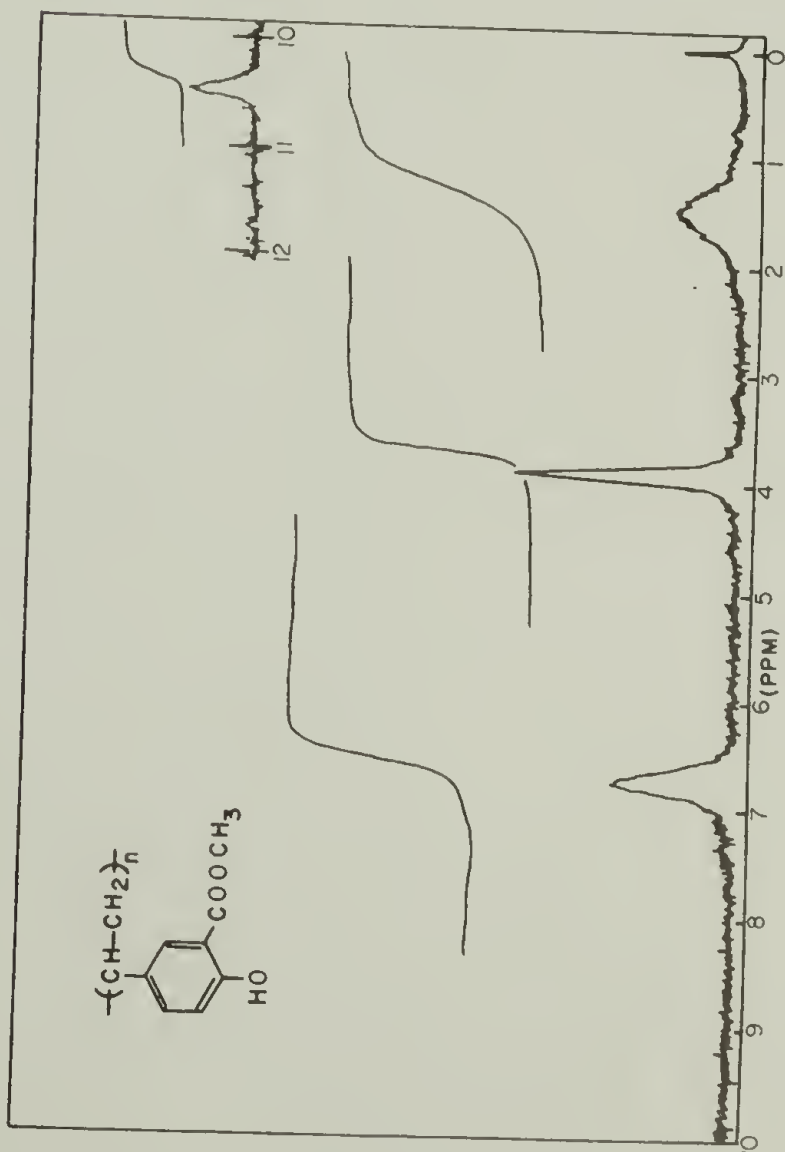
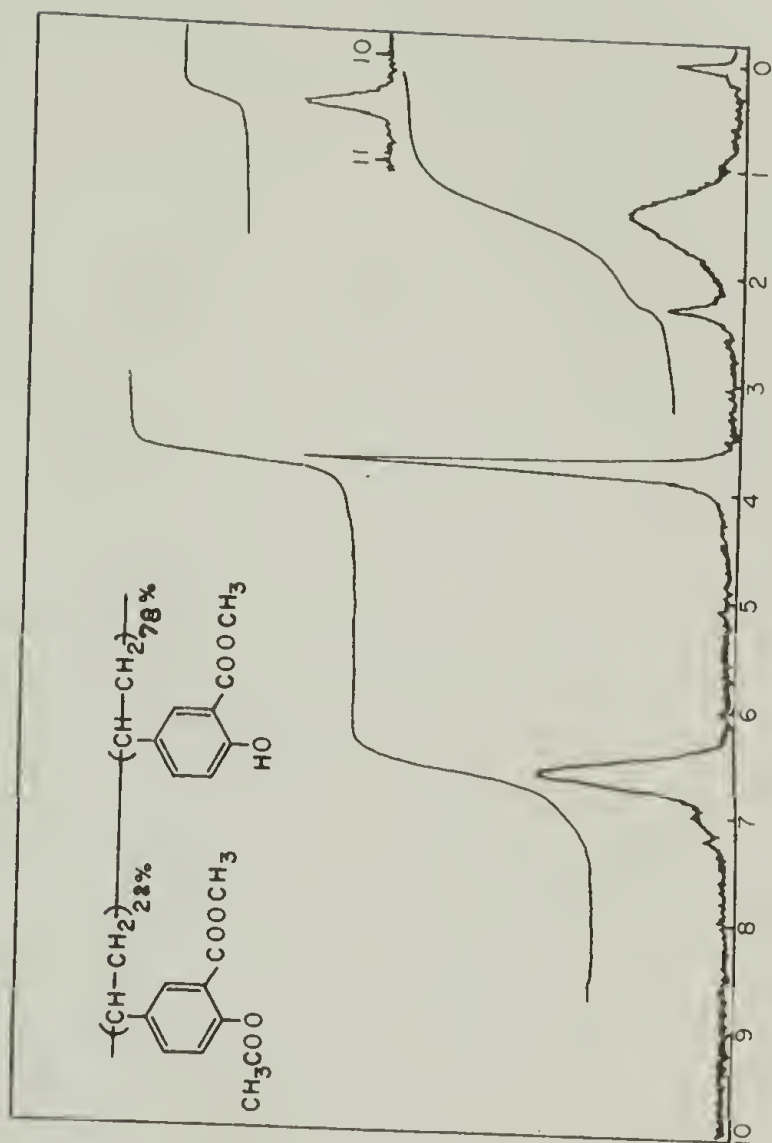
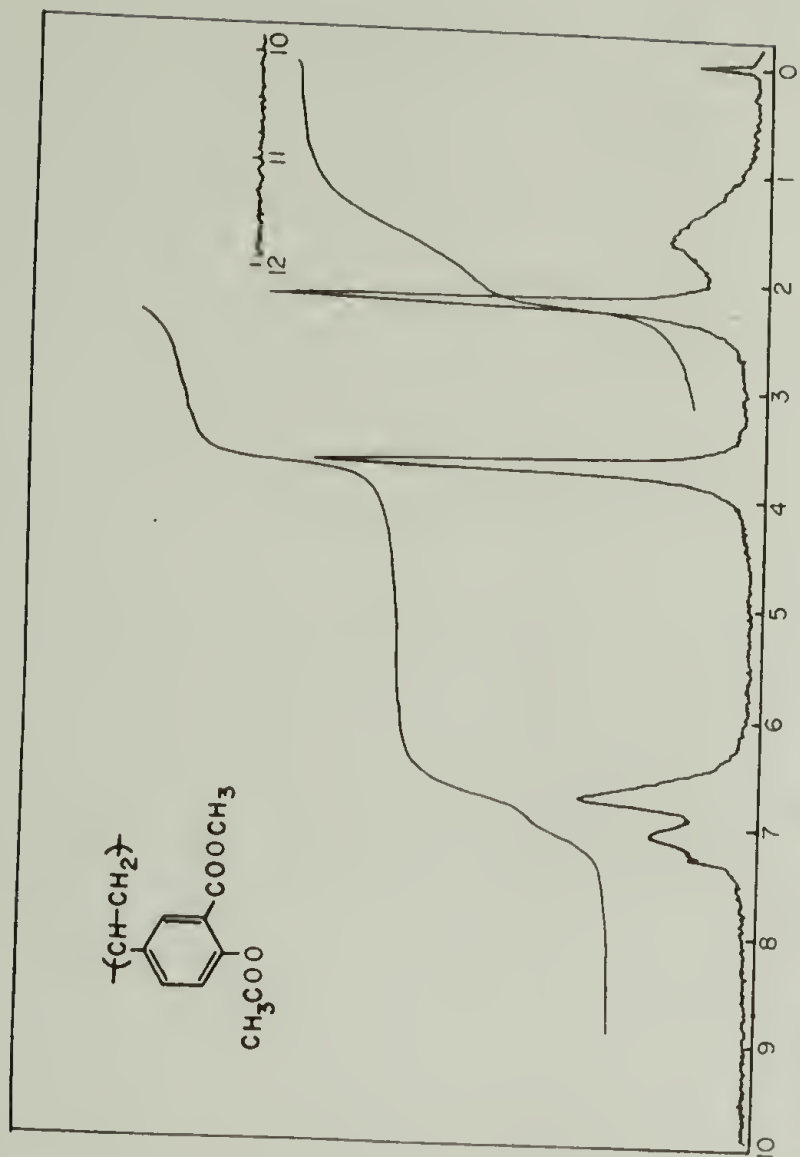


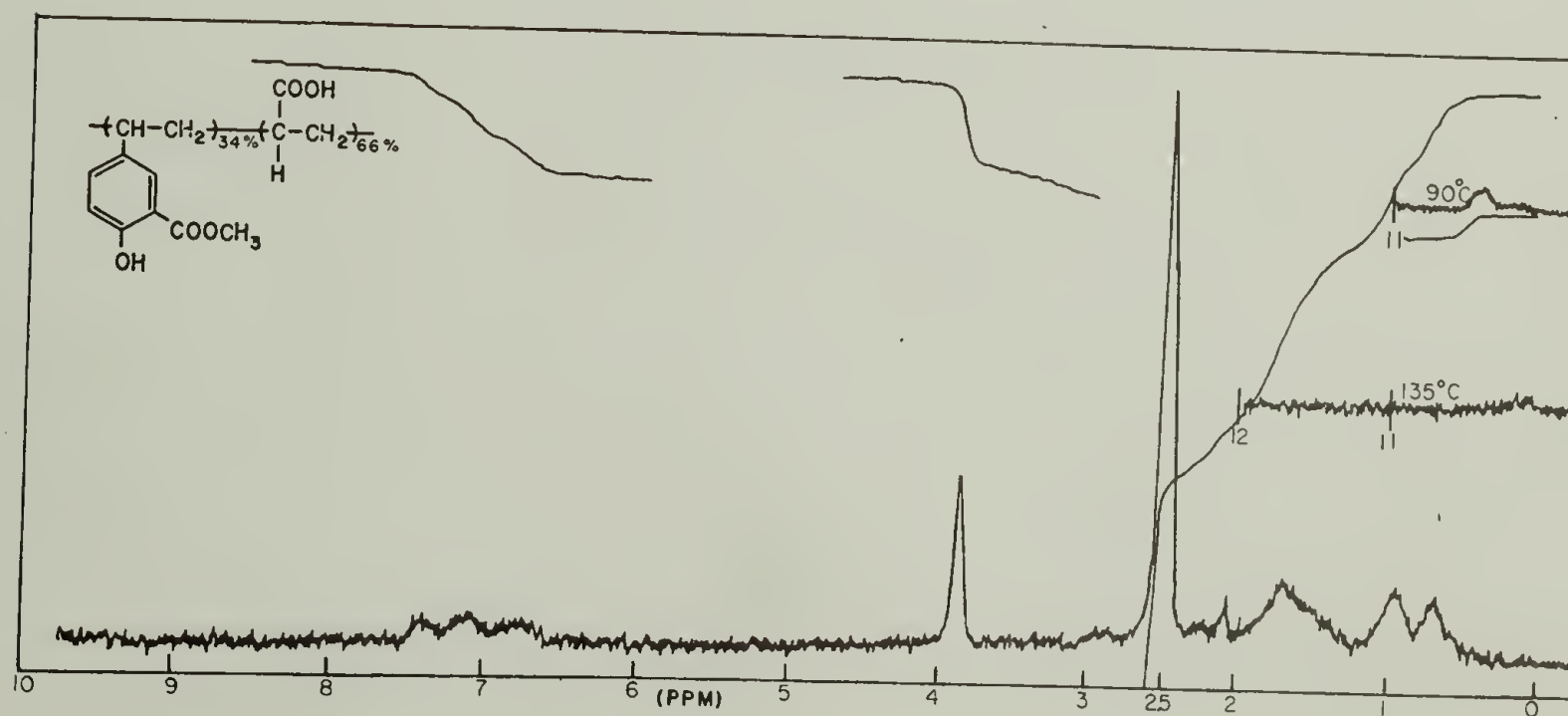
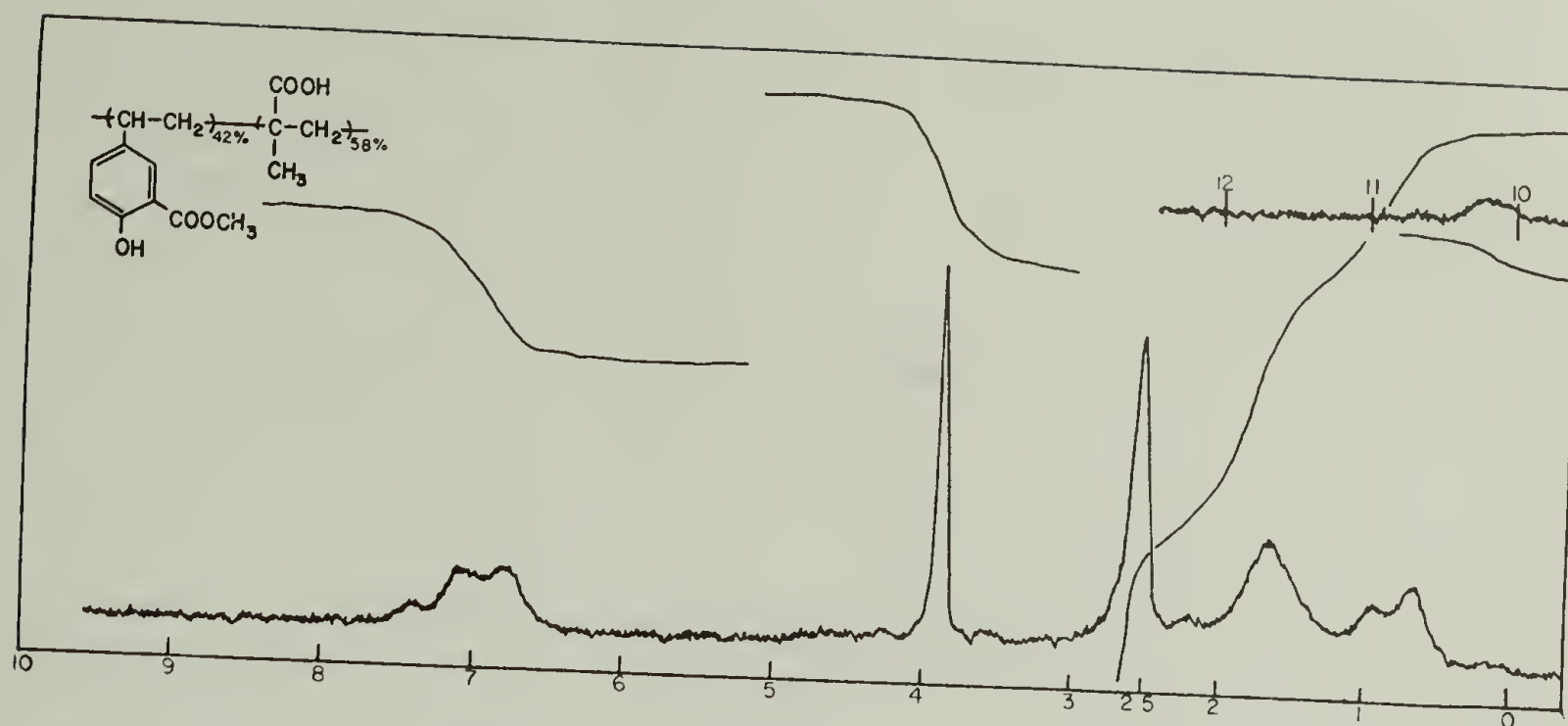
<u>n</u>	<u>E(1. mole⁻¹ cm.⁻¹)</u>	<u>λ(nm.)</u>
1	18.3 x 10 ³ 8.76 x 10 ³	238 306
2	18.0 x 10 ³ 8.56 x 10 ³	238 306
3	18.6 x 10 ³ 8.80 x 10 ³	238 306

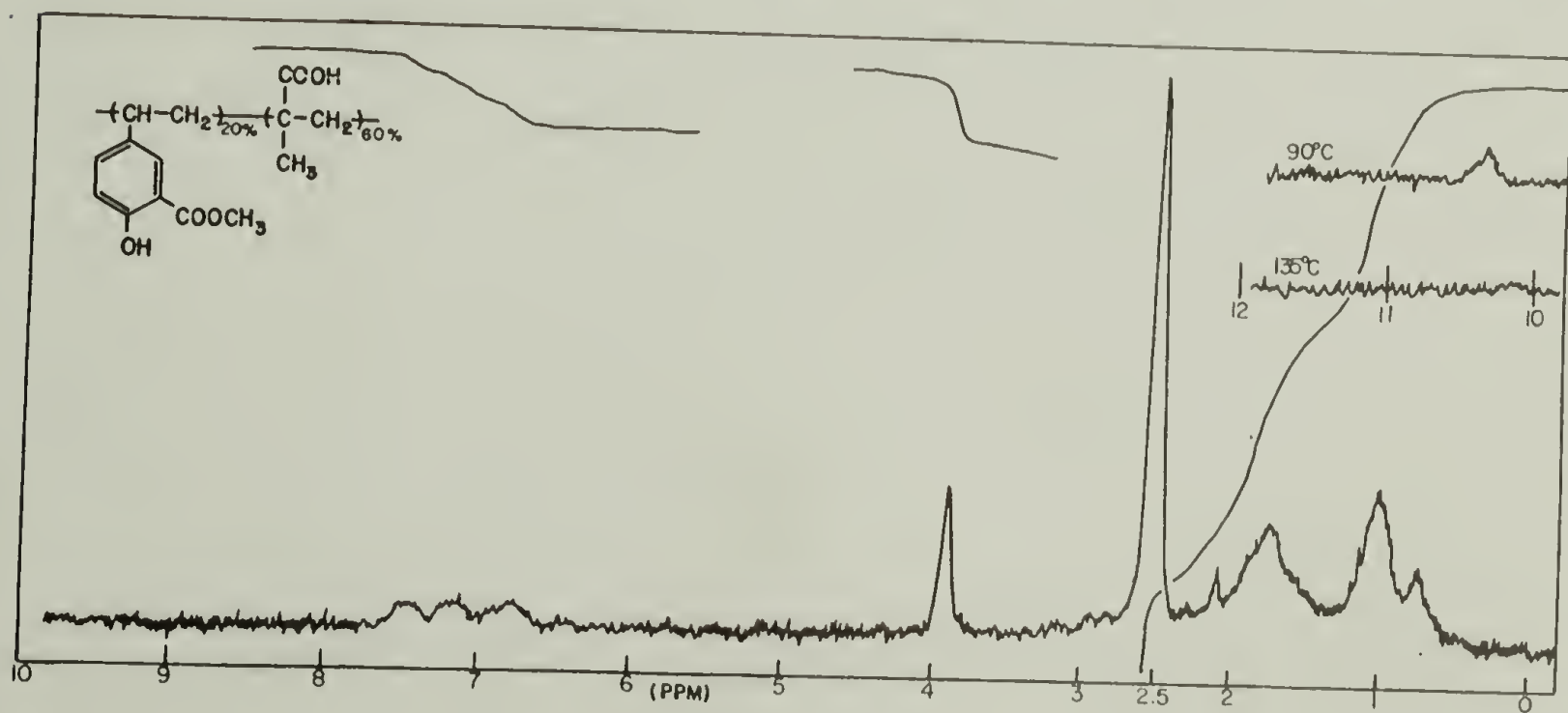
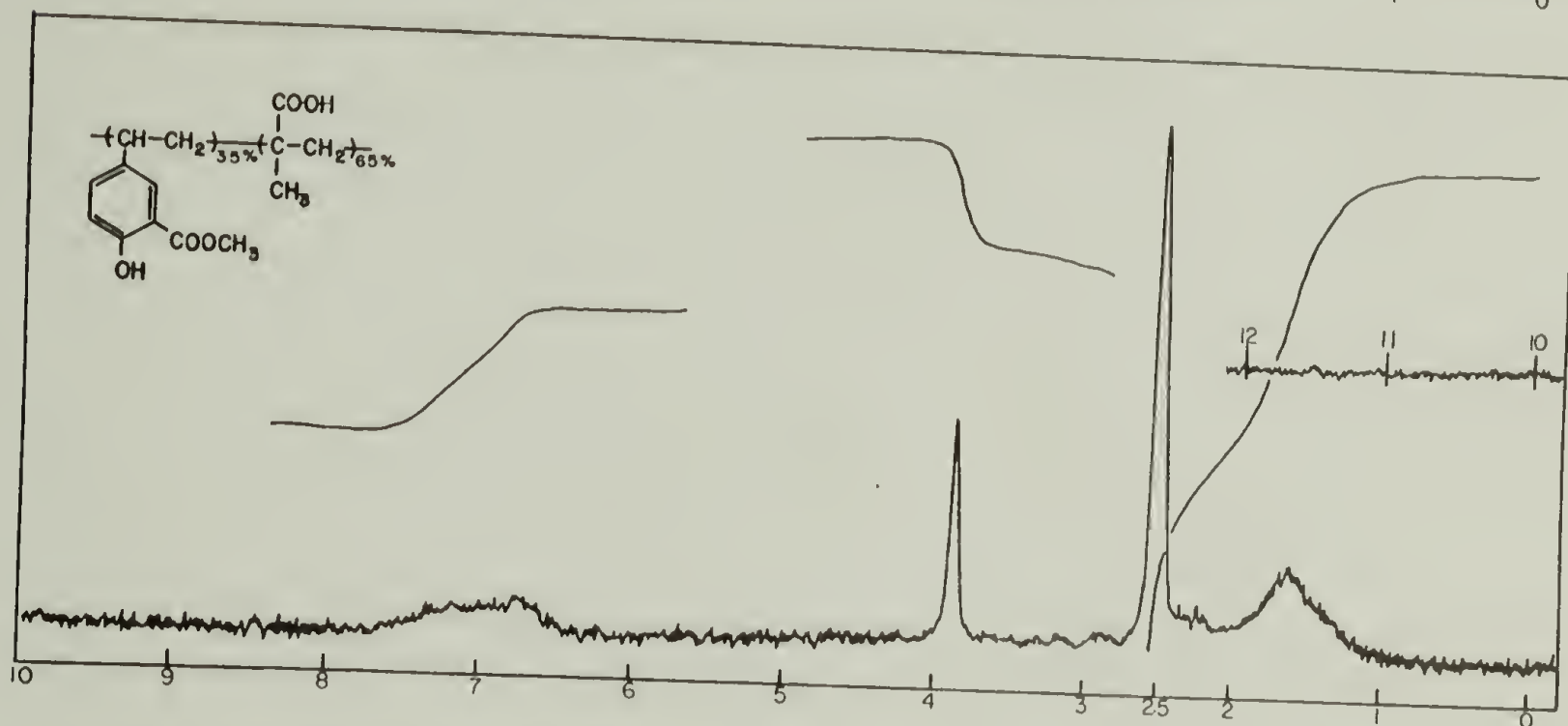
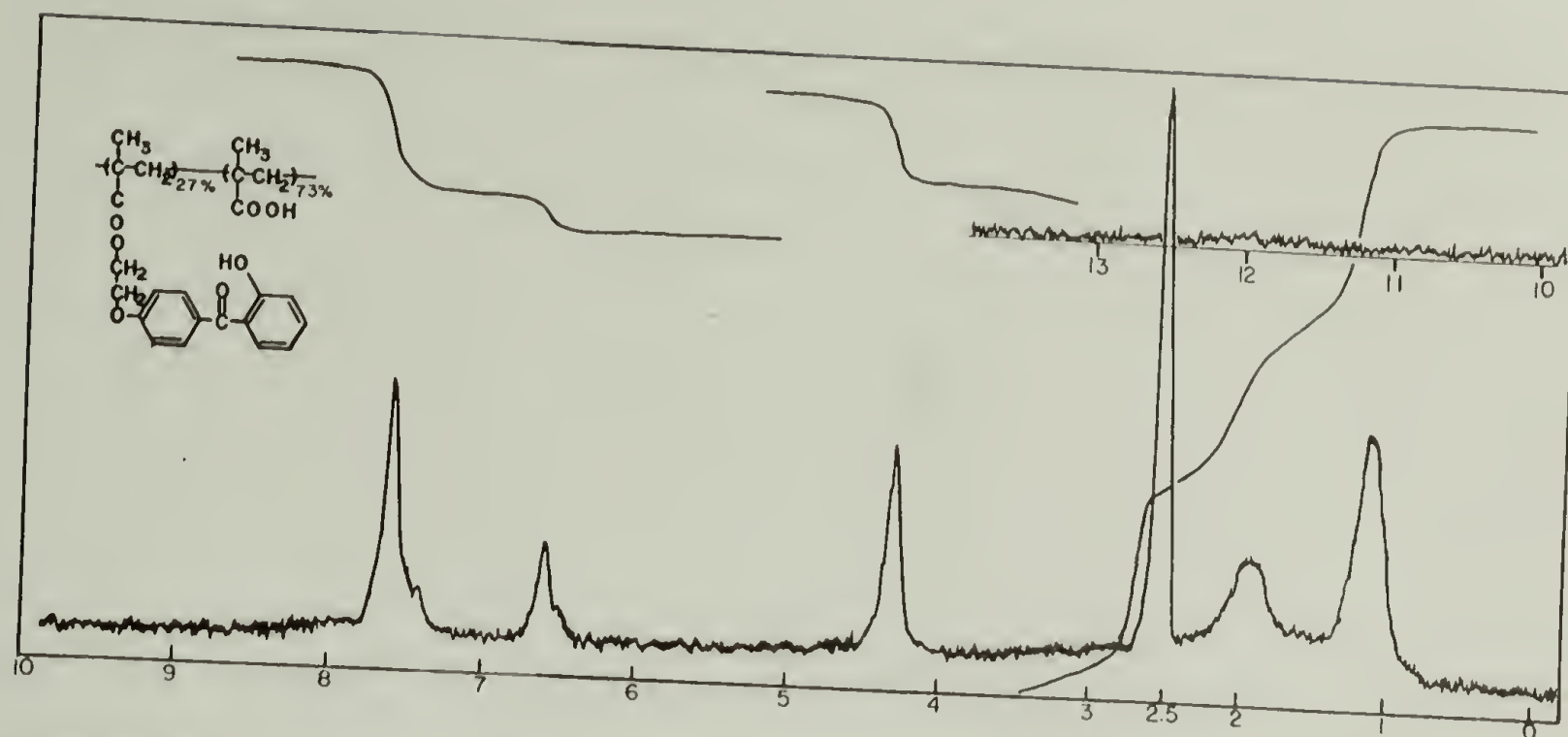
APPENDIX A

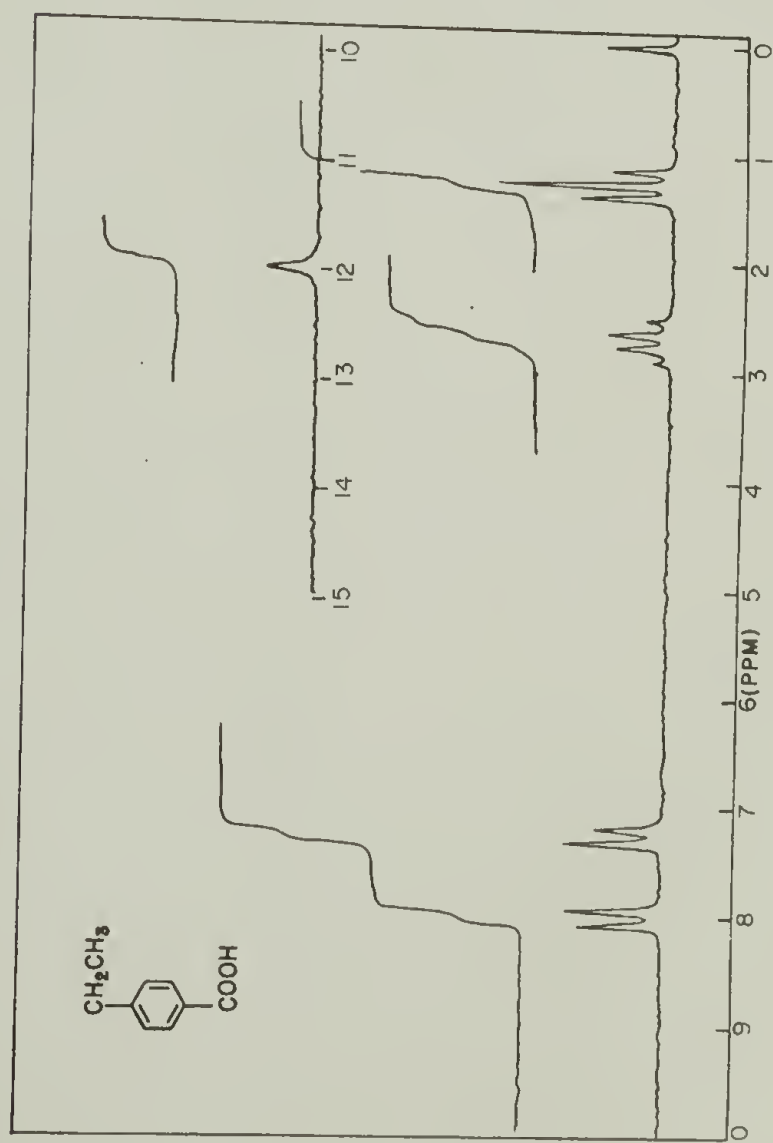
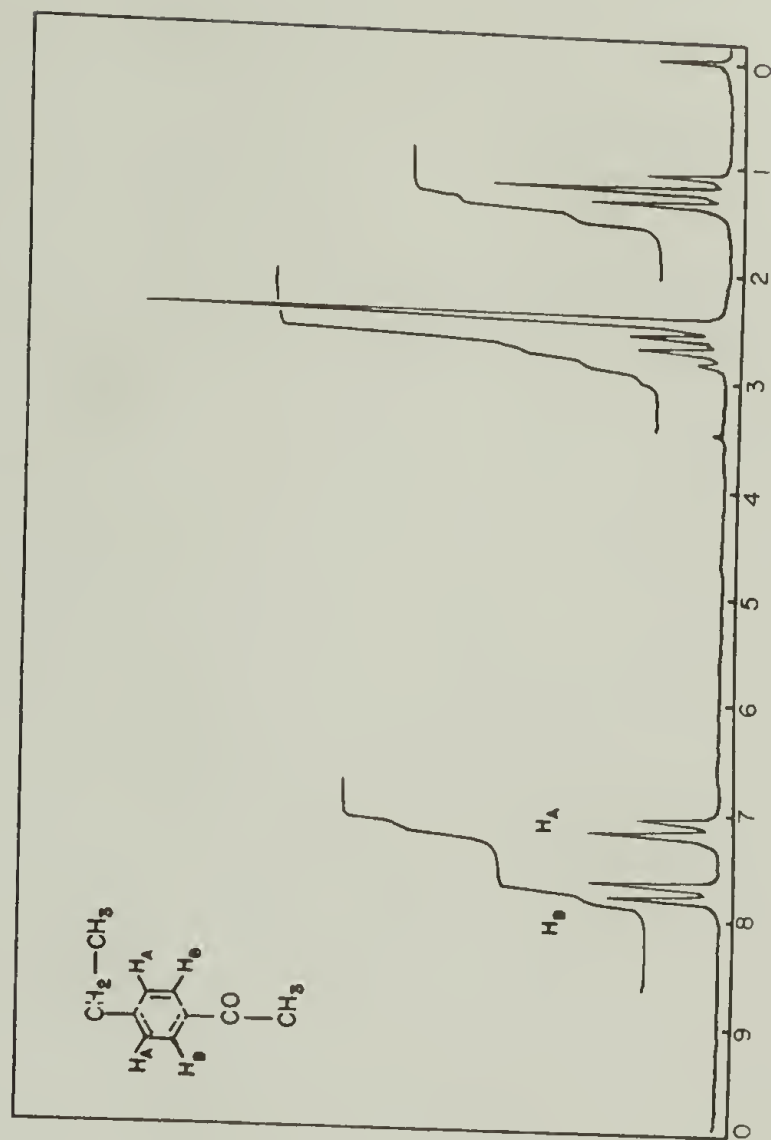
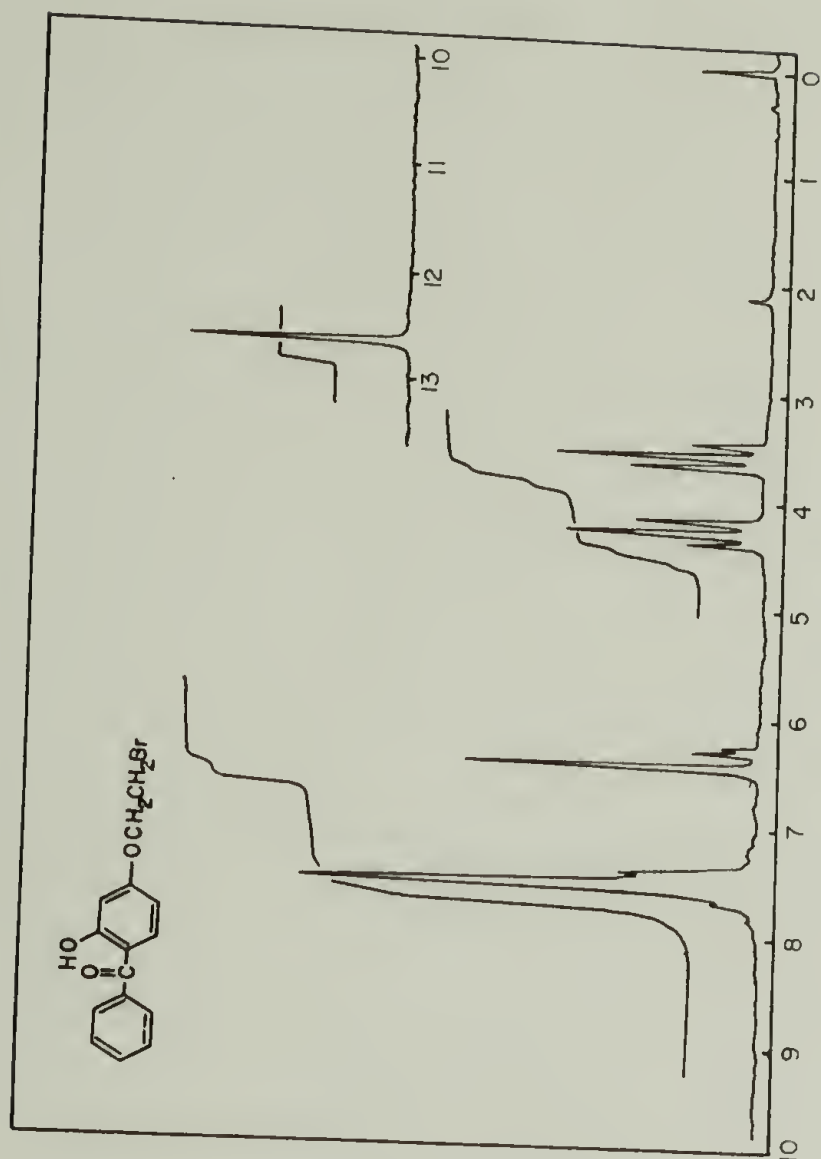
PROTON MAGNETIC RESONANCE SPECTRA

