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POLYESTERS WITH AROMATIC GROUPS IN THE BACKBONE FROM REACTIONS OF 3- AND 4-BROMOMETHYLBENZOIC ACIDS WITH TRIETHYLAMINE†

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ABSTRACT

Aromatic polyesters were obtained in relatively good yields (~70%) from reactions of 3- and 4-bromomethylbenzoic acids with triethylamine in chlorobenzene. A copolymer was prepared in 58% yield by reaction of a 1:1 mixture of the two acids under similar conditions. The polyesters were characterized by IR, ¹H- and ¹³C-NMR spectra, x-ray powder diffraction, DSC behavior, solution viscosity, and hydrolysis to the corresponding hydroxymethylbenzoic acids. Molecular weights were determined by ¹H-NMR endgroup analysis. Possible mechanisms for the reactions are discussed.

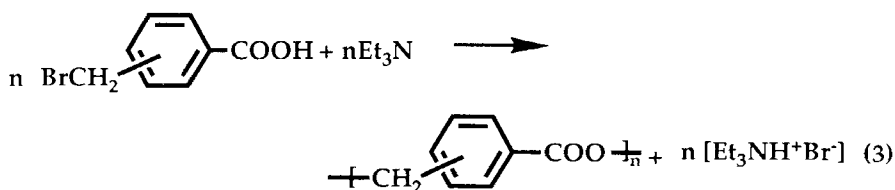
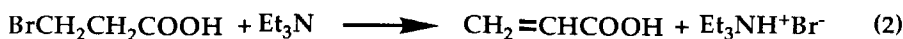
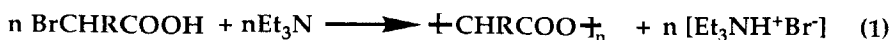
INTRODUCTION

α -Bromocarboxylic acids were reported [1, 2] to form polyesters when reacted with amines such as triethylamine (Eq. 1) whereas with a β -bromo-substituted acid, 3-bromopropanoic acid, hydrogen bromide elimination occurred to form acrylic acid and triethylammonium bromide in about 40% yield [3] (Eq. 2). It was of

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interest to see if compounds containing reactive bromine and in which dehydrobromination is precluded as in benzyl bromides, such as 3- and 4-bromomethylbenzoic acids, would undergo polymerization when reacted with amines to form the corresponding polyesters, poly(oxycarbonyl-1,3-phenylenemethylene) (**1**)* and poly(oxycarbonyl-1,4-phenylenemethylene) (**2**)* (Eq. 3). The possibility of formation of copolymers of **1** and **2** was also investigated. Results of this study are described.



Polyesters **1** and **2** were previously prepared by other methods. The *para*-polyester (**2**) was prepared by heating 4-hydroxymethylbenzoic acid esters in the presence of various catalysts [4–10], heating 4-hydroxymethylbenzoic acid under nitrogen without a catalyst [11], and also obtained as an oligomer ($DP = 3$) by phase-transfer catalysis [12]. The *meta*-polyester (**1**) has been prepared by catalytic heating of 3-hydroxymethylbenzoic acid ester [7, 10]. Higher molecular weights were obtained when catalysts were used.

Polyester **2** has been known since 1948 [4] to have useful properties [4–9, 13–15] as fibers, films, high-impact strength materials, foamed thermoplastic resins, and to have good weatherability. According to Cook et al. [4], these polyesters with intrinsic viscosities in *m*-cresol of 0.3 to 1.5 have satisfactory fiber-forming capabilities. Polyester **1** has been more recently investigated [7, 13, 14].

MEASUREMENTS

¹H-NMR spectra were recorded on a JEOL FX 90 Q Fourier transform spectrometer with an internal deuterium lock using DMSO-*d*⁶. The ¹H-NMR spectra of the polyesters were obtained as saturated solutions in dimethylsulfoxide-*d*⁶ and also in hexafluoroisopropanol (HFIP) in which they are slightly more soluble. An internal deuterium lock of DMSO-*d*⁶ in a capillary tube was used with HFIP solutions. ¹³C-NMR spectra were obtained on the HFIP solutions with a Bruker AMX-360 FT spectrometer. TMS was the internal standard for all the NMR spectra. Infrared (IR) spectra were recorded with a Matson FTIR spectrophotometer with the samples as pressed KBr pellets. Differential scanning calorimetry (DSC) studies were carried out with a Perkin-Elmer DSC-1B instrument with the samples in sealed aluminum pans under nitrogen atmospheres. Melting points were obtained in glass capillaries by using a Buchi 510 mp apparatus or a Thomas Hoover mp instrument. X-ray

*Trivially named as *m*- and *p*-poly(hydroxymethylbenzoic acids).

powder diffraction patterns were obtained with a Philips wide-range x-ray diffractometer model PW 1720 using Ni-filtered CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). Inherent viscosity measurements were carried out at 30°C in 60:40 phenol/*s*-tetrachloroethane with an Ostwald viscometer using procedures and calculation methods previously described [17–19].

MATERIALS

The following compounds were commercial products used in the purity grades listed: *p*-toluic acid (98 + %), *m*-toluic acid (99%), chlorobenzene (ACS grade, 99%), triethylamine (ACS grade, 99%), bromine (99.5%), and *s*-tetrachloroethane (100% by GC). Hexane, ether, ethyl acetate, and phenol were lab reagent grades. Benzene (lab reagent grade) was distilled.

Preparation of 3- and 4-Bromomethylbenzoic Acids

The acids were prepared by slight modification of previously described [16] light-catalyzed bromination of the corresponding toluic acids in yields of 77–80% for 3- (mp $153\text{--}154^\circ\text{C}$; literature [16], 153°C) and 89–92% for 4-bromomethylbenzoic (mp $227\text{--}228^\circ\text{C}$; literature [16], 228°C) acids after crystallization from ethyl acetate. R_f values of 0.81 and 0.26 were obtained for the 3- and 4-acids, respectively, using a 50:50 hexane/ether mixture with 2% acetic acid eluent on silica gel plates.

