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SYNTHESIS OF POLY(METHYLENE TEREPHTHALATE) AND COPOLYMERS WITH POLY(ETHYLENE TEREPHTHALATE)

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SYNTHESIS OF POLY(METHYLENE TEREPHTHALATE) AND COPOLYMERS WITH POLY(ETHYLENE TEREPHTHALATE)

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Key Words: Poly(methylene terephthalate) (PMT) Synthesis, PMT/PET Copolymers, Feed/Product Correlation for PMT/PET Copolymer

ABSTRACT

Poly(methylene terephthalate) (PMT) and poly(ethylene terephthalate) (PET) were synthesized by triethylamine-mediated reactions of terephthalic acid and dihalomethanes or 1,2-dihaloethanes, respectively. Reactions with chloro compounds required longer reaction times and higher temper-atures than those with bromo. Copolymers were synthesized by using proportionate amounts of dihalomethane/1,2-dihaloethane mixtures. Copolymer compositions were determined by inte-grations of relative areas of methylene and ethylene ^{1}H NMR peaks. Mn values were determined from ^{1}H NMR end group signals. Mole fraction feed is linearly related to CH_2/CH_2CH_2 incorporation into copolymer products. Mechanisms are proposed to explain results.

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INTRODUCTION

Poly(ethylene terephthalate) (PET) (1, n=2) is the world's leading synthetic fiber [1].

$$[\text{-OCOC}_6\text{H}_4\text{COO(CH}_2)_n\text{-}]$$

1

It has been termed [2] the workhorse of the polyester industry, having enjoyed widespread commercial use (as both fiber and plastic) since the 1940s. The worldwide consumption of PET in 1997 was approximately 4 million metric tons and growth rates of up to 15% are expected up to the year 2000. Its share of global fiber production increased by 58% from 1977-1997 from a third of the market in 1977, to over half (52-56%) [3, 4] of all fibers processed in 1997 [3]. It has been recently noted [5] that poly(1,3-propylene terephthalate) (PPT) [a. k. a. poly(trimethylene terephthalate) (PTT)] (n=3) as a "new" material which can fall back on a low-cost monomer base is undergoing process, product, and market development. Shell Chemical Co. has reported [6] a process which lowers the cost of producing PTT (their trade name: Conterra) to between 90 cents and $1 per pound down from the previous production cost between $8-$15 per pound. DuPont is reported [7, 8] to be developing a low-cost synthesis of 1,3-propanediol needed for the preparation of PTT. More recently, poly(trimethylene terephthalate) (dubbed 3GT by Dupont) has been produced directly by fermentation of glucose (produced from corn) to which terephthalic acid has been added [9]. By early next year DuPont expects to have a pilot plant in operation and to bring 3GT to market within five years. Poly(1.4-butylene terephthalate) (PBT) (n=4) is also being produced by several companies.

Poly(methylene terephthalate) (PMT) (1, n=1) [systematic name: poly(oxymethyleneoxycarbonyl-1,4-phenylenecarbonyl) or poly(oxymethyleneoxyterephthaloyl)] is the lowest homolog of the series, but until fairly recently it has not been possible to prepare it by methods used in the synthesis of other poly(alkylene terephthalates which depend on the availability of the glycol since the needed glycol, methylene glycol [$CH_2(OH)_2$] (dihydroxymethane) is not stable. In a synthesis [10] based on our previous synthesis [11] of polyglycolide from reaction of haloacetic acids and trialkylamines as applied to reactions of dihalides and dicarboxylic acids [12, 13], it was found that methylene dihalides were reactive enough to undergo the polymerization reaction (Rx. 1).

$HOOCC_6H_4COOH$ + $X(CH_2)_nX$ + Et_3N ($Et_3NH^+ X^-$
+ $Et_3NH^{+\ -}OOC[C_6H_4COO$(CH2)nOOC]x C6H4COO- +HNEt3 (Rx. 1)
<u>2</u>

1 has also been synthesized by reaction of cesium or potassium terephthalates with dibromo- or bromochloro-methane in N-methylpyrrolidone [14]. In our reaction using triethylamine [10, 12] to form PET, since 1,2-dihaloethanes were also reactive enough, this made possible the synthesis of copolymers (3) consisting of PET and PMT (Rx. 2).

$HOOCC_6H_4COOH$ + CH_2X_2 + $X(CH_2)2X$ + Et_3N ($Et_3NH^+X^-$
$Et_3NH^{+-}OOC\{[C_6H_4COOCH_2OOC]_m[C_6H_4COO(CH_2)_2OOC]_n\}xC_6H_4$
$COO^-\ {}^+HNEt_3$ (Rx. 2)
<u>3</u>

Thus, properties of PET could be modified in a controlled manner by varying the amounts of of PMT in the copolymer. In the present initial explorative study of PMT in the copolymer. In the present initial explorative study, a broad range of relative ratios of the two constituents were employed in order to study the overall copolymer composition range. It was also of interest to determine compositions of the copolymers in relation to feed ratios of reactants since feed/product correlations have rarely been reported for condensation-type polymerizations as compared with extensive free radical addition polymerizations.