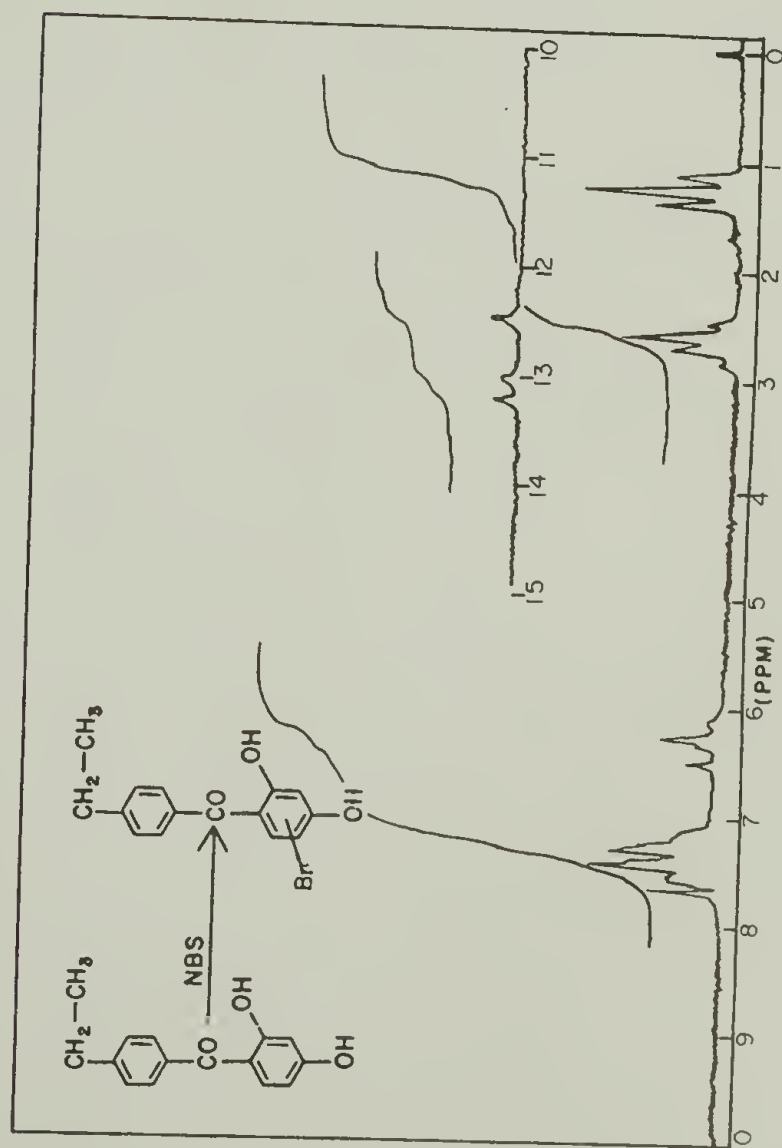
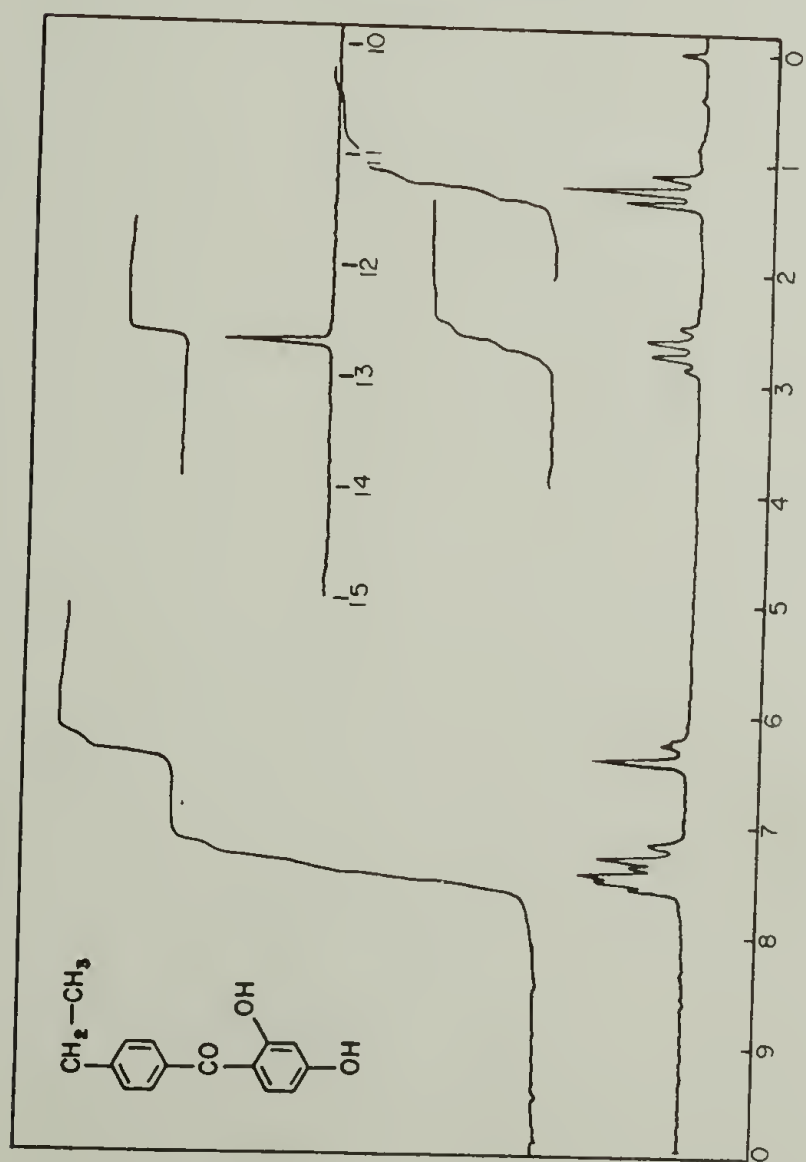
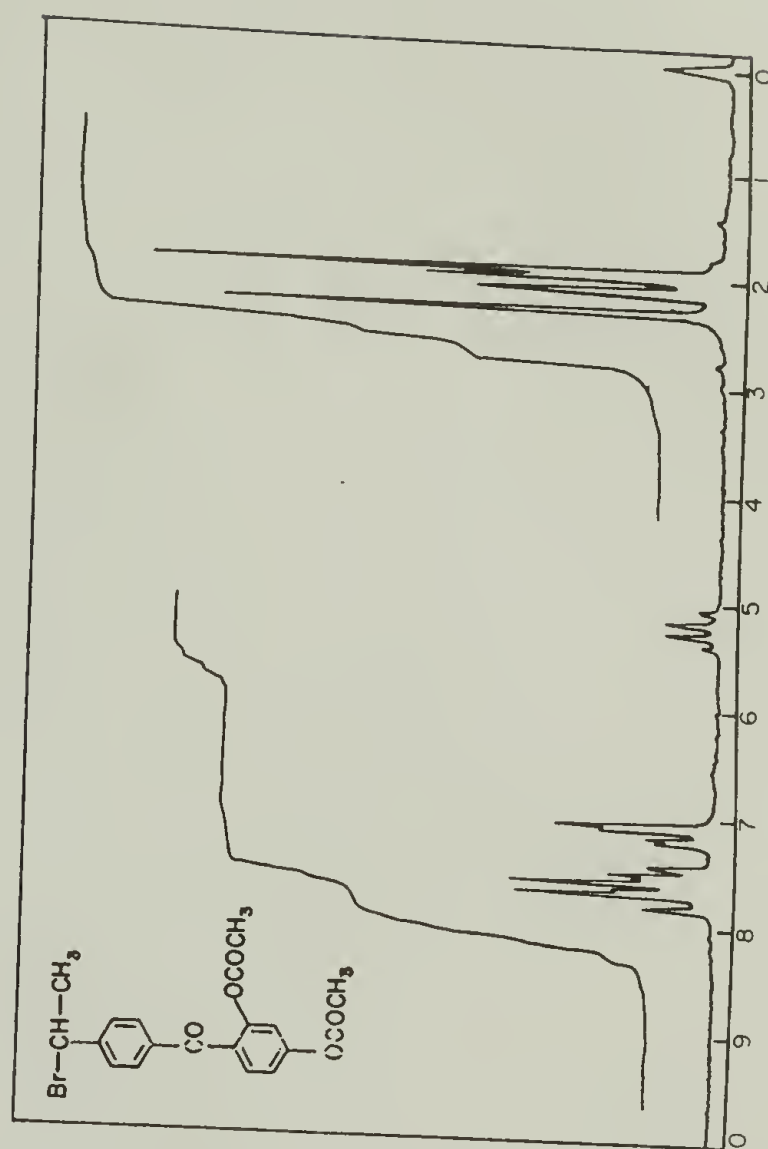
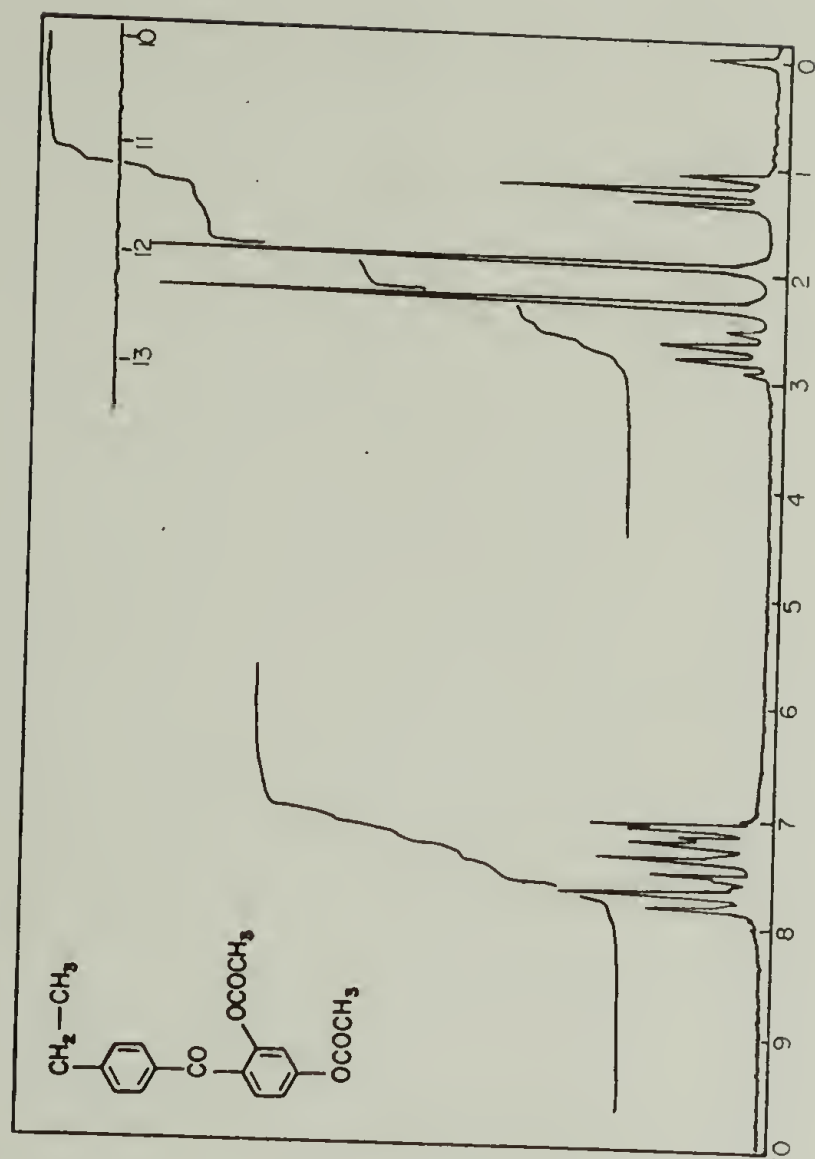


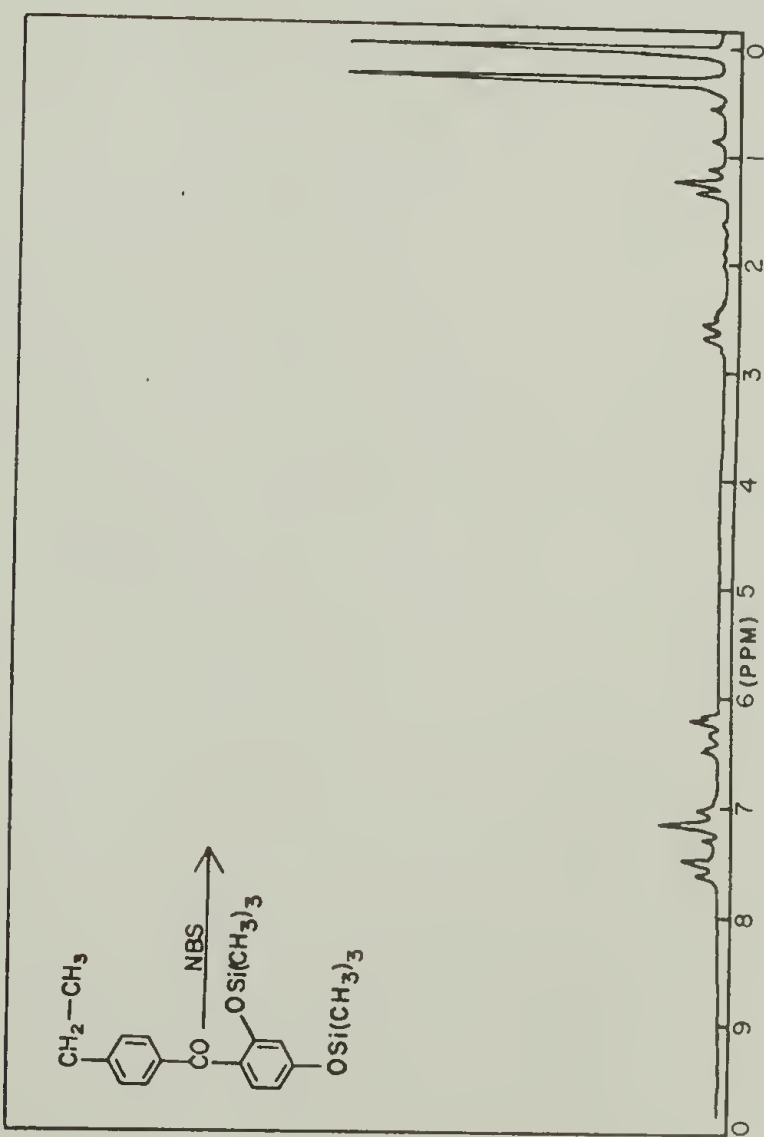
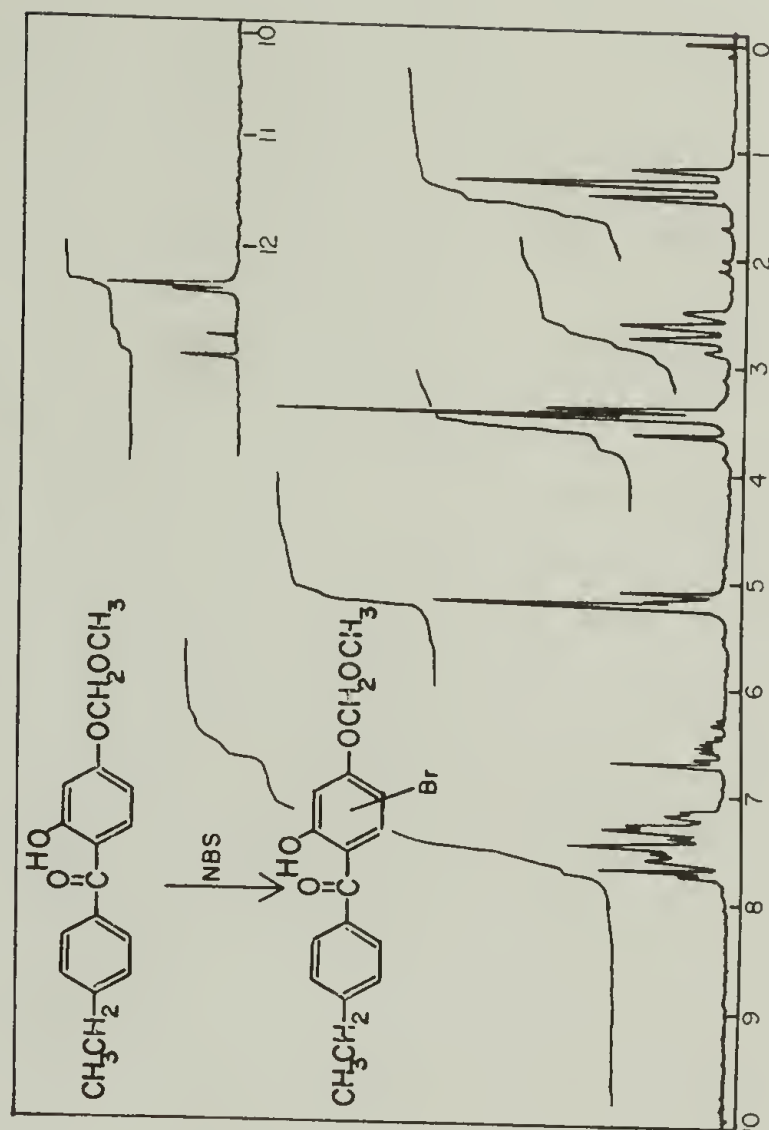


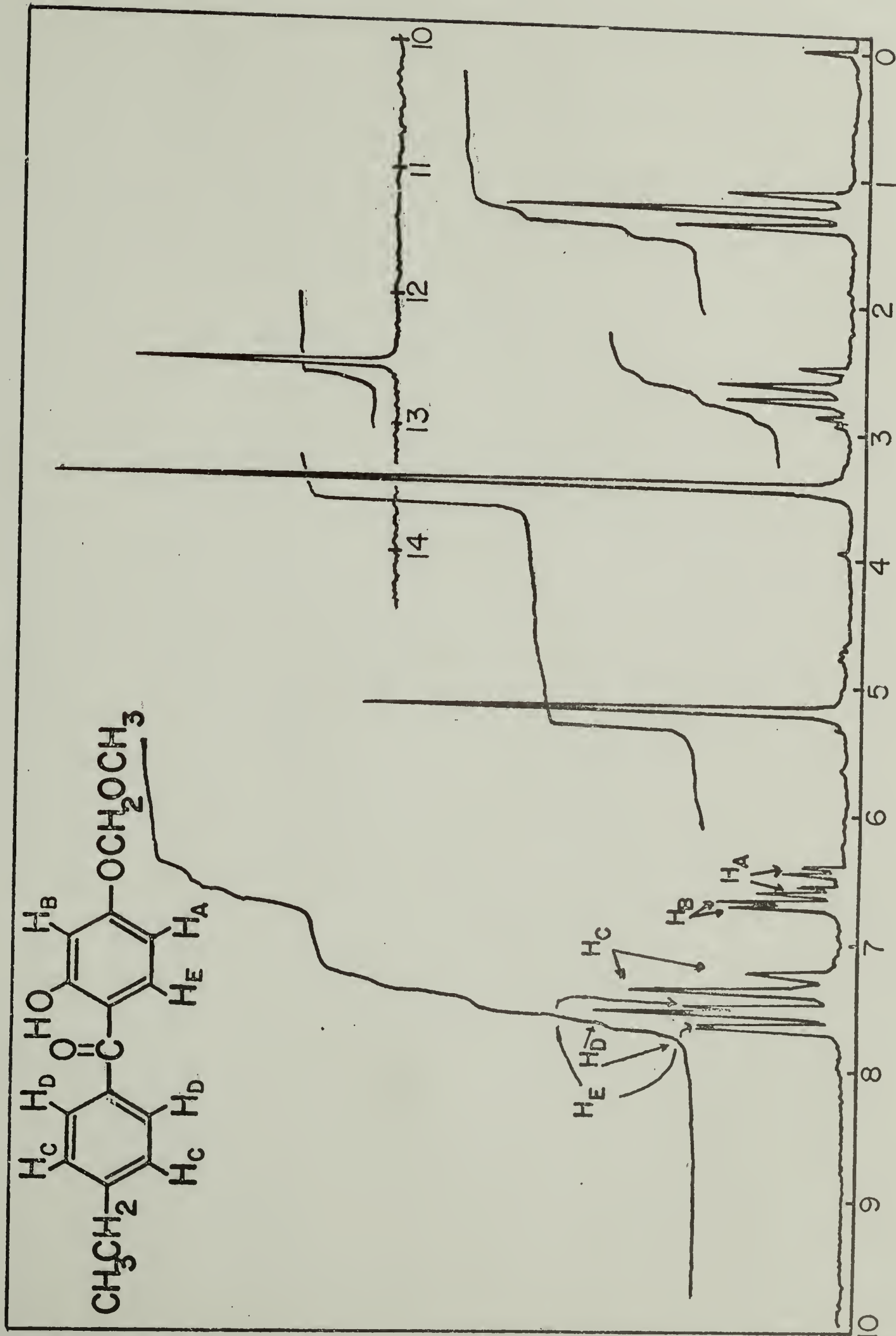


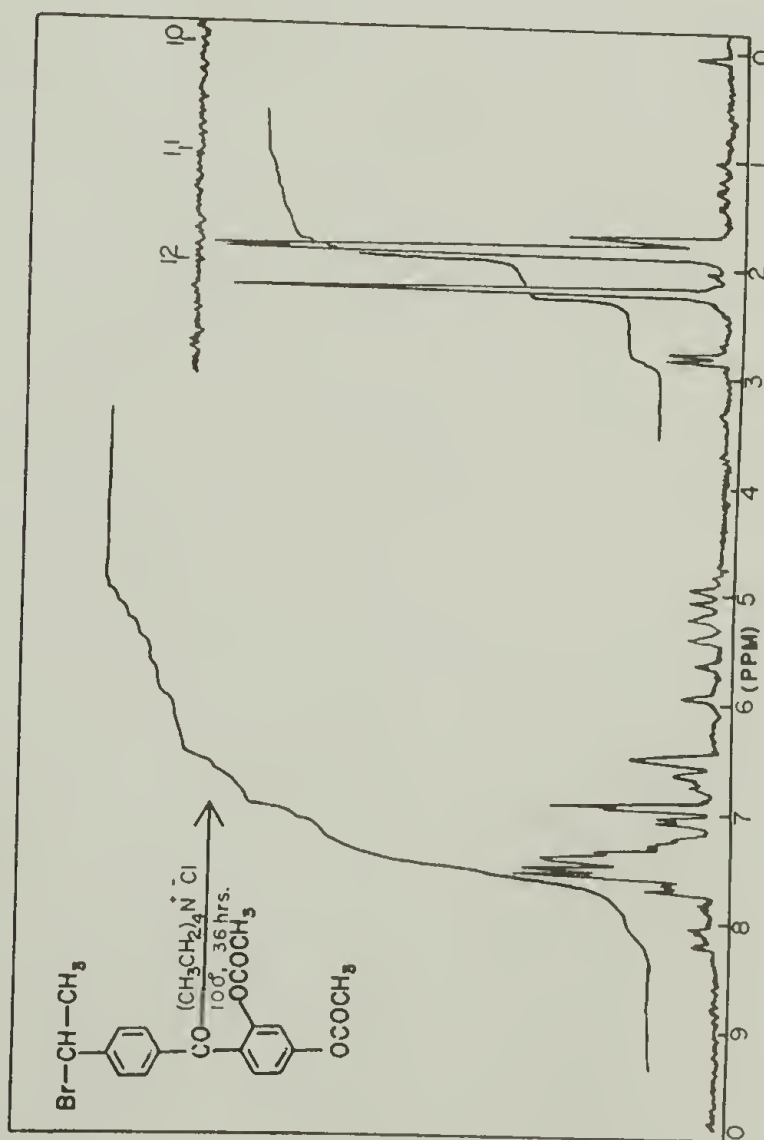
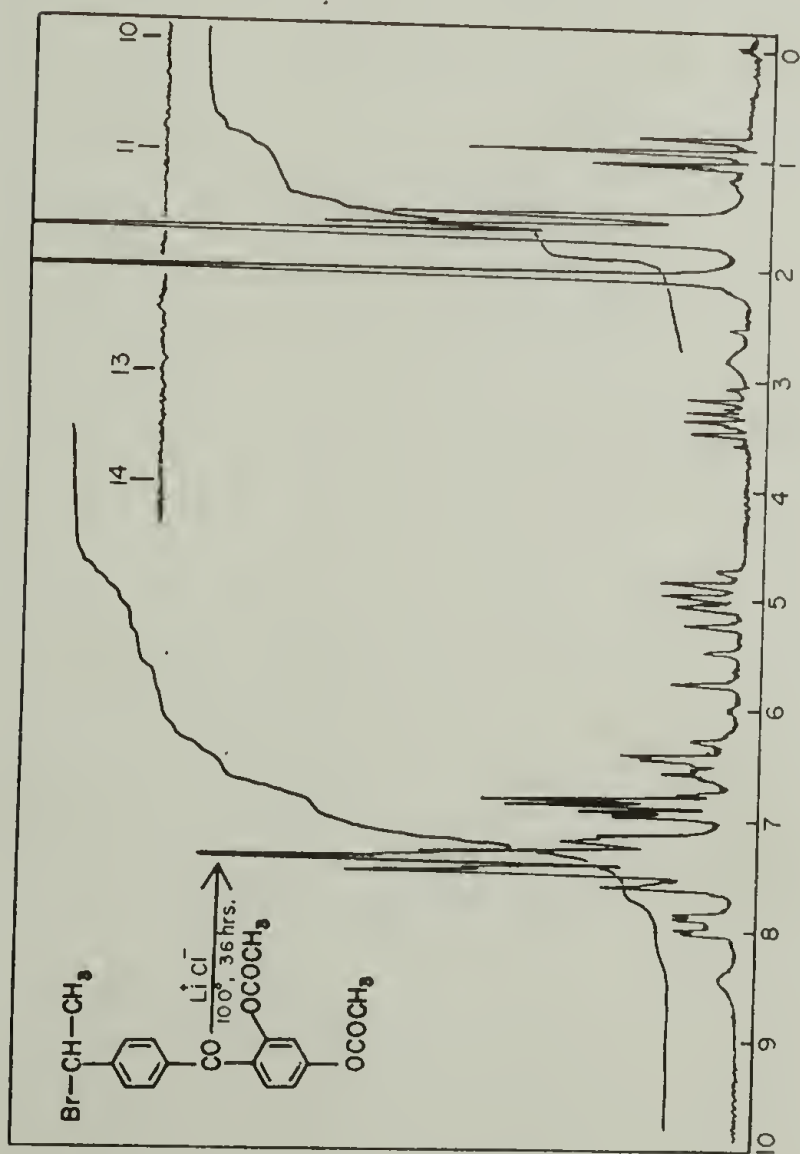
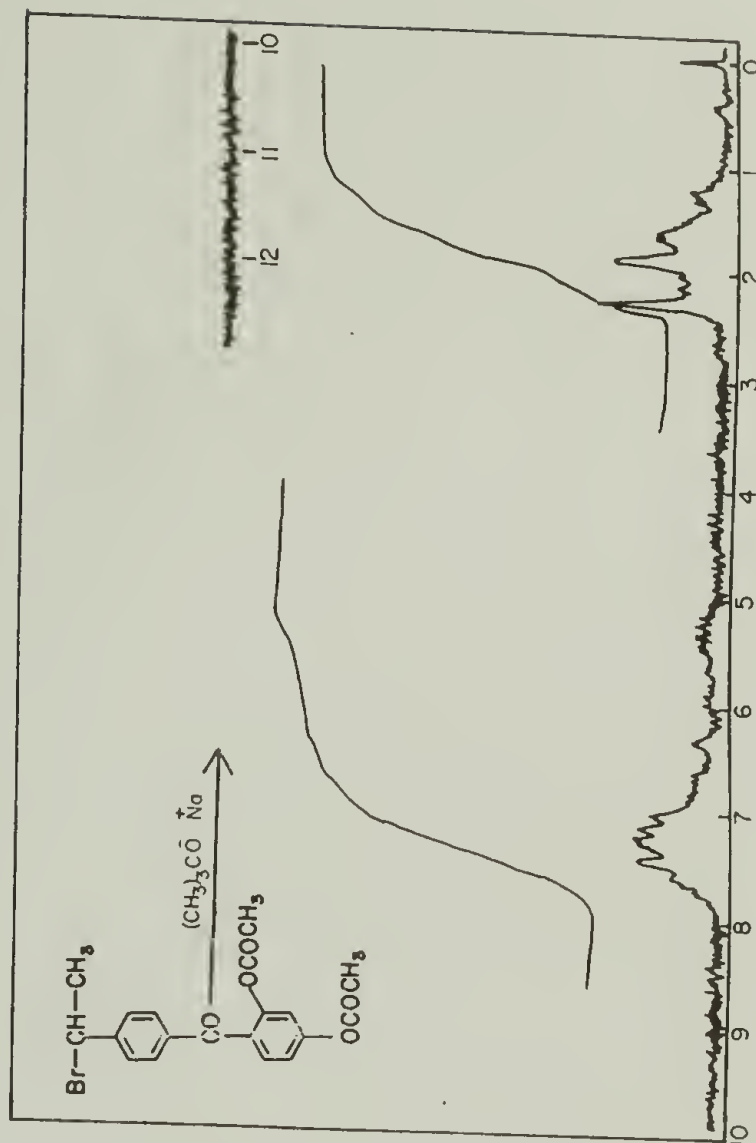
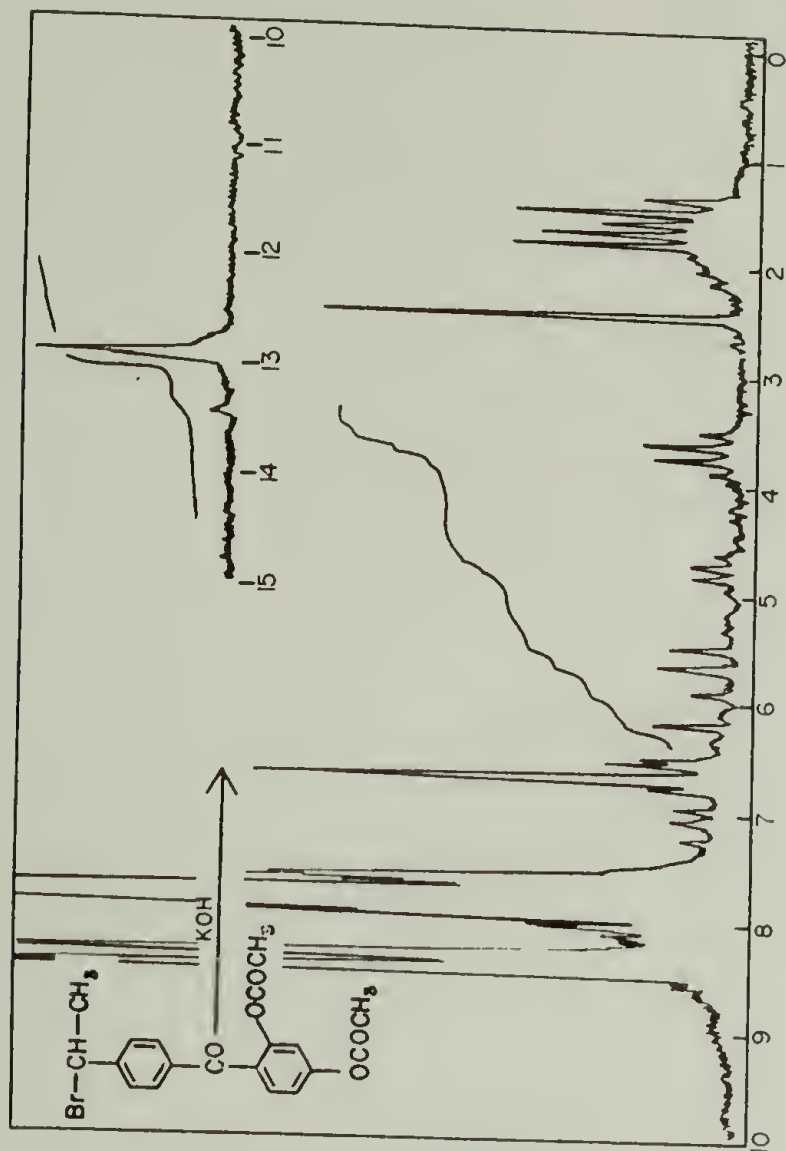


