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Functional Polymers. III. Endcapping and Substitution on Polymers with Compounds Containing Ultraviolet-Absorbing Groups

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Functional Polymers. III.* Endcapping and Substitution on Polymers with Compounds Containing Ultraviolet-Absorbing Groups

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ABSTRACT

Endcapping of oligo(oxyethylene) glycols was carried out by transesterification of methyl N,N-dimethylaminobenzoate with sodium methoxide as the catalyst or by the reaction of sodium salicylate with the ditosyl ester of the oligo(oxyethylene) glycols. Several other common reactions were tried for the endcapping of the oligo(oxyethylene) glycols but were found to be either more cumbersome or unsuccessful. All products were obtained in high yield and high purity. The reactions of tetraalkylammonium carboxylates with aliphatic halides were found to be very general and mild reactions for the preparation of esters in high yield and high purity. It was found that these reactions could be utilized for the preparation of esters on polymers even if the carboxylate group was directly attached to the polymer chain. It was also demonstrated that the aliphatic halide group could be on the polymer, as in the case of

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*For Part II see D. Bailey, D. Tirrell, and O. Vogl, J. Polym. Sci. Polym. Chem. Ed., 14, 2725 (1976).

polyepichlorohydrin. Copolymers of epichlorohydrin and glycidyl N,N-dimethylaminobenzoate with up to 90% glycidyl benzoate as the comonomer were prepared, and poly(tetrabutylammonium methacrylate) was effectively transformed with 4-(2-bromoethoxy)-2-hydroxybenzophenone into the corresponding ester. The products were characterized by the usual spectral means.

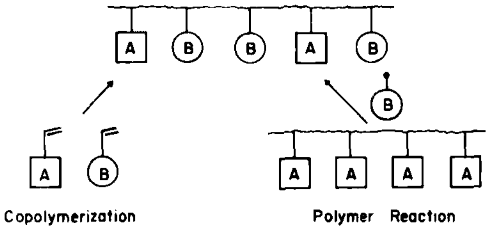
INTRODUCTION

Although synthetic polymeric materials have attained their present importance largely because of their physical and mechanical properties in bulk form, it is becoming increasingly clear that manipulation of the chemical properties of macromolecules provides opportunities which are equally promising. Drastic modifications of polymer properties can and have been attained when space-filling groups or groups with chemical functionality are attached to the polymer chain. Glass transition temperature, crystallinity, melting point, solubility, and other fundamental properties depend directly upon the polarity, steric requirements, and interaction of pendant functional groups. These effects are readily found in comparisons of the physical and chemical properties of polymers of apparently similar structures. In addition, the widespread use of copolymers demonstrates the vast potential of copolymerization as a tool for producing materials of intermediate properties.

More recently, polymers with functionalities designed for more specific purposes have been prepared. These "functional polymers" are of value because of their specific chemical and spectroscopic properties, rather than their mechanical properties. Polymers have been produced which contain catalytically active groups [1], UV absorbers [2-4] and antioxidants [5], pharmaceuticals [6-8] and photo- [9], thermo- [10], and electro-active [11] groups. These materials are quite diverse, encompassing homopolymers and copolymers, soluble and insoluble materials, oligomers and high molecular weight polymers.

The value of the oligomeric type of functional polymers has been demonstrated in the area of stabilization of polymers. The attachment of short paraffinic chains to active stabilizers is an effective means of increasing compatibility, lowering mobility in the polymer matrix and decreasing solubility and volatility of additives [12]. Such alterations in properties greatly improve the performance of additives with respect to the processing and aging of polymeric materials. It has indeed been argued that future antioxidant and UV stabilizer systems may consist of mixtures of polymeric, oligomeric, and low molecular weight active compounds with compatibilizing groups attached. This combination would provide a long-term balance of the mobility of these materials with their availability at the parts of the polymer matrix where stabilization is needed. Convenient methods of preparation of functional oligomers are (a) the attachment of a short chain, for example, a paraffin chain, for compatibilization of the functional compound and (b) the endcapping of low molecular weight oligomers with reactive compounds containing the desired functional group, e. g., functionalization of hydroxyl-terminated oligomers of ethylene oxide or butadiene.

High molecular weight polymers with specific functional groups are suitable in many of the same applications as the functional oligomers, and may offer distinct advantages over the lower molecular weight materials. Functional polymers of high molecular weight can be prepared via two principal routes: by preparation of functionally substituted monomers followed by polymerization or copolymerization, and by reaction on polymers (Scheme I). The advantages and disadvantages of the two approached are in many ways complementary; one of the two methods may be preferred for the preparation of a particular functional polymer while being totally impractical in another system. The requirements of the desired system must be thoroughly examined in order to exploit the advantages of each of the preparative techniques.



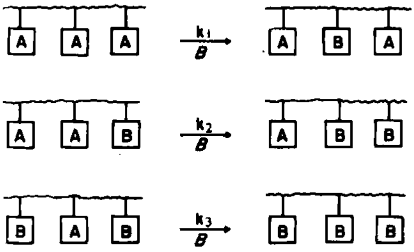
SCHEME I

When functional polymers are prepared by the synthesis and polymerization of functional monomers, the advantages of high monomer purity and diversity of comonomers may be realized. Monomer synthesis can, however, be difficult, and low yields of the desired monomers often result from the required multistep syntheses. The polymerization of functional monomers to polymers of optimum molecular weight and molecular weight distribution may not be easily realized, and sequence distribution and compositional homogeneity of copolymers may be difficult to control.

Some of these problems may be avoided through the use of the polymer reaction approach. In particular, the desired molecular weight and molecular weight distribution may be obtained by selection of the appropriate base polymer. The amount of functional group introduced may be easily varied, and more than one functional group may be introduced in sequence. Anchoring groups, solubilizing groups, etc., may therefore be attached to the polymer chain in order to modify the properties of the polymer. Several attractive, high yield reactions are now available for the successful introduction of functional groups.

The major problem in carrying out polymer reactions is the necessity of avoiding completely all side reactions involving functional groups attached to the polymer chain. It may be necessary to introduce activating groups in order to increase the yield and selectivity of the desired functional group transformation. The possibility of less than quantitative yields in each step must be kept in mind, and molecular weight degradation is always a danger. The character of polymer reactions is influenced by a variety of factors which have no parallel in the reactions of low molecular weight compounds; of these, the so-called "neighboring group effect" is of particular importance through its influence, not only on the overall kinetics of the reaction, but on unit sequence distribution and compositional heterogeneity of the product.

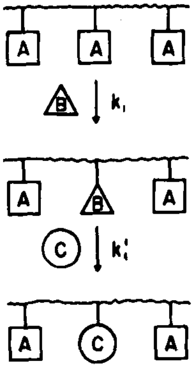
The course of a transformation of functional groups (A → B) on a polymer chain is determined, to a first approximation, by the rates of three reactions [13]. Considering only first neighbor effects, these reactions are given in Scheme II. If $k_1 \geq k_2 \geq k_3$, the transformation will be retarded and the reaction will not go to completion.



SCHEME II

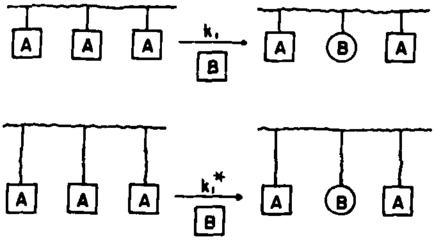
This situation is frequently encountered in reactions on polymers. For example, in the alkaline hydrolysis of poly(methyl methacrylate) $k_1 : k_2 : k_3 = 1.0 : 0.18 : 0.10$ [14]. If $k_1 = k_2 = k_3$, the reaction may go to completion if allowed to proceed long enough, and if $k_1 \leq k_2 \leq k_3$, the reaction will be accelerated and will go easily to completion. It is apparent that the different types of reaction kinetics will produce different products in terms of the distribution of A and B units, both intramolecularly and intermolecularly.

In some cases, the transformation (A→C) may proceed through active intermediates (Scheme III). If, as should be the case, k_1' is greater than k_1, the reaction should be readily driven to completion.

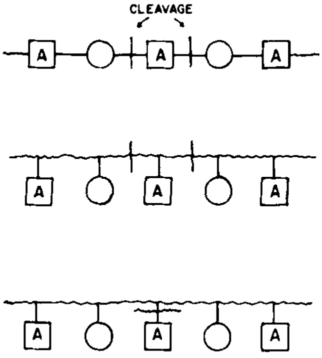


SCHEME III

A second means of avoiding problems associated with retarding neighboring group effects is the use of a "spacer" group (Scheme IV). The spacer group removes the reactive functionality from direct contact with the chain backbone and may provide a more favorable environment for functional group transformation. Indeed, the spacer link may be essential for the success of some reactions on polymers.



SCHEME IV



SCHEME V

The use of functional polymers provides an additional option; that of controlled polymer degradation and release of active agents (Scheme V). This is of particular value in the use of polymers carrying biologically active agents, such as herbicides, pesticides and pharmaceuticals. The agent may be incorporated into the chain backbone, for example, through condensation polymerization of a difunctional active compound, or alternatively, may be linked to the chain as a pendant group, either directly or via a spacer group. Scheme V illustrates the possible degradation routes which provide for release of low molecular weight active species. This concept has attracted particular attention because desirable release kinetics may be readily obtained, enhancing and/or prolonging the effectiveness of the active agent.