EXPERIMENTAL

Materials, Instruments, and Procedures

Triethylamine was stored over KOH pellets. Other chemicals were commercial reagent grades. Tm values were obtained with a Mettler or Thomas Hoover Unimelt instrument. NMR spectra were obtained with Bruker 300 and/or 360 MHz instruments. The CDCl3/TFAD (trifluoroacetic acid-d) solvent mixture for NMR spectra of polymers was prepared by a previously published procedure [15]. The reference deals with the use of this solvent mixture suitable for obtaining NMR spectra of polymers insoluble in the usual NMR solvents. Solvent peaks in the ^{13}C NMR spectra are quartets centered at 161.6 and 114.5 (for C=O and CF_3, respectively for carbons coupling to fluorine and a triplet resulting from coupling to deuterium in $CDCl_3$. In ^1H NMR spectra, signals at about 10.7 and 7.27 δ are from exchangeable hydrogen in Et_3NH^+ end groups and trifluoroacetic acid and, from $CHCl_3$, respectively. Mn values were obtained from ^1H NMR spectra by integration of areas of end group protons in the ethyl groups of triethylammonium (shown in the offsets of ^1H NMR spectra) and comparison with areas of protons in repeating units. IR spectra were obtained with a Mattson FTIR instrument. DSC measurements were made with a Perkin-Elmer 1B instrument using sealed Al pans under nitrogen atmospheres. Yields of copolymers were calculated [16] as based on product compositions obtained from NMR spectra.

Synthesis of Poly(methylene terephthalate) (PMT)

(a) From Dibromomethane

Triethylamine (2.2 mL, 1.6 g, 0.016 mol) was added dropwise from a syringe to terephthalic acid (1.1 g, 0.0066 mol). DMF (15 mL) was added and the mixture was stirred for 0.5 hours. Dibromomethane (0.70 mL, 1.7 g, 0.0099 mol) was added with a syringe. The solution was stirred under argon and heated

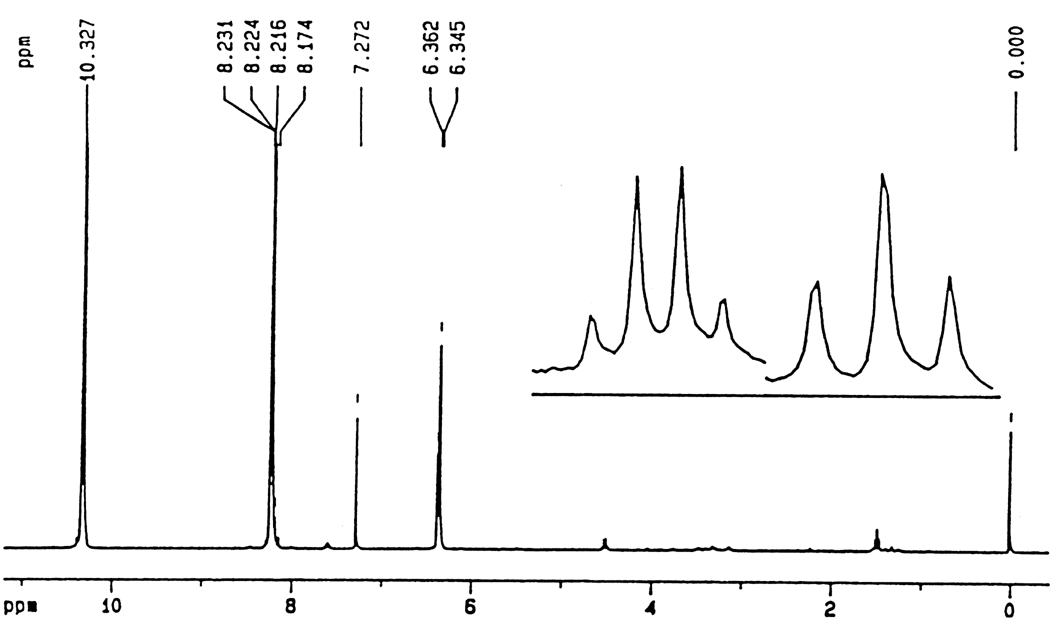


Figure 1. ^1H NMR spectrum of poly(methylene terephthalate) in TFA/$CDCl_3$ synthesized by triethylamine-promoted polymerization of terephthalic acid and dibromomethane.