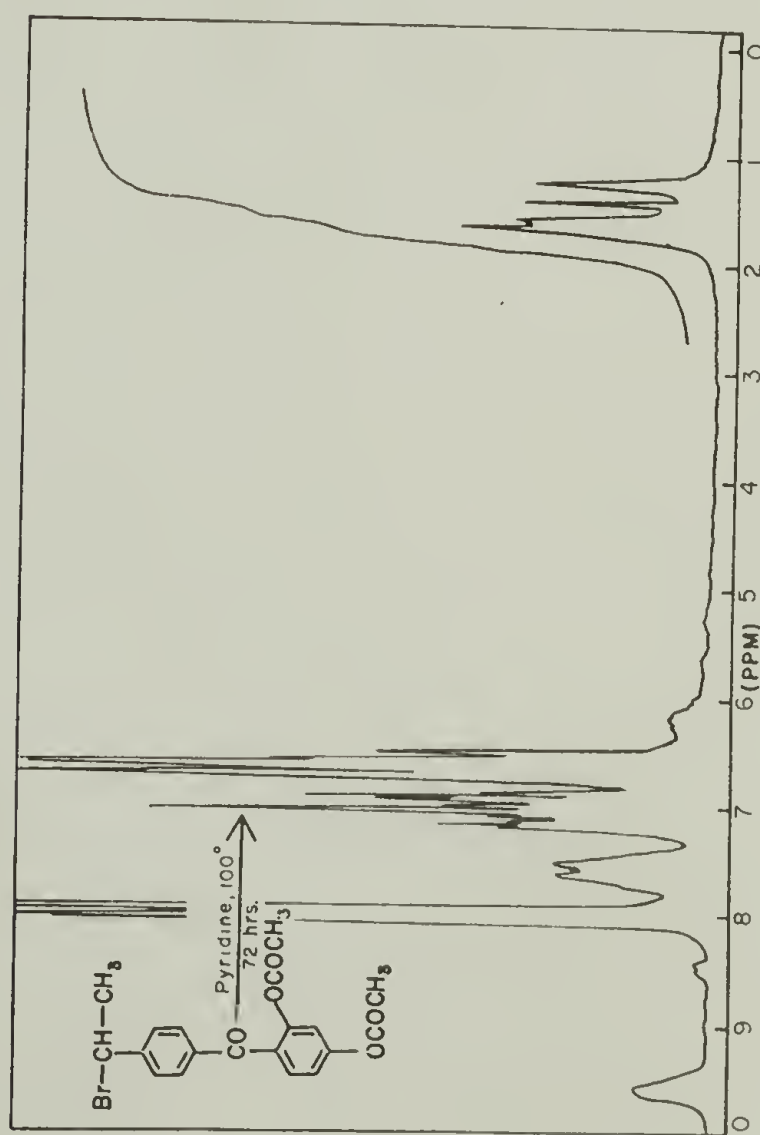
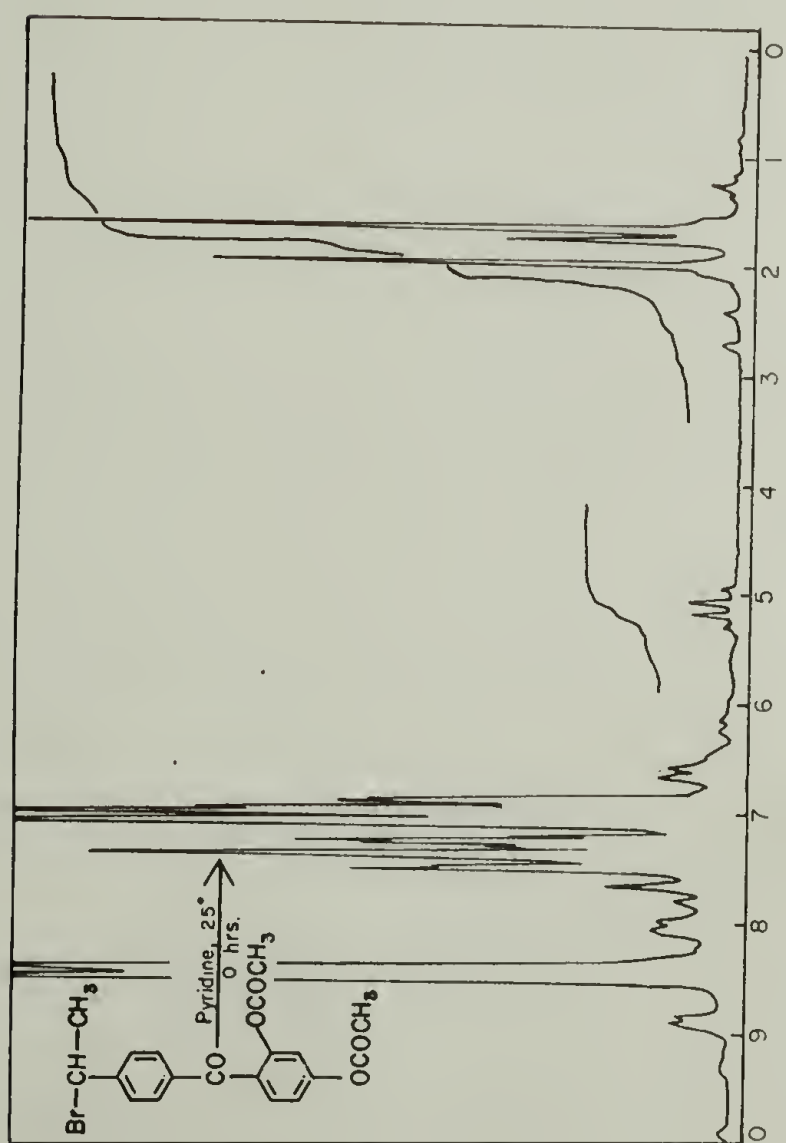
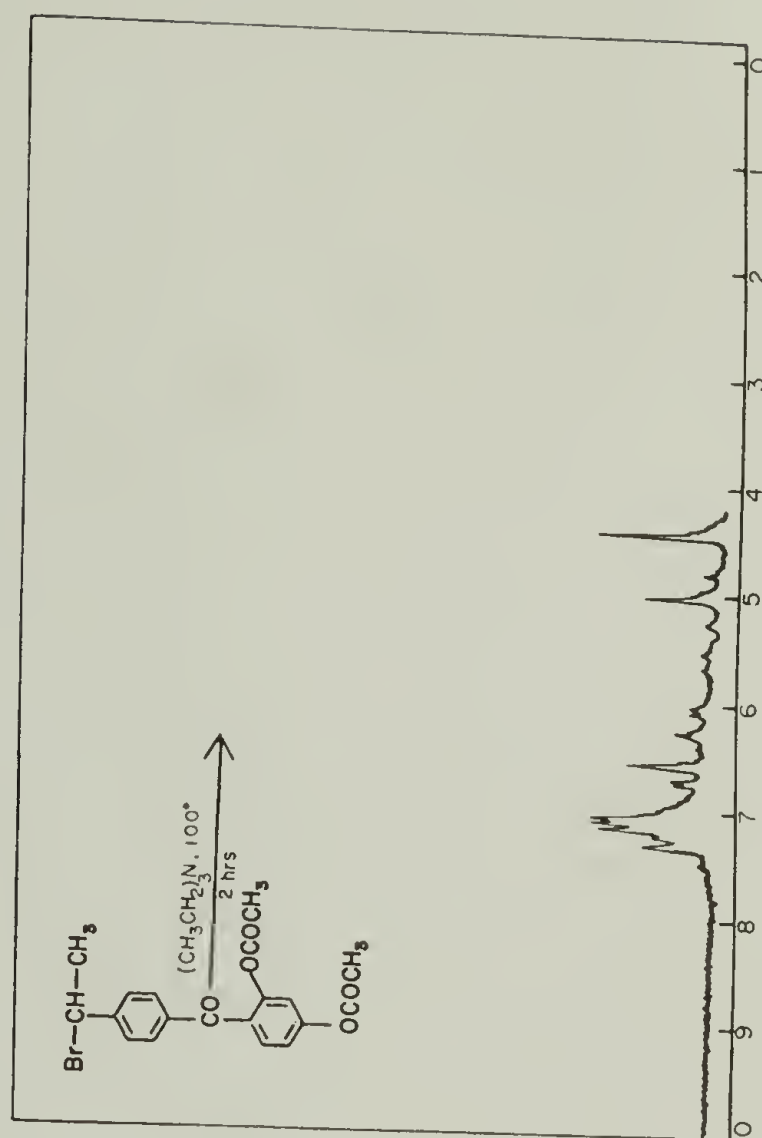
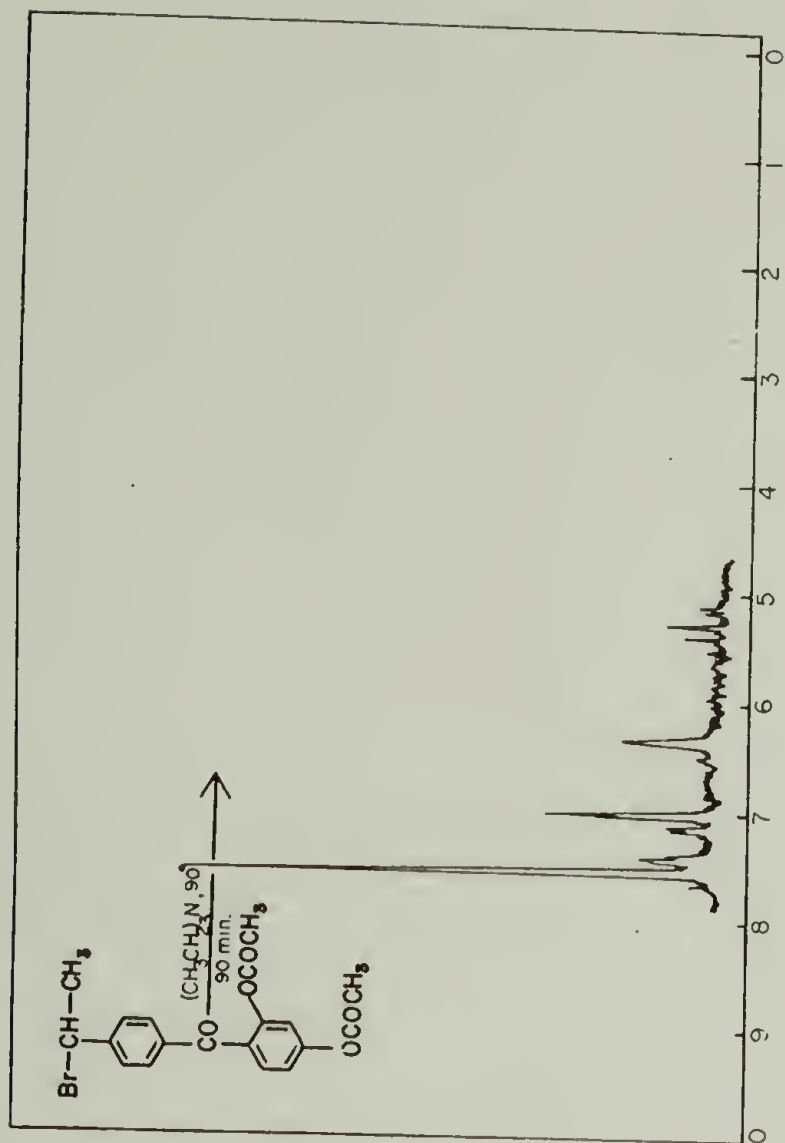


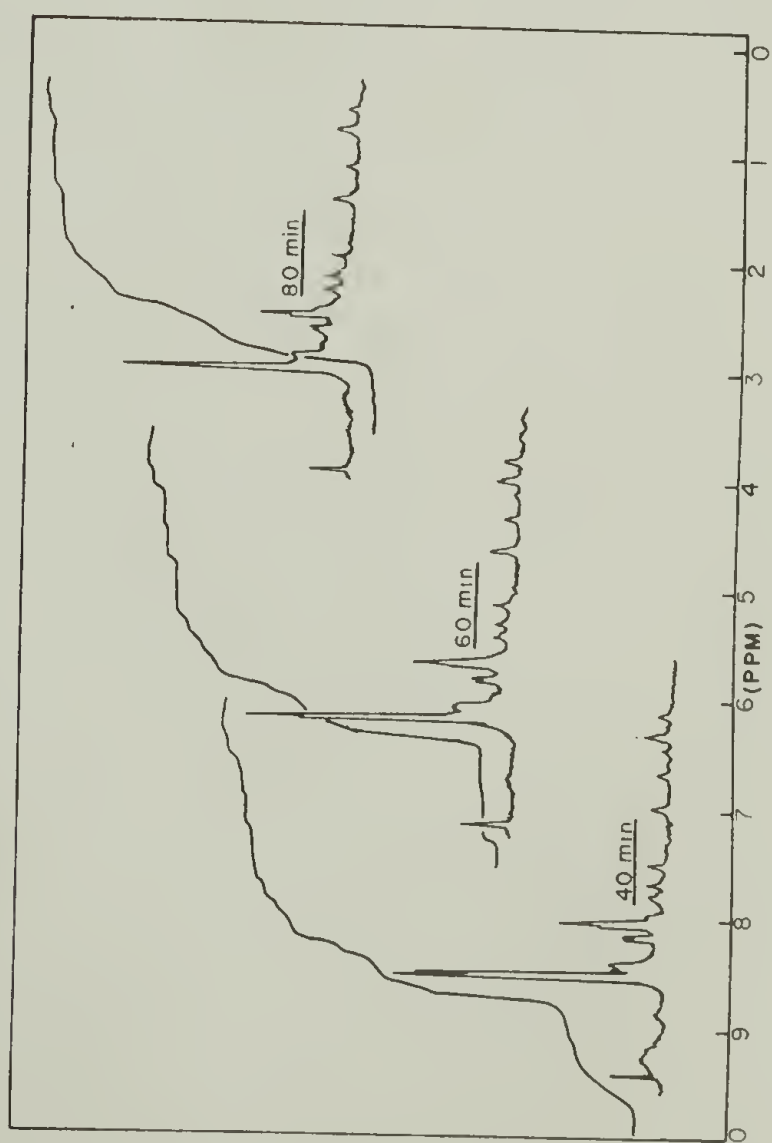
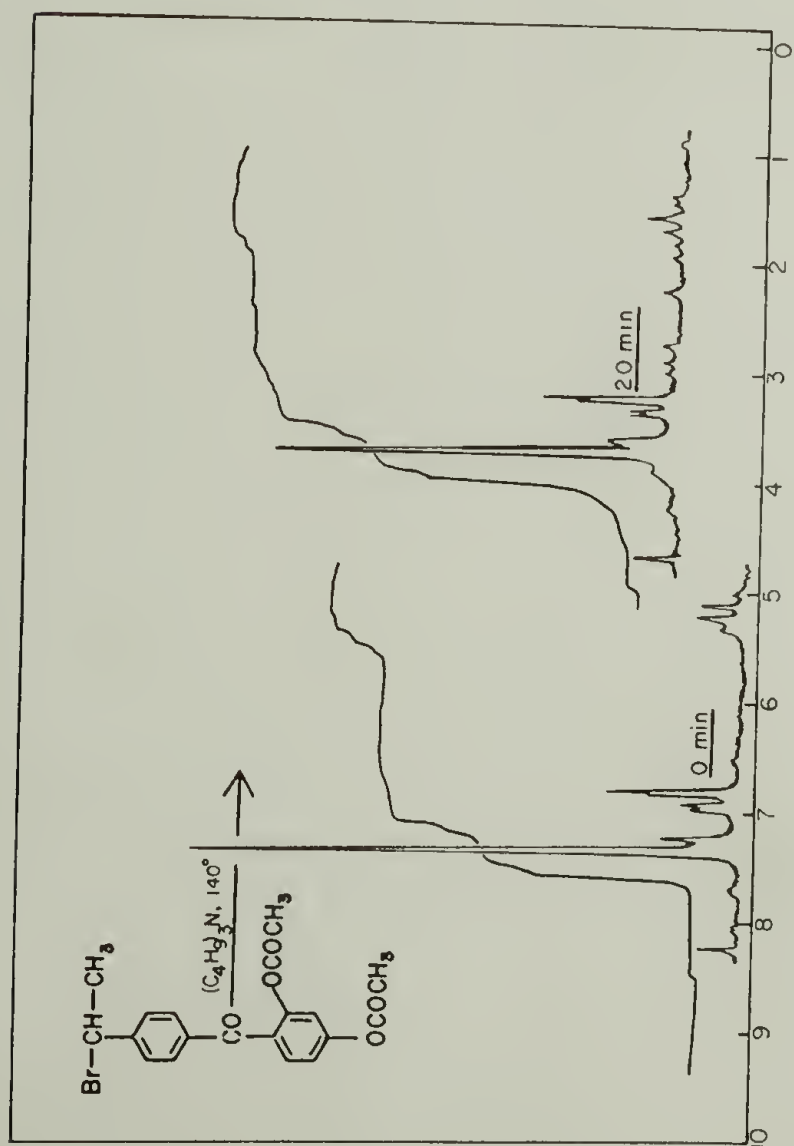
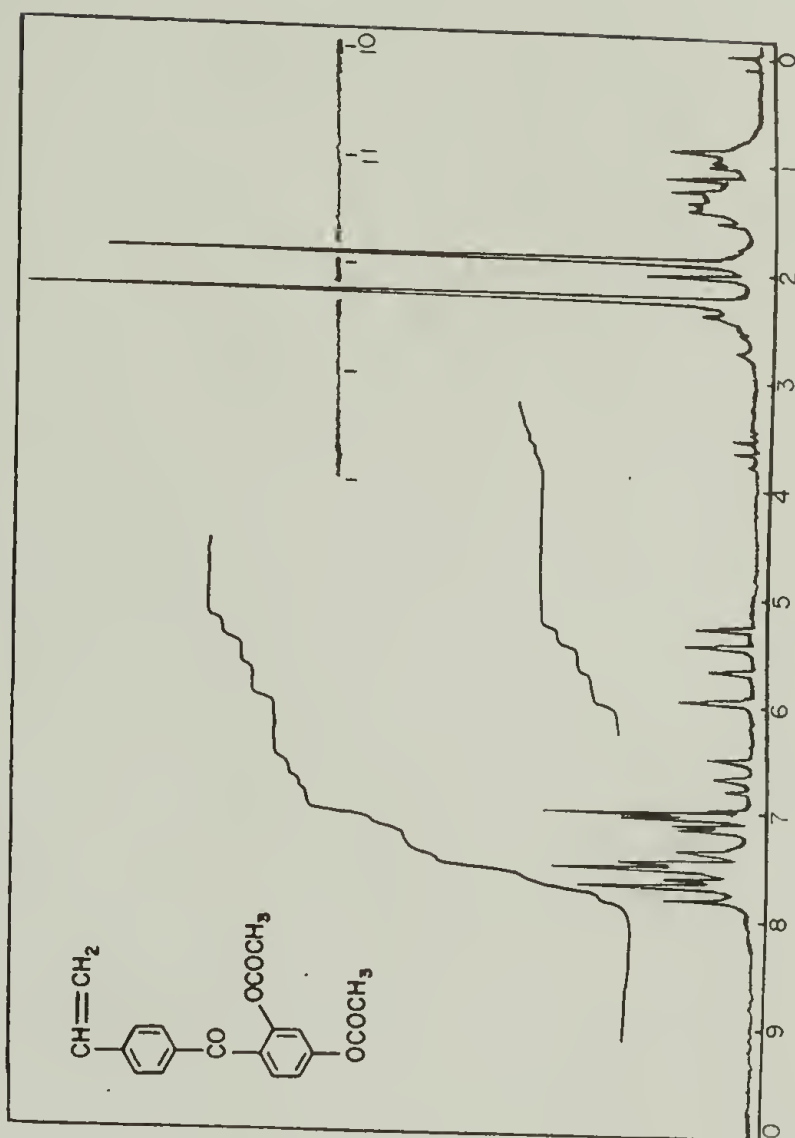
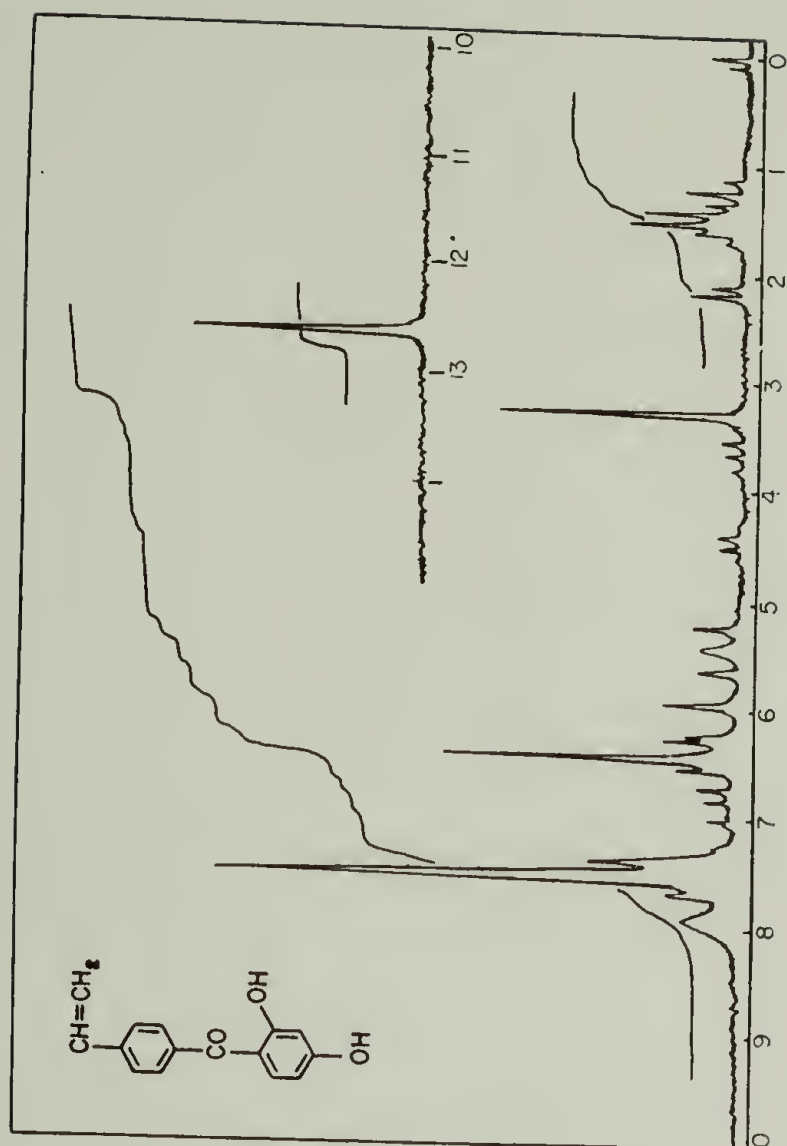


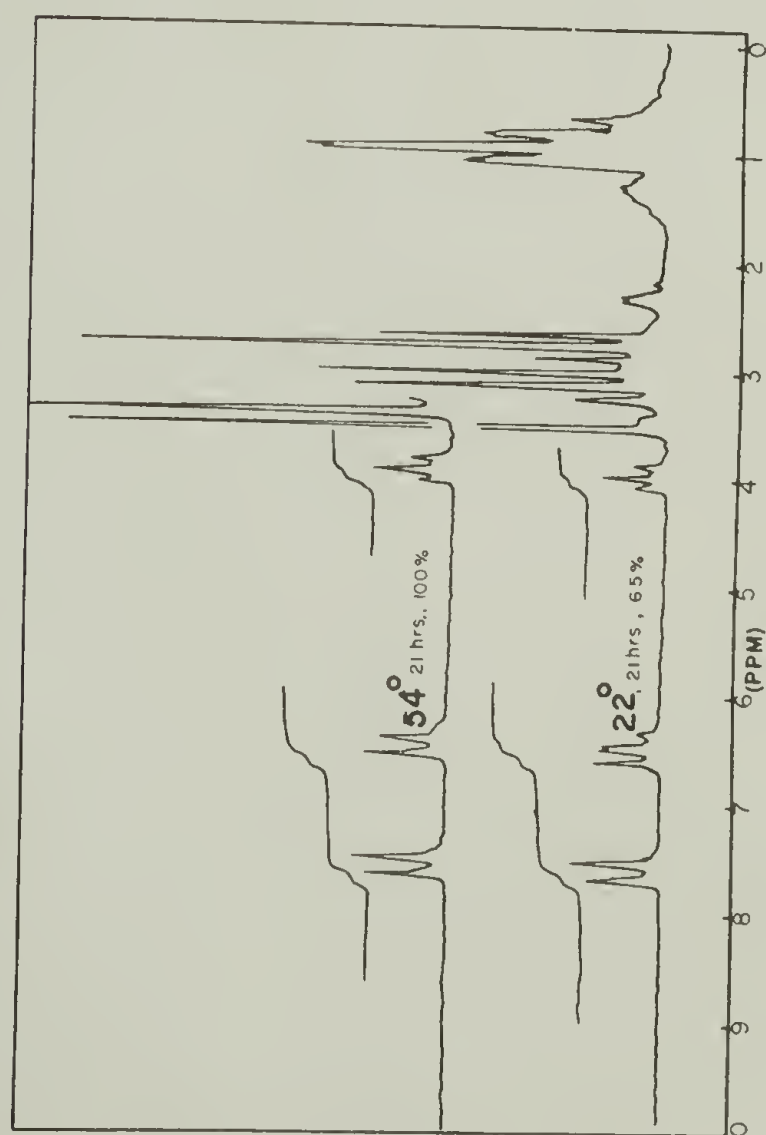
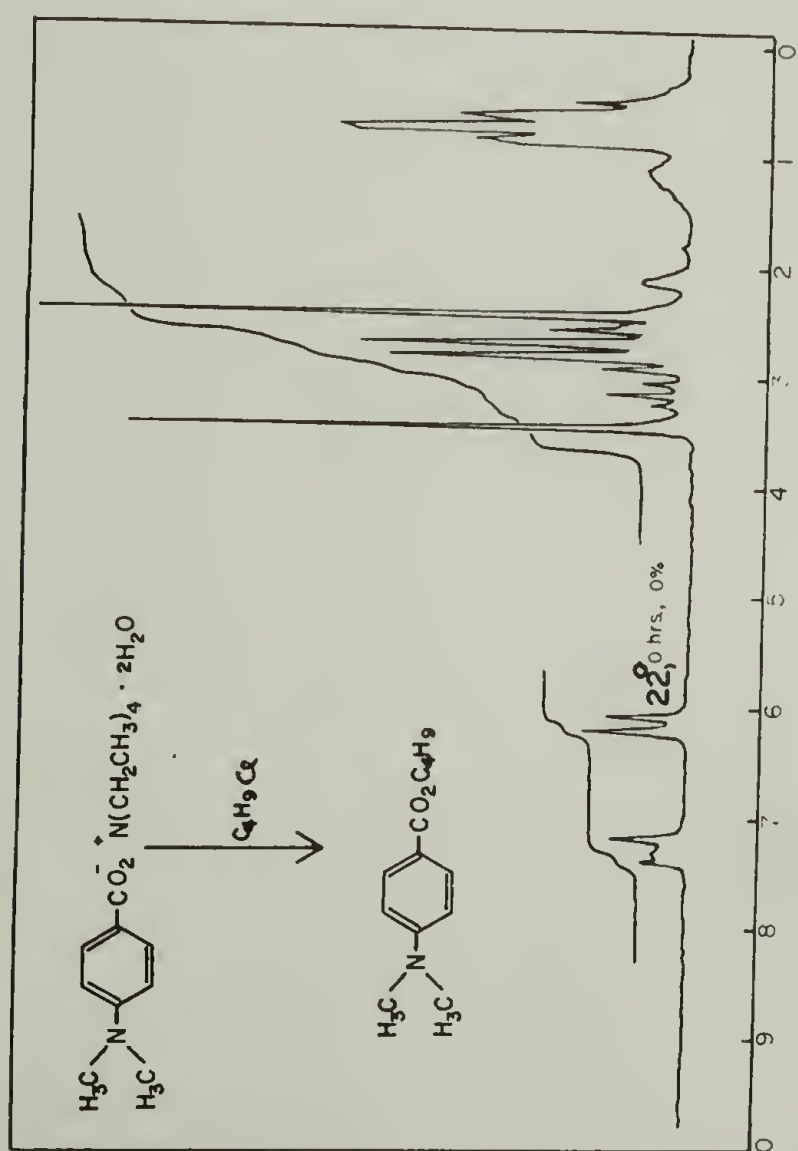
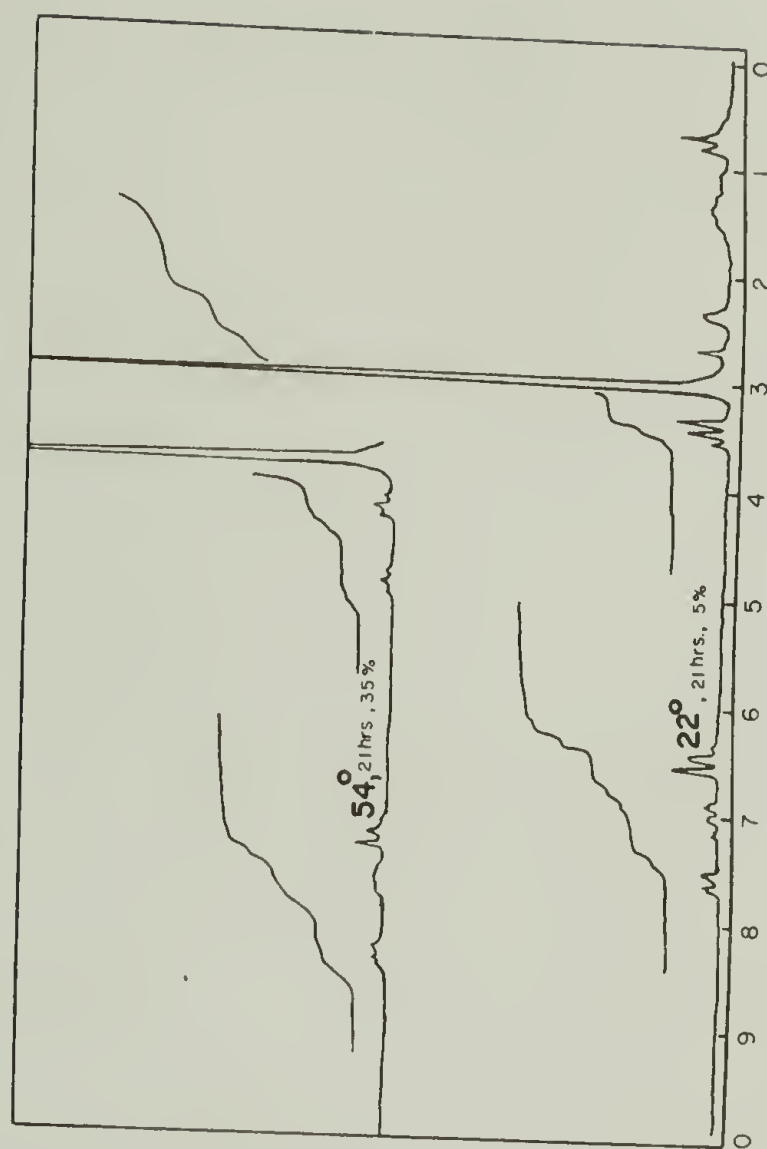
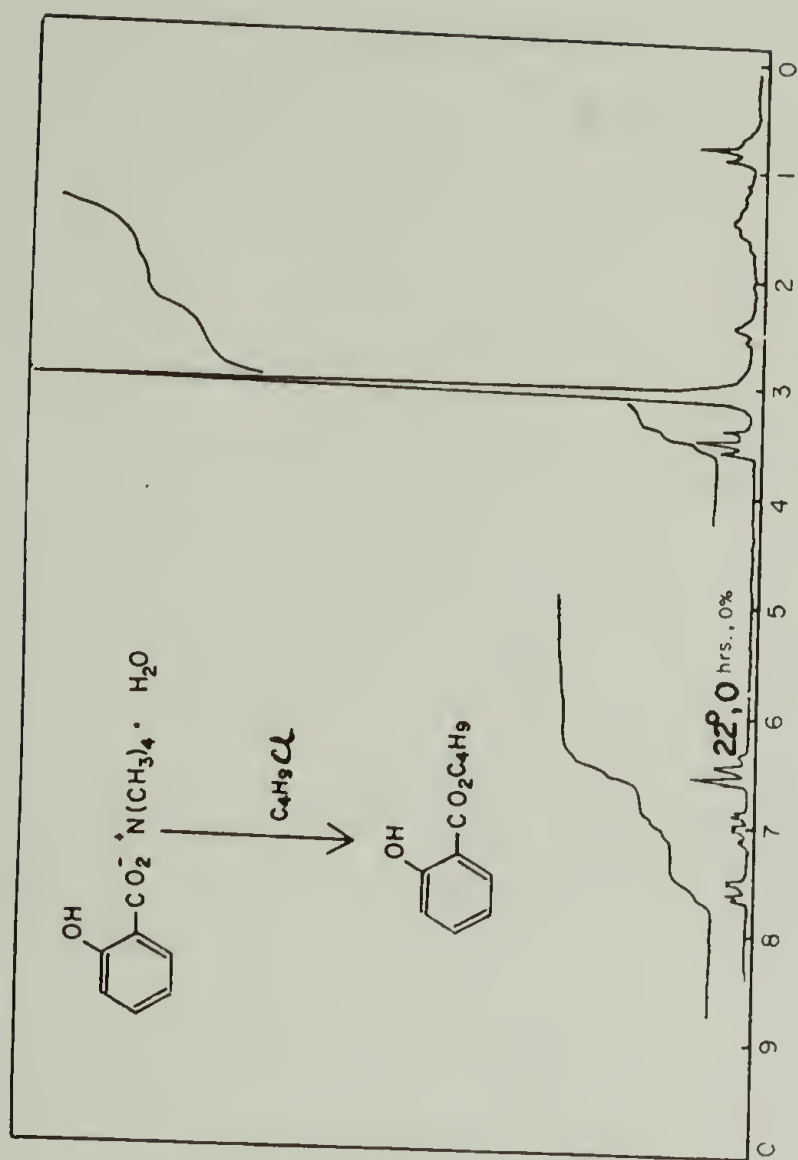