In our work on functional polymers we are exploring the preparation of functional oligomers, reactions on high molecular weight polymers with special emphasis on spacer length and flexibility of the backbone chain, and homo- and copolymerization of functional monomers with suitable comonomers.

In this paper, endcapping of hydroxyl-terminated oxyethylene oligomers with N,N-dimethylaminobenzoate and salicylate groups will be discussed, as well as reactions on polyepichlorohydrin and poly(methacrylic acid).

A comparative study of the esterification of oligo ethylene oxides has been undertaken in order to establish the most convenient preparative route for the esterification of hydroxyl end groups by functional low molecular weight compounds. Particular attention was paid to the more recently recognized reaction conditions using highly polar compounds as solvents.

Reactions in highly polar, nonprotic solvents such as DMSO, DMAc, and DMF were found to be very convenient for the high-yield esterification of polymers under mild conditions. It has recently been shown that ammonium salts, particularly butylammonium salts, rather than the potassium or sodium salt, react rapidly at or slightly above room temperature with alkyl halides to give high yields of alkyl esters [15]. This reaction is a very desirable reaction because it is relatively easy to prepare ammonium salts from acids, and the reaction with aliphatic halides can be readily carried out. In addition, commercial polymers are available which are either polymeric carboxylic acids or polymeric halides. The best-known examples are poly(acrylic acid) or poly(methacrylic acid), and polyepichlorohydrin. Well known, well characterized polymers may thus be employed as nucleophiles or as substrates for the introduction of functional groups via ester formation. The reaction of polyepichlorohydrin should be particularly facile due to the proximity of the ether oxygen.

Poly(methacrylic acids) and poly(acrylic acids) have been subjected to a wide variety of modification reactions. In most cases, however, the carboxylic acid group had to be functionalized by reactions more complicated than simple salt formation. Acid chlorides were prepared, or good leaving groups were introduced, such as in the case of poly-N-methacryloxysuccinimide [16]. Nucleophilic displacement reactions of poly(sodium acrylate) with organometal halides have been accomplished by interfacial techniques [17]. Neighboring group effects in nucleophilic displacement reactions of salts of poly(methacrylic acid) have also been studied; it was found that carboxylates in partially ionized poly(methacrylic acid) were four times as reactive with bromacetamide than were monomeric dicarboxylic acids [18].

Modifications on polyepichlorohydrin and poly(glycidyl p-toluenesulfonate) have also been studied quite extensively. One of the better studied examples is the reaction of polyepichlorohydrin with potassium cinnamate [19-21]. Displacements of more than 80% have been obtained, but degradation of the polyoxyethylene chains occurred as a serious side reaction during the course of the displacement reaction under the conditions used (HMPA, 100°C). Reaction times of greater than 6 hr did not increase the degree of esterification appreciably but did significantly decrease the molecular weight of the polymer. In the copolymers obtained by this reaction, the number average molecular weight was reduced to one-tenth of its original value.

Quaternization of polyepichlorohydrin with various nitrogen-containing tertiary bases has been studied [22-24]. Most of these reactions were carried out at temperatures higher than 100°C, where the molecular weight degradation becomes a serious problem. Thiolates were found to be better nucleophiles than oxygen containing groups, particularly in the phenol series, and mild reaction conditions could be used for this substitution [25]. Of the many reactions which were carried out with polyepichlorohydrins or with copolymers of epichlorohydrin and ethylene oxide, those with sodium thiosulfate [26], sodium N,N-dimethyldithiocarbamate [27], 2-mercaptoethanol [28], thiourea [29], sodium sulfite [30], and sodium thiocyanate [31] are of interest.

As indicated earlier, the degradation of polyepichlorohydrin is a serious side reaction, and its mechanism at 65°C in DMSO with sodium hydroxide has been studied [32]. With butyllithium, the polymer is cleaved in toluene solution at -78°C, and equal amounts of hydroxyl and carbonyl end groups are found in the main reaction product. There was severe discoloration at temperatures of 100°C and higher in the presence of bases and solvents such as DMSO.

It was the objective of this work to find and develop convenient methods for the esterification of oligomeric and polymeric materials, for the introduction of functional groups under mild reaction conditions.

EXPERIMENTAL

Materials

Pyridine, 1-bromobutane, tetrabutylammonium hydroxide, tetraethylammonium chloride, tetraethylammonium hydroxide, tetramethylammonium hydroxide, triethylene glycol, tetraethylene glycol, and 1,2-dibromoethane were obtained from the Eastman Chemical Company. Oxalyl chloride, N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and chloromethyl methyl ether were obtained from the Aldrich Chemical Company. Polyepichlorohydrin was obtained from the Hercules Chemical Company, poly(methacrylic acid) from Polysciences, and polyoxyethylenes 300 and 400 from the Union Carbide Company.

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 magnetic stirring and a Claisen head. The pressure was stabilized with a manostat.

Dimethyl sulfoxide was distilled from calcium hydride at reduced pressure (bp 60°C/8 Torr) and stored over Molecular Sieves.

N,N-Dimethylformamide was dried with magnesium sulfate, filtered, distilled (bp 78-80°C/40 Torr), and stored over Molecular Sieves.

N,N-Dimethylacetamide (1 liter) was stirred with barium oxide

(10 g) for 2 days, distilled (bp 55-58°C/11 Torr), and stored over Molecular Sieves.

Ethanol was reacted first with sodium and then with diethyl succinate and distilled.

Methanol was dried by distillation from calcium hydride.

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

Pyridine was distilled from sodium hydroxide pellets. Sodium salicylate was recrystallized from aqueous ethanol.

p-Toluenesulfonyl chloride (72 g) was dissolved in chloroform (80 ml) and diluted with petroleum ether (700 ml, bp 30-60°C); 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 in a vacuum desiccator under reduced pressure (0.05 Torr). The recovery of p-toluenesulfonyl chloride was 51 g (71%).

N,N-Dimethyl-p-aminobenzoic acid was received as a tan powder and had to be purified via the methyl ester. Methyl N,N-dimethyl-p-aminobenzoate was recrystallized three times from 80% aqueous methanol, and the white crystals were saponified by dissolving them in 15% sodium hydroxide solution by heating to 90°C for 30 min. After cooling, the solution was acidified with dilute hydrochloric acid which caused the N,N-dimethyl-p-aminobenzoic acid to precipitate. Two recrystallizations from 60% aqueous ethanol gave white needles of N,N-dimethyl-p-aminobenzoic acid (mp 245-247°C, lit. [33] mp 242-243°C). The overall yields were generally greater than 80%.

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.

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 thermal properties of the polymers were determined on a

Perkin-Elmer DSC-1B differential scanning calorimeter at a scan rate of 20°C/min.

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

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.

Characterization of Reagents

Polyepichlorohydrin (Herculon H elastomer) was soluble in chloroform, benzene, DMSO, DMF, 2-butanone, and acetone and insoluble in carbon tetrachloride and alcohols; the density was 1.36 g/cm. The polymer had a glass transition (by DSC) at -17°C. The inherent viscosity of a 0.5% DMF solution was 1.52 dl./g and the number-average molecular weight was 350,000. The infrared spectrum of a film prepared by evaporating a chloroform solution was as expected. The PMR spectrum (o-dichlorobenzene) at 110°C showed δ 3.58 ($C\underline{H}_2Cl$), 3.67 ($CHC\underline{H}_2O$).

Analysis. Calcd for $\left(C_3H_5ClO\right)_n$: 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. The PMR spectrum (d-DMSO) at 90°C showed δ 0.5-2.3 [$C\underline{H}_2C(C\underline{H}_3)$]; 2.3-2.6 (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 1.0 N 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 2.74 N in tetramethylammonium hydroxide (25% w/v, 27.8% w/w) and that a small amount of a weaker base, possibly trimethylamine (0.04 N), was present.

Tetraethylammonium hydroxide (10% in water, 10.0 ml, 9.98 g, diluted to 50 ml with water) was titrated potentiometrically with 0.25 N 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 0.75 N in tetraethylammonium hydroxide (11% w/v) and that a small amount of a weaker base, possibly triethylamine (0.01 N), was present.

Tetrabutylammonium hydroxide (10% in methanol, 10.0 ml, 8.10 g, diluted to 40 ml with water) was titrated potentiometrically with

0.10 N 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 0.31 N in tetrabutylammonium hydroxide (8.1% w/v, 10% w/w) and that a small amount of a weaker base, possibly tributylamine (0.02 N), was present.

Procedures

Synthesis of Oligo(oxyethylene)di-N,N-dimethyl-p-aminobenzoates

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 min. 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 min to dissolve the unreacted N,N-dimethyl-p-aminobenzoic acid. The product was filtered with suction, dried in a vacuum oven at 60°C and reduced pressure (50 Torr), 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%, mp 202-208°C) of yellow crystals of ethylene glycol di-N,N-dimethyl-p-aminobenzoate. 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 pure ethylene glycol di-N,N-dimethyl-p-aminobenzoate (mp 212-213°C). The infrared spectrum (KBr) showed absorptions at 1690 cm^{-1} (C=O stretching) and 1610 cm^{-1} (aromatic).

Analysis. Calcd for $C_{20}H_{24}N_2O_4$: C, 67.39%; H, 6.79%; N, 7.86%. Found: C, 67.33%; H, 7.00%; N, 7.65%.

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 hr by an oil bath at 90°C. 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%, mp 202-210°C).