Reaction of 4-Bromomethylbenzoic Acid and Triethylamine; Preparation of Poly(Oxycarbonyl-1,4-phenylenemethylene) (2)

4-Bromomethylbenzoic acid (3.39 g, 0.0158 mol) was placed in a flask equipped with magnetic stirring and protected from moisture with a drying tube filled with phosphorus pentoxide. (*Caution:* The acid is lachrymatory.) Chlorobenzene (50 mL) was added and gently warmed to dissolve the acid. An equimolar quantity (2.2 mL, 0.015 mol) of triethylamine was dissolved in 15 mL chlorobenzene and added dropwise with stirring to the acid solution. After about three-fourths of the mixture was added, a clear solution formed. Addition was continued with stirring until all of the triethylamine was added. The reaction was stirred for 30 min at room temperature, at which time a precipitate formed. The reaction mixture was then refluxed for 10 h at 145°C and allowed to cool to room temperature. The chlorobenzene was removed *in vacuo* to leave a solid residue. The residue was washed several times with absolute ethanol to remove triethylammonium bromide. The solid residue was collected by filtration. When ethanol was evaporated from the filtrate, triethylammonium bromide was obtained, yield 76%. The polymer was purified by reprecipitating it from hot chlorobenzene and by washing it with ethanol in which the starting material and the reagents are soluble and the polymer is insoluble. The product was a white powdery solid. It was dried *in vacuo* for several hours; yield, 1.48–1.52 g (70–72%); mp, $217\text{--}223^\circ\text{C}$ (reported mp, $200\text{--}210^\circ\text{C}$ [4]; $205\text{--}215^\circ\text{C}$ and $220\text{--}230^\circ\text{C}$ [7]).

The reaction was also carried out in ether at room temperature and reflux, ether/benzene (4:1) at reflux, acetone at reflux, and acetonitrile at reflux. However,

lower yields (45–52%) were obtained from these preparations. After purification by dissolving in hot nitromethane followed by cooling, the following melting point ranges were obtained from the ether (RT), ether/benzene, and acetone reactions, respectively: 195–200, 197–202, and 225–230°C.

Reaction of 3-Bromomethylbenzoic acid and Triethylamine; Preparation of Poly(Oxymethylene-1,3-phenylenecarbonyl) (1)

The same procedure for preparation of the polymer from 4-bromomethylbenzoic acid was followed by using 1.75 g (0.00820 mol) of 3-bromomethylbenzoic acid in 30 mL chlorobenzene and an equimolar amount (1.14 mL, 0.00820 mol) of triethylamine in 15 mL chlorobenzene. (*Caution:* The acid is lachrymatory.) After adding triethylamine, the reaction mixture was refluxed at 145°C for 10 h. The isolation and purification of the 3-polyester was carried out in the same way as described for the 4-polyester. The product was a white powdery solid, yield, 0.75–0.77 g (68–70%); mp, 147–151°C (literature mp 135–145 and 160–170°C [7]). The yield of triethylammonium bromide isolated was 74%.

The reaction was also carried out in refluxing acetone from which the melting point of the polyester after purification from hot nitromethane was 117–120°C and the yield of triethylammonium bromide isolated was 80–85%. An oily product was obtained from anhydrous ether at reflux in 45% yield.

Preparation of Copolymer 3 from 3- and 4-Bromomethylbenzoic Acids

For the copolymerization reaction, the same procedure was adopted as described above. The 3- and 4-bromomethylbenzoic acids (1.39 g, 0.00650 mol each) were dissolved in 50 mL chlorobenzene and mixed with 1.8 mL (0.013 mol) triethylamine dissolved in 15 mL chlorobenzene. The reaction mixture was refluxed for 18 h. The isolation and purification of the product was carried out in the same way as described above in the preparation of the homo polymers. The product was a dirty white solid which was reprecipitated from hot chlorobenzene, yield 1.0 g (58%); mp 130–148°C. The yield of triethylammonium bromide isolated was 66%.

Hydrolysis of *p*- and *m*-Polyesters

Samples of the *p*- and *m*-polyesters were hydrolyzed by heating with sodium hydroxide solution followed by acidification. A solid which precipitated from the *p*-polyester was crystallized from water. The melting point of 4-hydroxymethylbenzoic acid was 181°C (literature mp 179–181°C [20]). An oil which formed from the *m*-polyester was dissolved in benzene. On dropwise addition of ethanol, a precipitate formed which was recrystallized from benzene/ethanol. The melting point of 3-hydroxymethylbenzoic acid was 112°C (literature mp 114.5–115°C [21] and 111°C [22]).

RESULTS AND DISCUSSION

Physical Properties

Solubility

The homopolyesters were insoluble in most of the common organic solvents. They were soluble in hot dimethylsulfoxide, hot nitrobenzene, a 60:40 mixture of phenol and *s*-tetrachloroethane, hot 2-ethoxyethyl ether, hot 2-methoxyethyl ether,

hot polyethylene glycol (MW 400), and hot chloro- and bromobenzenes. In general, the trend was that the *p*-polyester was less soluble than the *m*-polyester, which in turn was less soluble than the copolyester.