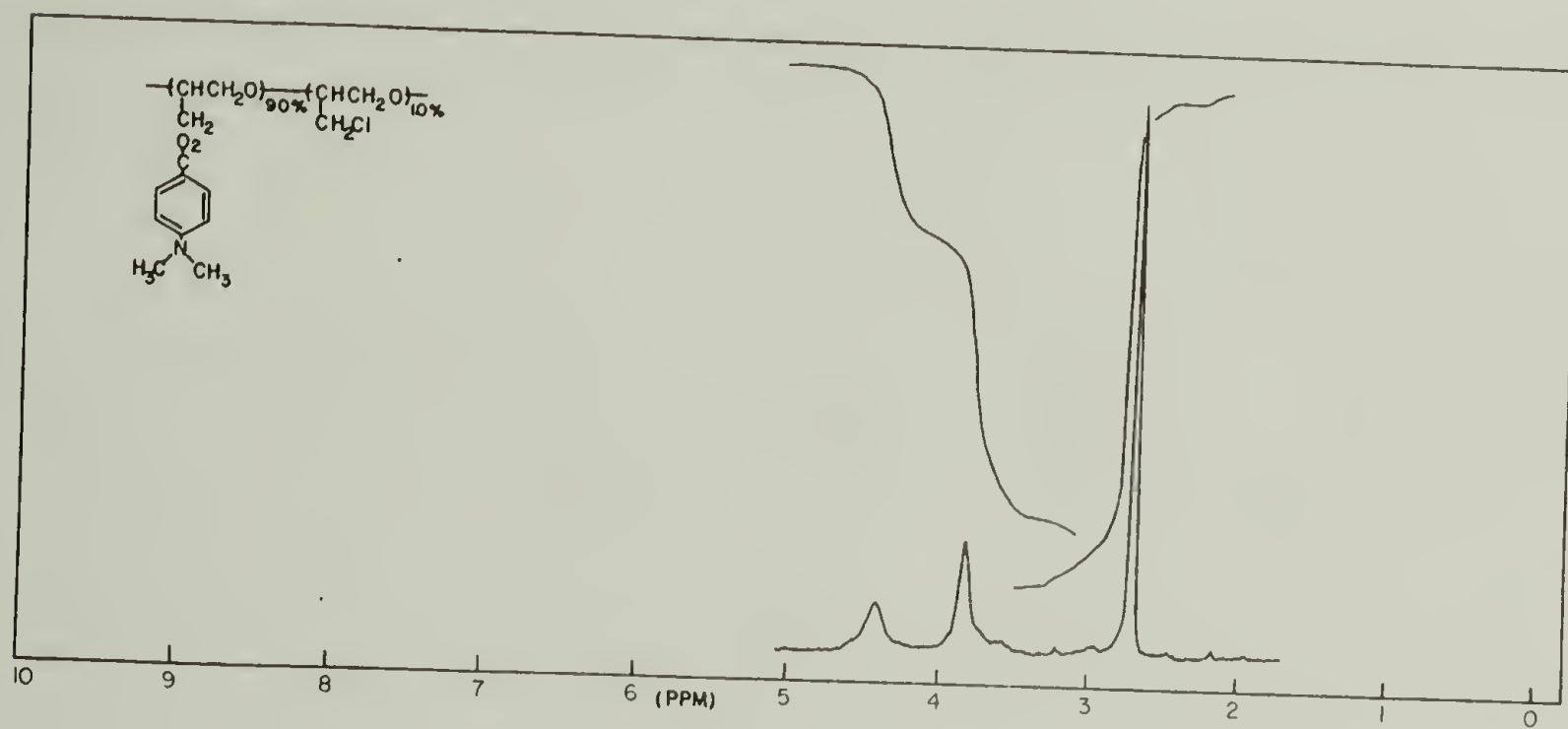
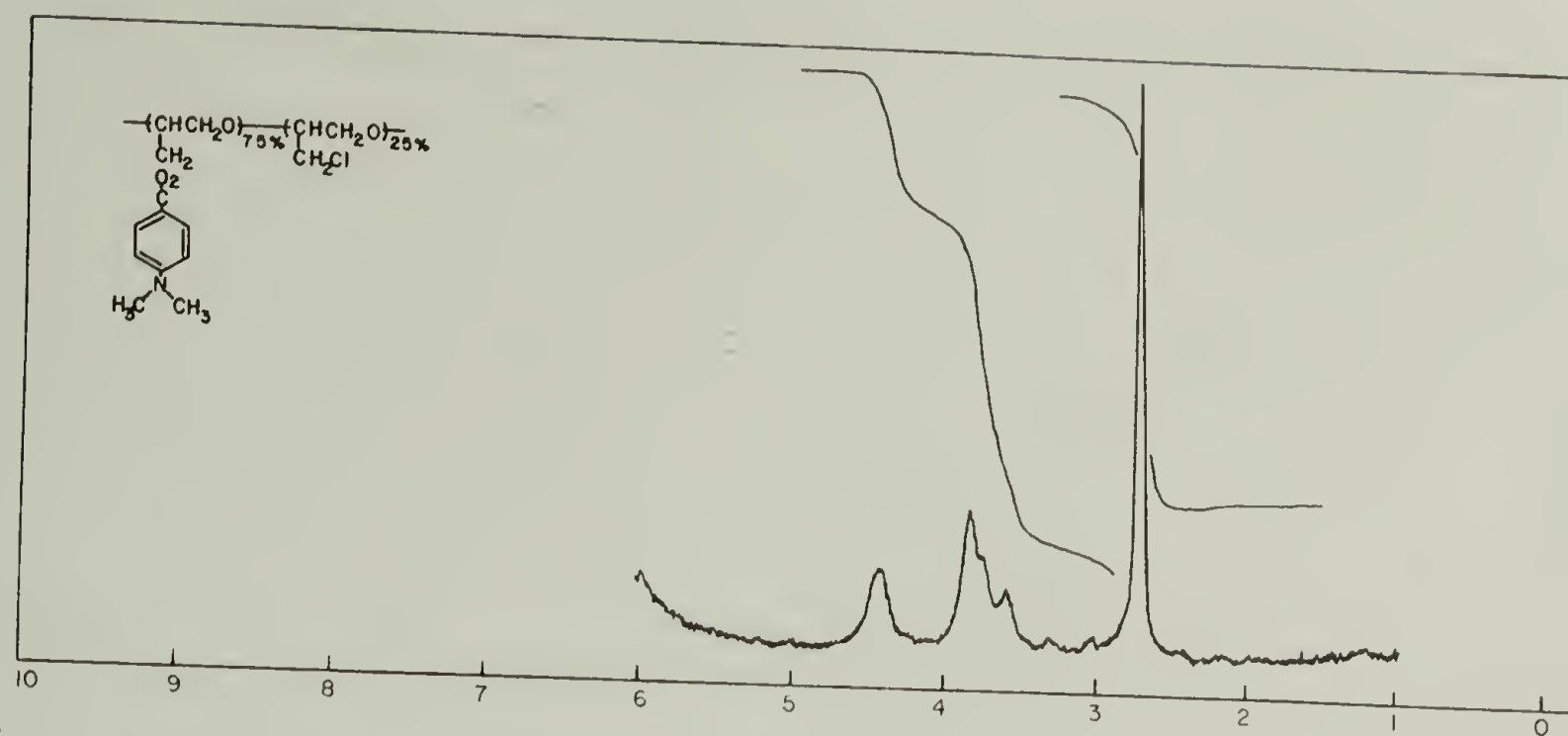


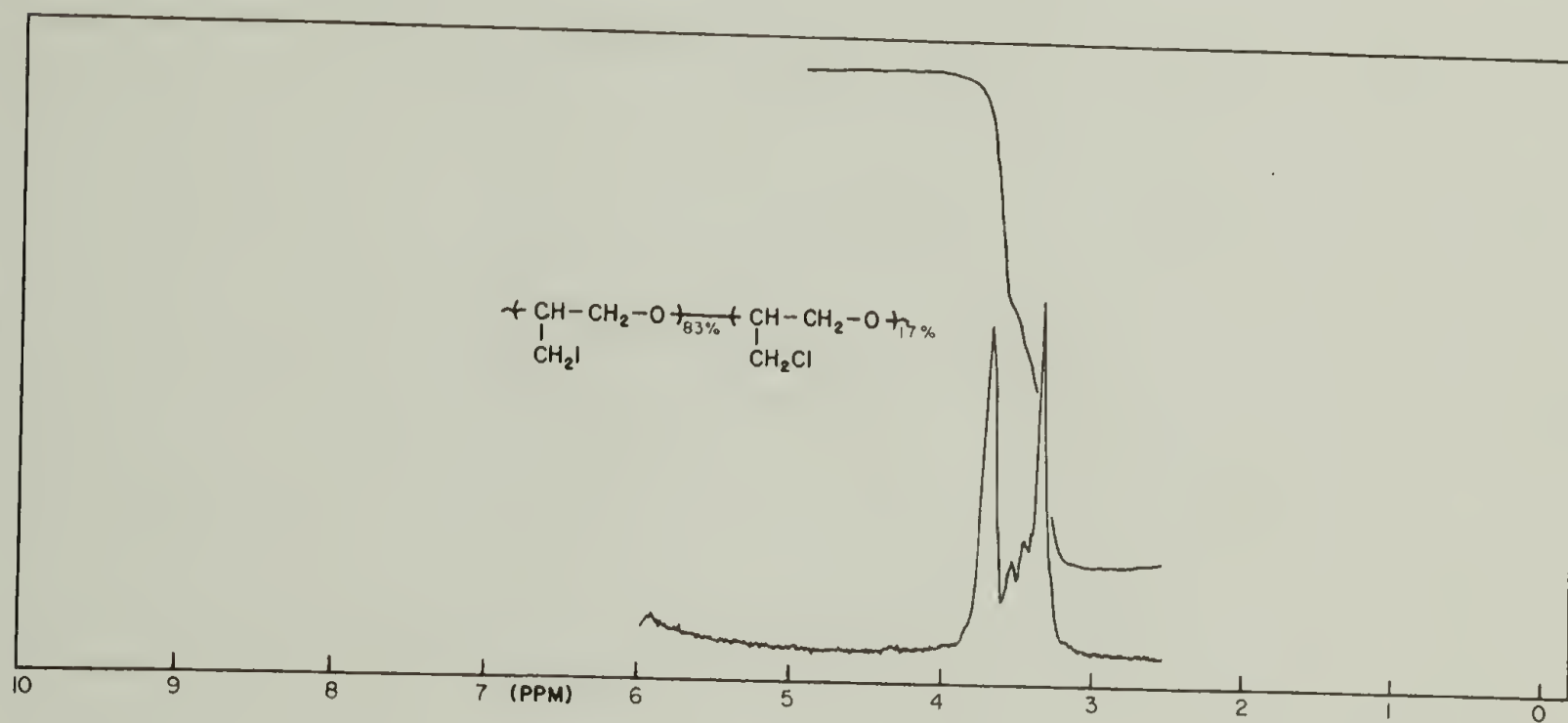
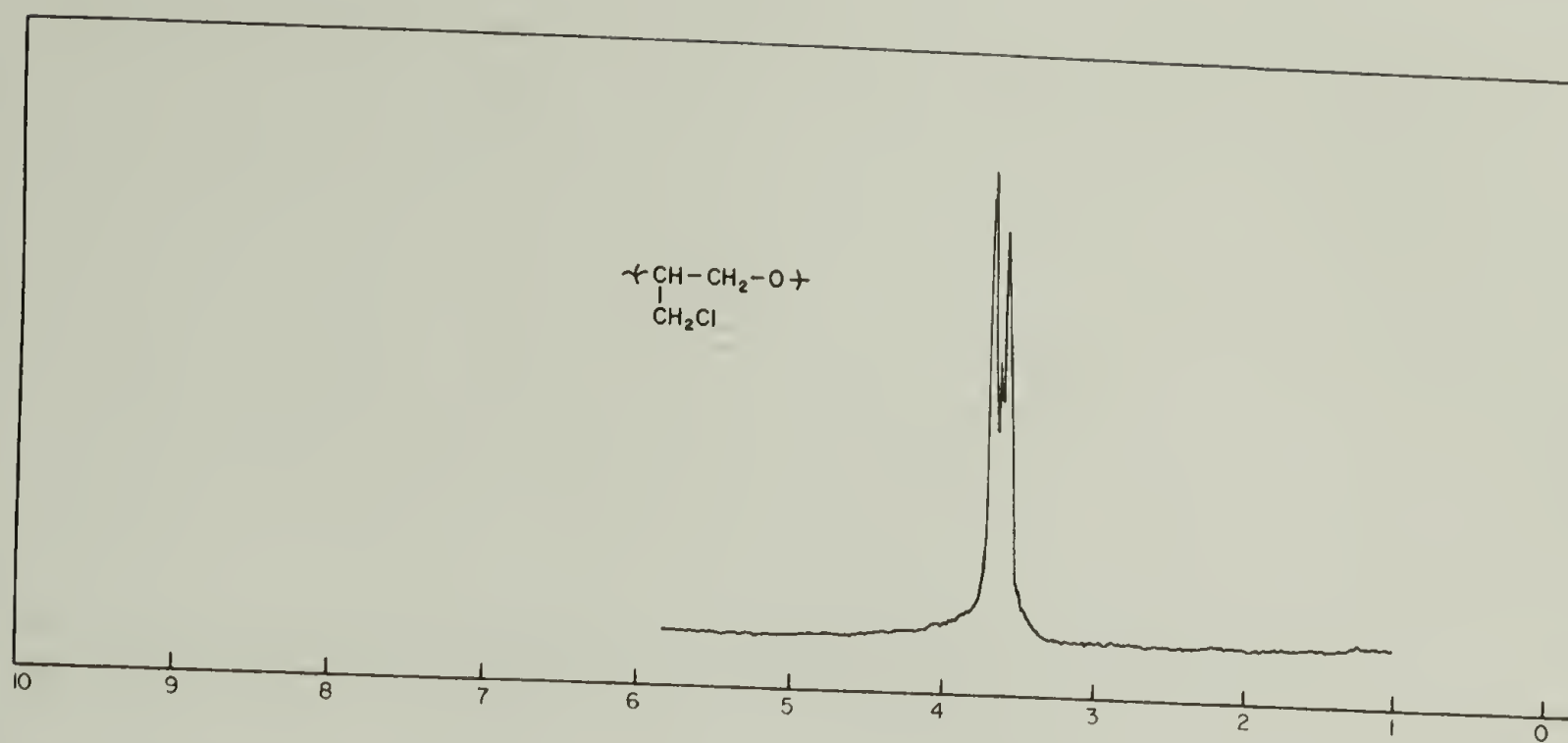


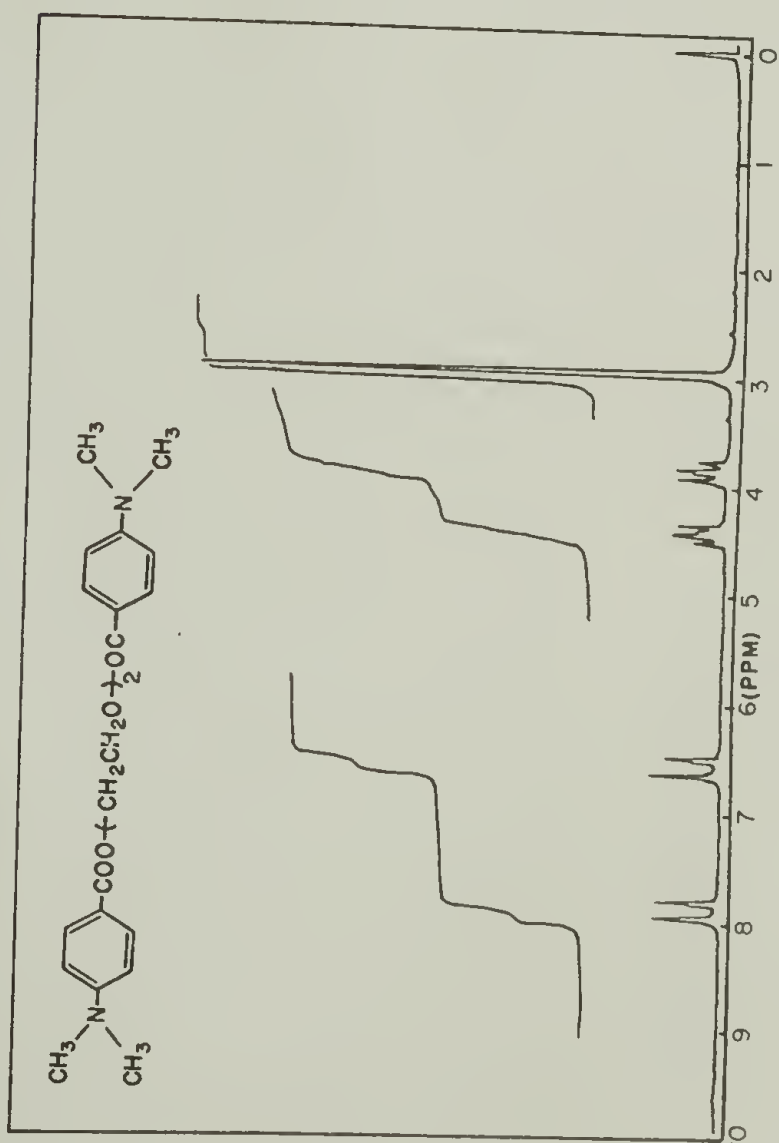
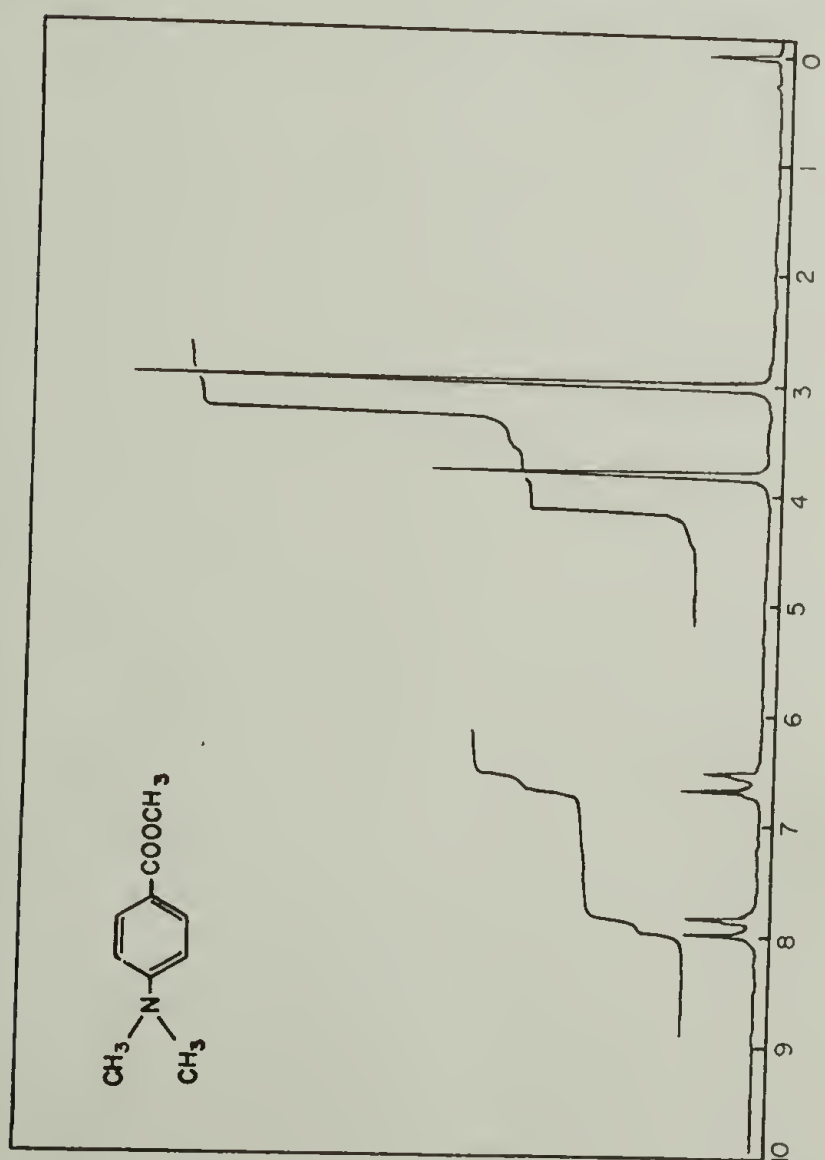
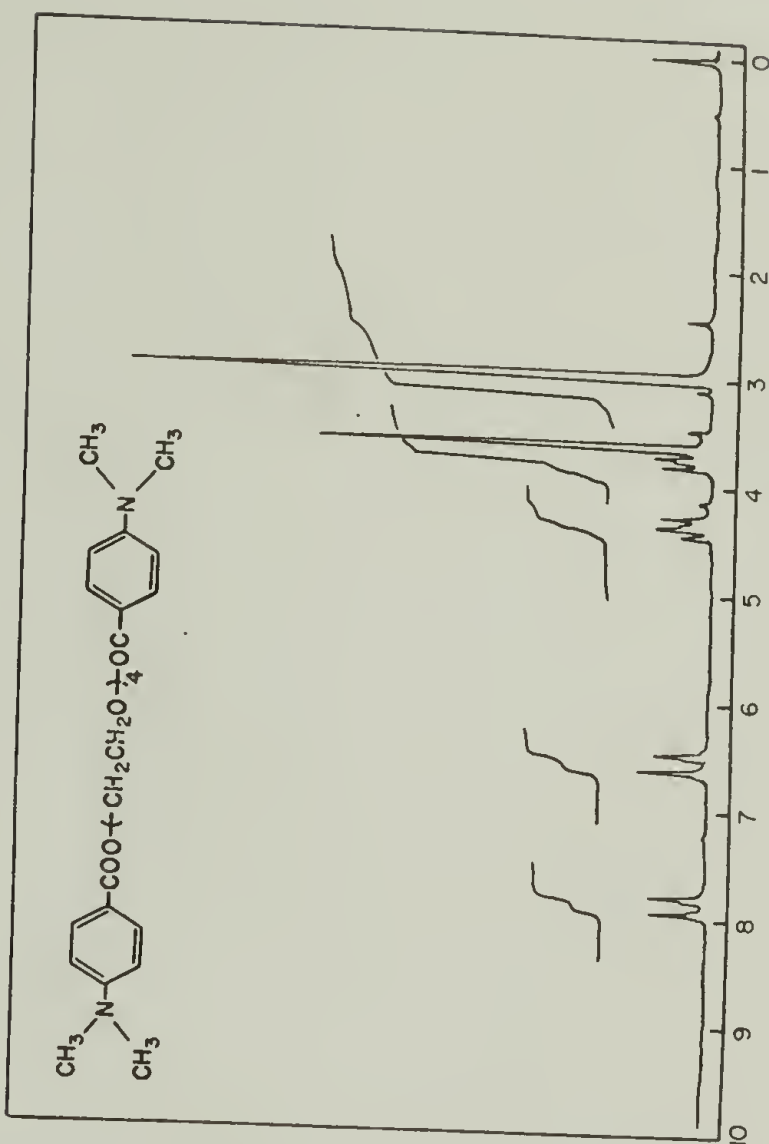
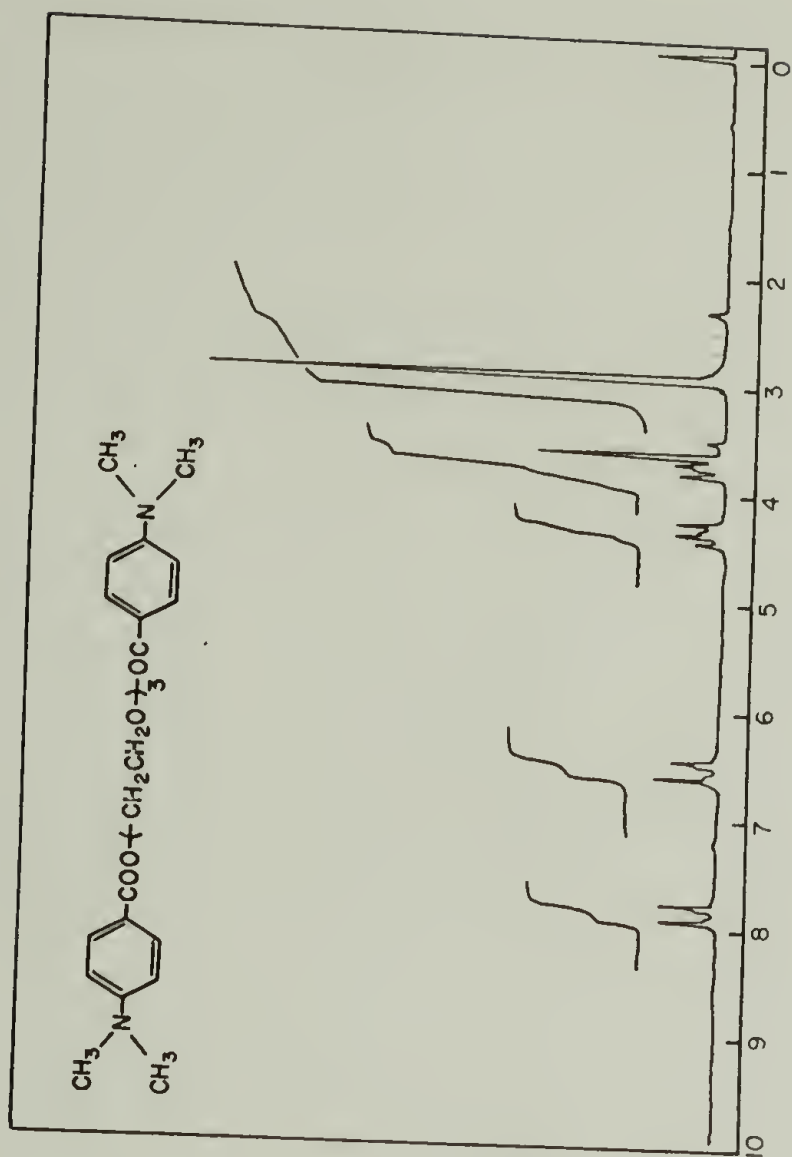


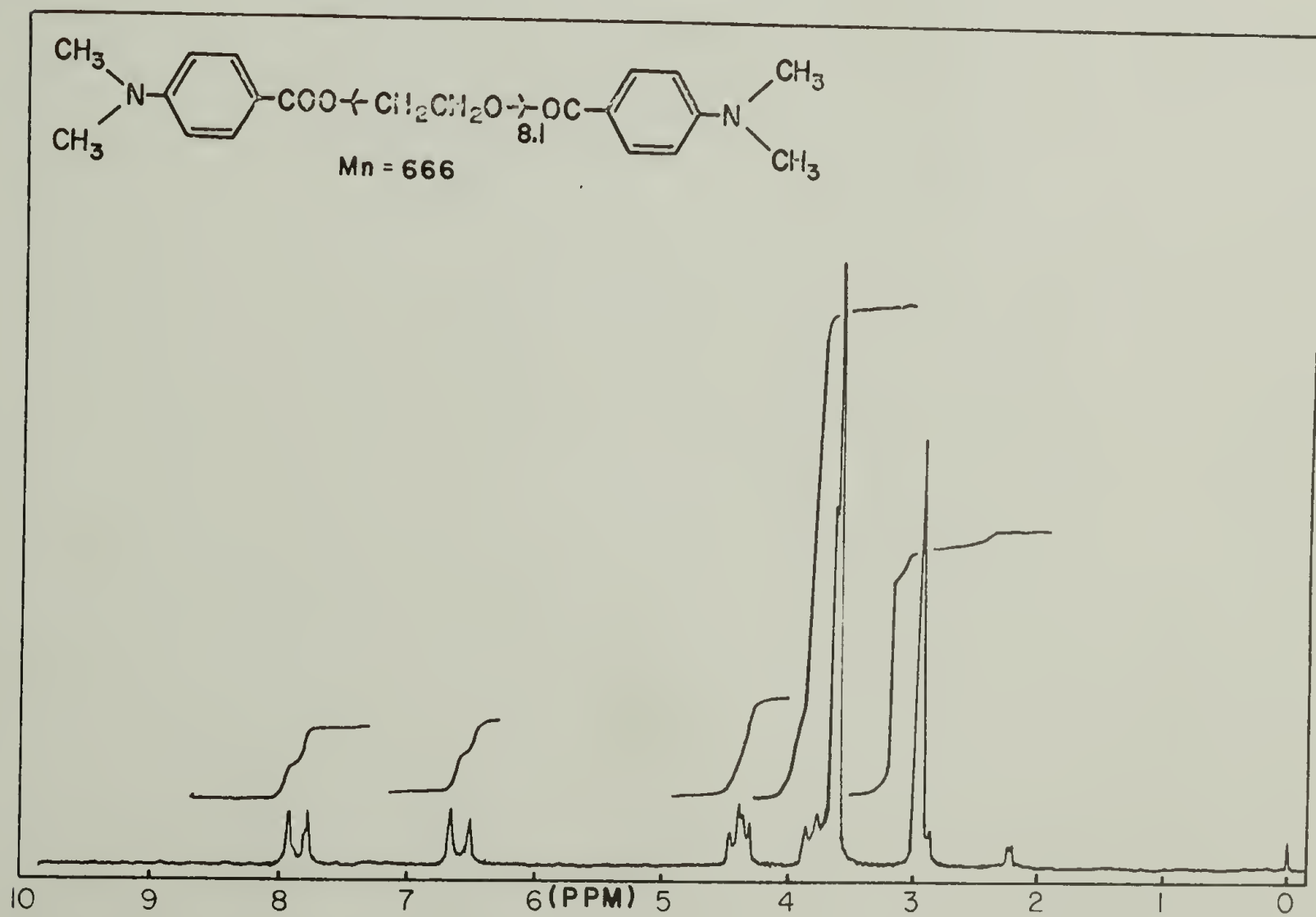
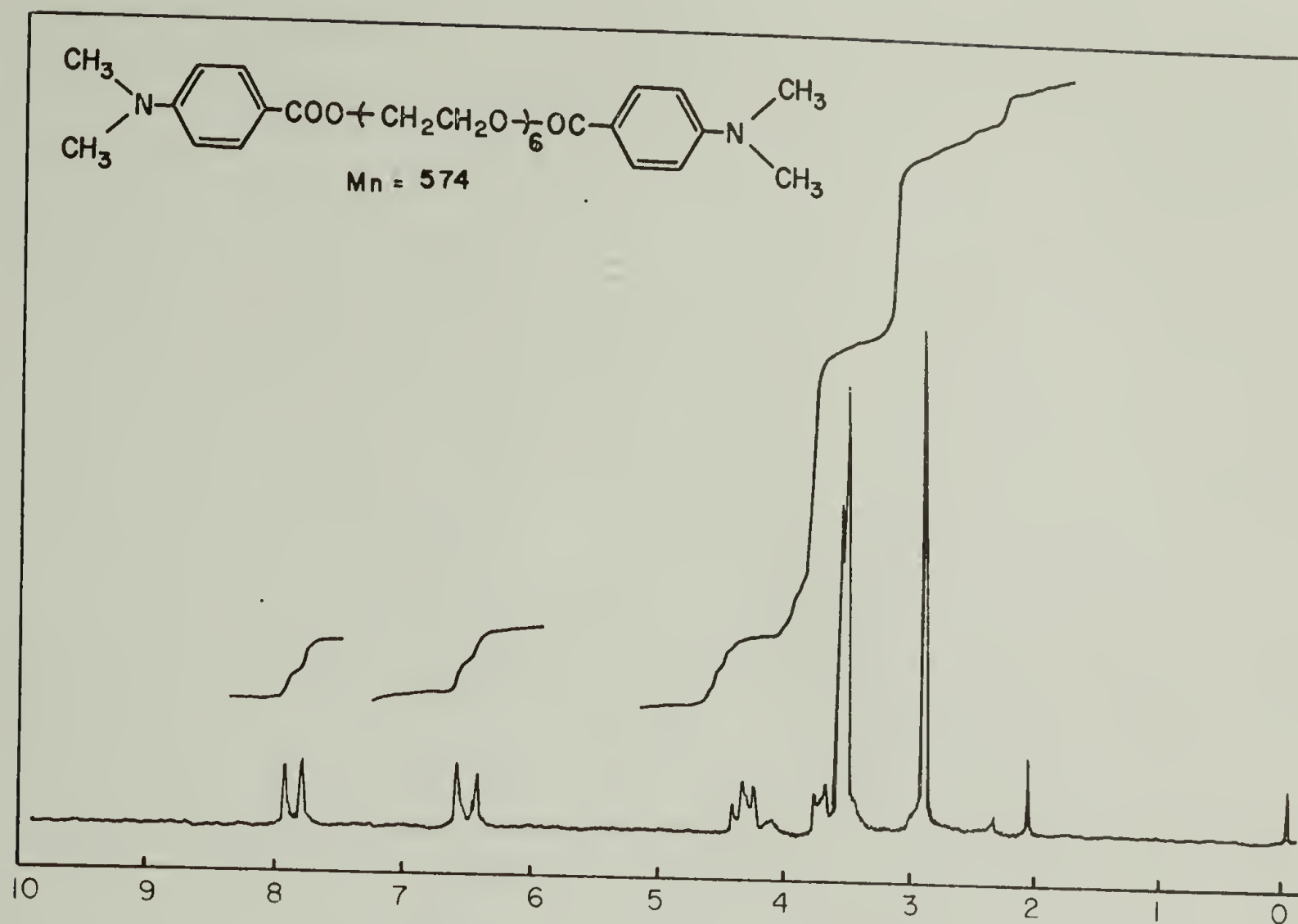