Procedure III. A 100-ml round-bottomed flask was charged with 1,2-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 hr by an oil bath at 94°C. 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%, mp 195-200°C).

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), (mp 100-102°C, lit. [33] mp 101-102°C), 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 extractor 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. As the reaction proceeded, white ethylene glycol di-N,N-dimethyl-p-aminobenzoate precipitated. After 3.5 hr 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 and with acetone, and dried at 50°C for 4 hr at reduced pressure (50 Torr) to yield impure ethylene glycol di-N,N-dimethyl-p-aminobenzoate (13.3 g, 83%, mp 197-205°C). The product was recrystallized once from toluene (400 ml) and once from methyl benzoate to yield 9.9 g (62%, mp 212-214.5°C) of ethylene glycol di-N,N-dimethyl-p-aminobenzoate.

Synthesis of Diethylene Glycol di-N,N-dimethyl-p-aminobenzoate. 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), were treated as described above. Linde type 5A Molecular Sieves were used in the extractor. After 3 hr at reflux, the reaction mixture was diluted with benzene and washed with water to remove the base catalyst. After drying with $MgSO_4$, the product was precipitated by the addition of hexane, giving 15.6 g (86%) of diethylene glycol di-N,N-dimethyl-p-aminobenzoate. The product was dissolved in dichloromethane and the yellow solution was decolorized through a 1 × 10 cm column of alumina. Recrystallization from dichloromethane-hexane yielded pure diethylene glycol di-N,N-dimethyl-p-aminobenzoate (14.1 g, 79%, mp 129-130°C). The infrared spectrum (KBr) showed absorptions at 1700 cm^{-1} (C=O stretching) and 1605 cm^{-1} (aromatic). The PMR spectrum ($CDCl_3$) showed δ 2.95 [$(CH_3)_2N$, 12]; 3.75-3.92 [$O(\underline{CH_2}CH_2)_2$, 4]; 4.35-4.50 ($CO_2\underline{CH_2}$, 4); 6.50-6.65 and 7.80-7.95 (aromatic protons, 8). 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 liter/mole-cm, respectively.

Analysis. Calcd for $C_{22}H_{28}N_2O_5$: C, 65.98%; H, 7.05%; N, 7.00%. Found: C, 65.98%; H, 6.76%; N, 6.97%.

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 hr in the presence of Molecular Sieves as described above and gave 17.6 g (88% yield) of impure triethylene glycol di-N,N-dimethyl-p-aminobenzoate. The crude product was dissolved in dichloromethane, the yellow solution was decolorized and the product recrystallized from a dichloromethanehexane mixture to yield 10.7 g (51.4%, mp 94.5-96.5°C). The infrared spectrum (KBr) showed absorptions at 1690 cm^{-1} (C=O stretching) and 1610 cm^{-1} (aromatic). The PMR spectrum ($CDCl_3$) showed δ: 3.0 [$N(CH_3)_2$, 12]; 3.70-3.86 [$\text{-(}C\underline{H}_2OC\underline{H}_2CH_2)_2$, 8]; 4.33-4.50 ($CO_2C\underline{H}_2$, 4); 6.50-6.65 and 7.83-7.98 (aromatic protons, 8). The UV spectrum (methanol) showed maxima at 310 and 228 nm with molar extinction coefficients of 56.8×10^3 liter/mole-cm, respectively. Analysis. Calcd for $C_{24}H_{32}N_2O_6$: N, 6.30%. Found: N, 6.58%.

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) treated as described above gave 13.1 g (60%) of tetraethylene glycol di-N,N-dimethyl-p-aminobenzoate. The product oiled out initially when the solution was added to n-hexane and the oil solidified on standing. Once crystallized, the product could be recrystallized by dissolving 1 g in 50 ml of warm ether and cooling the solution to -20°C (mp 70.5-71°C). The infrared spectrum showed absorptions at 1685 cm^{-1} (C=O stretching) and 1605 cm^{-1} (aromatic). The PMR spectrum ($CDCl_3$) showed δ: 2.98 [$N(CH_3)_2$, 12]; 3.62-3.82 [$O(C\underline{H}_2C\underline{H}_2OC\underline{H}_2CH_2O)_2$, 12]; 3.62-3.82 [$O(C\underline{H}_2C\underline{H}_2OC\underline{H}_2CH_2O)_2$, 12]; 4.30-4.48 ($CO_2C\underline{H}_2$, 4); 6.50-6.65 and 7.80-7.95 (aromatic protons, 8). The UV spectrum (methanol) showed maxima at 310 and 228 nm with molar extinction coefficients of 56.3×10^3 and 14.2×10^3 liter/mole-cm, respectively. Analysis. Calcd for $C_{26}H_{36}N_2O_7$: N, 5.74%. Found: N, 5.82%.

Synthesis of Poly(oxyethylene) ($\overline{M}_n$ 300) di-N,N-dimethyl-p-aminobenzoate. Methyl N,N-dimethyl-p-aminobenzoate (21.5 g, 0.12 mole), poly(oxyethylene glycol) (13.5 g, 0.045 mole), and benzene (45 ml) were charged as above, 30 g of dry Linde type 5A Molecular Sieves were added to the modified Soxhlet extractor, and the solution was refluxed for 30 min under nitrogen to remove water that may have been present in the poly(oxyethylene) glycol. After the solution had cooled, sodium methoxide (0.2 g) was added and the mixture was refluxed for 3 hr. 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), and water (50 ml), dried with magnesium sulfate, and filtered. The benzene solution was added to n-hexane (850 ml) which caused an oil to precipitate. The precipitation from benzene with n-hexane was repeated and the slightly yellow oil was decolorized by passing a dichloromethane (50 ml) solution through a 1 × 16 cm column of neutral alumina. The solvent was removed at reduced pressure (0.2 Torr) and 50°C for 6 hr 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). The PMR spectrum ($CDCl_3$) showed δ 2.94 [$N(C\underline{H}_3)$, 12]; 3.55-3.80 [$CH_2C\underline{H}_2O(C\underline{H}_2CH_2O)$[illegible]$C\underline{H}_2CH_2$, 20]; 4.30-4.45 ($CO_2C\underline{H}_2$, 4); 6.45-6.62 and 7.83-7.95 (aromatic protons, 8). 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 liter/mole-cm, respectively. The nitrogen analysis was calculated on assuming the product had an average molecular weight of 574.

Analysis. Calcd: N, 4.88%. Found: N, 4.91%.

Synthesis of Poly(oxyethylene) ($\overline{M}_n$ 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) ($\overline{M}_n$ 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). The PMR spectrum ($CDCl_3$) showed δ 2.97 [$N(C\underline{H}_3)_2$, 12]; 3.62-3.88 [$CH_2C\underline{H}_2O(C\underline{H}_2C\underline{H}_2O)_{6.1}C\underline{H}_2CH_2$, 28]; 4.32-4.50 ($CO_2C\underline{H}_2$, 4); 6.53-6.60 and 7.80-7.94 (aromatic protons, 8). 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 15.2×10^3 liter/mole-cm, respectively. The nitrogen analysis was calculated assuming the product had an average molecular weight of 666.

Analysis. Calcd. N, 4.20%. Found: 4.48%.

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

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°C, in an ice-water bath. p-Toluenesulfonyl chloride (34 g, 0.18 mole) was added, and the flask was left in a refrigerator at 5°C for 2 days. 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 Torr). 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 (mp 124-127°C; lit. [34] mp 126-127°C.

Synthesis of Ethylene Glycol Disalicylate: 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°C. In a few minutes, the reactants dissolved to form a clear, yellow solution, and after 30 min, sodium p-toluenesulfonate started to precipitate. After 12 hr, 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 Torr) 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 (mp 78.5-79.5°C, lit. mp 78.5°C [35] and 84°C [36]). The infrared spectrum (KBr) showed an absorption at 1665 cm^{-1} (C=O stretching). The PMR spectrum ($CDCl_3$) showed δ 4.57 ($CO_2C\underline{H}_2$, 4); 6.63-7.85 (aromatic protons, 8); 10.55 ($O\underline{H}$, 2). The UV spectrum (methanol) showed maxima at 306 and $\overline{2}38$ nm with molar extinction coefficients of 8.76×10^3 and 18.3×10^3 liter/mole-cm, respectively.

Analysis. Calcd for $C_{16}H_{14}O_4$: 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.

Procedure II. A 250-ml round-bottomed flask was charged with 1,2-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°C with magnetic stirring. Within a few minutes, a clear solution formed, and after 30 min, a precipitate started to form. The mixture was allowed to cool to room temperature after 5 hr of heating and was then added to water (250 ml). A yellow oil separated which solidified to a white solid and which was recrystallized from aqueous methanol to yield 7.1 g (79%) of ethylene disalicylate (mp 84.5-86°C, lit. mp 78.5°C [35] and 84°C [36]). DMSO and 2-butanone were also used as solvents for the reaction of dibromoethane and sodium salicylate; however, the yields were not as high with these solvents as with DMAc.

Synthesis of Diethylene Glycol Di-p-toluenesulfonate. Diethylene glycol (5.1 g, 0.048 mole), dry pyridine

(35 ml), and purified p-toluenesulfonyl chloride (21 g, 0.11 mole), when treated as described above, yielded 16.6 g of diethylene glycol di-p-toluenesulfonate (83%, mp 88-89°C, lit [37] mp 88-89°C, after recrystallization from DH_2Cl_2/hexane. The PMR spectrum ($CDCl_3$) showed δ 2.41 (CH_3, 6); 3.48-3.64 ($C\underline{H_2}OC\underline{H_2}$, 4); 4.00-4.18 ($SO_3C\underline{H_2}$, 4); 7.25-7.39 and 7.68-7.81 (aromatic protons, 8).