Infrared Spectra

The IR spectra of the *para*-, *meta*-, and copolyesters are shown in Figs. 1, 2, and 3, respectively. A comparison of the IR absorption frequencies and vibrational assignments is in Table 1. The carbonyl peak for the *para*-polyester appears at 1719 cm^{-1} and for the *meta*-polyester at 1720 cm^{-1} . Ozgun and Tuzun [10] reported these peaks at 1750 and 1702 cm^{-1} , respectively, in KBr but did not publish their spectra. The IR spectral pattern of the *p*-polyester closely resembles the IR spectral curves reported by Sweeny [11] and Brindell et al. [6] who did not report their data. The relative intensities of the C—O stretching peaks for the *para*- and *meta*-polymers can be used to estimate the relative amounts of these units incorporated into the copolymer. Since the intensity of the symmetric stretching peak of the *para*-polymer at 1096 cm^{-1} evident at 1102 cm^{-1} in the copolymer spectrum is much stronger than that for the *meta*-polymer at 1195 cm^{-1} , it is clear that a larger amount of *para* units were incorporated into the copolymer when monomers were reacted in a 1:1 ratio. Additional evidence is that the peak at 1018 cm^{-1} for the *para*-polymer also appears in the copolymer spectrum but the 1108 cm^{-1} peak for the *meta*-polymer does not.

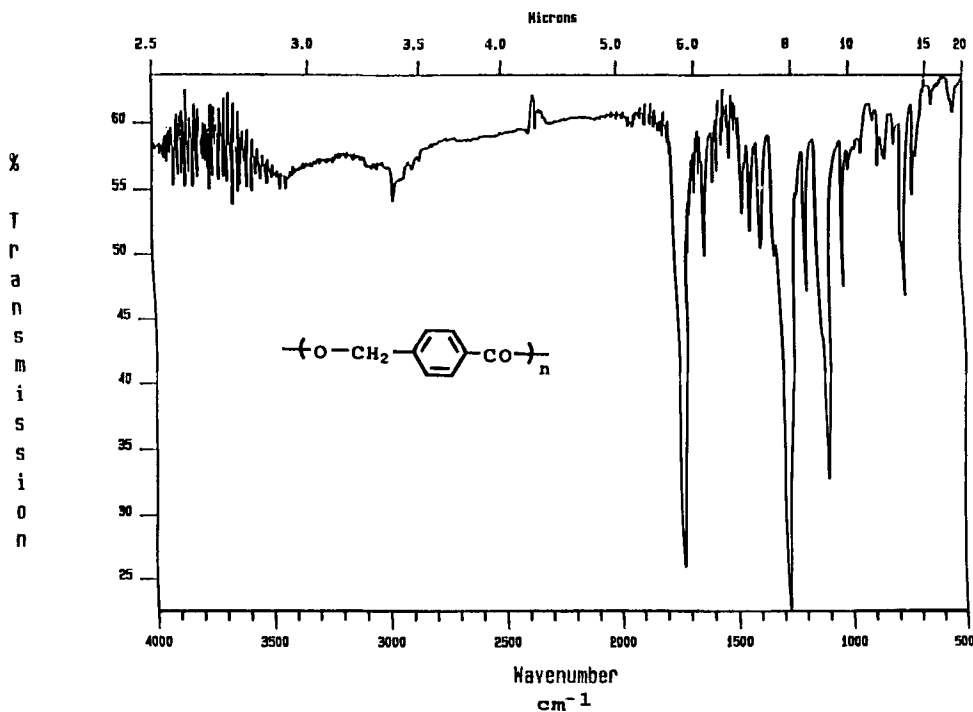


FIG. 1. IR spectrum of *p*-polymer in KBr pellet.

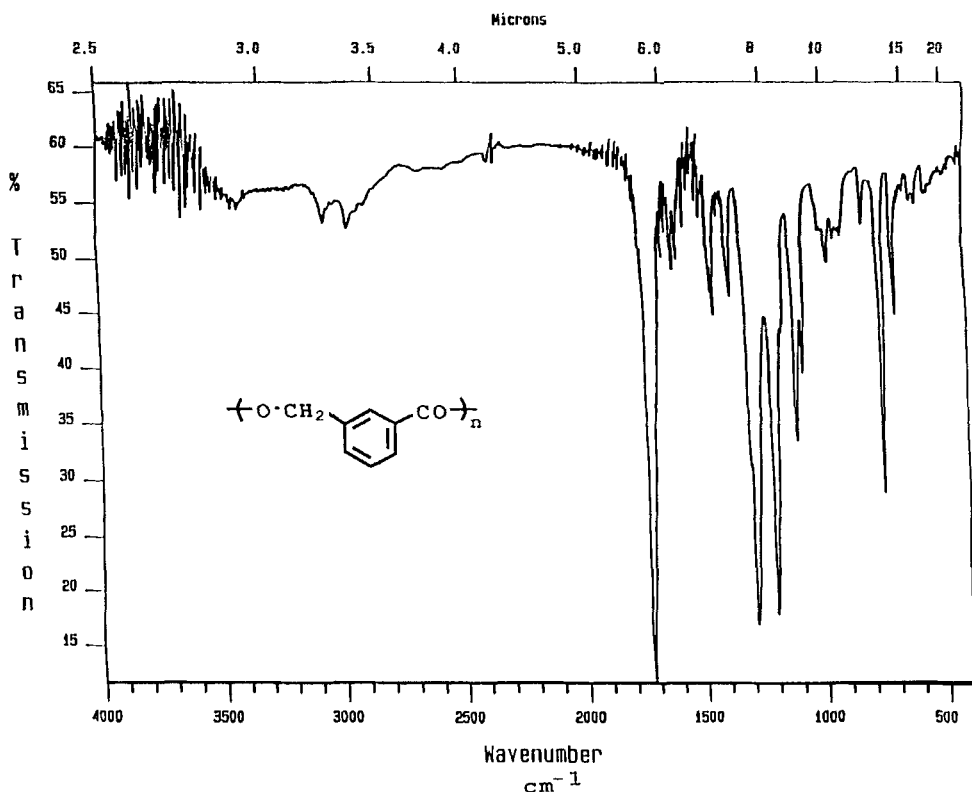


FIG. 2. IR spectrum of *m*-polymer in KBr pellet.