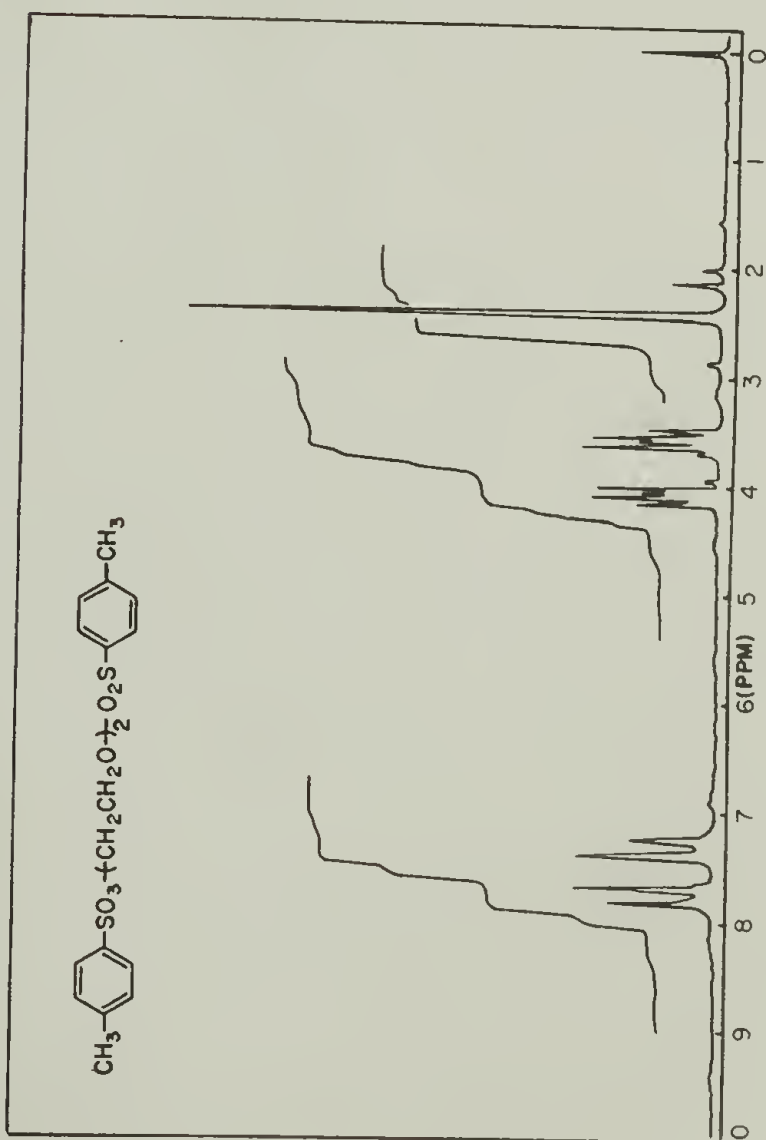
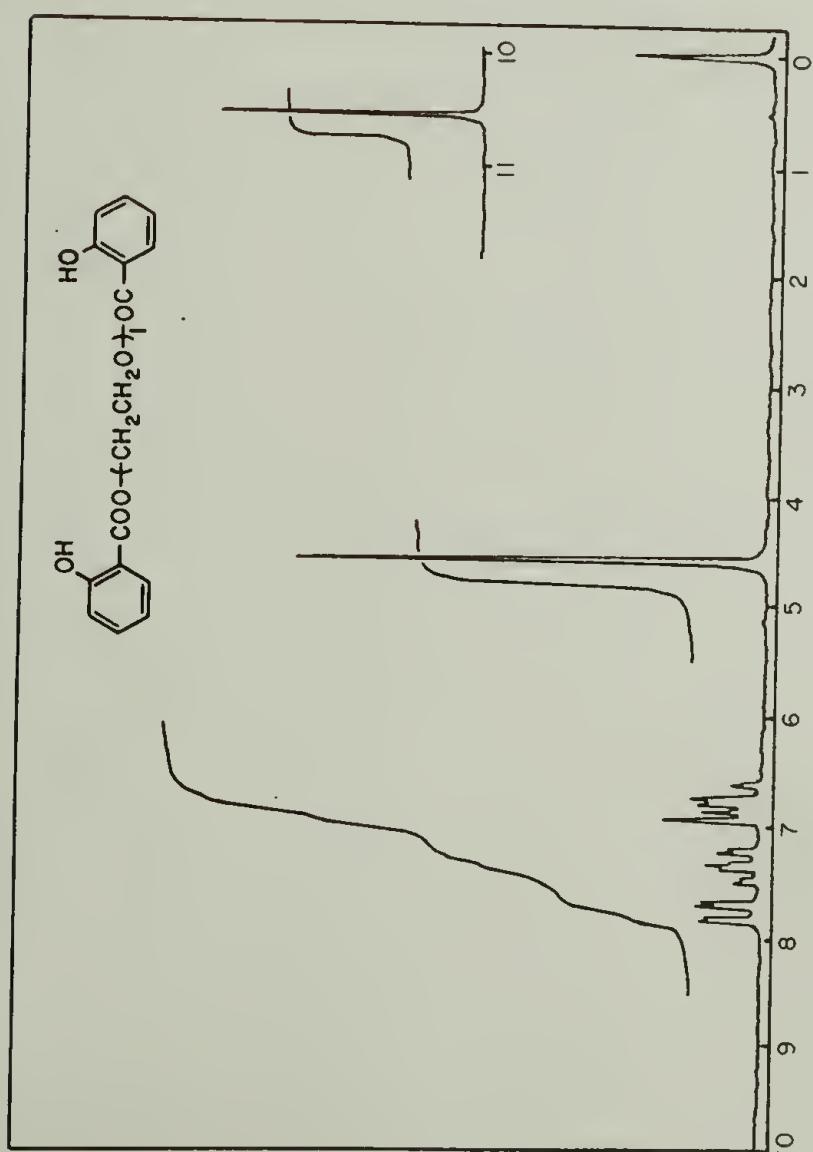
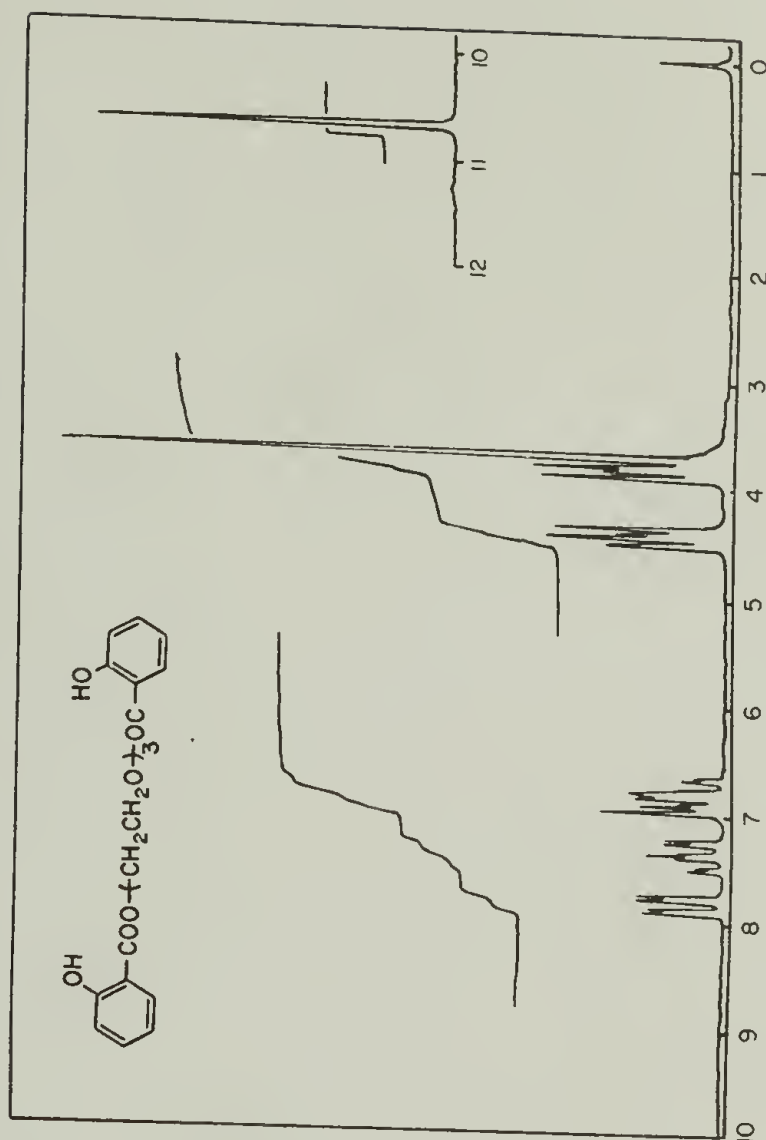
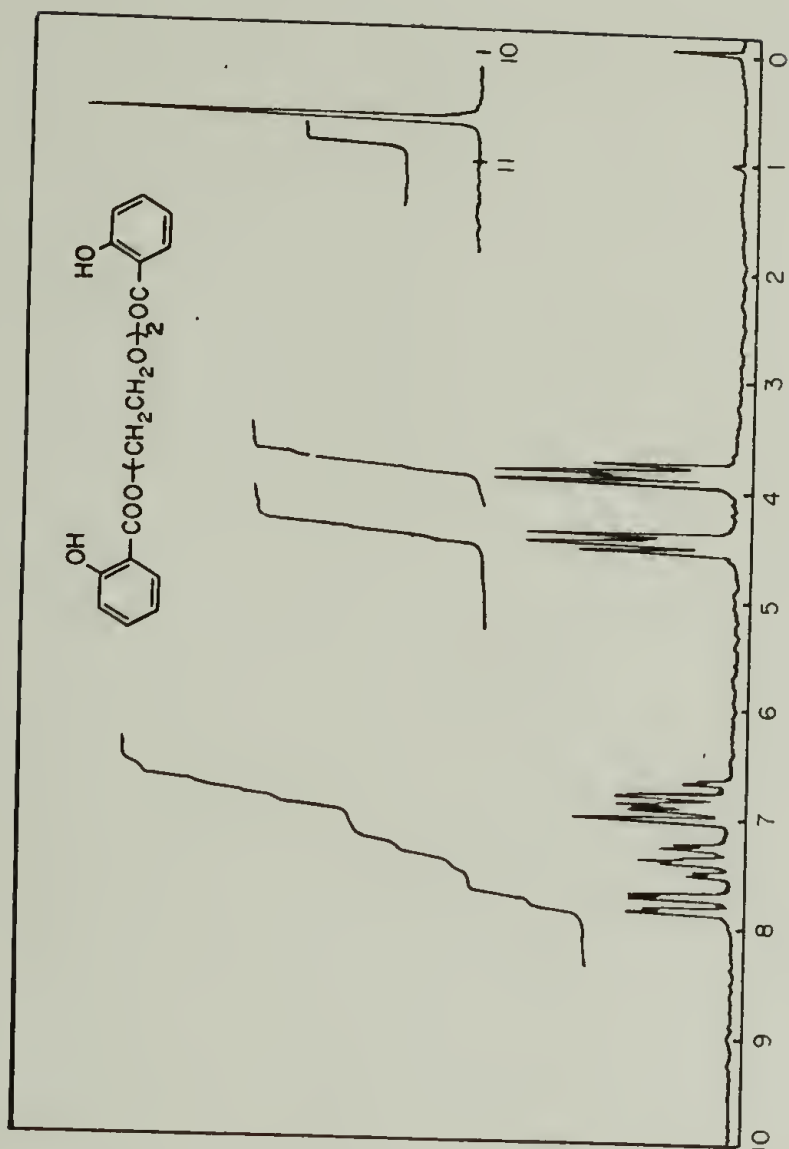






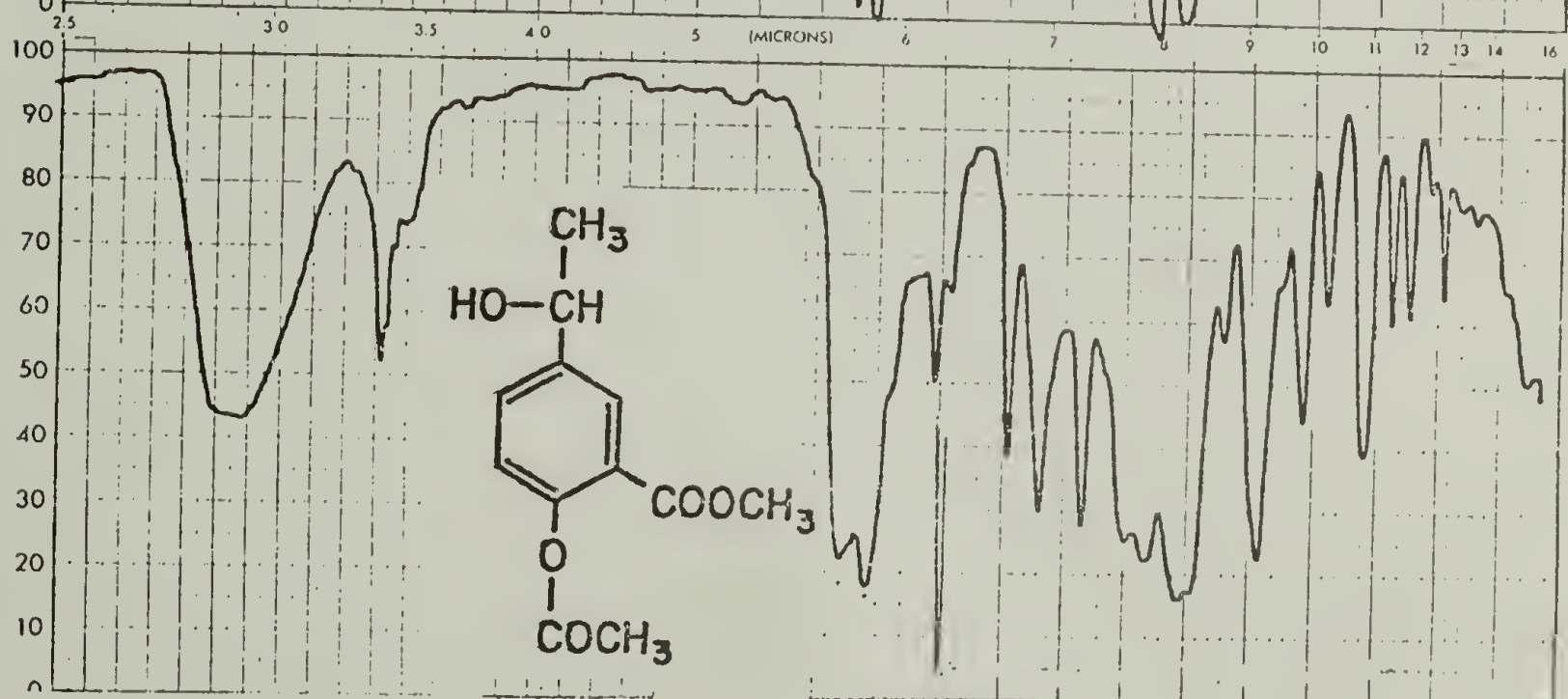
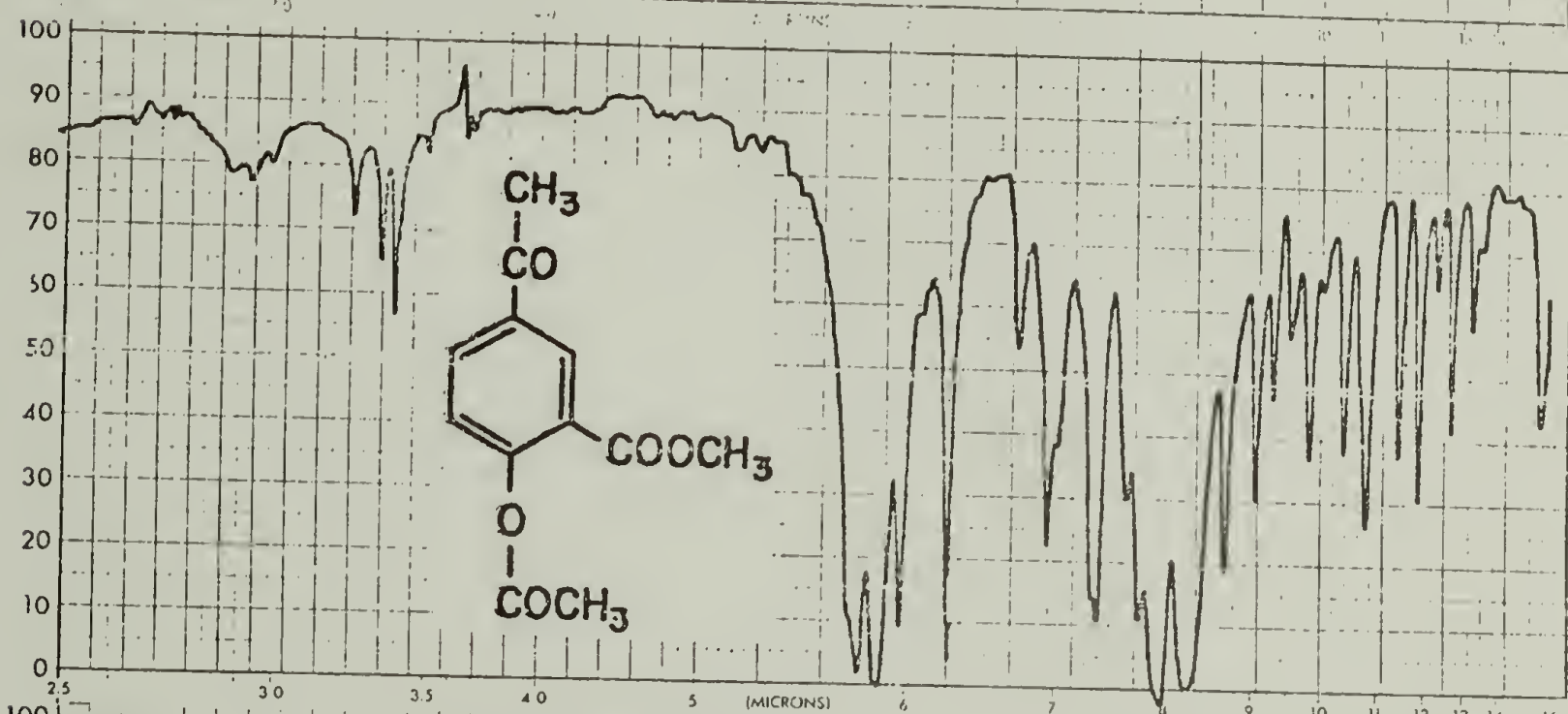
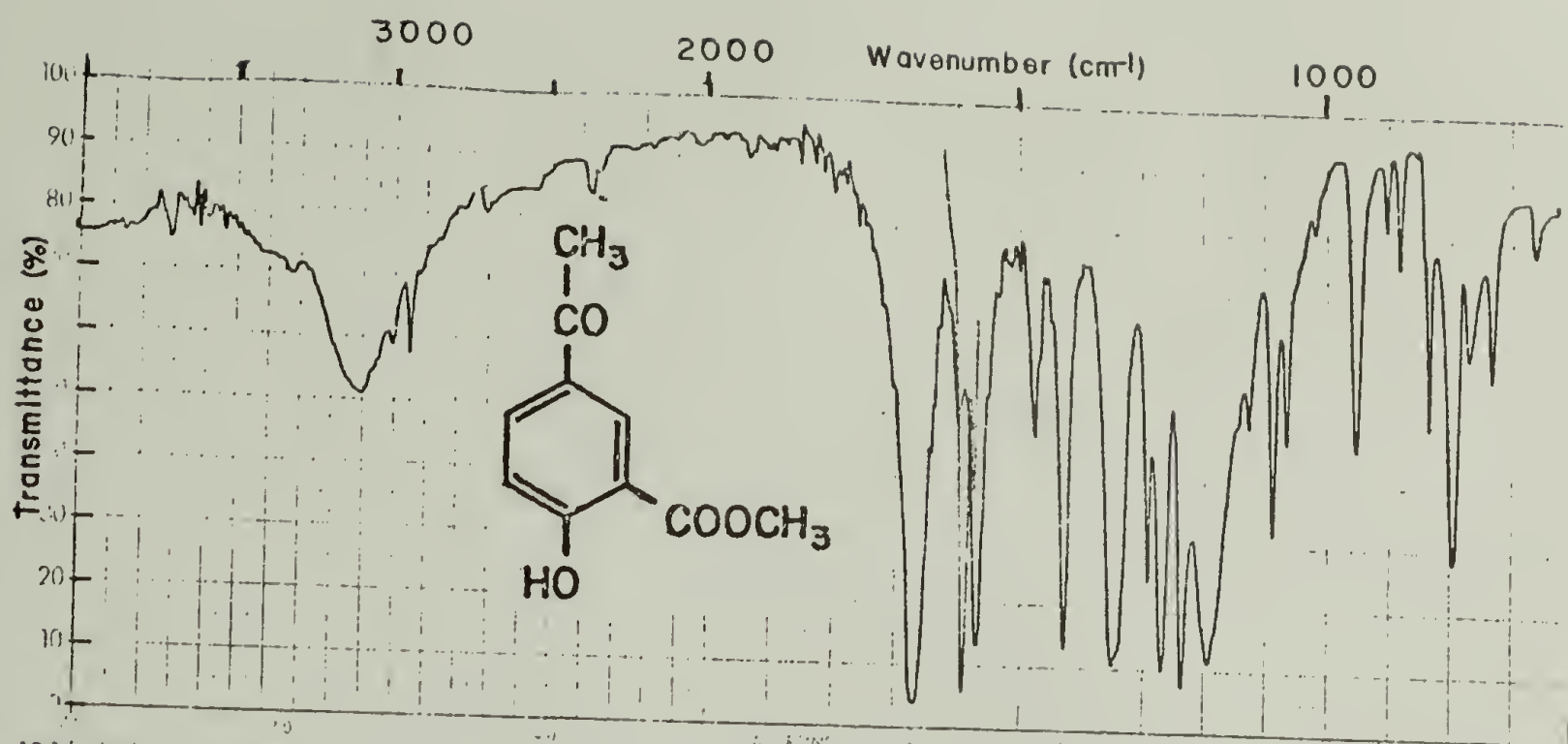


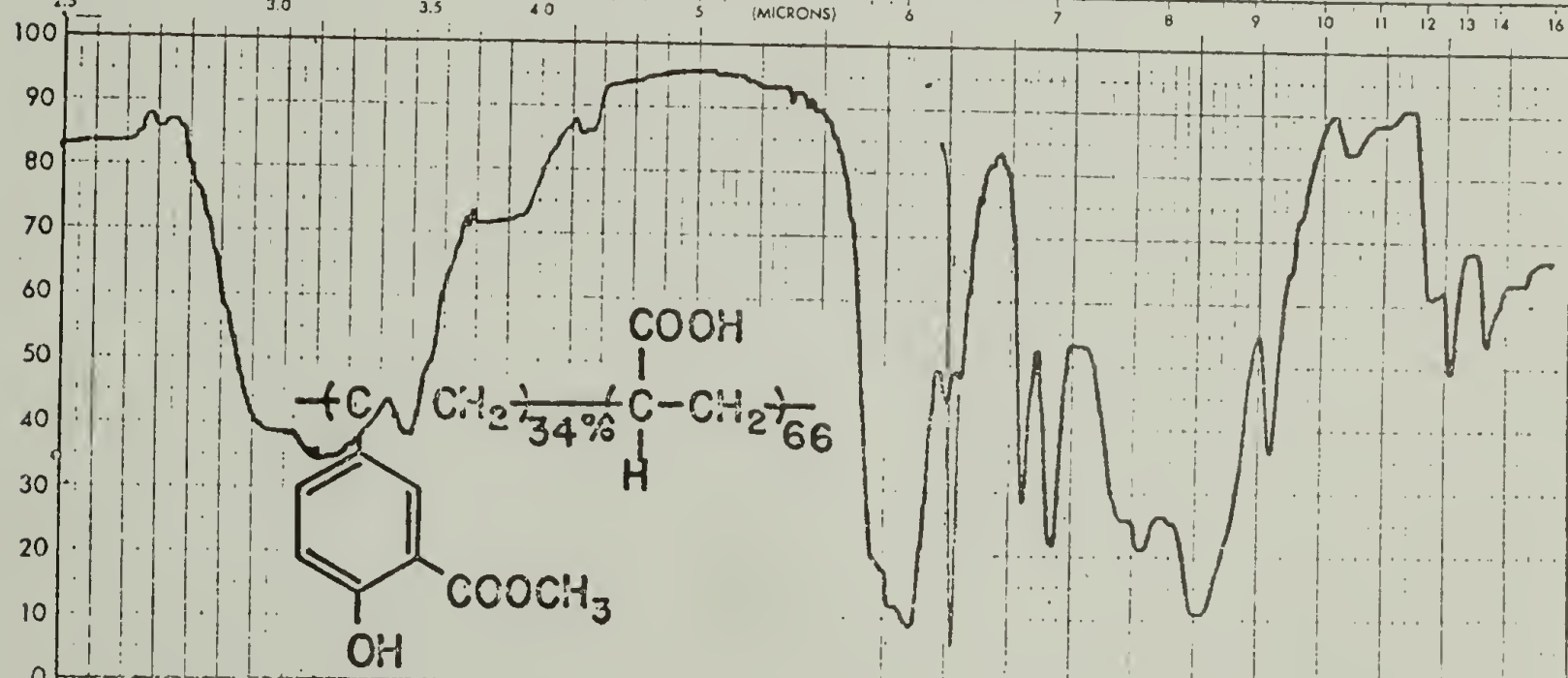
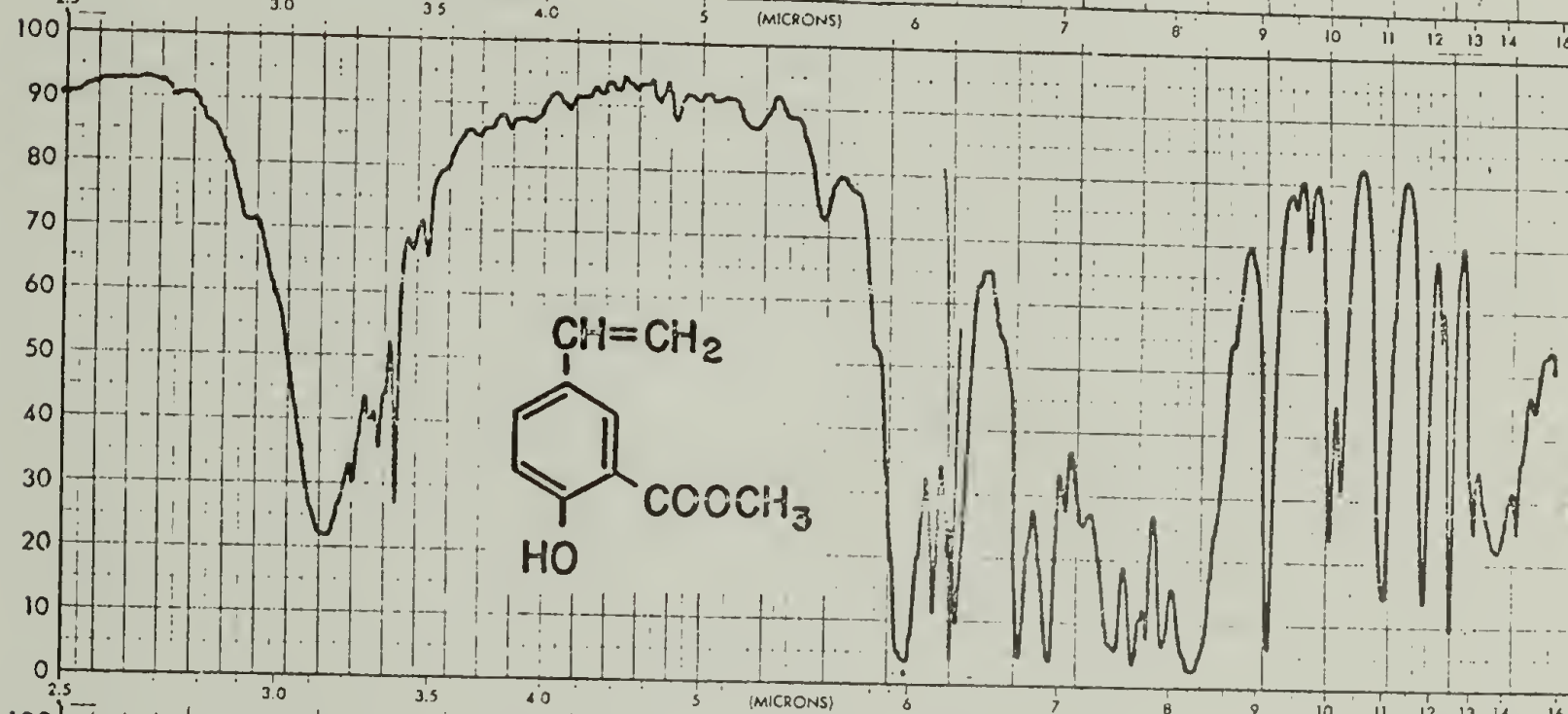
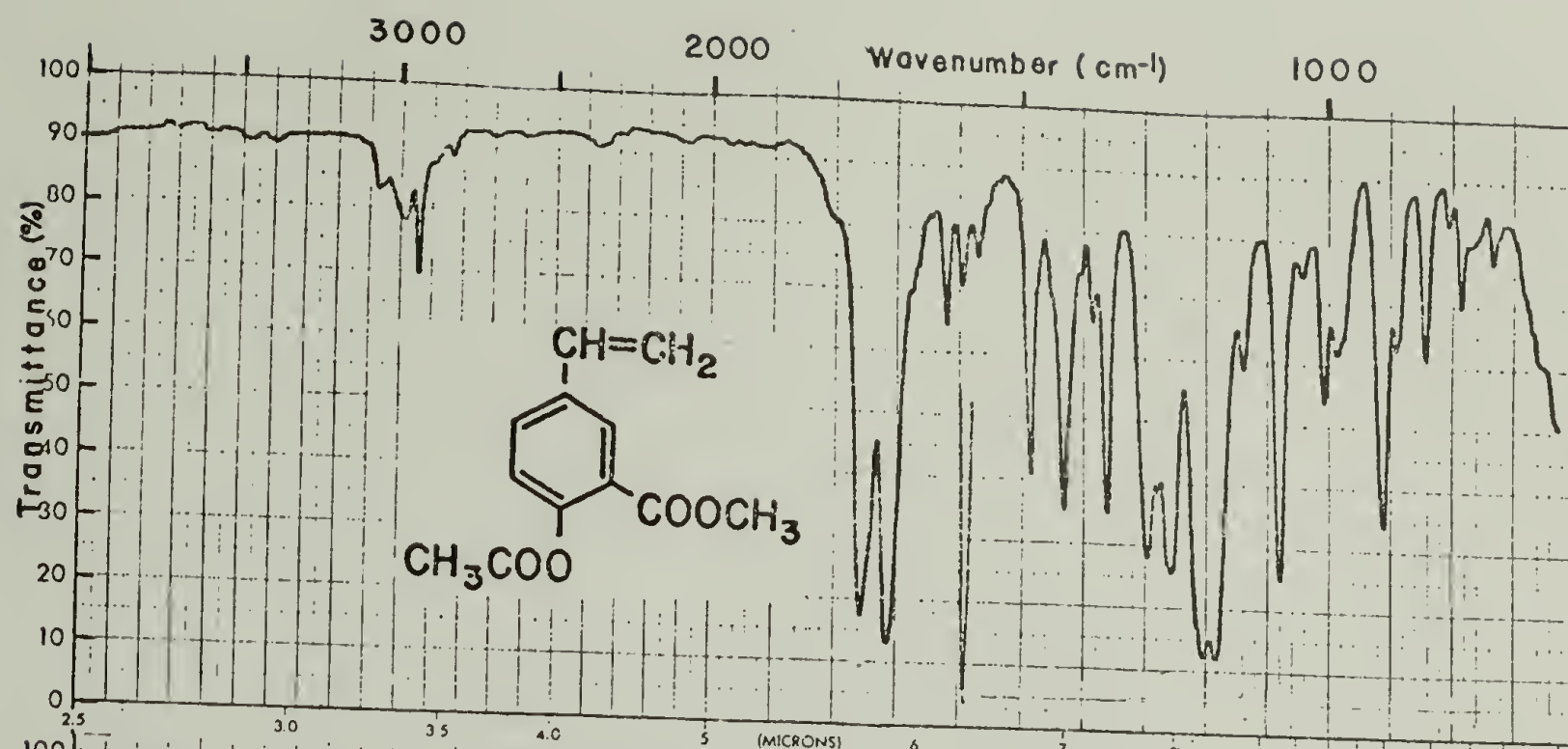