Synthesis of Diethylene Glycol Disalicylate. DMAc (50 ml), sodium salicylate (25.6 g, 0.16 mole), and diethylene glycol di-p-toluenesulfonate (16.6 g, 0.04 mole) were heated with magnetic stirring by an oil bath at 75°C. 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). A 0.5-ml aliquot of the reaction mixture was added to a test tube containing 1 ml each of water and CCl_4. The test tube was shaken, and the organic layer was separated and washed with 5% aqueous $NaHCO_3$ and with water, dried with $MgSO_4$, and filtered. The PMR spectrum of the clear, colorless solution revealed that the conversion of tosylate groups to salicylate groups was 73% after 2 hr, 86% after 3 hr, and 93% after 4 hr. After 4.5 hr, the reaction mixture was cooled and added to water with stirring. Diethylene glycol disalicylate precipitated as a yellow oil. The oil was dissolved in CH_2Cl_2, and the solution was washed with 5% aqueous $NaHCO_3$, with water, and with dilute HCl, dried with $MgSO_4$, and filtered. The clear, colorless solution was added to n-hexane to precipitate the product. Diethylene glycol disalicylate was recrystallized from a solution of ether (40 ml) and n-hexane (50 ml) to yield 9.2 g (67%, mp 67.5-68.5°C, lit. [36] mp 68°C). The infrared spectrum (KBr) showed an absorption at 1670 cm^{-1} (C=O stretching). The PMR spectrum ($CDCl_3$) showed δ 3.85-4.00 [$O(C\underline{H_2}CH_2)_2$, 4]; 4.45-4.60 ($CO_2C\underline{H_2}$, 4); 6.75-7.95 (aromatic protons, 8); 10.6 ($O\underline{H}$, 2). The UV spectrum (methanol) showed maxima at 306 and 238 nm with molar extinction coefficients of 8.56×10^3 and 18.0×10^3 liter/mole-cm.

Analysis. Calcd. for $C_{18}H_{18}O_5$: C, 62.42%; H, 5.24%. Found: C, 62.59%; H, 5.39%.

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%, mp 80.5-81.5°C, lit. [38] mp 81-82°C) of product.

Synthesis of Triethylene Glycol Disalicylate. The same procedure used in converting diethylene glycol di-p-toluenesulfonate to diethylene glycol disalicylate was used to convert triethylend glycol di-p-toluenesulfonate to triethylene glycol disalicylate and gave after the usual workup 9.8 g (90%) of a slightly yellow oil. The oil was purified and crystallized to a white solid and was dried in a vacuum desiccator at reduced pressure (0.05 Torr). The yield of triethylene glycol disalicylate was 6.0 g (55%, mp 46.5-49°C).

Acid-Catalyzed Esterification of Triethylene Glycol with Salicylic Acid. A 250-ml round-bottomed flask equipped with a Dean-Stark trap and reflux condenser 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 4 days the reaction mixture was worked up 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 of triethylene glycol disalicylate (mp 47.5-49°C). The infrared spectrum (KBr) showed an absorption at 1675 cm^{-1} (C=O stretching). The PMR spectrum showed δ 3.65-3.85 ($C\underline{H}_2OCH_2CH_2OCH_2$, 8); 4.33-4.48 ($CO_2C\underline{H}_2$, 4); 6.63-7.88 (aromatic protons, 8); 10.65 (ArO$\underline{H}$, 2). The UV spectrum (methanol) showed maxima at 305 and 238 nm with molar extinction coefficients of 8.80 × 10^3 and 18.6 × 10^3 liter/mole-cm, respectively.

Analysis. Calcd for $C_{20}H_{22}O_8$: C, 61.53%; H, 5.68%. Found: C, 61.74%; H, 5.59%.

Synthesis of Tetraethylene Glycol Di-p-toluenesulfonate. The procedure used to prepare tetraethylene glycol di-p-toluenesulfonate was the same as that used in the preparation of diethylene glycol di-p-toluenesulfonate; however, purification was accomplished by passage of a CH_2Cl_2 solution of the oily product through a 1 × 10 cm column of neutral alumina. The yield was 78% (21.5 g) of a slightly yellow oil.

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 65°C or at 75°C in DMAc (25 ml) with sodium salicylate (13.7 g, 0.085 mole). The progress of the reaction was followed by PMR spectroscopy. The total yield of impure tetraethylene glycol disalicylate after 6 hr at 75°C or 20 hr at 65°C was 9.4 g (81%), and after purification, a slightly yellow oil (6.0 g, 64%) was obtained.

Analysis. Calcd for $C_{22}H_{26}O_5$: C, 60.82%; H, 6.03%. Found: C, 60.40%; H, 5.89%.

Synthesis of Polyepichlorohydrin Derivatives

Synthesis of Tetraethylammonium N,N-Dimethyl-p-aminobenzoate. A 250-ml round-bottomed flask was charged with aqueous tetraethylammonium hydroxide (0.75 N, 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°C and reduced pressure in a rotary evaporator. The slightly yellow oil was placed in a vacuum desiccator (0.05 Torr) over phosphorus pentoxide for 24 hr, during which time it solidified. The tetraethylammonium N,N-dimethyl-p-aminobenzoate was dissolved in dichloromethane at room temperature. Ethyl acetate was added and crystals formed when the mixture was placed 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 Torr) and 50°C for 2 hr (mp 64-67°C, sealed capillary) and then at 70°C for 18 hr. The hygroscopic white powder (7.1 g, 47% yield) then melted at 117-120°C. The elemental analysis and potentiometric titration with perchloric acid in acetic acid showed that anhydrous tetraethylammonium N,N-dimethyl-p-aminobenzoate was obtained.

Analysis. 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.

Synthesis of Tetraethylammonium N,N-Dimethyl-p-aminobenzoate Hemihydrate. Tetraethylammonium hydroxide (81 ml, 0.75 N, 61 mmole) was added to a 250-ml Erlenmeyer flask which contained an excess of N,N-dimethyl-p-aminobenzoic acid (11.0 g, 66 mmole). The mixture was stirred for 30 min 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°C and reduced pressure. The oil partially solidified on cooling and completely solidified on further drying in a vacuum desiccator over phosphorus pentoxide at reduced pressure (0.05 Torr) for 1 week. The PMR spectrum (d-DMSO) showed δ 1.00-1.30 [$N(CH_2C\underline{H}_3)_4$, 12]; 2.85 [$N(C\underline{H}_3)_2$, 6]; 3.05-3.43 [$N(C\underline{H}_2CH_3)_4$, 8]; 4.10 ($^1/_2$ $\underline{H}_2O$, 1); 6.50-7.70 (aromatic protons, 4). The PMR spectrum ($CDCl_3$) showed δ 0.90-1.27 [$N(CH_2C\underline{H}_3)_4$, 12]; 2.90 and 2.90-3.25 [$N(C\underline{H}_3)_2$ and $N(C\underline{H}_2CH_3)_4$, 14]; 6.50-6.65 (aromatic protons, 2); 7.75-7.90 (aromatic protons and $^1/_2$ H_2O, 3). The salt melted at 73-94°C.

Analysis. Calcd for $C_{17}H_{30}N_2O_2 \cdot {}^1/_2\ H_2O$: C, 67.28%; H, 9.97%; N, 9.23%. Found: C. 66.74%; H, 9.99%; N, 9.03%.

Synthesis of Tetramethylammonium Salicylate Monohydrate. Salicylic acid (7.5 g, 55 mmole) was added to tetramethylammonium hydroxide in methanol (2.74 N, 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. Further distillation of the solvents at reduced pressure resulted in the precipitation of a solid. The crude product was crystallized three times from a mixture of isopropanol, ethyl acetate, and petroleum ether (bp 60-70°C) and dried at 90°C and reduced pressure (0.05 Torr) for 16 hr. The yield of product was 5.9 g (47%, mp 141-143.5°C, sealed capillary). The PMR spectrum (d-DMSO) showed δ 3.15

[$(C\underline{H}_3)_4$ and $\underline{H}_2O$, 14]; 6.5-7.8 (aromatic protons, 4); 16.75 (O$\underline{H}$, 1). The elemental analysis and potentiometric titration with perchloric in acetic acid showed that the salt was a monohydrate.

Analysis. Calcd for $C_{11}H_{17}NO_3 \cdot H_2O$: N, 6.11%; 229.5 g/equiv. Found: N, 6.34%; 230 g/equiv.

Titration with Perchloric Acid in Acetic Acid. Perchloric acid in acetic acid (0.10 N) was prepared according to the published procedure [39]. The reagent was stored in an automatic buret which was sealed from the atmosphere with clamped rubber hoses when not in use. 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.

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, 37 mmole), and tetraethylammonium N,N-dimethyl-p-aminobenzoate (1.10 g, 3.7 mmole). (All transfers 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, 105°C; detector temperature, 245°C; injector temperature, 215°C; helium flow rate, 25 ml/min; current, 125 mA; attenuator, 4 and 16; sample size, 0.20 μl; chart speed, 5 in./min; column, 3% SE 30 on Varport 100/120 5 ft. × 1/8 in. The retention times were 62 sec for DMSO and 35 sec 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 reaction was carried out a second time with heating by an oil bath maintained at 44°C.