¹H-NMR Spectra

The ¹H-NMR spectra of *p*-, *m*-, and copolyesters as saturated solutions in DMSO-*d*⁶ and in hexafluoroisopropanol (HFIP) are shown in Figs. 4, 5, and 6, respectively. Peaks from HFIP solvent are identified as S in the spectra. The signal for the methylene group for the *meta*-polymer appears under one of the HFIP peaks but can be seen in the spectrum in DMSO-*d*⁶ at 5.5 d. Since the solubility in HFIP is greater, triethylammonium end groups can be seen. Since solubility of the *para*-polymer is least of the three, the endgroup signals are barely visible at the expected chemical shift positions in Fig. 4, but were more evident in a partial spectrum in which the Y scale was increased and on which area integrations were made. Molecular weights were obtained from comparison of the areas of the end groups with methylene and aromatic signals. The chemical shift data are in Table 2. The methylene protons for the *p*-polyester appear as a broad singlet at 5.4 d. Aromatic protons appear as a broad doublet at 7.5 and 8.0 d. For comparison, ¹H-NMR data have only been reported in the literature [6] for a *para*-polymer with *DP* = 3. They reported an aromatic peak at 5.4 d in CDCl₃ and formation of another singlet at 4.58 d corresponding to the CH₂Br end group. No literature NMR data for the *meta*-polymer have been reported. The methylene and the aromatic protons were in a 1:2 ratio for all of the polymers.

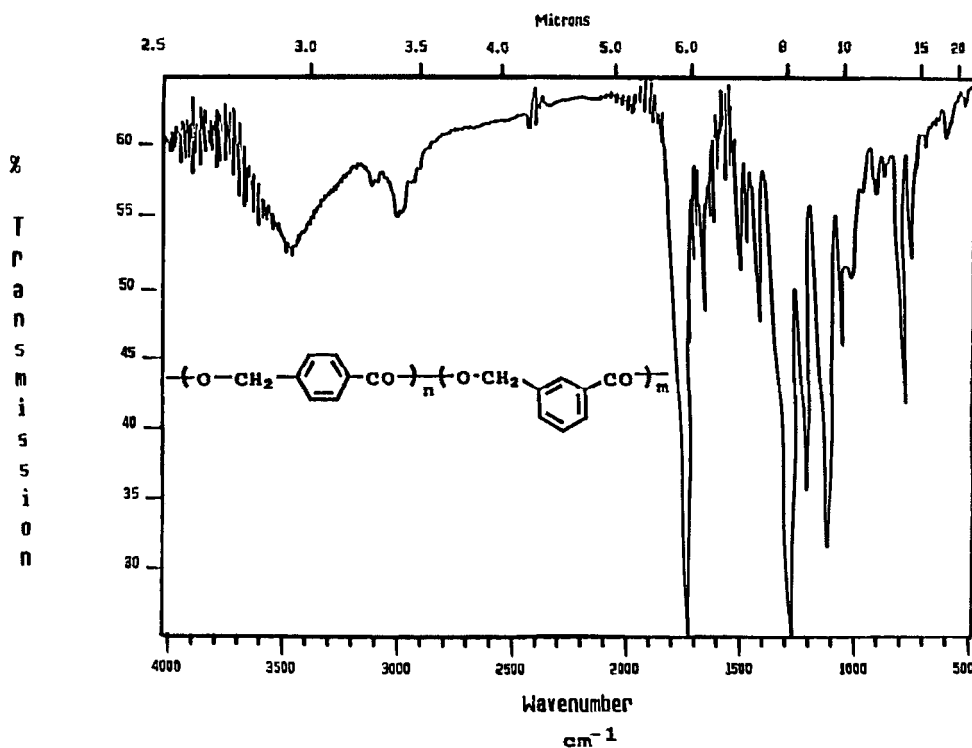
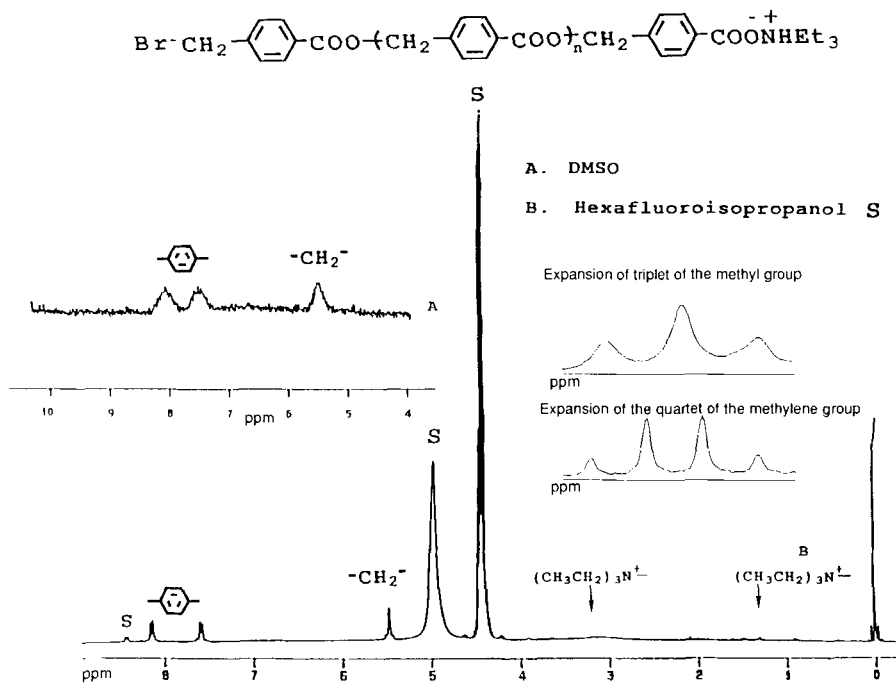
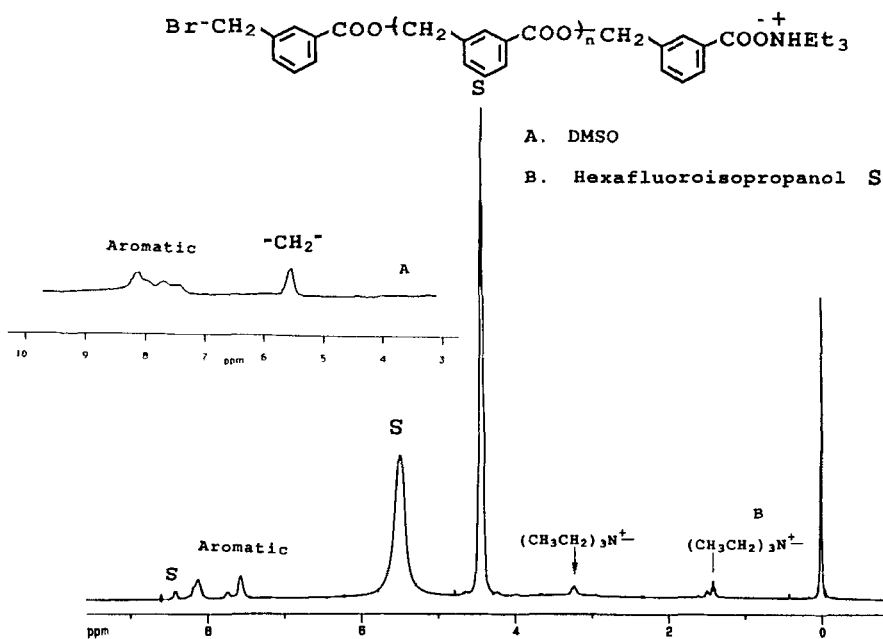