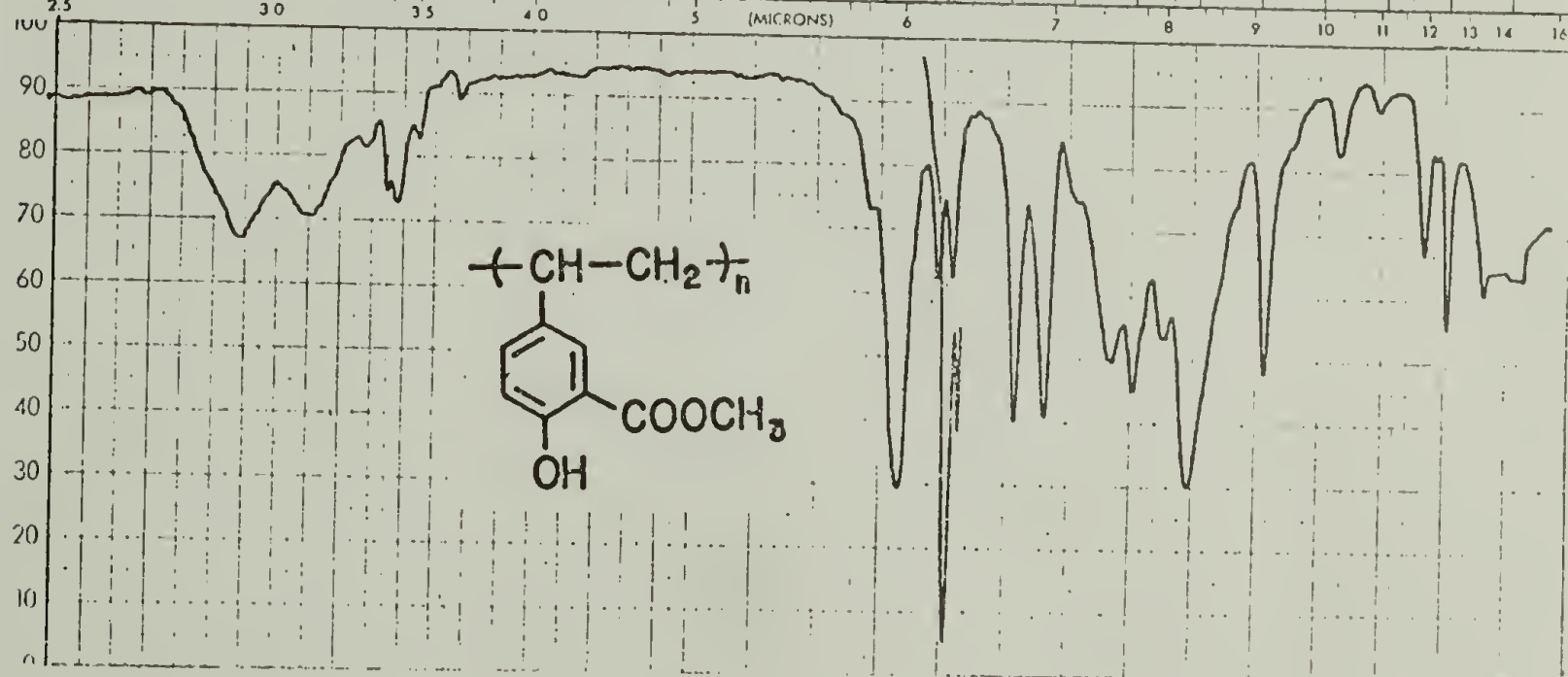
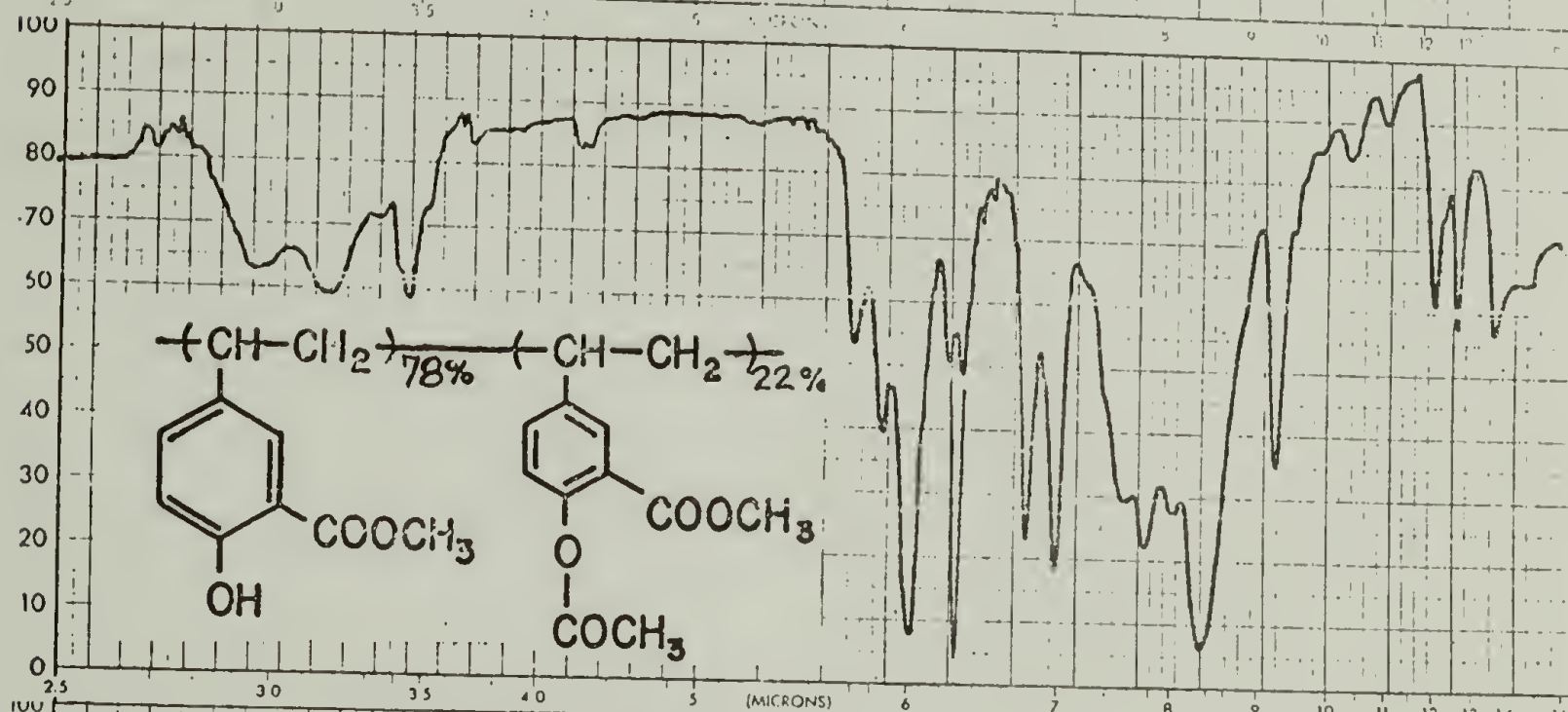
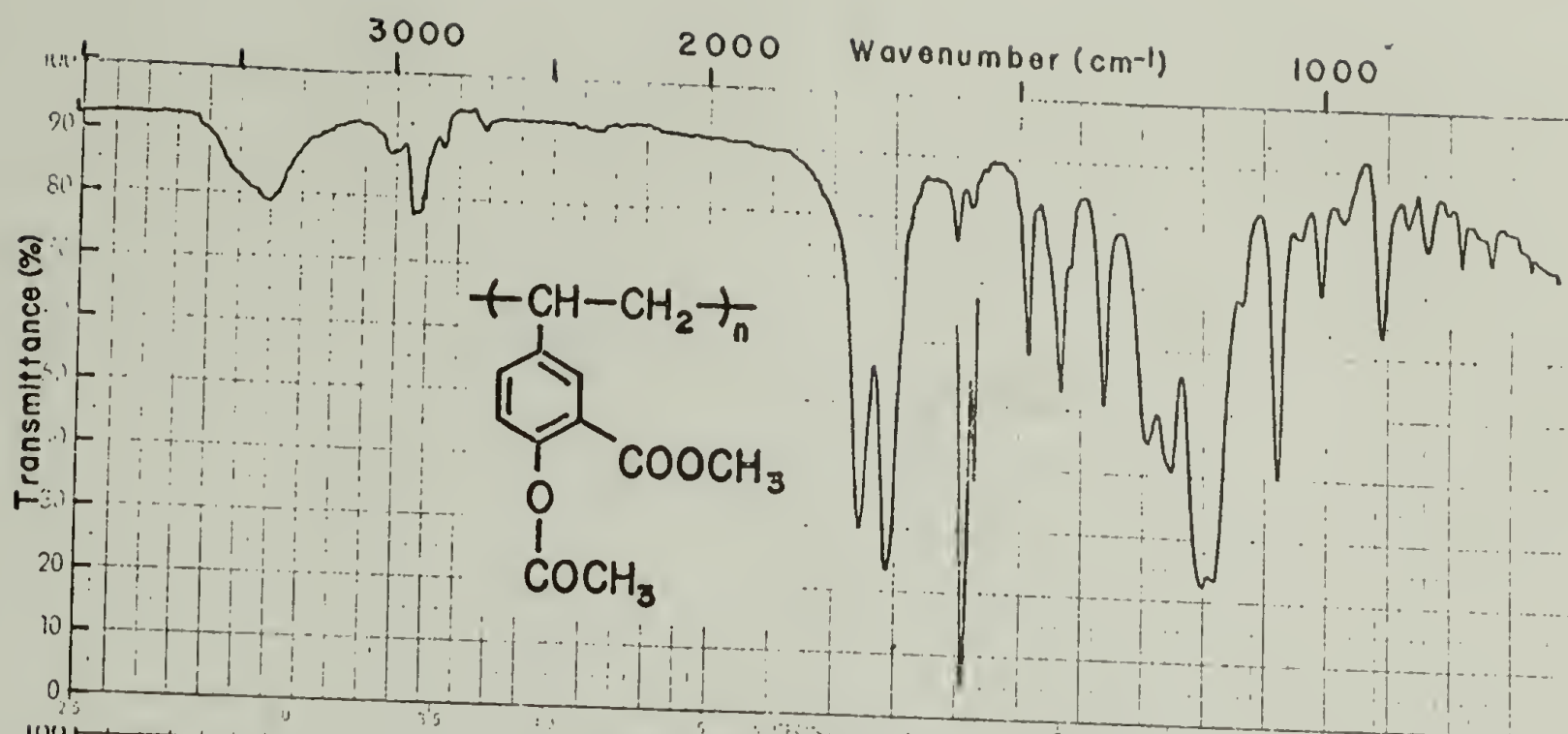


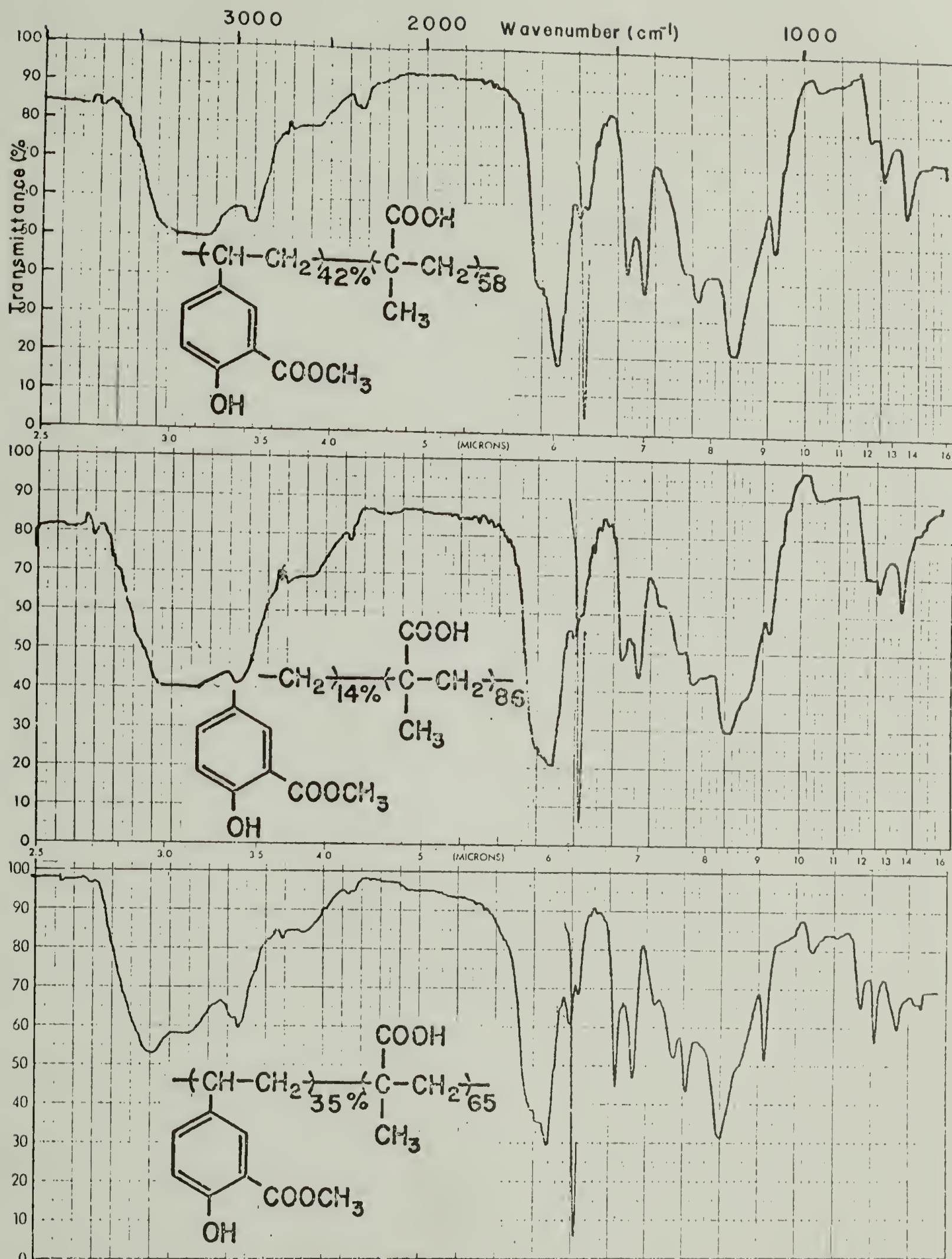
APPENDIX B

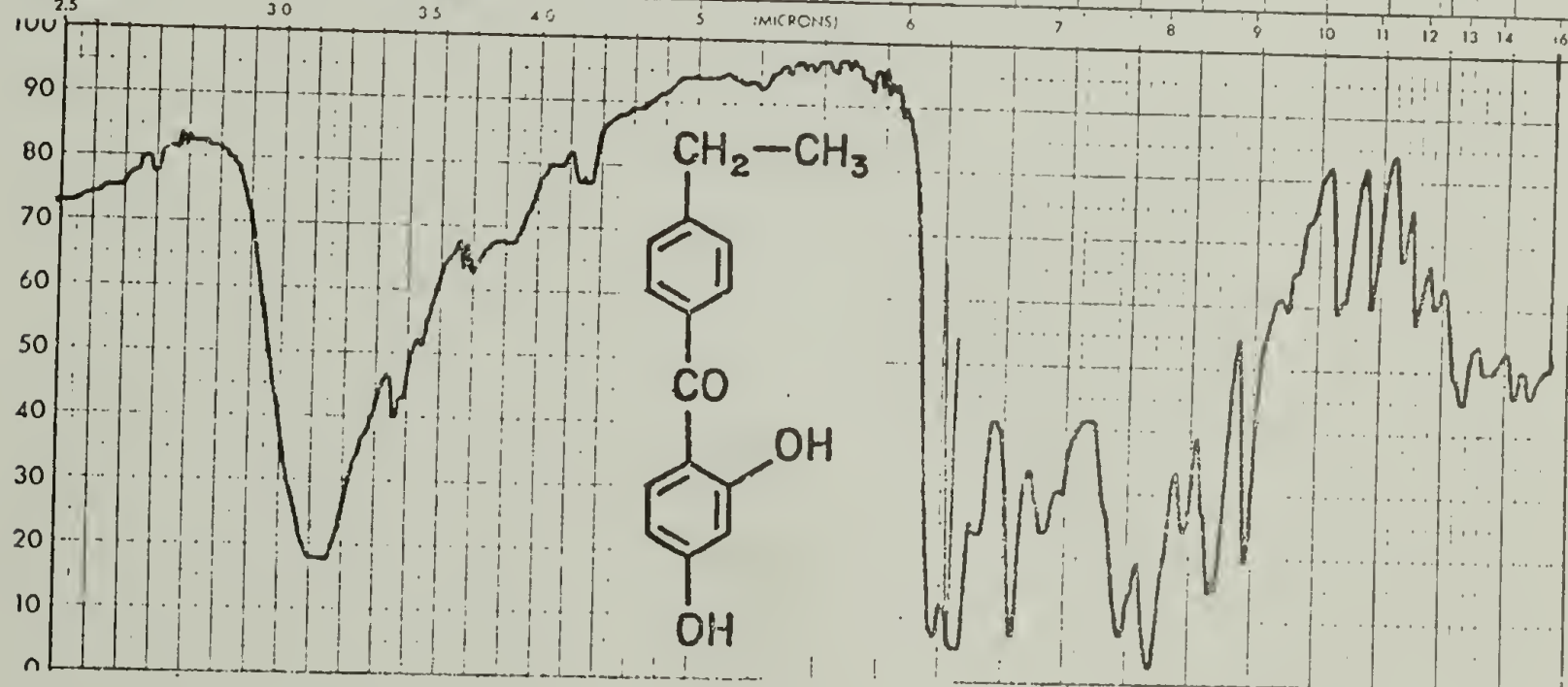
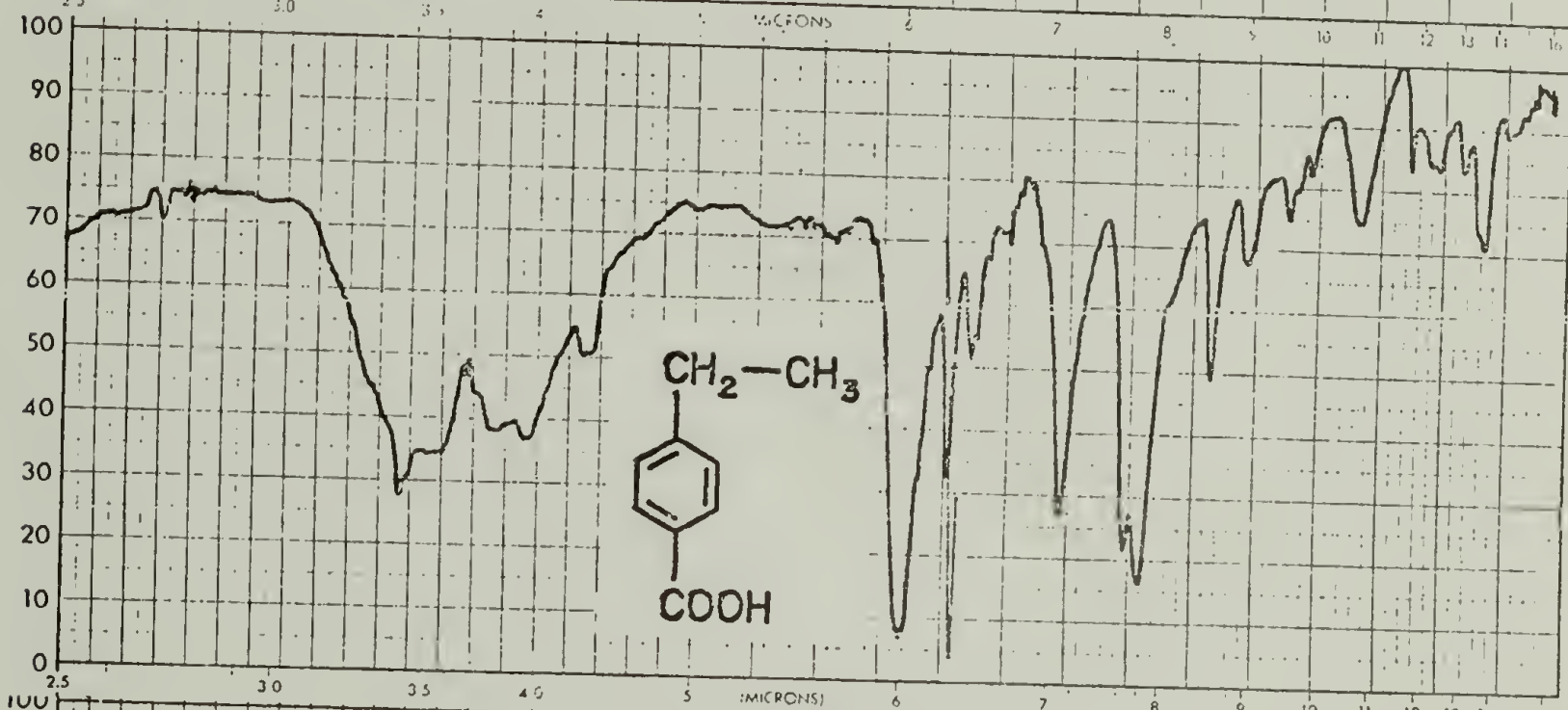
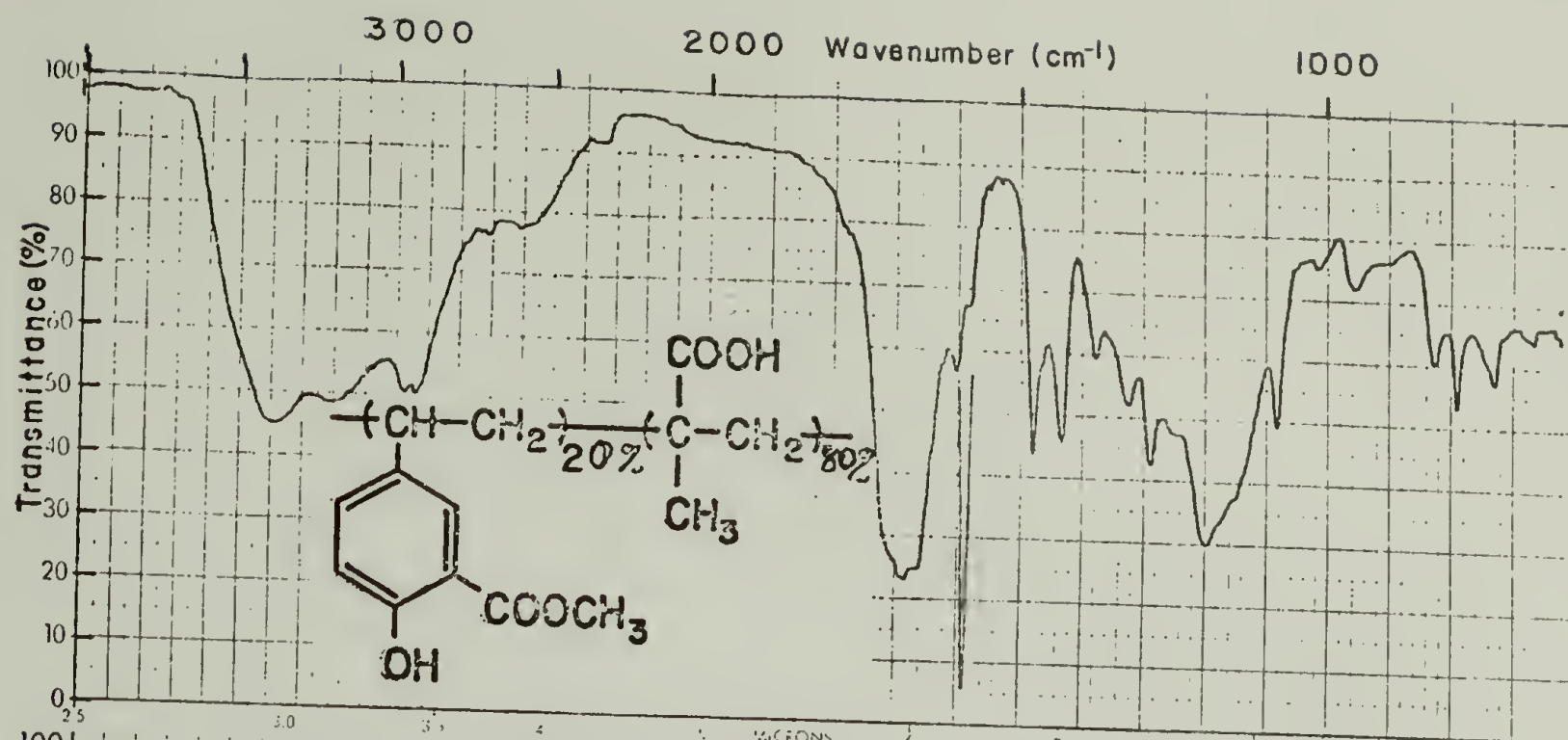
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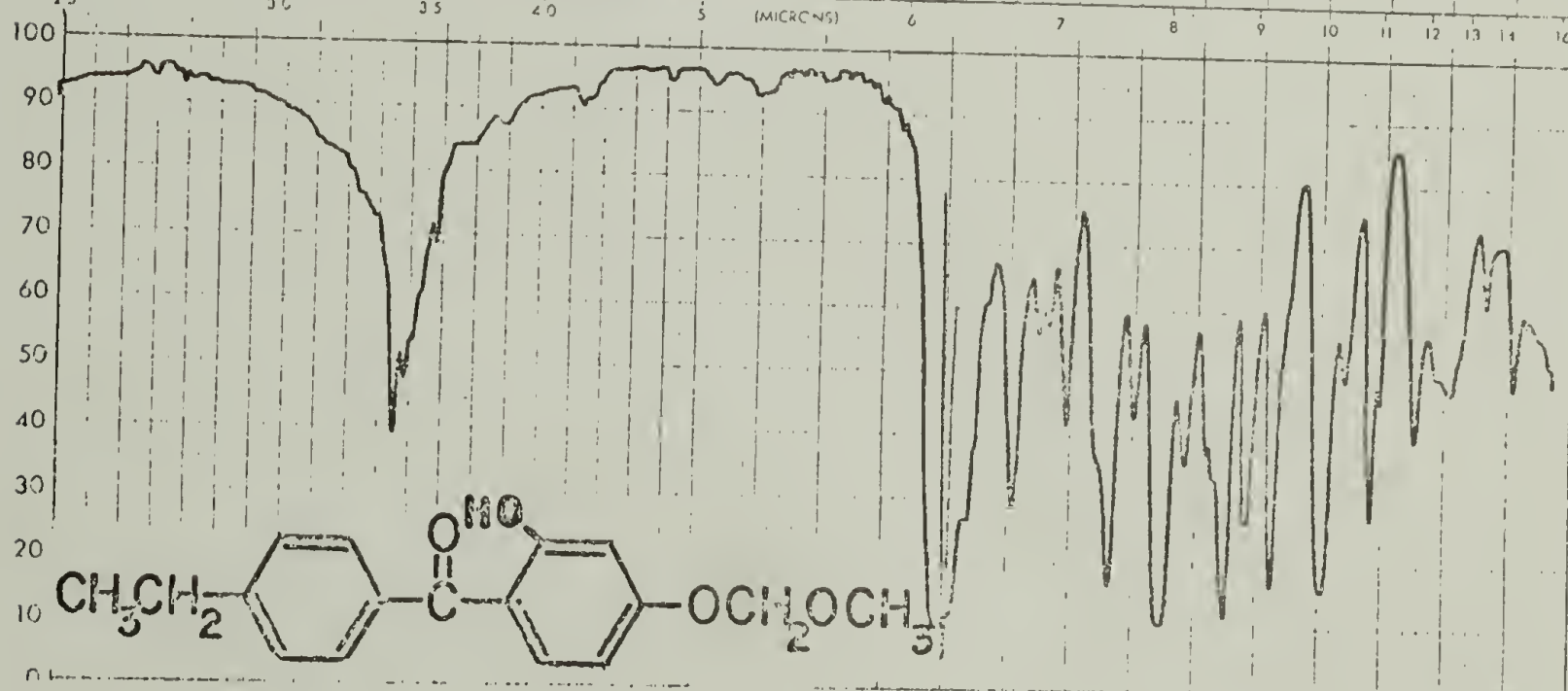
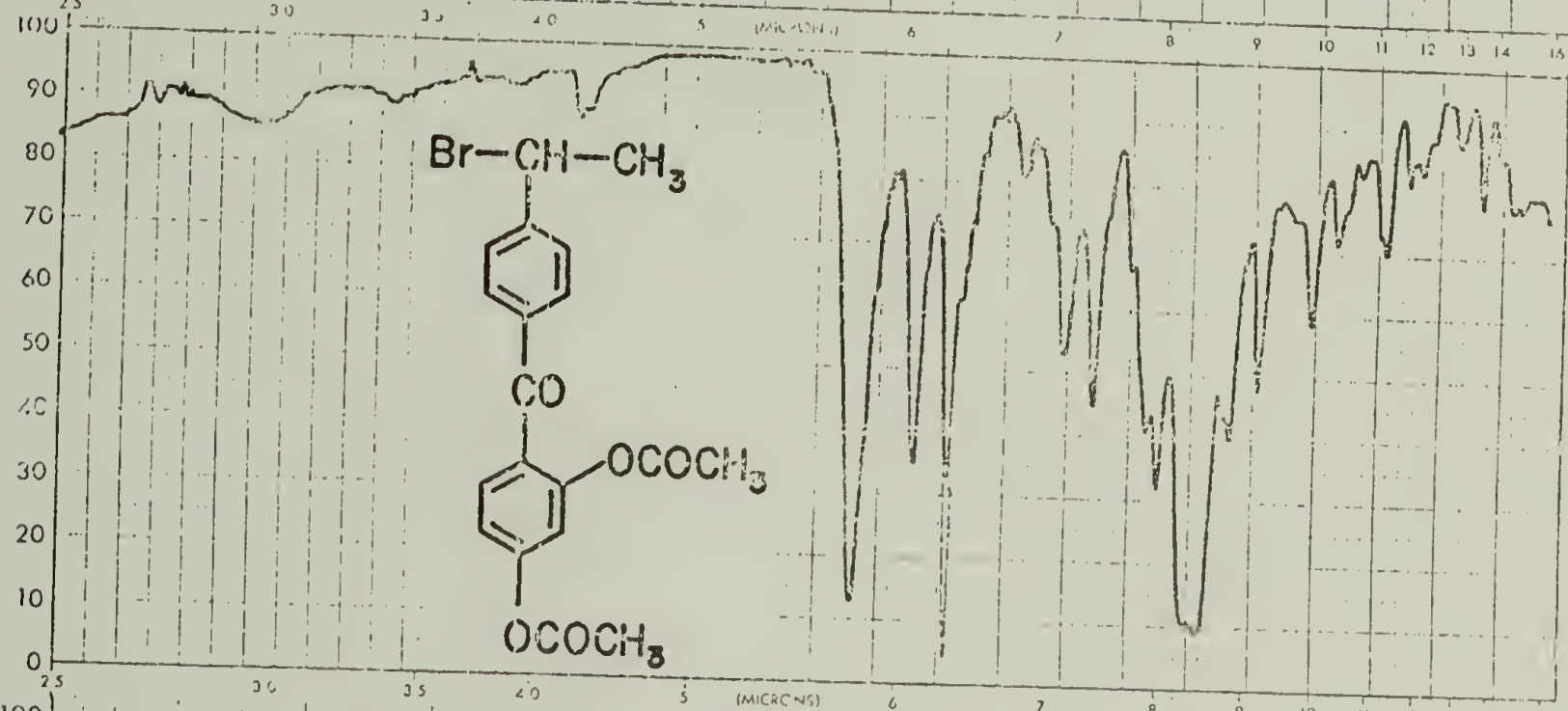
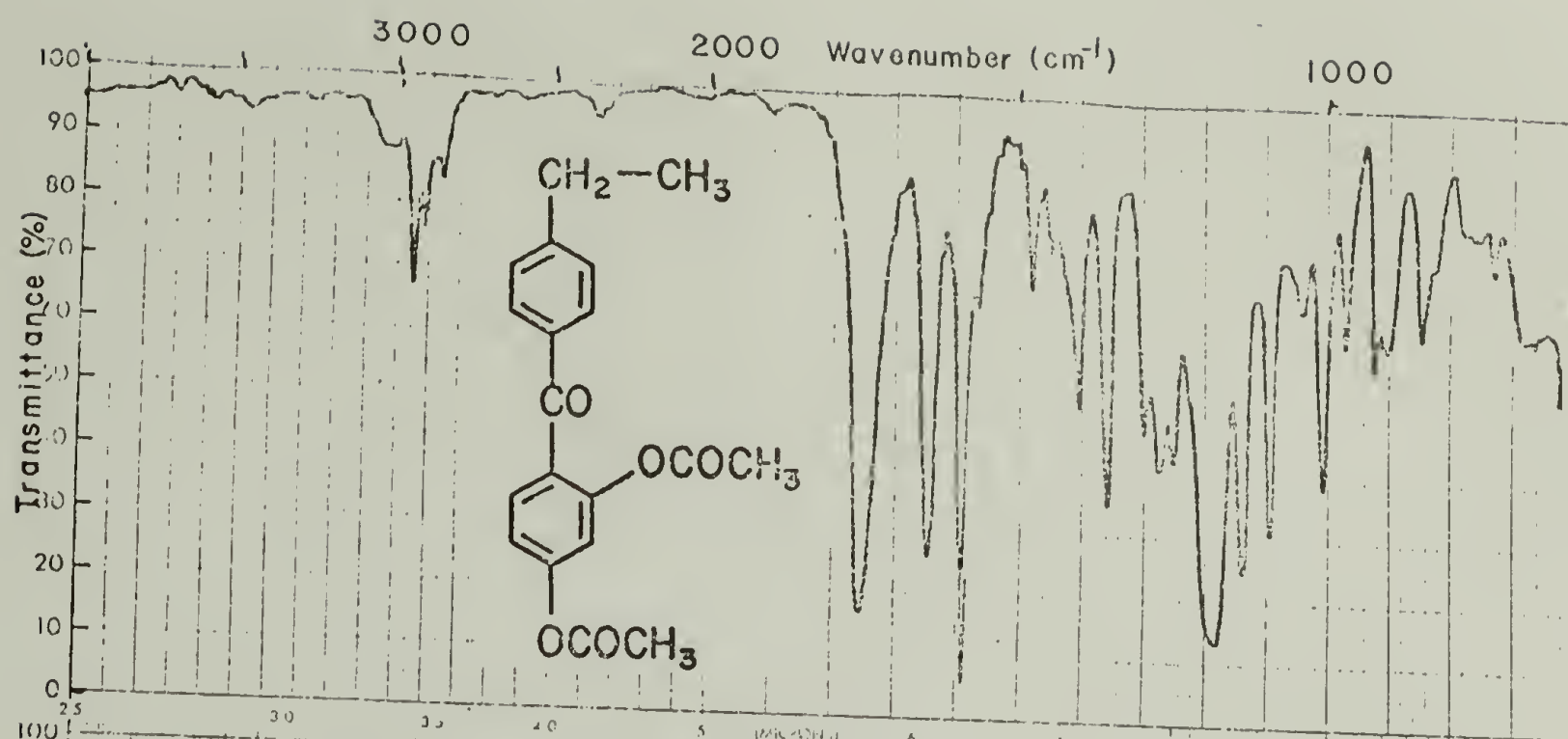