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 min). 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°C. The PMR spectra of the solutions were measured 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 hr, respectively, at room temperature. The conversion of the reaction at 54°C was 75 and 100% after 4 and 21 hr, respectively.

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°C. 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.

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°C 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 showed a progressive decrease in the integrated signal intensity of the triplet (3.45-3.65 ppm) of the methylene protons in the 1-position of butyl chloride and an increase in the integrated signal intensity of the triplet (4.15-4.35 ppm) of butyl salicylate. The reaction conversion was 0 and 5% after 4 and 21 hr, respectively, at room temperature, and was 25 and 35% after 4 and 21 hr, respectively at 54°C.

Reaction of Tetraethylammonium N,N-Dimethyl-p-aminobenzoate Dihydrate with Polyepichlorohydrin. Polyepichlorohydrin (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°C (oil bath heating). During the course of the reaction, a colorless gel separated from the solution. After 24 hr, 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 phosphorus pentoxide at 78°C and reduced pressure (0.05 Torr) for 24 hr. 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°C. 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-dichloroethan solution were 0.75 and 1.4 dl/g, respectively. The copolymer had a glass transition (by DSC) at 60°C. 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). The PMR spectrum (o-dichlorobenzene, R-32) at 120° showed δ 2.72 [$N(C\underline{H}_3)_2$, 54]; 3.4-4.1 ($C\underline{H}C\underline{H}_2O$ and $C\underline{H}_2Cl$, 43); 4.2-4.7 ($C\underline{H}_2O_2O-$, 19). The relative integrated signal intensities indicated that the degree of substitution was 75%. A 1-ml portion 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 (6.61×10^{-3} g/liter) showed maxima at 310 nm (103 liter/g-cm) and 229 nm (27.0 liter/g-cm).

Analysis. Calcd for $\text{-(}C_{12}H_{15}NO_3\text{)-}_{75\%}\text{-(}C_3H_5ClO\text{)-}_{25\%}$: 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%.

Reaction of Tetraethylammonium N,N-Dimethyl-p-aminobenzoate Hemihydrate with Polyepichlorohydrin. Polyepichlorohydrin (1.9 g, 21 mmole) was dissolved in DMF (20 ml) with stirring in a 100-ml three-necked round-bottomed flask for 16 hr 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°C (oil bath heating). After 30 hr, the clear, viscous solution was cooled and added to water (200 ml) which caused a slighly off-white elastomeric material to precipitate. The product was completely dissolved in chloroform (30 ml) and the solution was stirred for 45 min 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 hr at 50°C in a vacuum oven at reduced pressure (0.4 Torr) and further dried in a drying pistol over phosphorus pentoxide at 61°C and reduced pressure (0.05 Torr) for 24 hr. The yield of slightly off-white polymer was 3.9 g. A 50-mg portion 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°C. The solution was filtered from a trace amount of insoluble material. The copolymer concentration of the DMF solution was 0.48% and the inherent viscosity was 0.60 dl/g. The viscosity of a 0.23% 1,2-dichloroethane solution was 0.37 dl/g. The number-average molecular weight (by VPO) was greater than 20,000. The copolymer had a glass transition (by DSC) of 63°C. The infrared spectrum of a film prepared by evaporating a chloroform solution on a sodium chloride plate showed an absorption at 1695 cm^{-1} (C=O stretching). The PMR spectrum at 120°C (o-dichlorobenzene, R-32) showed δ 2.70 [$N(CH_3)_2$, 63]; 3.4-4.1 ($C\underline{H}C\underline{H}_2O$ and $C\underline{H}_2Cl$, 37); 4.2-4.7 ($C\underline{H}_2O_2C-$, 21), and the integration indicated that the degree of substitution was 90%. The UV spectrum of a dichloroethane solution (9.18 × 10^{-3} g/liter) showed maxima at 309 nm (104 liter/g-cm) and 229 nm (29.81 liter/g-cm).

Analysis. Calcd for $\text{-}(C_{12}H_{15}NO_3)\underset{90\%}{\text{---}}(C_3H\ ClO)\underset{10\%}{\text{---}}$: 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°C and reduced pressure (0.05 Torr) over phosphorus pentoxide for 36 hr.

Analysis. Found: C, 63.56%; H, 6.71%; N, 5.83%; Cl, 1.49%.

Synthesis of Poly(methacrylic Acid) Derivatives

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 hr. 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.

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 hr 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°C and reduced pressure over a period of 30 min. The poly(tetrabutylammonium methacrylate), which probably contained some water, was a yellow solid.

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 min of the addition, a considerable amount of gel separated from solution. The mixture was magnetically stirred for 16 hr at room temperature and then added to 0.1 N 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; a large excess of water was added to the mixtures before decanting the liquids from the precipitate. The addition of water to the 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 Torr) in a drying pistol over phosphorus pentoxide at room temperature for 90 min and then at 78°C for 16 hr. The yield of white product was 0.82 g (76% based on a 100% degree of esterification). The infrared spectrum (KBr) was identical to the published spectrum of poly(butyl methacrylate) [40].

Analysis. 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%.

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 hr and then added to 100 ml of a 0.15 N 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 Torr) in a vacuum desiccator over phosphorus pentoxide for 16 hr. The copolymer was then stirred with benzene, filtered, and dried in a drying pistol over phosphorus pentoxide at reduced pressure (0.05 Torr) at 78°C. The yield of fluffy off-white powder was 1.02 g (calculated 1.14 g).

The polymer was further purified by reprecipitation from DMSO into ether, and then from DMSO/aqueous HCl into water, followed by 24 hr extraction with ether.

Analysis. Calcd for $-(C_4H_6O_2)_{73\%}-(C_{19}H_{18}O_5)_{27\%}$: C, 64.05%;

H, 6.17%; Br, 0%; N, 0%. Found: 60.83%; H, 5.31%; Br, 0.0%; N, 0.18%.

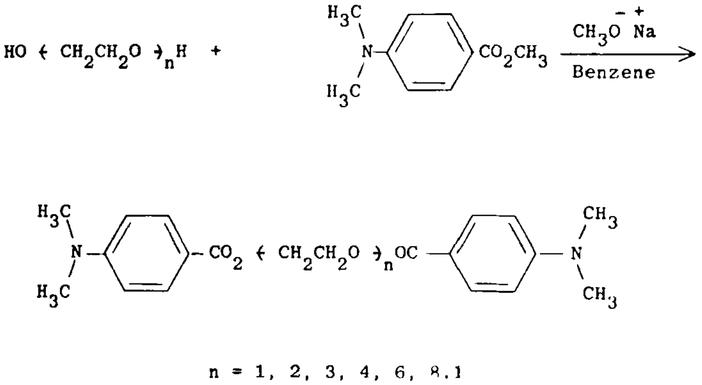
The copolymer had an inherent viscosity (0.5% DMSO solution) of 0.5 dl/g and did not show a glass transition by DSC. The infrared spectrum (KBr) showed a broad peak at 1700 cm^{-1} (C=O stretching) and a broad peak at 1615 cm^{-1}. The PMR spectrum (d-DMSO, R-32) at 135°C showed δ 0.7-2.4 [$C\underline{H}_2C(C\underline{H}_3)$, 51]; 2.4-2.6 (DMSO); 4.1-4.5 ($OC\underline{H}_2C\underline{H}_2O_2C$, 12); 6.4-6.8 and 7.2-7.9 (aromatic protons, 5 and 16). A signal was not present between 10 and 20 ppm; however, at 90°C a signal was observed at 11.7-12.1 ppm. 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 liter/g-cm, respectively.

RESULTS AND DISCUSSION

Encapping reactions on ethylene glycol and on oligomeric polyethylene glycols were carried out to form N,N-dimethyl-p-aminobenzoates and salicylates. Nucleophilic displacement reactions on poly(epichlorohydrin) with tetraalkylammonium N,N-dimethyl-p-aminobenzoates were carried out to form various copolymers of glycidyl N,N-dimethyl-p-aminobenzoates and epichlorohydrin. Substitution of poly(methacrylic acid) as its tetrabutyl ammonium salt, with substituted alkyl halides provided an effective way of preparing esters of poly(methacrylic acid).

Oligo(oxyethylene) glycols of molecular weights from 62 to 400 were endcapped with N,N-dimethyl-p-aminobenzoate by a 3-hr sodium methoxide-catalyzed ester interchange reaction of the oligo(oxyethylene) glycol with methyl N,N-dimethyl-p-aminobenzoate in refluxing benzene, using a recently modified method to remove methanol in the presence of molcular sieves [41]. Good yields, in excess of 60%, of purified product were obtained [Eq. (1)]. The reaction of the glycols with N,N-dimethyl-p-aminobenzoyl chloride in the presence of pyridine, the reaction of the di-p-toluenesulfonate with potassium N,N-dimethyl-p-aminobenzoate in DMAc, or the reaction of potassium N,N-dimethyl-p-aminobenzoate with 1,2-dibromoethane to form the endcapped esters offered no advantage over the first method. These methods had the disadvantage that the starting material had to be transformed by introduction of an activating group. This additional reaction was undesirable in view of our objective of exploiting simple reactions of readily available materials for the introduction of functional groups.