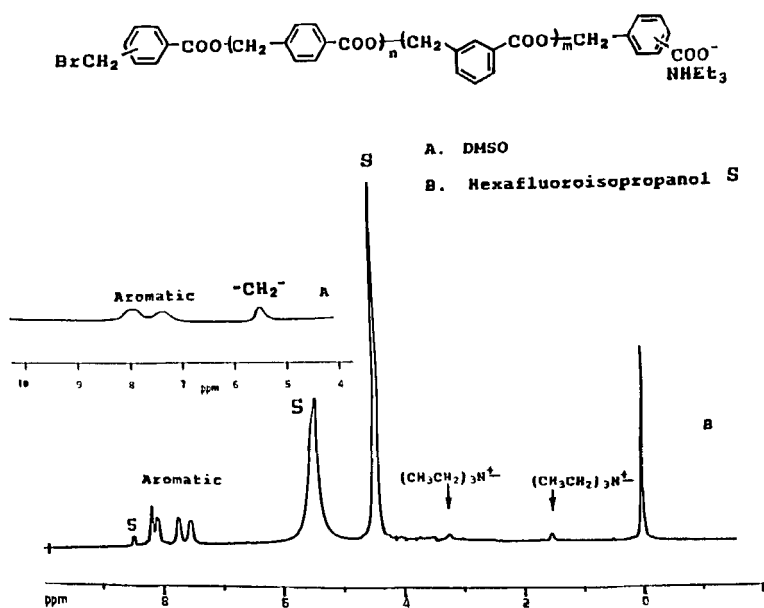
FIG. 3. IR spectrum of copolymer in KBr pellet.

TABLE 1. Infrared^a Vibrational Assignments (cm⁻¹) for *para*- and *meta*-Polymers and *p,m*-Copolymer

<i>para</i> -Polymer	<i>meta</i> -Polymer	Copolymer	Vibrational assignments
2962	2961, 3058	2939, 3068	C—H stretching
1719	1720	1720	C=O Stretching
1614	1611, 1592	1613, 1592	Aromatic C—C stretching
1279	1278	1269	Asymmetric —C—O Stretching
1096	1198	1195, 1102	Symmetric —C—O stretching
1018	1108	1018	
752	751	750	

^aKBr pellet.

FIG. 4. ^1H -NMR spectrum of *p*-polymer.FIG. 5. ^1H -NMR spectrum of *m*-polymer.

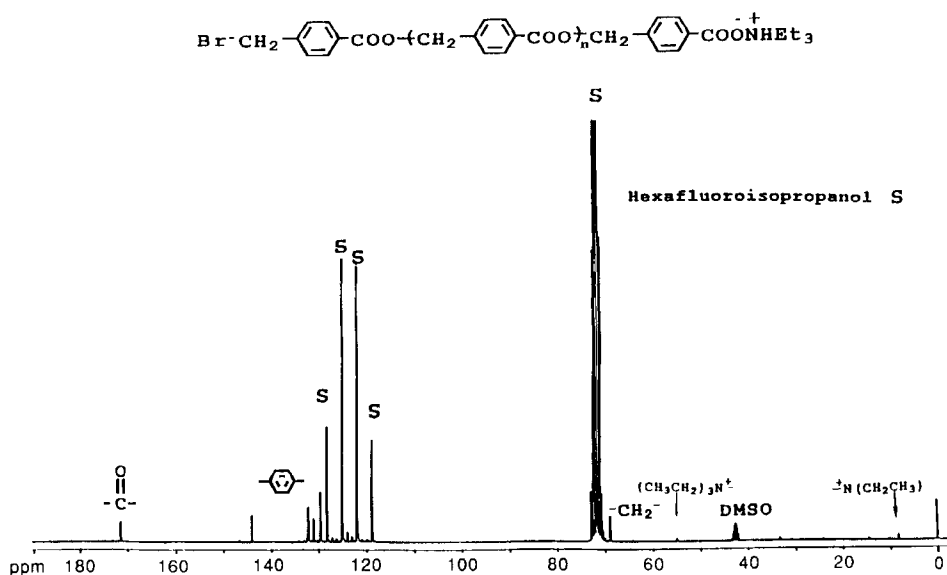
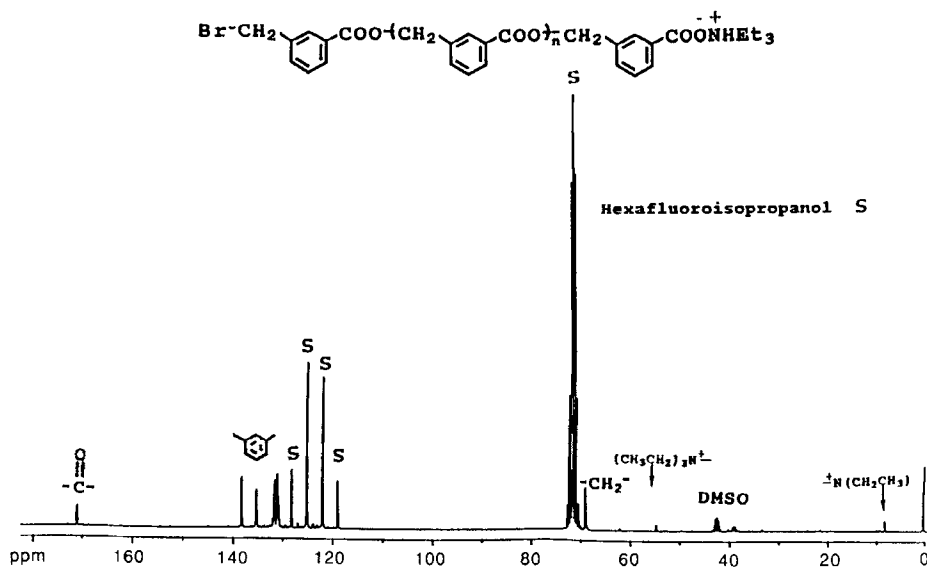
FIG. 6. ^1H -NMR spectrum of copolymer. ^{13}C -NMR Spectra