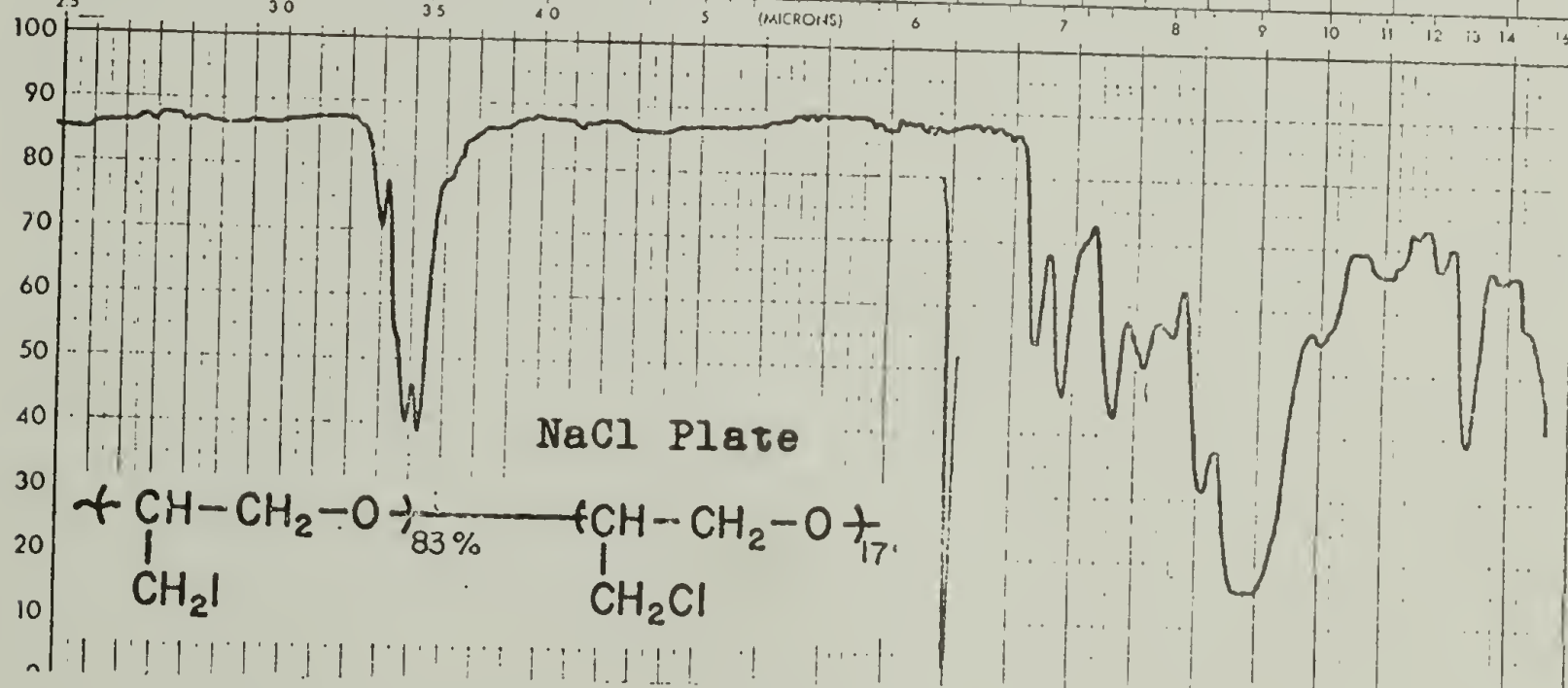
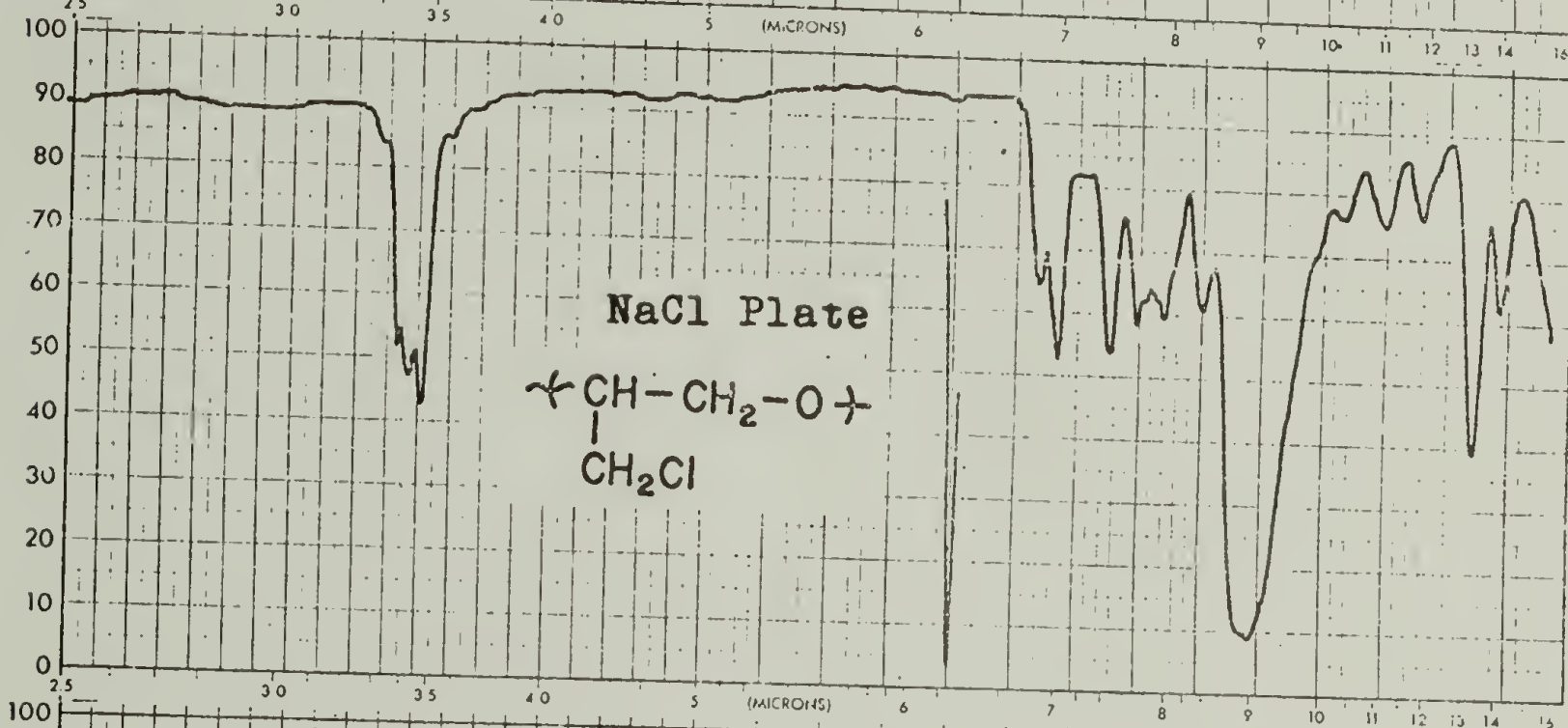
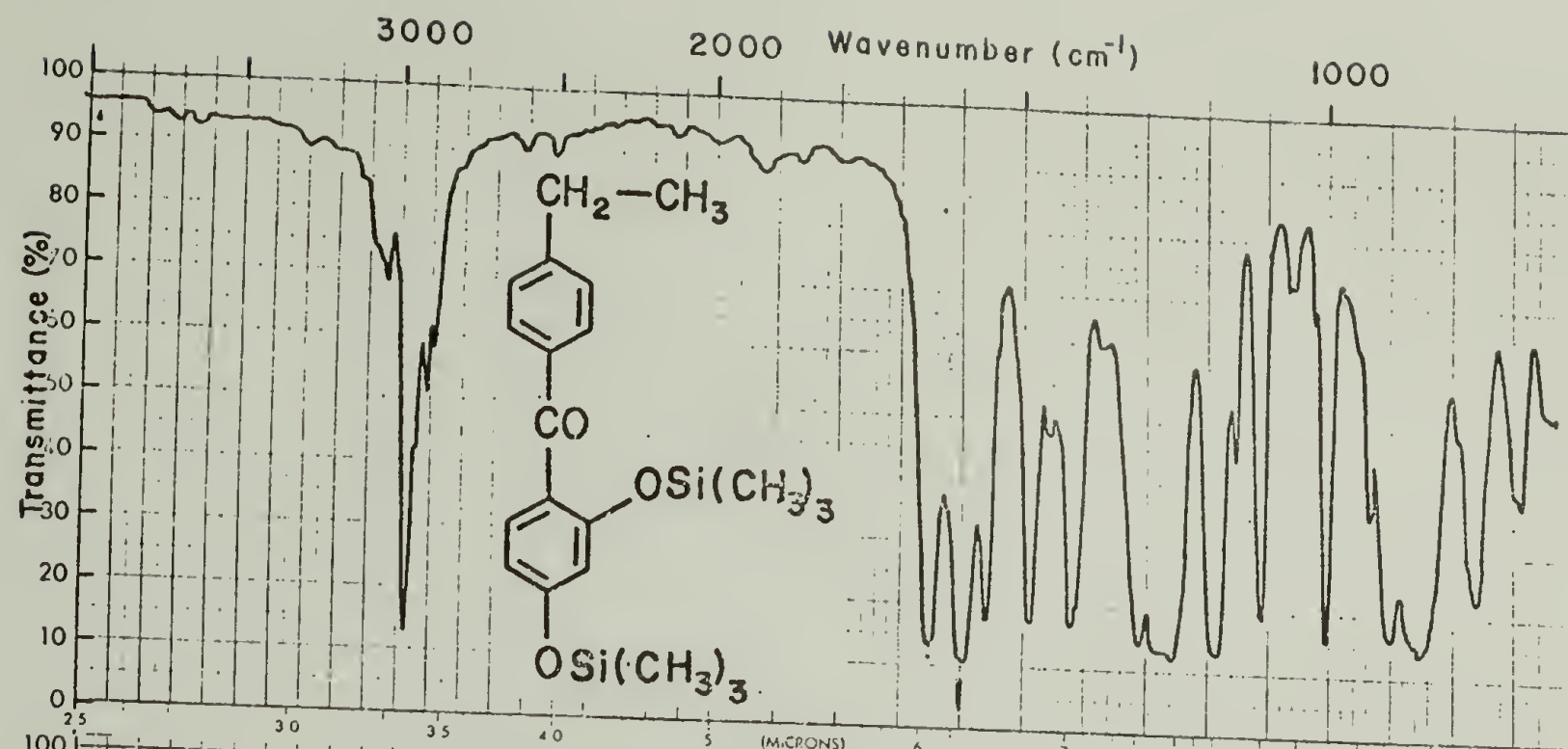


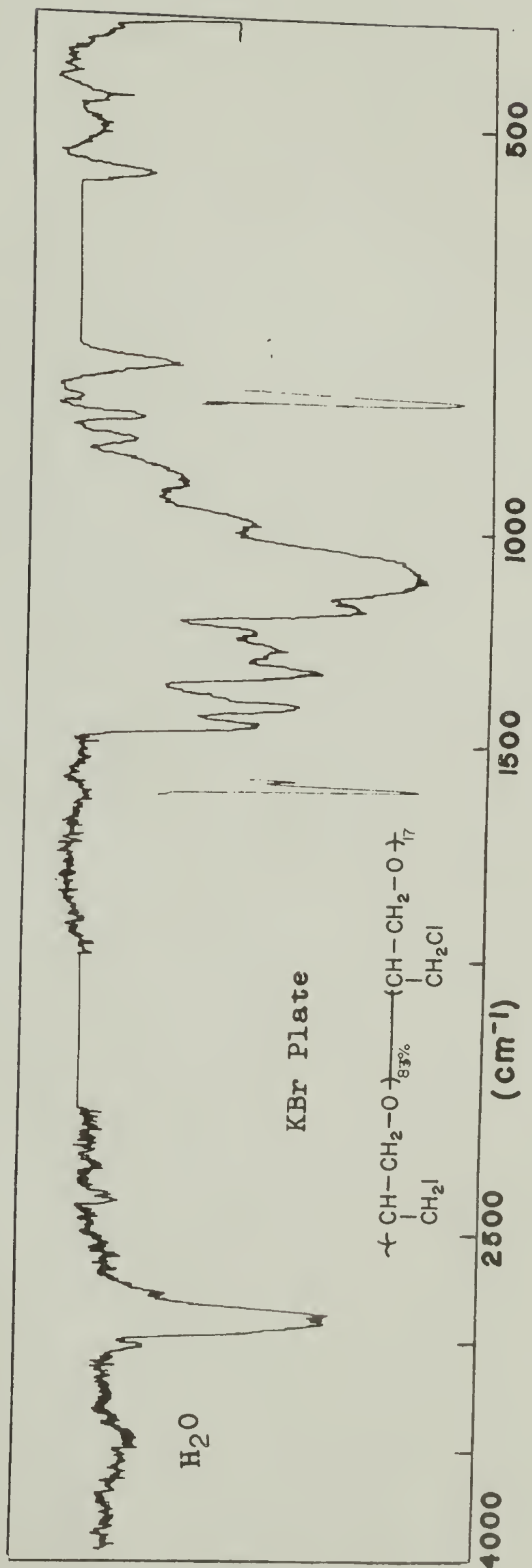
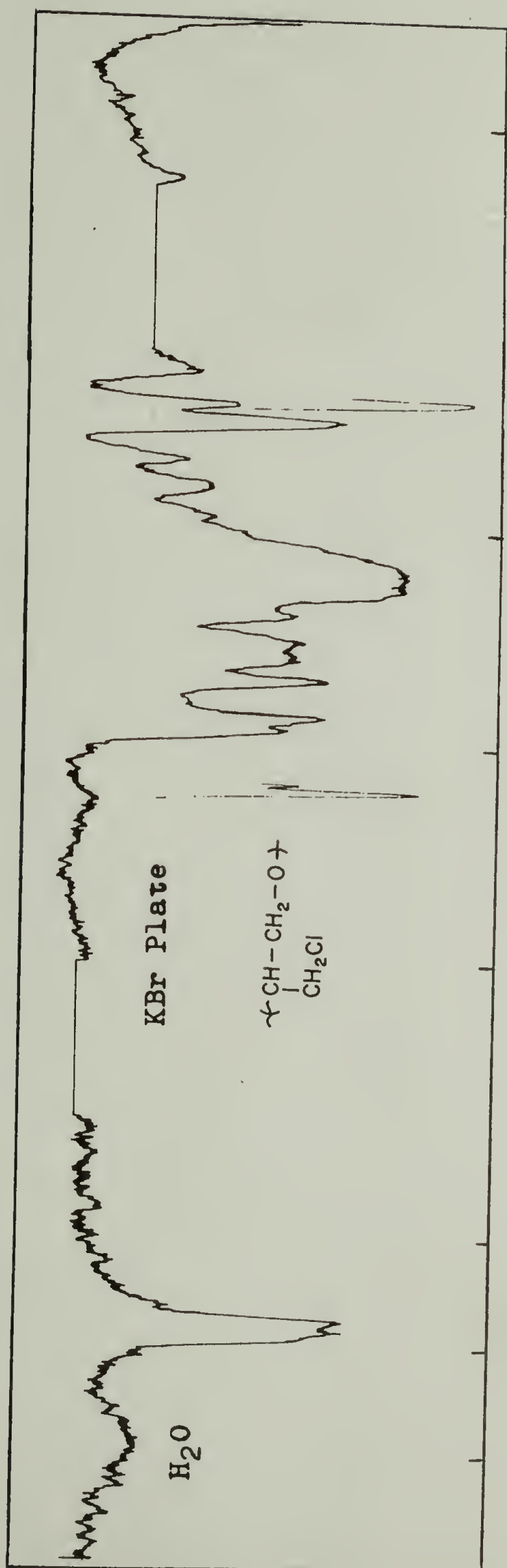


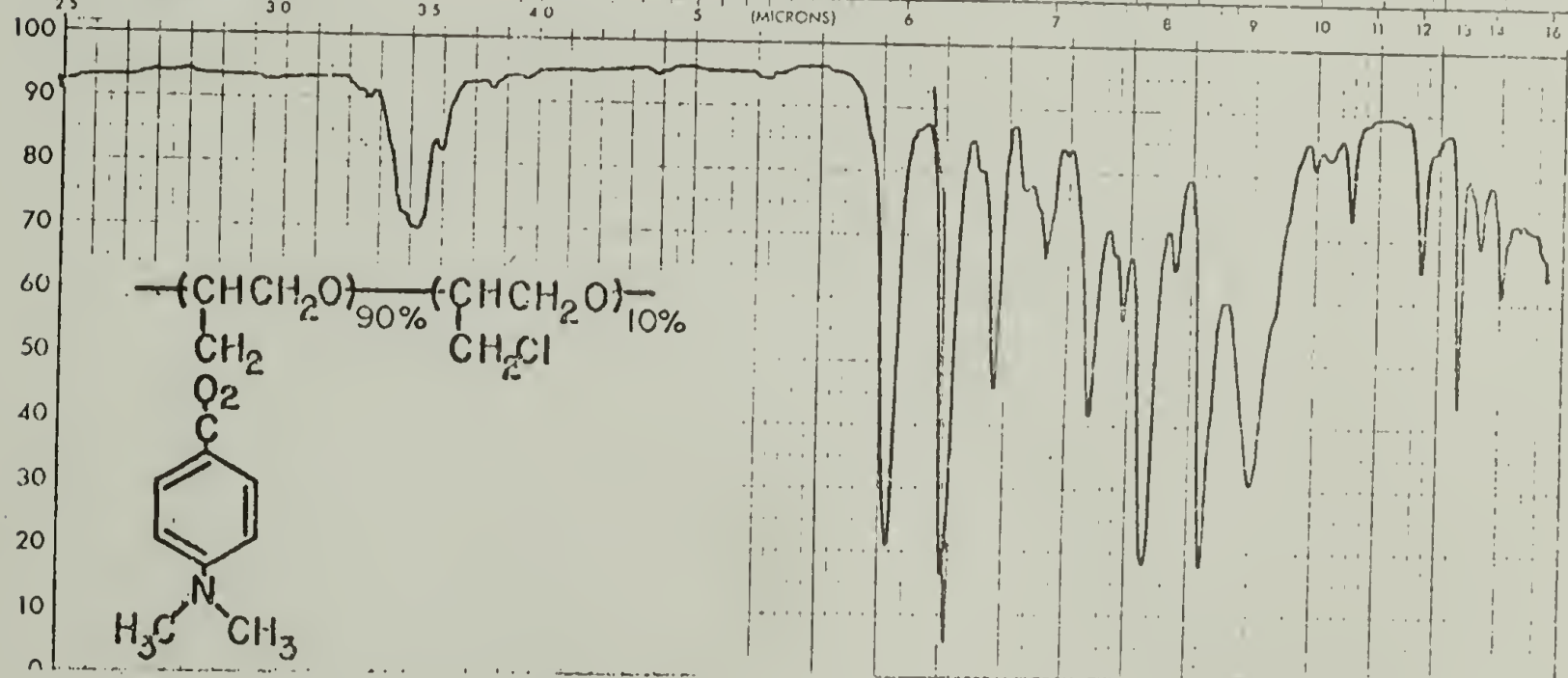
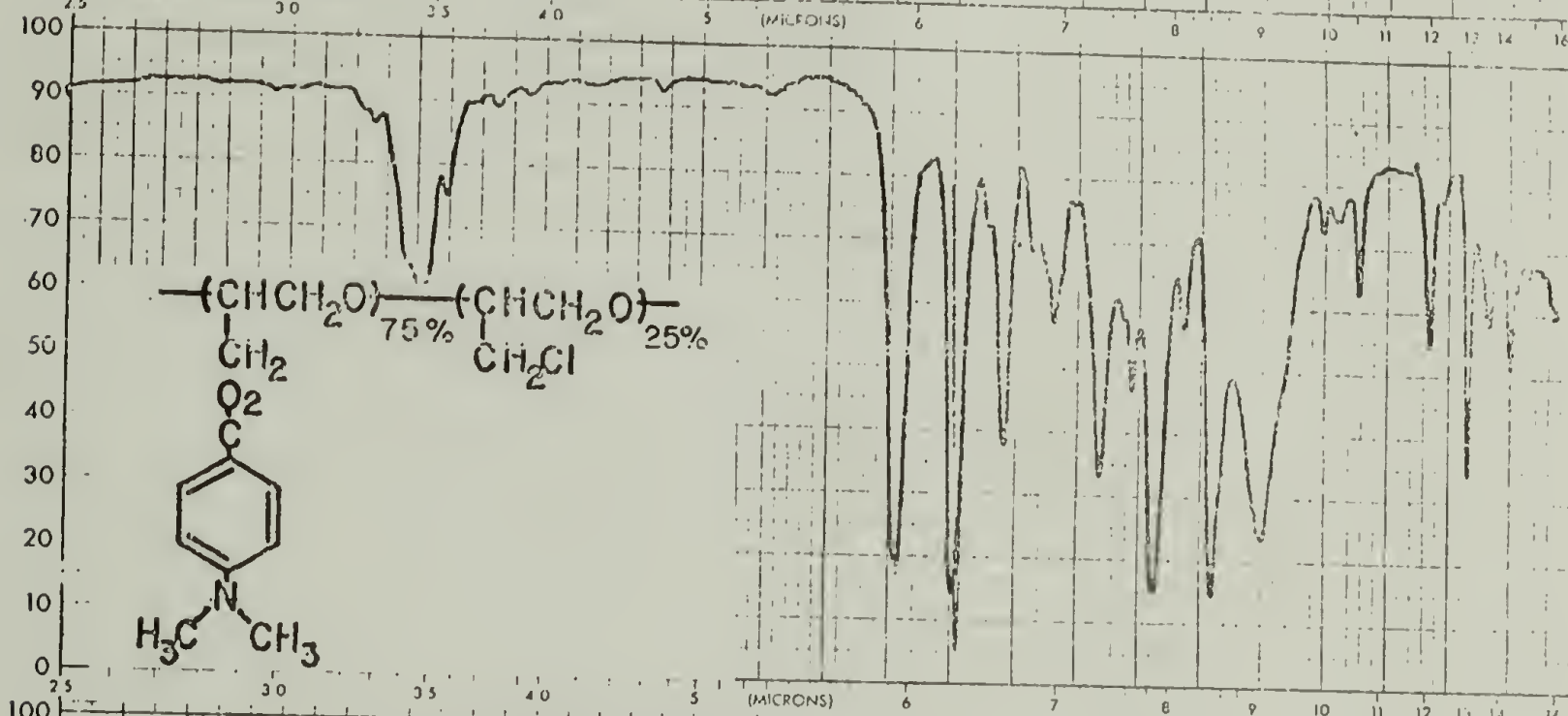
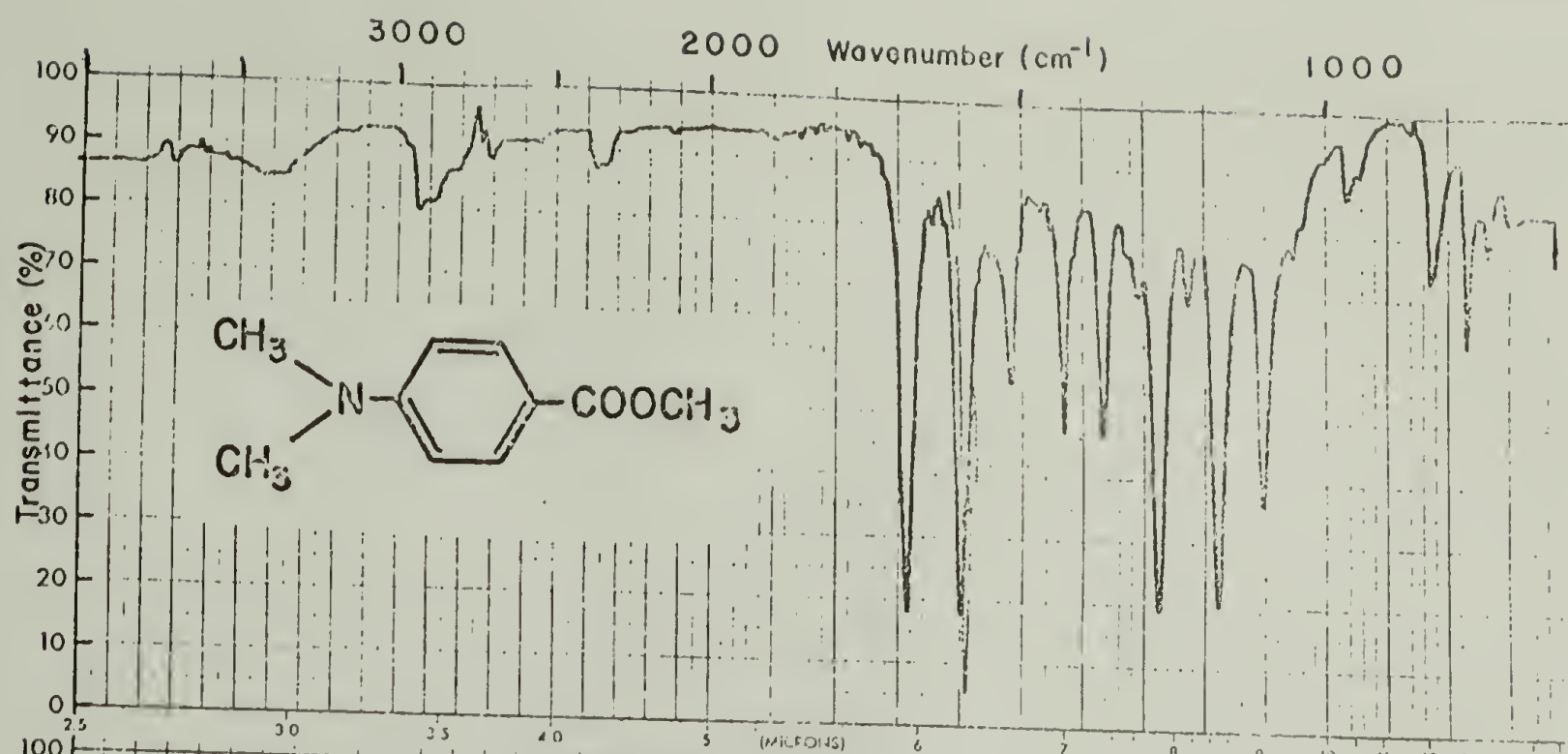


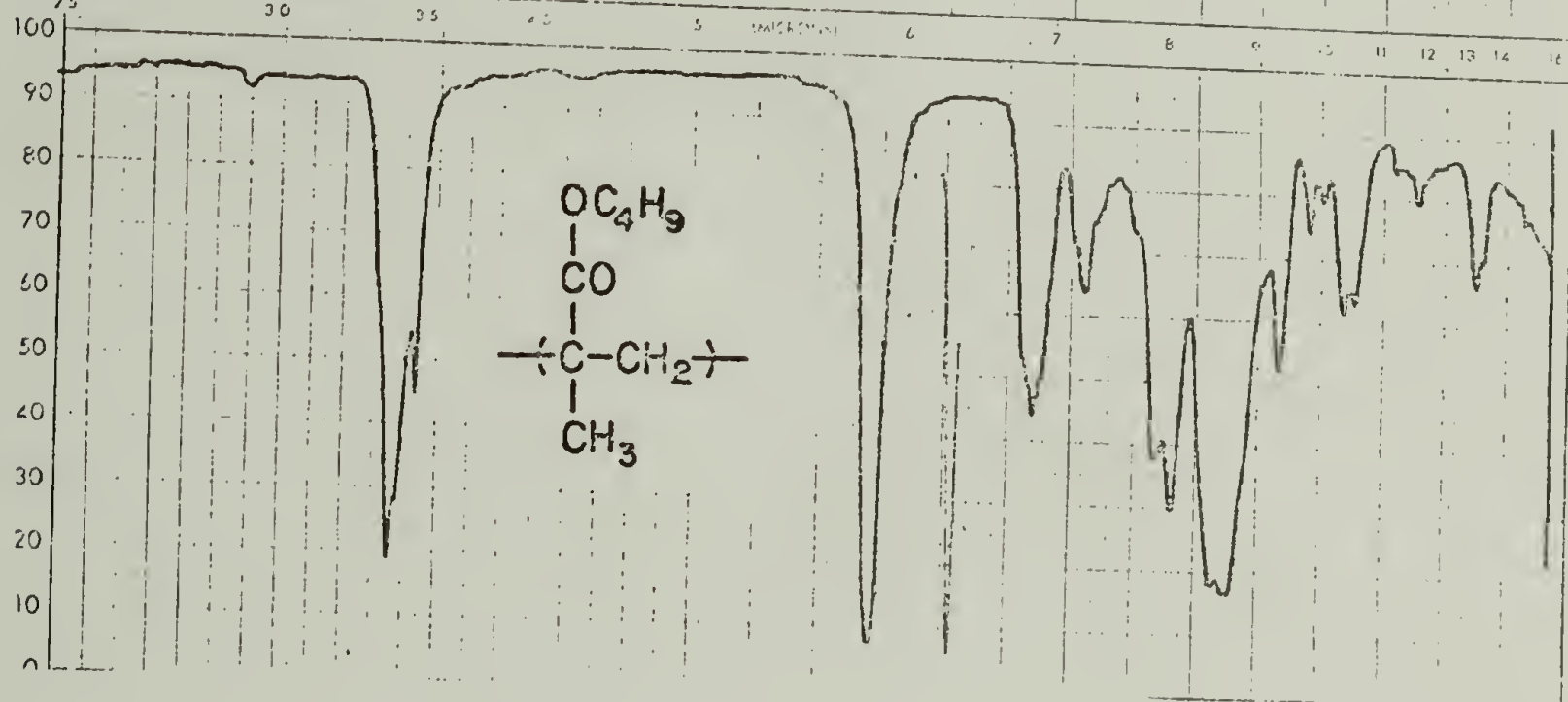
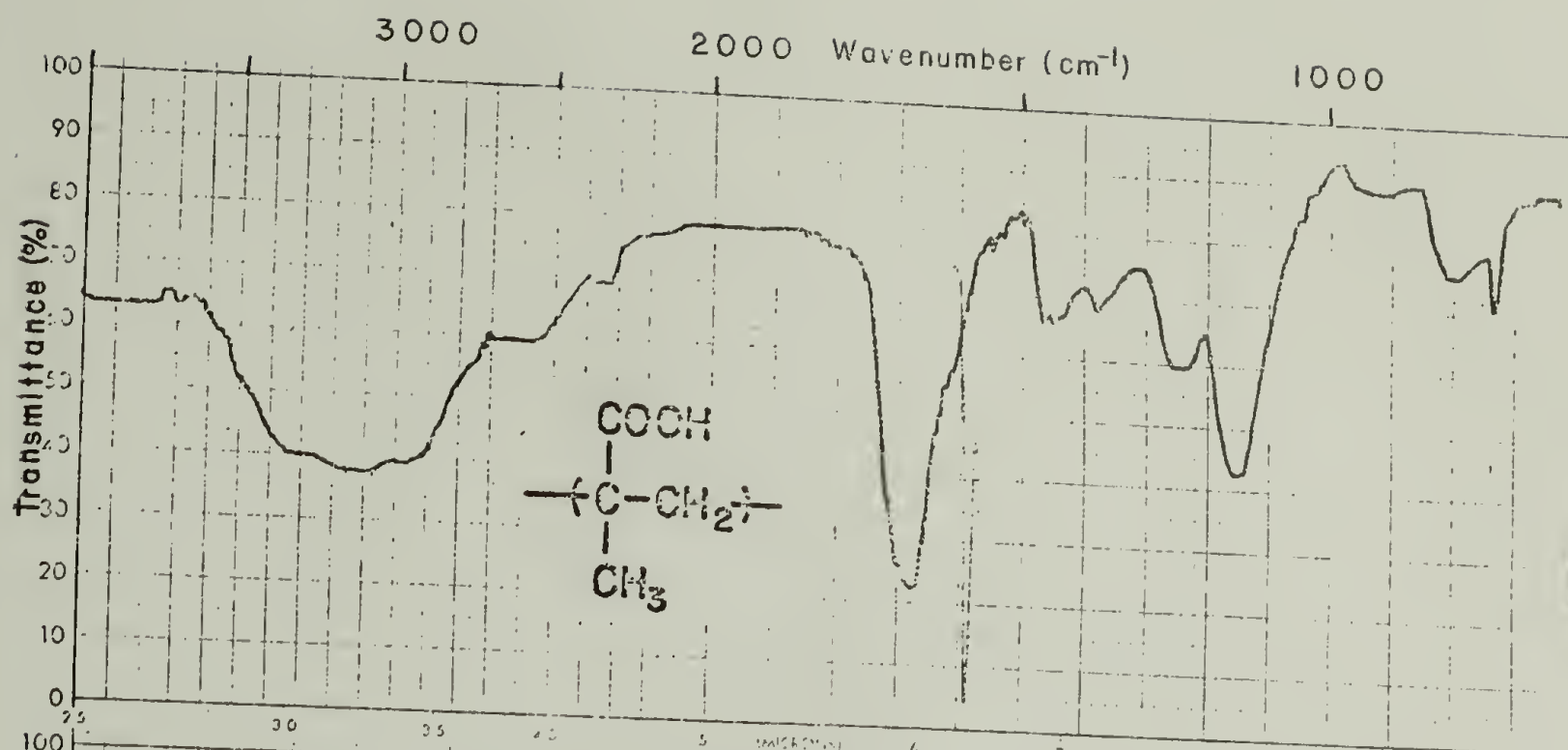