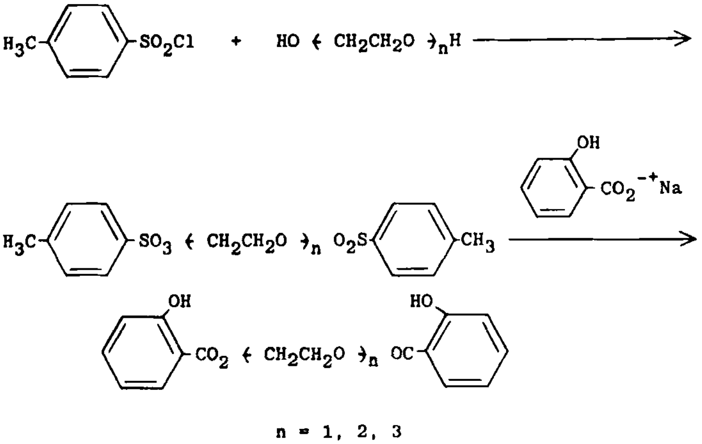
The infrared, PMR, and UV spectra of the diethylene glycol, triethylene glycol, tetraethylene glycol, and poly(oxyethylene) (MW 300



(1)

or 400), di-N,N-dimethyl-p-aminobenzoates were all similar. The UV spectral data are presented in Tables 1 and 2, and the PMR spectrum of the highest member of the series is shown in Fig. 1.

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 hr at 75°C or for 20 hr at 65°C [Eq. (2)]. The



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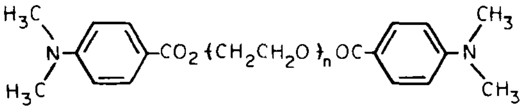
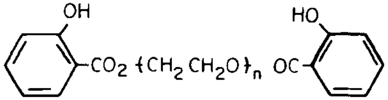
progress of some of these displacement reactions was monitored by PMR spectroscopy (Fig. 2). The infrared, PMR, and UV spectra of the ethylene glycol, diethylene glycol, and triethylene glycol disalicylates are very similar. The UV spectral data are presented in

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

Compound	Extinction coefficient	Molar extinction coefficient of the UV-absorbing group	λ_{max} (nm)
Methyl N,N-dimethyl-p-aminobenzoate	26.3×10^3 [a]	26.3×10^3	310
	7.31×10^3 [a]	7.31×10^3	228
Diethylene glycol di-N,N-dimethyl-p-aminobenzoate[b]	53.8×10^3 [a]	26.9×10^3	310
	14.7×10^3 [a]	7.35×10^3	229
90/10 Copolymer[c]	104[d]	24×10^3	309
	29.8[d]	6.9×10^3	229
75/25 Copolymer[c]	103[d]	26×10^3	310
	27.0[d]	6.8×10^3	229

[a] In liter/mole-cm.
[b] In methanol.
[c] Copolymer of glycidyl N,N-dimethyl-p-aminobenzoate and epichlorohydrin.
[d] In liter/g-cm.

TABLE 2. Ultraviolet Absorption Properties of Oligo(oxyethylene) Di-N,N-dimethyl-p-aminobenzoates and Disalicylates

	n	Extinction coefficient (liter/mole-cm)	λ_{max} (nm)
	2	14.7×10^3	229
		53.8×10^3	310
	3	14.8×10^3	229
		56.8×10^3	310
	4	14.2×10^3	229
		56.3×10^3	310
	$\overline{M}_n = 574$	14.4×10^3	229
		53.4×10^3	310
	$\overline{M}_n = 666$	15.2×10^3	229
		55.6×10^3	310
	1	18.3×10^3	238
		8.76×10^3	306
	2	18.0×10^3	238
		8.56×10^3	306
	3	18.6×10^3	238
		8.80×10^3	306

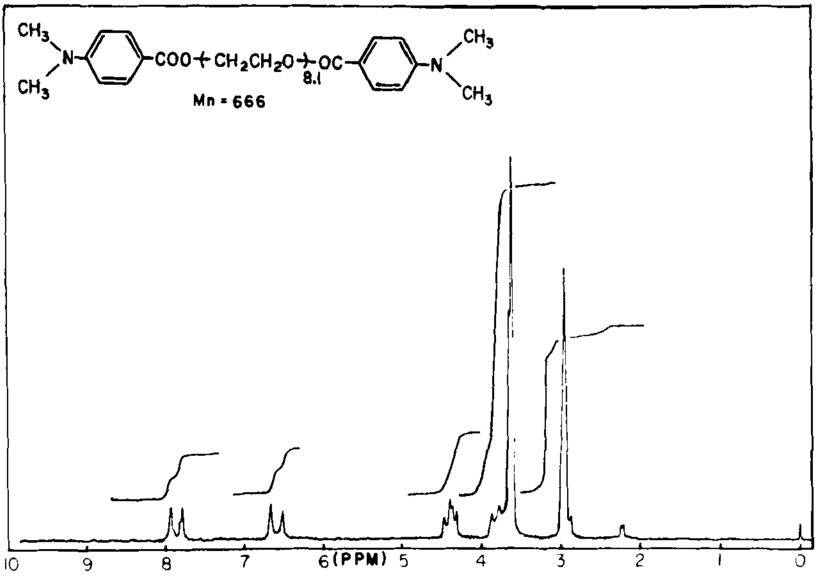


FIG. 1. PMR spectrum of oligo(oxyethylene) (8.1) N,N-dimethyl-p-aminobenzoate.

Table 2, and the PMR spectrum of the triethylene glycol derivative is shown in Fig. 3.

Another procedure investigated for the preparation of disalicylates was the direct esterification of triethylene glycol by salicylic acid, with p-toluenesulfonic acid as the catalyst in refluxing toluene. This technique required approximately 4 days to reach high conversion while the displacement reactions required only 4-5 hr at 75°C. The reaction of sodium salicylate in DMAc with dibromoethane was also investigated and gave reasonably good yields. While this method is convenient for the preparation of ethylene glycol disalicylate, it is less convenient for higher oligomers because the hydroxyl terminal group has to be replaced by a bromine end group.

The reactions of tetraalkyl ammonium salts of carboxylic acids with polyepichlorohydrin, as well as the reactions of substituted alkyl halides with tetraalkyl ammonium salts of polymethacrylic acid, are based on a recent discovery that mild esterification reactions could be carried out if the tetraalkyl ammonium, preferably the tetrabutyl ammonium, salts of carboxylic acids, were allowed to react in DMAc with alkyl halides [15]. Essentially quantitative yields were obtained with butyl chloride.

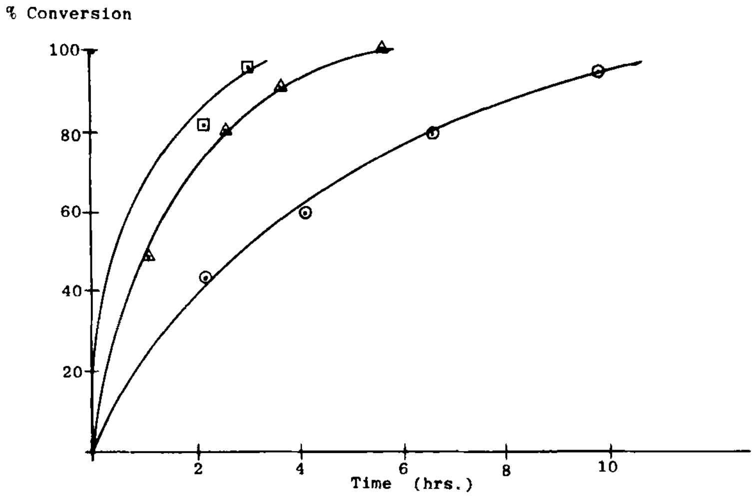


FIG. 2. Alkylation of sodium salicylate with oligo(oxyethylene) di-p-toluenesulfonates: (▣) diethylene glycol di-p-toluenesulfonate (0.8 M) and sodium salicylate (3.4 M) in DMAc at 75°C; (◬) tetramethylene glycol di-p-toluenesulfonate (0.9 M) and sodium salicylate (3.4 M) in DMAc at 75°C; (⊙) tetraethylene glyco di-p-toluenesulfonate (0.9 M) and sodium salicylate (3.4 M) in DMAc at 65°C.

The displacement reactions on polyepichlorohydrin were carried out with tetraethylammonium N,N-dimethyl-p-aminobenzoate hemihydrate in DMF at 55°C for 30 hr. The copolymer consisted of a 90% glycidyl N,N-dimethyl-p-aminobenzoate repeat units and 10% epichlorohydrin repeat units as determined by PMR spectroscopy. The reaction of tetraethylammonium N,N-dimethyl-p-aminobenzoate dihydrate with polyepichlorohydrin in DMSO at 52°C for 24 hr yielded a colorless product in which 75% of the epichlorohydrin repeat units had been converted to glycidyl N,N-dimethyl-p-aminobenzoate repeat units. This composition was confirmed by PMR spectroscopy and by elemental analysis. The PMR spectrum (in o-dichlorobenzene, 120°C) is shown in Fig. 4. With this polymer it was observed that a substantial insoluble fraction was obtained after drying at 80°C for 24 hr. It is believed that the 20% of copolymer insoluble in DMSO was crosslinked by quaternization of the dimethyl amino group of the N,N-dimethyl aminobenzoate units with unreacted epichlorohydrin units. Polymers of 90% substitution apparently are not as sensitive to such a crosslinking reaction and could be dried without change in solubility.