^{13}C -NMR spectra of these polymers have not been previously reported. In order to obtain good ^{13}C -NMR spectra, hexafluoroisopropanol (HFIP) in which the polymers were more soluble was used with DMSO- d_6 in a capillary as an internal deuterium lock. The spectra for *para*- and *meta*-polymers and the copolymer are given in Figs. 7, 8, and 9 respectively and the data are in Table 3. For the *para*-polymer, there are 4 signals in the aromatic region, 6 for the *meta*-polymer, and multiple peaks for the copolymer. Peaks also appear for the triethylammonium end groups.

TABLE 2. ^1H -NMR Spectral Data^a for Polymers

Groups	<i>p</i> -Polymer	<i>m</i> -Polymer	Copolymer
$-\text{CH}_2-\text{O}-$	5.4 ^b 5.5 ^c	5.5 ^b —	5.4 ^b —
Aromatic $-\text{CH}_3$ of	7.5–8.0 ^b	7.6–8.1 ^b	7.6–7.9 ^b
$\text{Et}_3\text{NH}^+\text{Br}^-$ end group	7.5–8.1 ^c 1.5 ^c	7.5–8.1 ^c 1.5 ^c	7.5–8.1 ^c 1.4 ^c
$-\text{CH}_2-$ of $\text{Et}_3\text{NH}^+\text{Br}^-$	—	3.2 ^c	3.2 ^c

^a δ in ppm.^bIn DMSO- d_6 .^cIn HFIP with DMSO- d_6 in capillary as internal lock.

FIG. 7. ^{13}C -NMR spectrum of *p*-polymer.FIG. 8. ^{13}C -NMR spectrum of *m*-polymer.

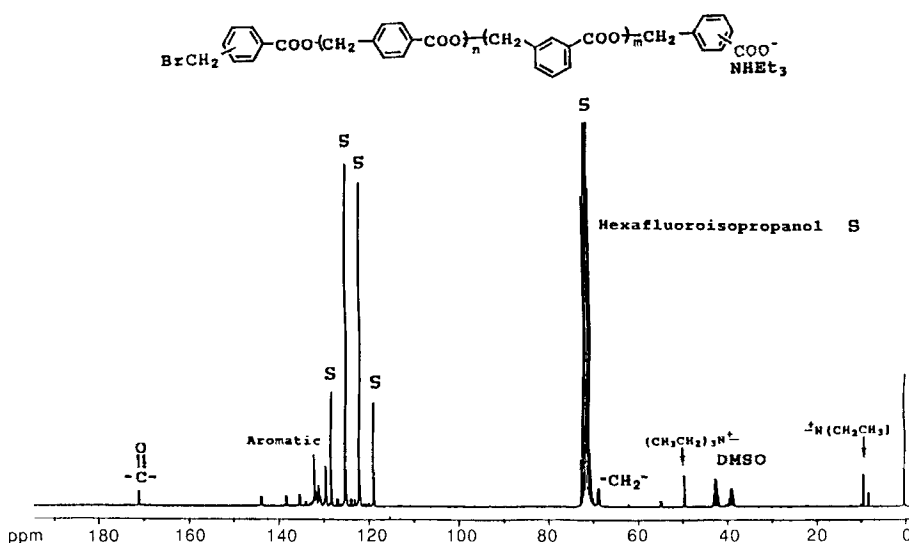


FIG. 9. ^{13}C -NMR spectrum of copolymer.

Viscosity Studies

The inherent viscosity values are listed in Table 4 along with the corresponding degrees of polymerization as determined by ^1H -NMR endgroup analysis. The inherent viscosities are 0.11, 0.15, and 0.19 for copolymer, *meta*-, and *para*-polymers respectively, and close to the lower range of values (0.23 to 1.0) reported for polymerizations of *p*-hydroxymethylbenzoic acid or methyl esters. No previous correspondence of viscosity values with independent molecular weight determinations has been reported.