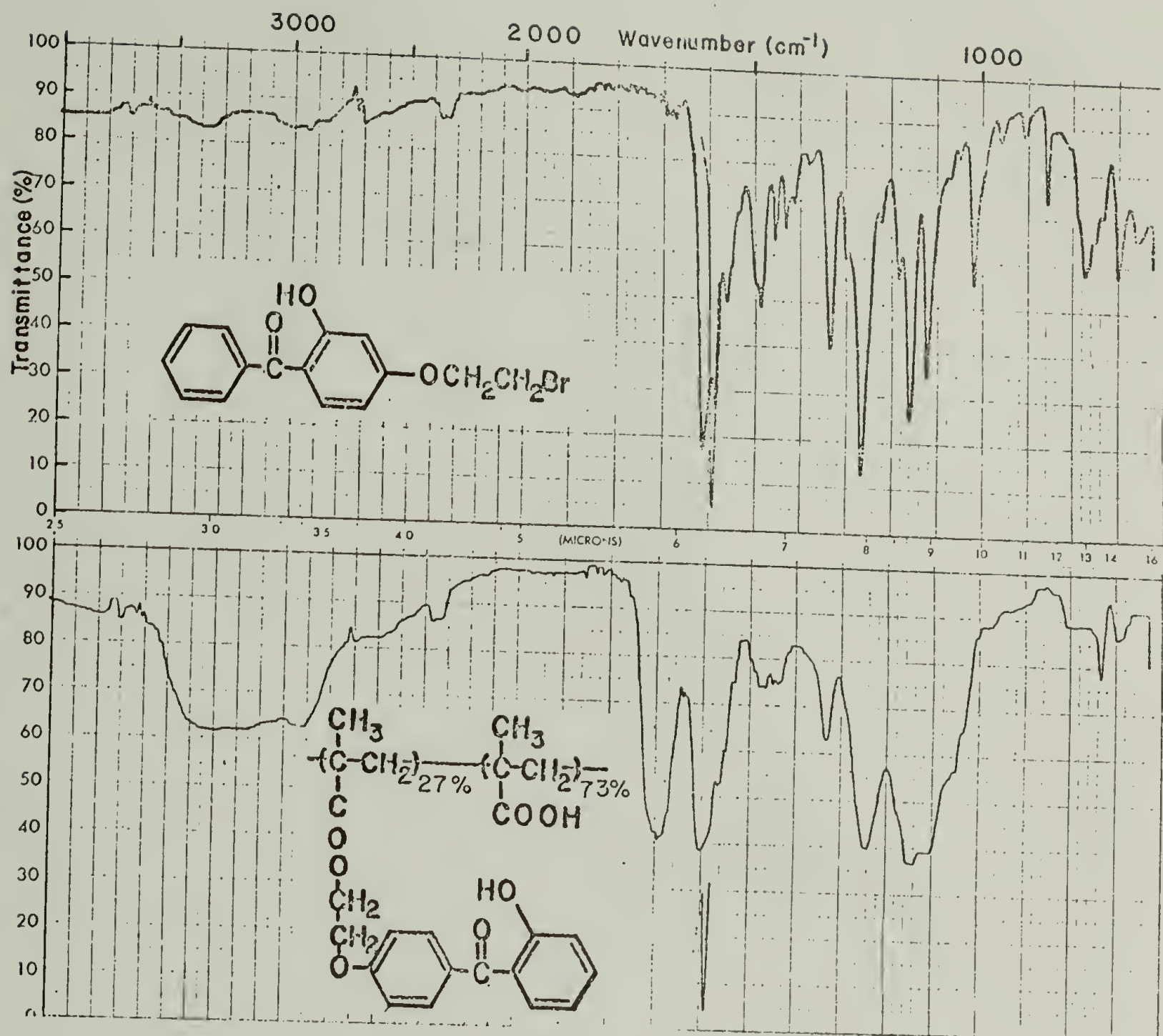


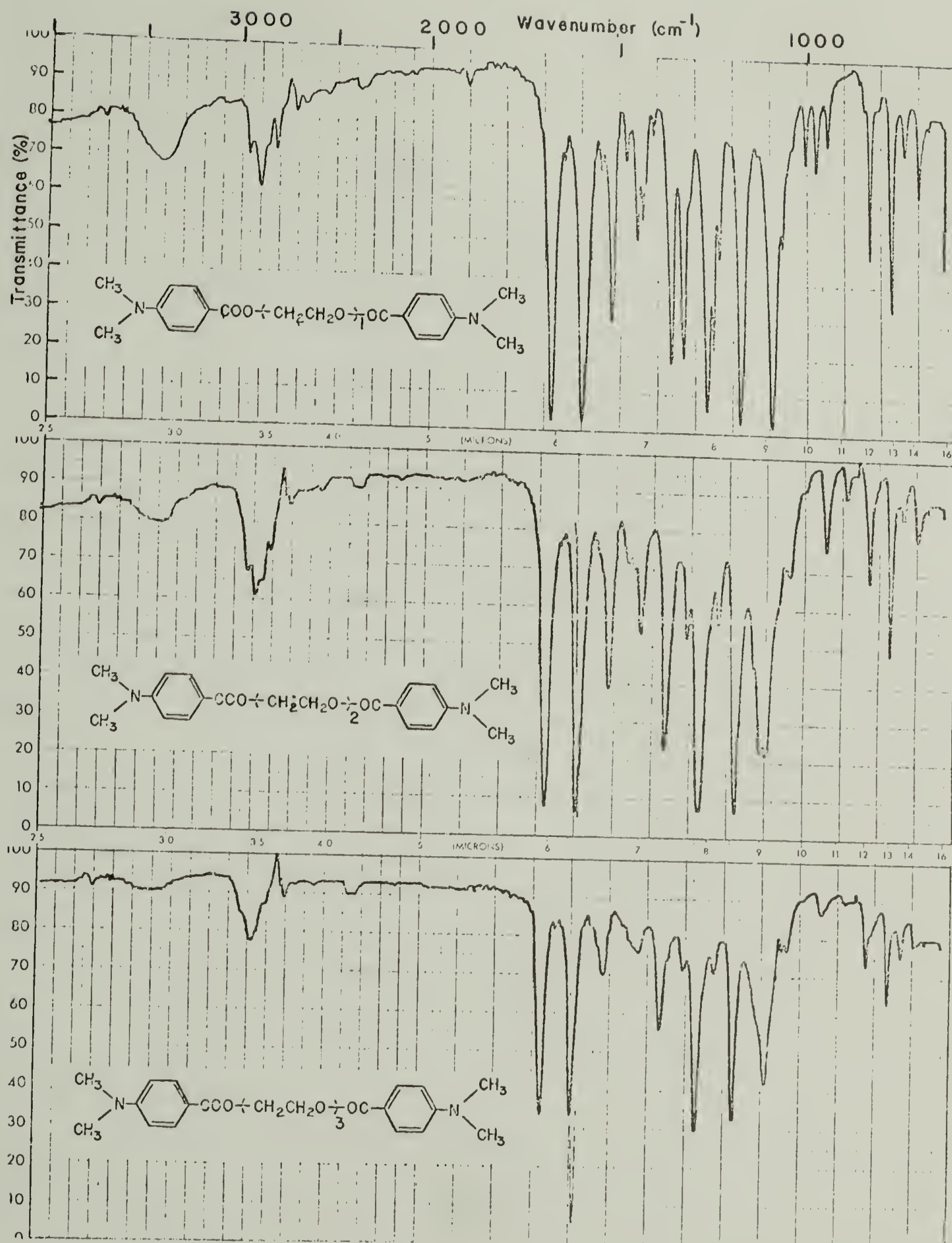


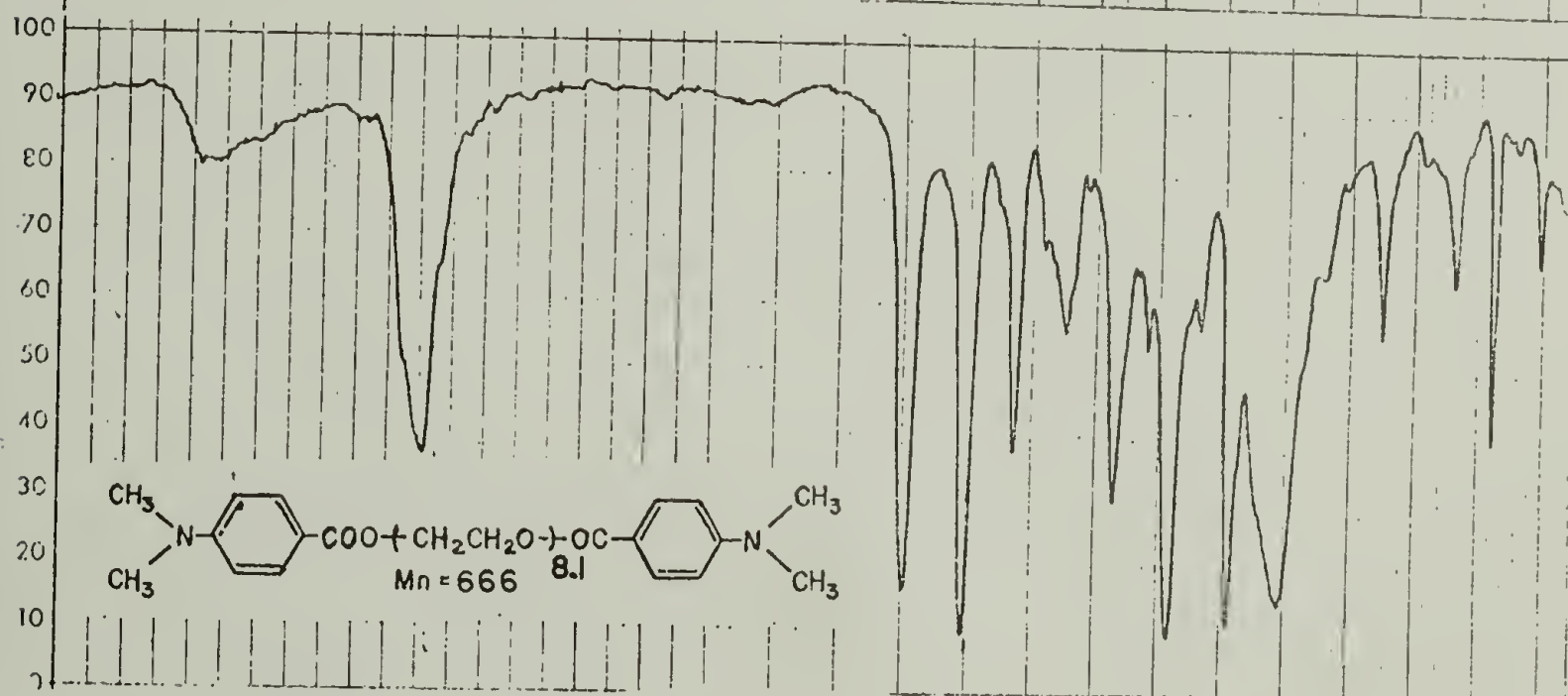
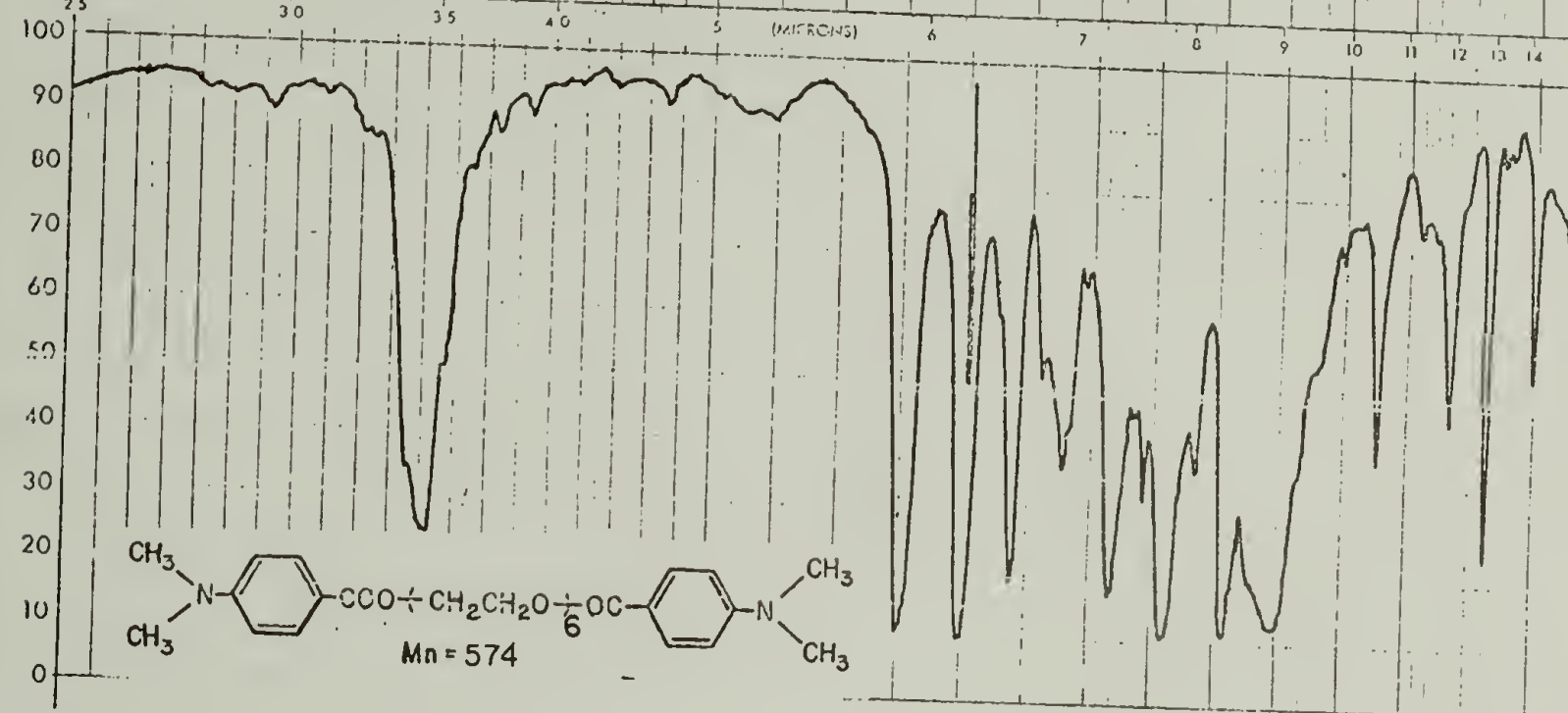
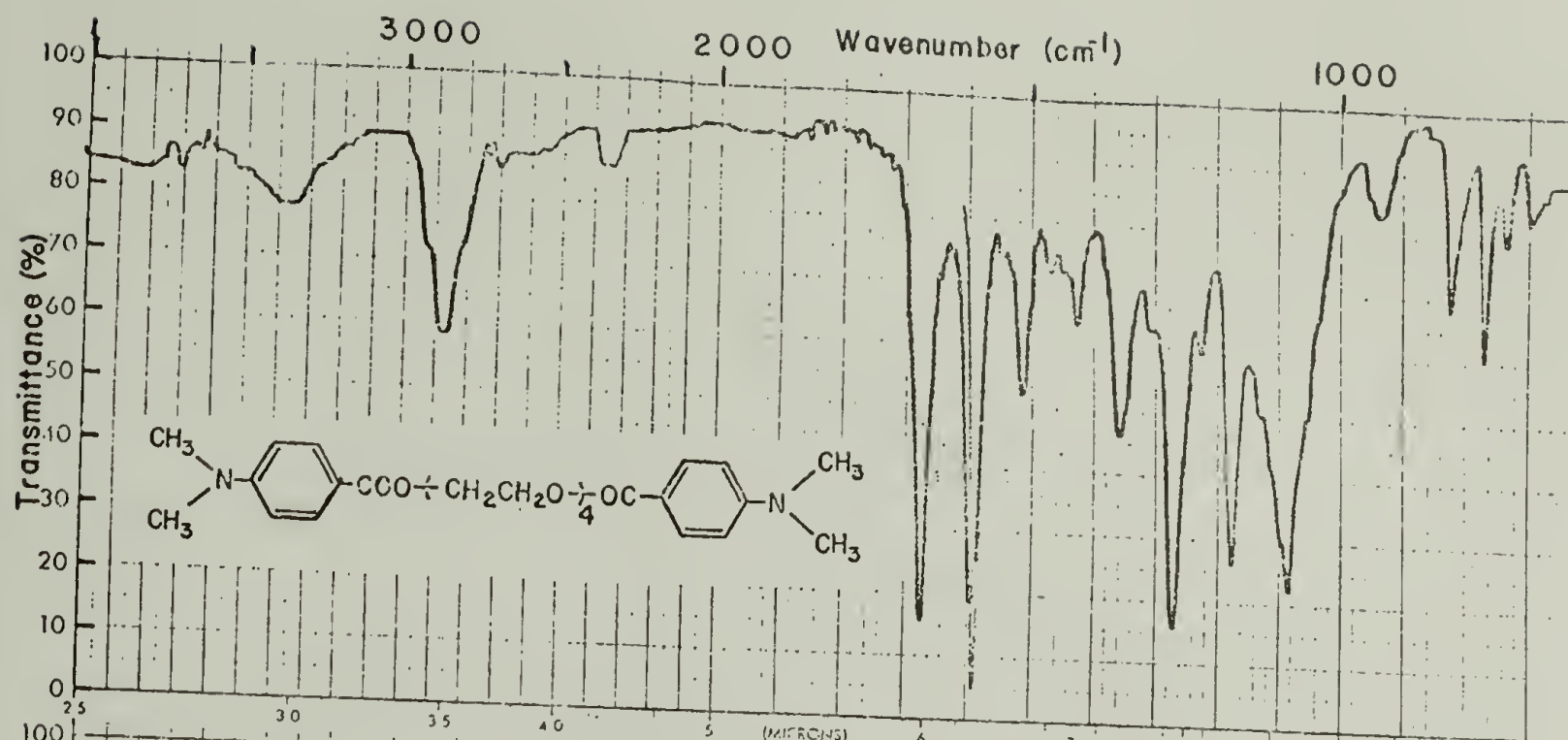


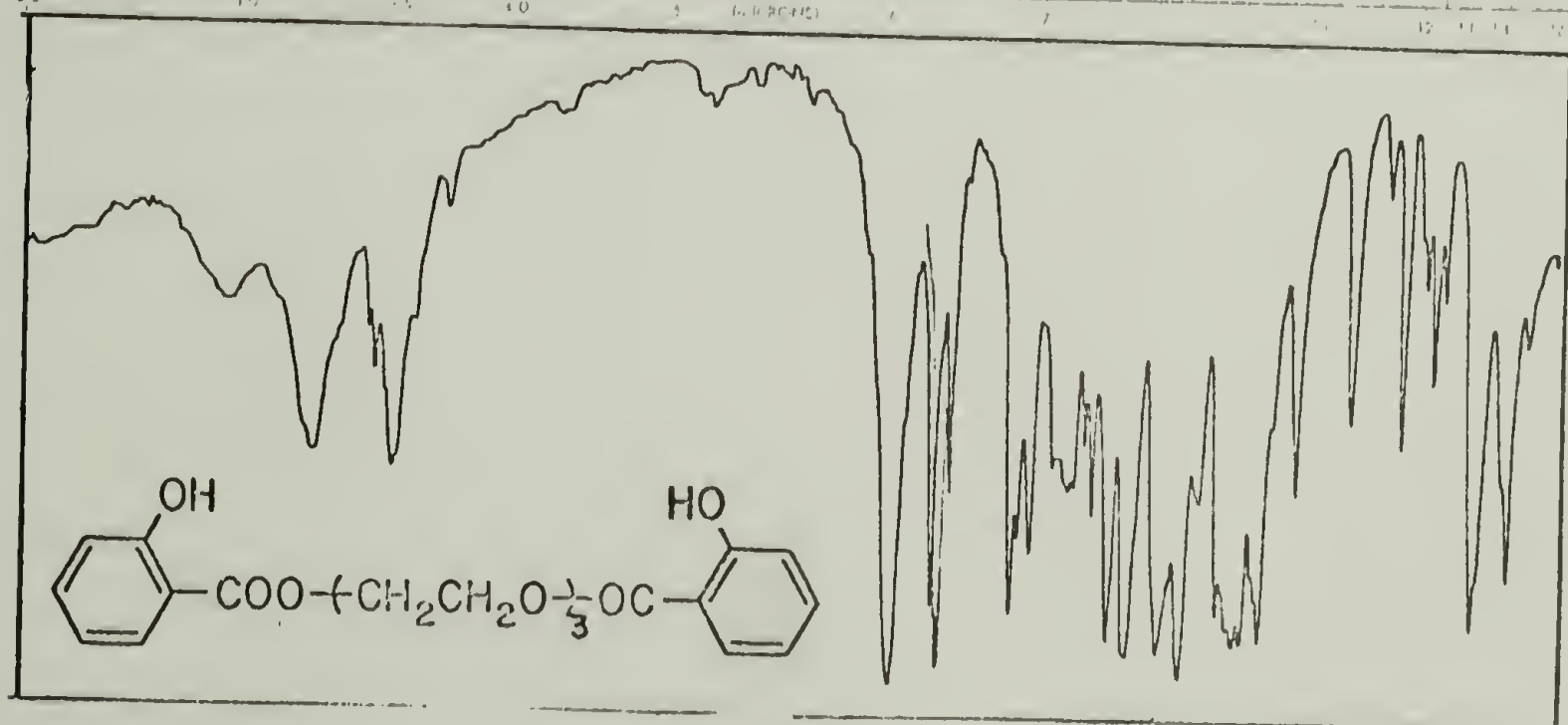
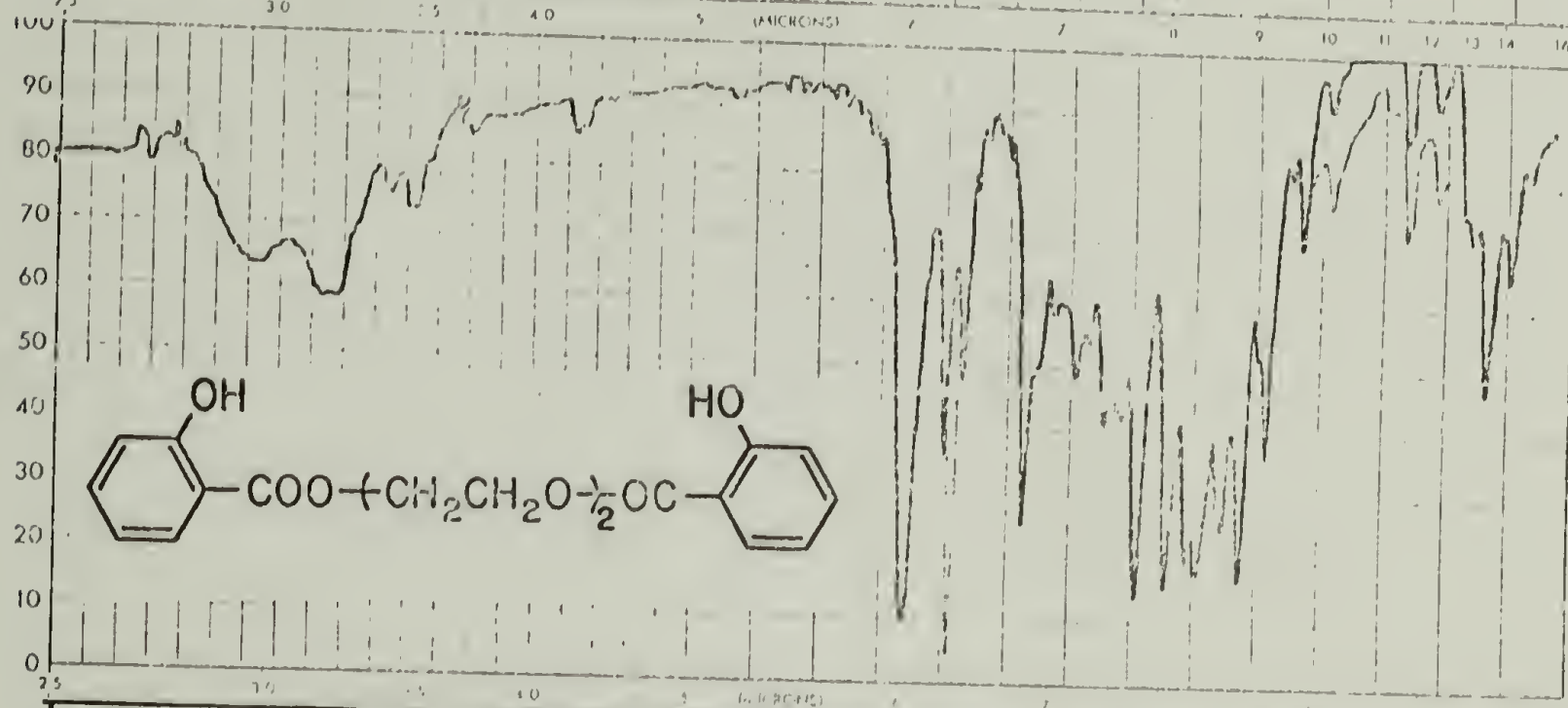
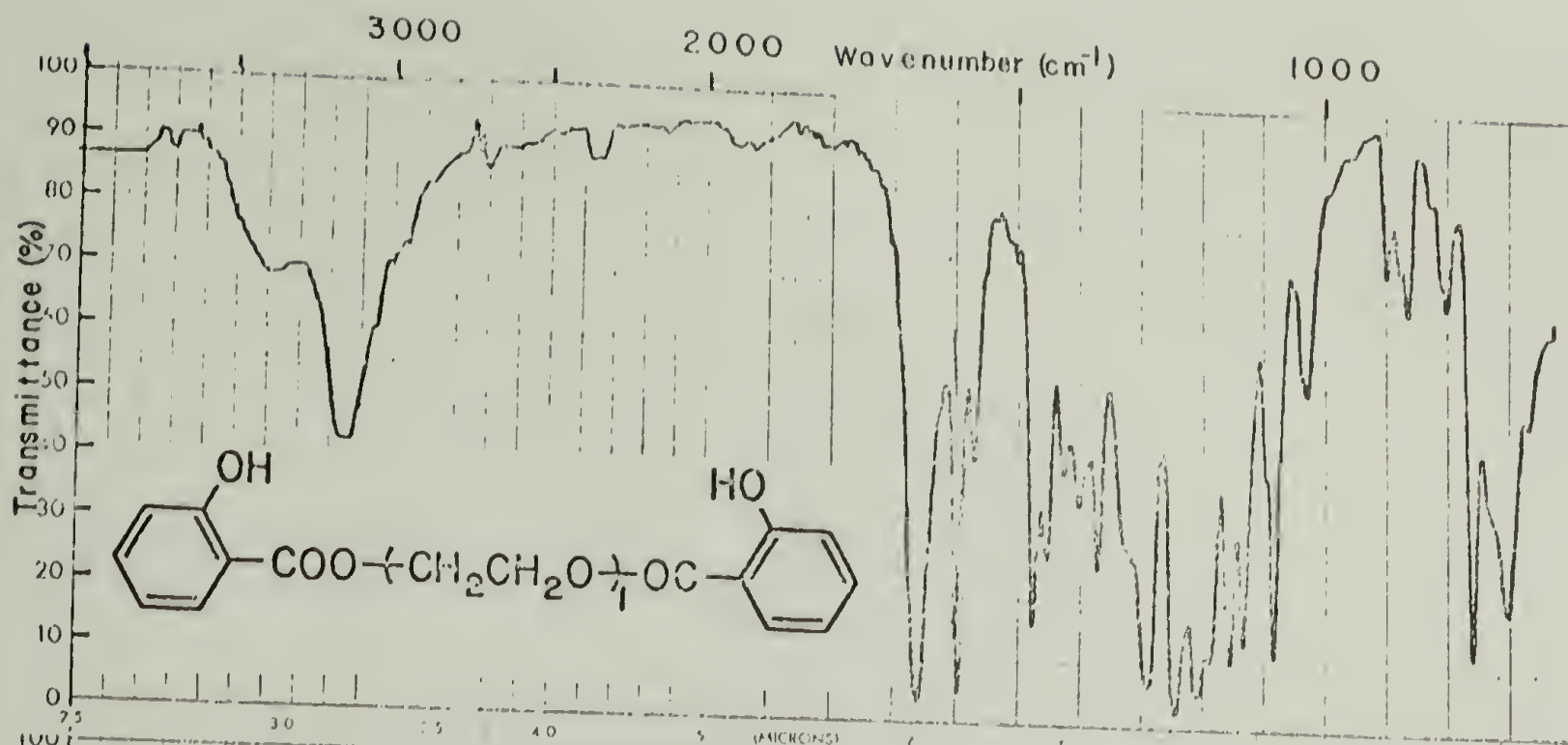












APPENDIX C

TRITIATION AND TESTING OF OLIGOMERIC
ULTRAVIOLET ABSORBERS

Arrangements were made with Dr. R. J. Scheuplein of the Massachusetts General Hospital to evaluate the ability of some of the oligomeric UV absorbers to penetrate and adhere to the skin. In order to determine the effectiveness of the compounds by his test procedure, it was first necessary to convert them to radioactive materials. This was achieved by having the nonradioactive compounds tritiated by a catalytic exchange technique at the New England Nuclear Corp. of Boston, Mass. Methyl N,N-dimethyl-p-aminobenzoate and the oligomeric UV absorbers, diethylene glycol disalicylate and tetraethylene glycol di-N,N-dimethyl-p-aminobenzoate, were successfully tritiated and then purified by repeated recrystallizations.

The diethylene glycol disalicylate tritiation is typical of the New England Nuclear tritiation procedure. Two hundred milligrams of diethylene glycol disalicylate dissolved in 0.3 ml. of DMAc were treated with 100 mg. of 5% Rh/Al₂O₃ catalyst and 10 curies of tritiated water. The reaction mixture was stirred overnight at 80°. The crude tritiated diethylene glycol disalicylate was isolated and labile tritium was then removed using a toluene-ethanol mixture as the solvent. The product was recrystallized with 715 mg. of unlabelled diethylene glycol disalicylate from a mixture of toluene and petroleum ether. After a second recrystallization, the yield of product was 282 mg.

The diethylene glycol disalicylate had an activity of 0.0606 millicuries/mg. Methyl N,N-dimethyl-p-aminobenzoate (621.4 mg.) was obtained with an activity of 5.47 millicuries/mg. and tetraethylene glycol di-N,N-dimethyl-p-aminobenzoate (69 mg.) was obtained with an activity of 0.017 millicuries/mg.

Samples of the radioactive methyl N,N-dimethyl-p-aminobenzoate, tetraethylene glycol di-N,N-dimethyl-p-aminobenzoate, and diethylene glycol disalicylate were delivered to Dr. R. J. Scheuplein and their ability to penetrate and adhere to the skin was evaluated. The results of Dr. Scheuplein's tests are included in the Final Technical Report (Grant No. DAHC 19-72-G-0014) "Sorption and Retention of Substances in the Surface Layers of the Skin" which was submitted to the U.S. Army Research Office - Durham in February, 1975.

No attempts were made to tritiate the polymeric UV absorbers. It was believed that the tritiation procedure (80°, overnight) would cause some polymer degradation. The partially degraded polymeric UV absorber, unlike the oligomeric UV absorbers, could not be purified by recrystallization or any other purification techniques available at the New England Nuclear Corp. Therefore, the results of subsequent skin adhering tests for the polymers would have been questionable.

The nonradioactive oligomeric and polymeric UV absorbers are currently being evaluated as sunscreens for skin protection at Fort Detrick, Frederick, Md. under the direction of Dr. Clarence Wade. These test procedures do not require radioactive materials.

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