Minoura [42] has reported that displacement reactions of sodium

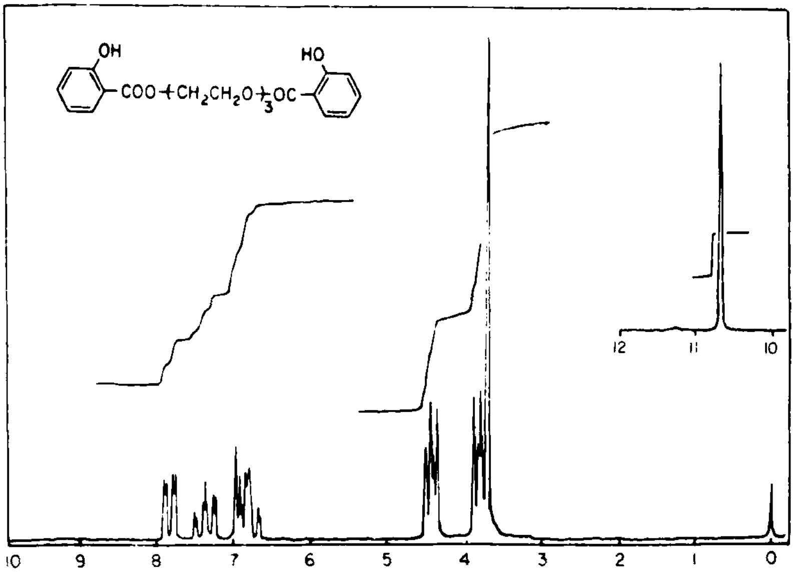


FIG. 3. PMR spectrum of trioxyethylene disalicylate.

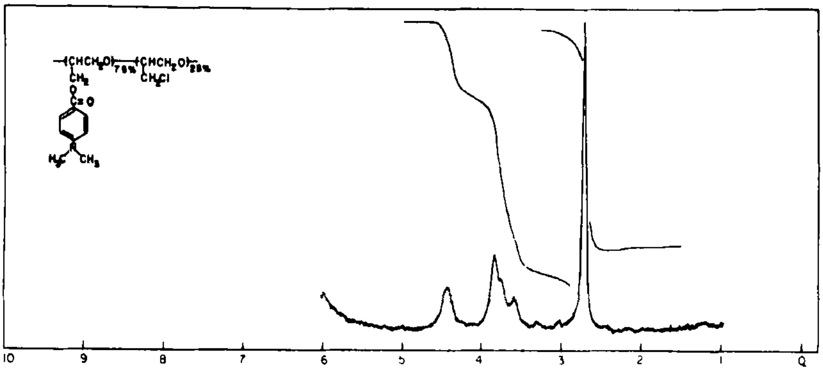
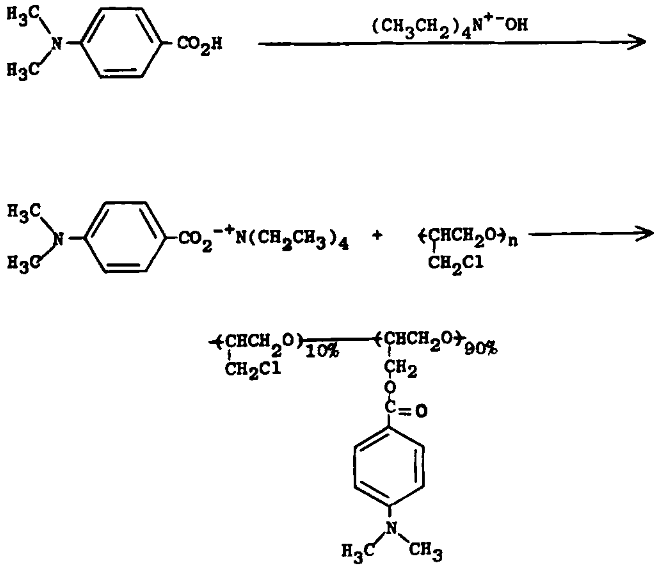


FIG. 4. PMR spectrum of copolymer of N,N-dimethyl-p-aminobenzoate (75%) and epichlorohydrin (25%).

acetate on poly-3,3-bis(chloromethyl)oxacyclobutane at 130°C were accompanied by a chain-scission reaction, leading to formation of hydroxyl end groups. Chain scission was also observed in our own attempts to prepare highly substituted, pure polyepiiodohydrin from polyepichlorohydrin by the Finkelstein reaction [43], but we have not been able to detect any significant absorption in the 3100 to 3500 cm^{-1} region of the infrared spectrum.

The copolymers of glycidyl N,N-dimethyl-p-aminobenzoate and epichlorohydrin had much higher glass transition temperatures than polyepichlorohydrin (T_g = -17°C). The 90/100 copolymer had a glass transition temperature of 63°C, and the 75/25 copolymer had a T_g of 60°C. The ultraviolet spectral data for these copolymers are presented in Table 1 and showed, as expected, that the 90/100 copolymer had a slightly higher extinction coefficient than the 75/25 copolymer [Eq. (3)].



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In the past, the alkylation of sodium or potassium salts of carboxylic acids with polyepichlorohydrin or poly-3,3-bis(chloromethyl)-oxacyclobutane at temperatures higher than 100°C has been reported to be accompanied by serious degradation reactions. It appears that these degradation reactions depend on the nucleophilicity of the reagent and on the temperature and solvent used. As a consequence, it was decided to utilize the much more reactive tetraalkyl ammonium salts of carboxylic acids rather than the potassium and sodium salts for the displacement reactions. Very mild conditions may be used for the reactions of these salts with alkyl halides in polar aprotic solvents. For example, the reaction of butyl chloride with tetraethyl ammonium acetate which contained a few moles of water per mole of salt, reached 50% conversion at 6 hr in room temperature in DMF [15]. The same reaction with butyl bromide reportedly reached 90% conversion in 30 min at room temperature. On the other hand, the reaction of butyl bromide with potassium acetate in DMF and DMSO reportedly required 2 hr at 90-100°C to obtain a high yield of butyl acetate.

In order to model the reactions of tetraalkyl ammonium carboxylate salts with polyepichlorohydrin, the conversion versus time data for the reactions of tetraethylammonium N,N-dimethyl-p-aminobenzoate and tetramethylammonium salicylate monohydrate with butyl chloride and with 2-ethoxyethyl chloride at room temperature and at 44 and 54°C, were studied. The rate data for these reactions are reported in Figs. 5 and 6. The reaction of tetraethylammonium N,N-dimethyl-p-aminobenzoate with 2-ethoxyethyl chloride reached 50% conversion in 7 hr at room temperature, similar to the data reported for the reaction of tetraethylammonium acetate with butyl chloride [15]. Tetramethylammonium salicylate was somewhat less reactive, probably because of hydrogen bonding of the o-phenol group to the carboxylate anion.

The tetraethylammonium N,N-dimethyl-p-aminobenzoate and tetramethylammonium salicylate salts were prepared in various stages of hydration in order to study the reactivity of individual hydrated forms. For example, anhydrous tetraethylammonium N,N-dimethyl-p-aminobenzoate became hydrated with 2 moles of water during storage as determined by PMR spectroscopy in deuterated DMSO. Tetraethylammonium N,N-dimethyl-p-aminobenzoate with approximately 0.5 mole of water was also prepared. This was accomplished by drying the salt at reduced pressure with P_2O_5 for 1 week at room temperature rather than at elevated temperatures. Tetramethylammonium salicylate monohydrate was prepared from salicylic acid and tetramethylammonium hydroxide. Extensive heating at reduced pressure (90°C, 0.05 Torr, 16 hr) could not remove the mole of water.

The presence of the small amount of water in the above salts was not considered to be a serious problem in nucleophilic displacement reactions. It has been reported that the tetraethylammonium acetate which was hydrated with a few moles of water reacted rapidly with butyl bromide [15]. It can be seen from Fig. 5 that the reaction of butyl bromide and 2-ethoxyethyl chloride is not sufficiently fast at room temperature but that at 50°C the reaction does proceed at a

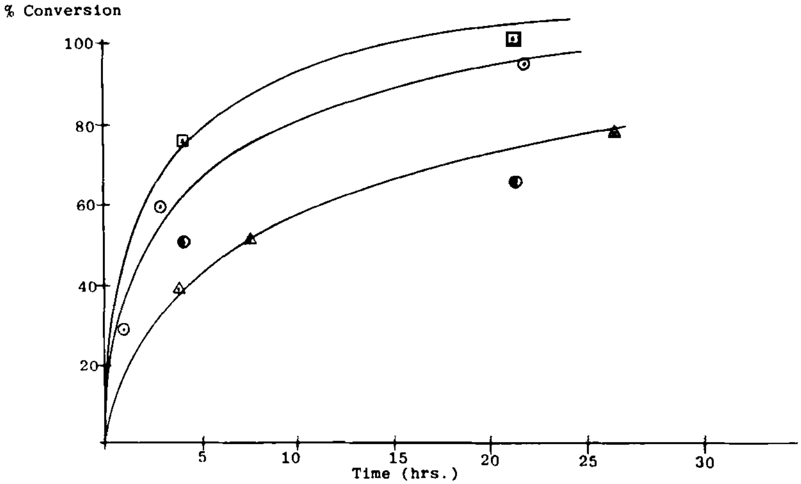


FIG. 5. Alkylation of tetraethylammonium N,N-dimethyl-p-aminobenzoate with butyl chloride and 2-ethoxyethyl chloride in DMSO. (◻) tetraethylammonium N,N-dimethyl-p-aminobenzoate dihydrate (1 M) and butyl chloride (1 M) at 54°C; (◐) tetraethylammonium N,N-dimethyl-p-aminobenzoate dihydrate (1 M) and butyl chloride (1 M) at 22°C; (⊙) tetraethylammonium N,N-dimethyl-p-aminobenzoate (0.9 M) and 2-ethoxyethyl chloride (0.9 M) at 44°C; (△) tetraethylammonium N,N-dimethyl-p-aminobenzoate (0.9 M) and 2-ethoxyethyl chloride (0.9 M) at 22°C.

reasonable rate. The presence of water in the tetraethylammonium N,N-dimethyl-p-aminobenzoate did not appear seriously to hinder the activity 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; the rate data are presented in Fig. 6. This was a slow reaction and could not be practically used for our anticipated displacement reaction on polyepichlorohydrin.