Fiber- and Film-Forming Properties

The *para*- and *meta*-polymers form thin brittle fibers when pulled from melts; the copolymer does not, probably because of the lower molecular weight. Brindell

TABLE 3. ^{13}C Spectral Data^a of Polymers in HFIP with DMSO-*d*⁶ in Capillary as Internal Lock

Groups	<i>p</i> -Polymer	<i>m</i> -Polymer	Copolymer
—CH ₂ —O—	69	69	69
Aromatic —CH ₃ of Et ₃ NH ⁺ Br ⁻ end group	131-144 8.3	131-144 8.1	131-144 9.3
—CH ₂ — of Et ₃ NH ⁺ Br ⁻ end group	54.9	54.7	49.5
Carbonyl	171	171	171

^aδ in ppm.

TABLE 4. Viscosities^a and Degrees of Polymerization (DP)^b of *para*- and *meta*-Polymers and *p,m*-Copolymer

Polymers	η_{inh}^c	DP
<i>p</i> -Polymer	0.19	81
<i>m</i> -Polymer	0.15	43
Copolymer	0.11	9

^aPhenol/*s*-tetrachloroethane (60:40).

^bBased on ¹H-NMR endgroup analysis.

^c η_{inh} = inherent viscosity.

et al. [6] and Owaki et al. [15] reported the formation of fibers having inherent and intrinsic viscosities of 0.35 and 0.50–0.65, respectively, from *para*-polymers. Although Cook et al. [4] reported the formation of fibers and filaments from the *para*-polymer, no viscosities were given.

Because of the insolubilities of the polymers in most solvents, film formation was only investigated from HFIP and DMSO solutions; only brittle, translucent films were formed. Brindell et al. [6] were the only ones to report the formation of a clear film by pressing from a melt.

X-Ray Powder Diffraction

The x-ray powder diffraction patterns of the *p*- and *m*-polyesters and the copolyester are presented in Fig. 10, and the data are given in Table 5. The curves of the *p*- and *m*-polyesters show a few sharp diffraction peaks which indicate a degree of crystallinity resulting from some regularity of chain orientation. For the copolyester, a broad featureless peak shows that it is amorphous, indicating randomness in the arrangement of chains. X-ray powder diffraction patterns for these polyesters have not been previously reported.

Differential Scanning Calorimetry (DSC)

The DSC curves are in Fig. 11. The curve for the *p*-polyester (2) showed a gradual endothermic change which began at about 289°C. The polyester started decomposing at about 370°C to form a white sublimate on the lid of the sample holder. The *m*-polyester (1) showed an endothermic change beginning at 237°C, similar to the *p*-polyester, with decomposition starting at 365°C. The scan for the copolyester (3) showed the endothermic change beginning at 167°C. It can be interpreted from the DSC data that the *p*-polyester is more stable to decomposition in a nitrogen atmosphere than the *m*-polyester, which in turn is more stable than the copolyester. No further studies were made using DSC to induce additional crystallinity. Sweeny [11] reported an exotherm for the *p*-polyester at 155°C and an endotherm maximum at 250°C.

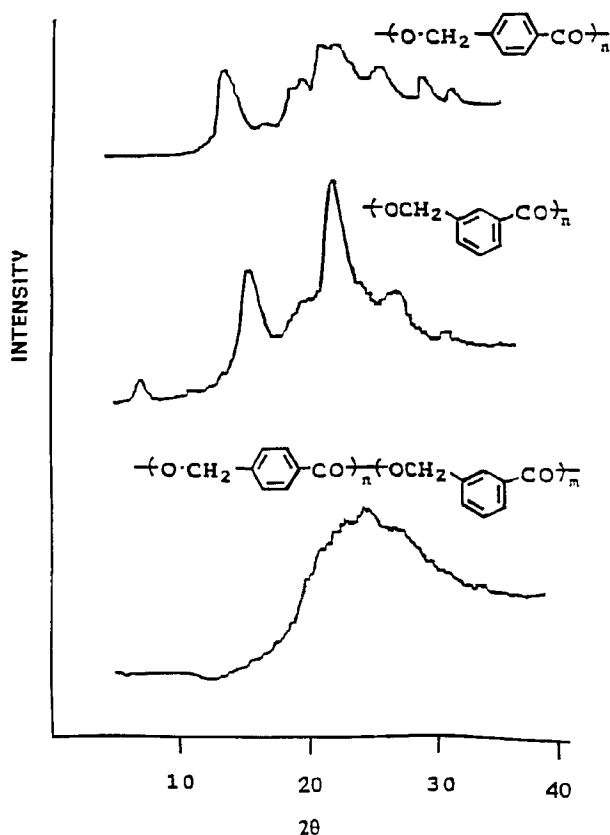


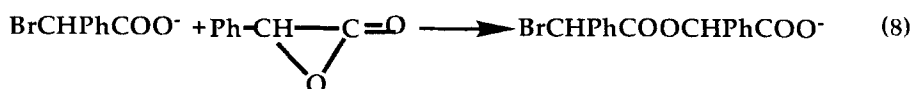
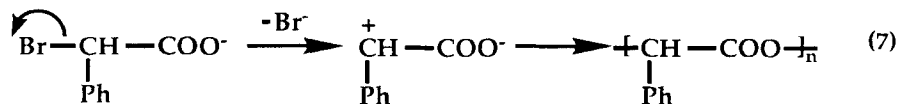
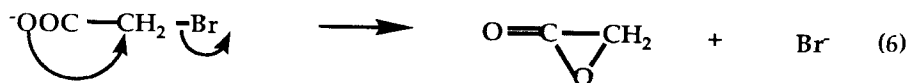
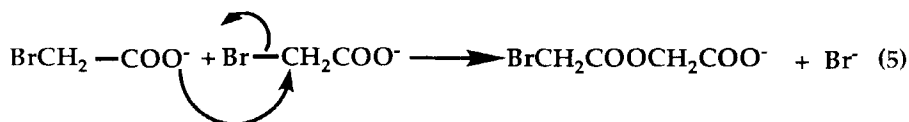
FIG. 10. X-ray powder diffraction peaks of *p*- and *m*-polymers and copolymer.

Mechanistic Aspects

The initial products from the reactions of α -halocarboxylic acids or 3- and 4-bromobenzoic acids with triethylamine are triethylammonium salts as expected for acid/base proton-transfer reactions (Eq. 4). Evidence for this is from the $^1\text{H-NMR}$ spectra of the reaction mixture of the two components (acid and triethylamine) which on mixing show peaks characteristic of the triethylammonium cation and carboxylate anion. In the propagation step as shown for haloacetate (Eq. 5), an S_N2 reaction between two haloacetate ions can be postulated. However, this would require high energy resulting from attack of a negatively charged species by another anion. Formation of an α -lactone intermediate by a carboxylate neighboring group reaction (Eq. 6) would be favored by entropy considerations but would need to overcome the strain energy of the 3-membered ring. In the case of the phenyl-substituted bromomandelide anion (a secondary halide), prior ionization is also a consideration to form a zwitterion (Eq. 7) or an α -lactone. α -Lactones have been previously postulated [23, 24]. Either of these species could then undergo propagation reactions to form the polyester (Eqs. 7 and 8).

TABLE 5. X-Ray Powder Diffraction Peaks for the Polymers

d^a	$2\theta^b$	I/I_0^c
<i>p</i> -Polymer		
5.33	16.6	75.4
4.66	19.0	3.5
4.06	21.8	43.9
3.90	22.7	57.9
3.65	24.3	61.4
3.51	25.3	100.0
3.12	28.5	61.4
2.70	32.0	43.9
2.63	33.9	31.6
2.16	41.5	26.3
<i>m</i> -Polymer		
10.52	8.4	13.8
5.24	16.9	70.8
3.77	23.6	100.0
2.52	28.3	32.3
2.76	32.4	7.7
Copolymer		
3.98	22.3	100

^aSpacings between planes.^bAngle of diffraction.^cRatio of intensity of diffraction to intensity of strongest line in percent.

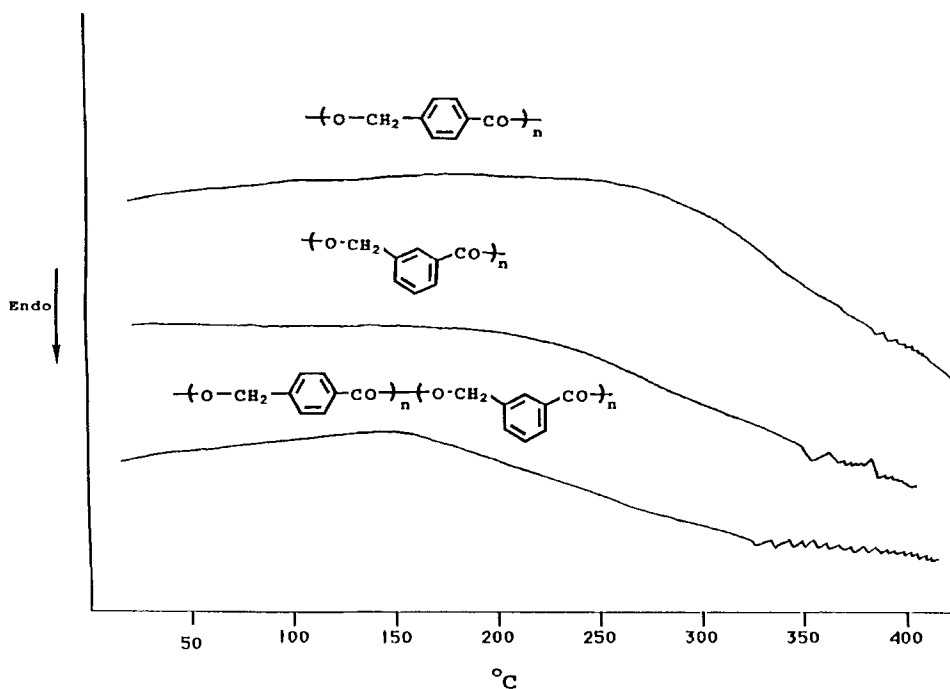


FIG. 11. Differential scanning calorimeter of *p*- and *m*-polymers and copolymer.

With the bromomethylbenzoate anions, α -lactone formation is precluded. S_N1 - or S_N2 -type reactions are known to occur with benzyl halides. Studies to elucidate the mechanistic aspects discussed above are planned.

CONCLUSIONS

A new method for the preparation in relatively good yields of polyesters with aromatic groups in the backbone from reactions of 3- and 4-bromomethylbenzoic acids with triethylamine is reported. The polyesters were characterized by IR, ^1H - and ^{13}C -NMR spectra, x-ray powder diffraction, DSC behavior, solution viscosity, and hydrolysis to corresponding hydroxymethylbenzoic acids.

Although the viscosities are slightly lower than those from the catalyzed polymerizations previously reported for hydroxymethylbenzoic acids and esters, undoubtedly these could be increased by further studies using other solvents, tertiary amines, and conditions. The main reason triethylamine was used in the present study was that it was the best of several tertiary amines investigated in the original polymerization of bromoacetic acid to polyglycolide [1].

Advantages of the present method over those previously reported can be compared. *p*- and *m*-Hydroxymethylbenzoic acids, which are the starting materials for the previously reported syntheses, are not available commercially [25] and are therefore undoubtedly expensive to synthesize. The starting compounds for the present syntheses, *m*- and *p*-toluic acids, are commercially available [25] and relatively

inexpensive. These have been converted to the bromomethylbenzoic acids in good yields by treatment with bromine using low energy radiation. Although bromine is relatively expensive, the hydrogen bromide and triethylammonium bromides can be readily recycled to bromine by mild oxidation. The triethylamine can also be recycled. Although *p*-bromomethylbenzoic acid is commercially available [25], synthesis by the present method [16] would probably be much less expensive. Overall, the present process would be environmentally compatible since the major by-products could be recycled.

Further work on the mechanisms of these polymerization reactions is planned.

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