The above model studies only approximated the reaction of the tetraalkyl ammonium salts of carboxylate acids with polyepichlorohydrin. It was, however, shown that the displacement on polyepichlorohydrin could be carried out under milder conditions (50°C, 30 hr, DMF) than that reported for the reaction of sodium or potassium salts of carboxylate acids on polyepichlorohydrin and poly-3,3-bis(chloromethyl)oxacyclobutane, consequently avoiding some of the side reactions that had resulted in severe molecular weight losses.

For the preparation of copolymers of glycidyl esters by polymer

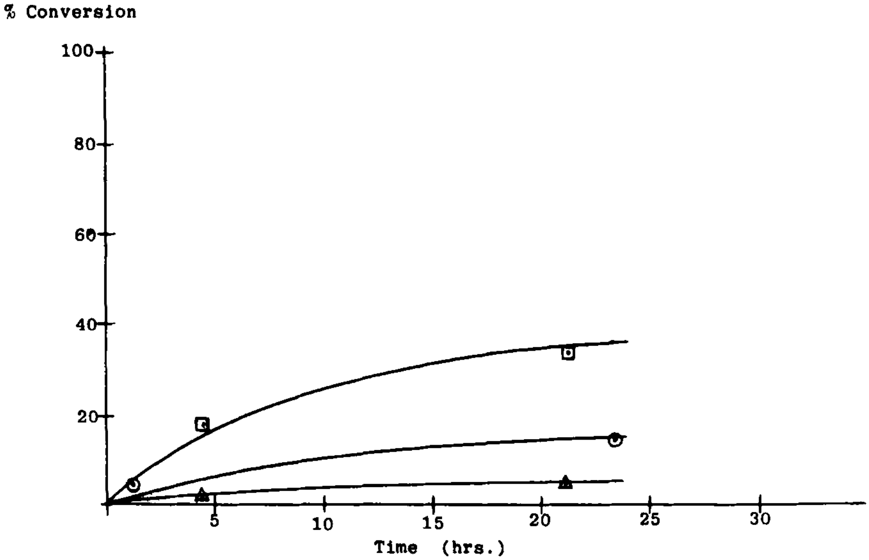
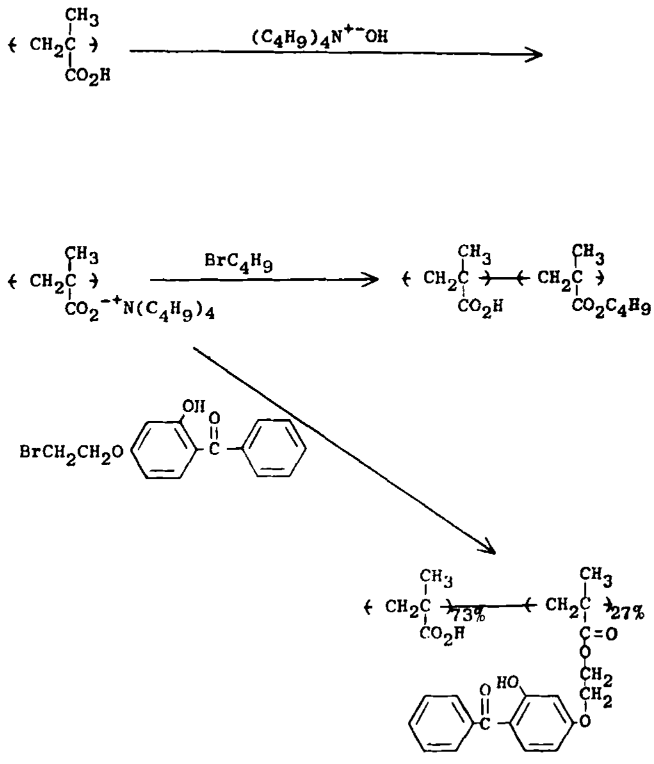


FIG. 6. Alkylation of tetramethylammonium salicylate monohydrate with butyl chloride and 2-ethoxyethyl chloride in DMSO: (▫) tetramethylammonium salicylate monohydrate (1 M) and butyl chloride (1 M) at 54°C; (△) tetramethylammonium salicylate monohydrate (1 M) and butyl chloride (1 M) at 22°C; (⊙) tetramethylammonium salicylate monohydrate (0.9 M) and 2-ethoxyethyl chloride (0.9 M) at 44°C.

reactions, more reactive oxyethylene polymers are desirable. In another paper we have reported on attempts which were effective but not completely successful, to prepare polyepiiodohydrin from polyepichlorohydrin with potassium iodide [43]. In this reaction, the degree of substitution obtained was in the neighborhood of 90%, but molecular weight losses were still very severe. Another approach to the preparation of glycidyl esters is the preparation of polyglycidol and its reaction with reactive acid derivatives. More reactive derivatives of polyglycidol, such as the tosylate, are also attractive.

Extensive studies of displacement reactions have been carried out in the past with the objective of preparing various derivatives of poly(acrylic acid) and poly(methacrylic acid). The reaction of tetraalkyl ammonium salts of carboxylate acids with alkyl bromides (90% conversion at room temperature in 30 min) is a new avenue which allows the preparation of esters of poly(methacrylic acid) under mild conditions. This reaction allows the greater reactivity of carboxylates as nucleophiles and the use of aprotic solvents in displacement reactions. The feasibility of the polymeric displacement reaction was tested by carrying out the reaction on butyl bromide with poly(tetrabutylammonium methacrylate) at room temperature for 24 hr [Eq. (4)]. As was shown previously, tetraethylammonium acetate reportedly reacted very rapidly with butyl



(4)

bromide, even in hydrated form; a few moles of water could be tolerated. Therefore, no attempts were made by us to dehydrate the polymeric salt, in order to avoid side reactions. After the butyl bromide was allowed to react with the polymeric salt of methacrylic acid, a product was obtained whose infrared and PMR spectra were identical to the published spectra of poly(butyl methacrylate). The elemental analysis indicated also that the degree of substitution was very high. It was, however, found that a small amount of nitrogen was left in the polymer.

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 hr. The infrared spectrum of the product showed that 2-hydroxybenzophenone groups had been incorporated into the polymer. The copolymer was analyzed by PMR spectroscopy and showed that 27 mole % 2-hydroxy-4-(2-methacryloxyethoxy) benzophenone and 73% methacrylic acid were present [Eq. (4)].

The ultraviolet spectrum of the product showed the characteristic absorptions of the 2-hydroxybenzophenone group at 327, 287, and 243 nm. Since the copolymer had 27 mole % (58 wt %), 2-hydroxy-4-(2-methacryloxyethoxy) benzophenone repeat units, the molar extinction coefficient of the UV absorbing repeat units was 9.3×10^3, 15×10^3, and 10×10^3 liter/mole-cm at 327, 287, and 343 nm, respectively. The PMR spectrum (in d-DMSO, 135°C) is shown in Fig. 7.

In this work it was outlined that endcapping of oligomeric materials can be used effectively to prepare oligomers whose characteristics as ultraviolet absorbers are similar to that of the parent compound, but whose physical properties, e. g., solubility and mobility, have been altered.

In selected examples, it has been shown that tetraalkylammonium salts of carboxylic acids may serve as nucleophiles in mild esterification reactions in highly polar aprotic solvents. This reaction is a particularly versatile reaction as the preparation of tetraalkyl ammonium salts of carboxylic acids is easily accomplished. These salts are very hygroscopic, but their reactivity is not too significantly influenced by water if the water content is held relatively low.

FIG. 7. PMR spectrum of copolymer of ester of 2-hydroxy-4-(2-methacryloxyethoxy) benzophenone (27%) and methacrylic acid (73%).

We have demonstrated that tetraethylammonium N,N-dimethyl-p-aminobenzoate can be readily alkylated with alkyl chlorides at 50°C in DMF. This model reaction was the basis for the reaction of tetraalkylammonium salts of low molecular weight carboxylic acids with polyepichlorohydrin. It has also been shown that the tetraalkylammonium salts of poly(methacrylic acid) can be readily prepared and utilized for the preparation of esters of poly(methacrylic acid). Poly(butyl methacrylate) was made as a model compound, through the reaction of poly(tetrabutylammonium methacrylate) and butyl bromide. When 4-(2-bromoethoxy)-2-hydroxybenzophenone was allowed to react with poly(tetrabutylammonium methacrylate) in an attempted low conversion reaction (28 mole percent), the corresponding ester was obtained in high yield.

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