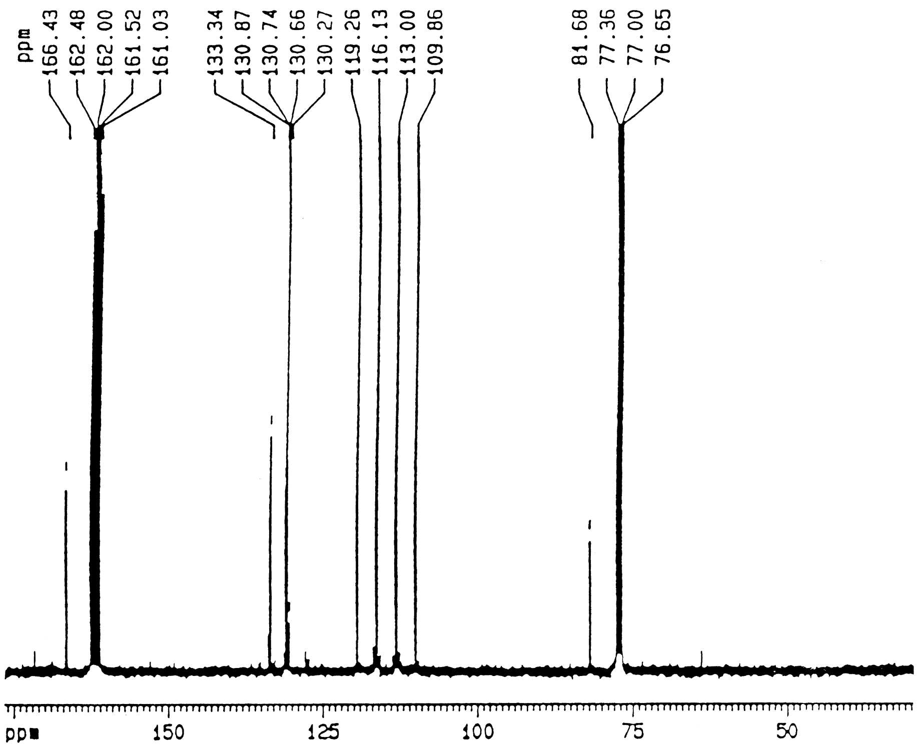


Figure 2. ^{13}C NMR spectrum of poly(methylene terephthalate) in TFA/$CDCl_3$ synthesized by triethylamine-promoted polymerization of terephthalic acid and dibromomethane.

by a sand bath at 120°C for 24 hours, during which time a precipitate formed. The mixture was allowed to cool to room temperature and the precipitate was collected by centrifugation, refluxed with DMF to remove any unreacted acid, collected by centrifugation, and washed with methanol to remove any triethylammonium bromide, and dried by heating *in vacuo* for 1 hour to obtain 0.70 g, 60% yield. On combination of the solution from the above precipitate with the methanol washings and removal of solvent by rotary flask vacuum evaporation, 1.4 g (70% yield) of triethylammonium bromide salt was recovered. ^{1}H NMR of PMT δ, ppm, $CDCl_3$/trifluoroacetic acid-d (Figure 1): 1.47 [t, CH_3 of $^+HN(CH_2CH_3)_3$ end group, J= 7.2 Hz], 4.50 [q, CH_2 of $^+HN(CH_2CH_3)_3$ end group, J=7.2 Hz; end group shown in offset of Figure 1], 6.35, 6.36 (CH_2), 8.17-8.23 (Ar). ^{13}C-NMR (, ppm) (Figure 2): 81.68 (CH_2), 130.3 (CH, Ar), 133.3 (C, Ar), 166.4 (C=O). IR (wavenumbers, cm^{-1}, KBr pellet) (Figure 3): 1741 (C=O

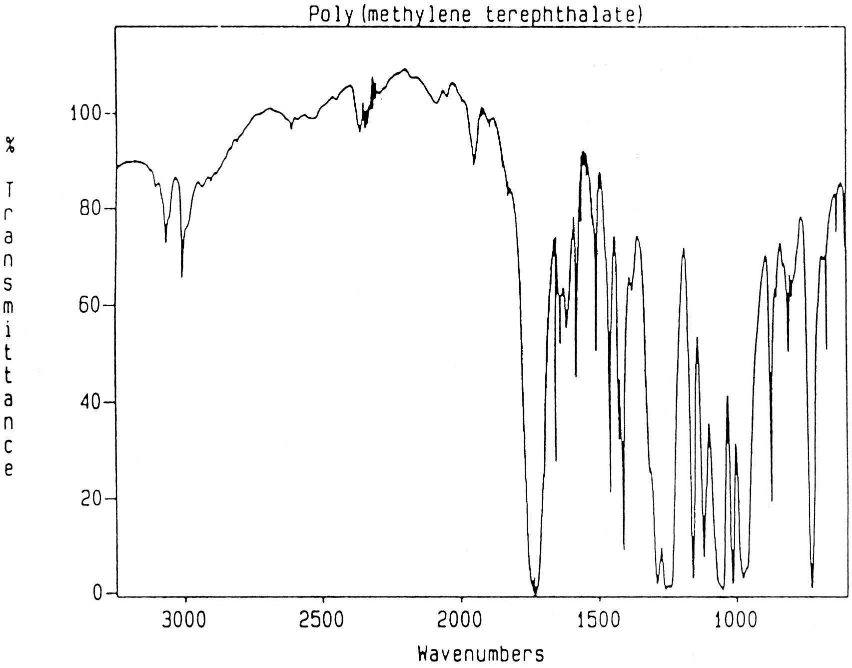


Figure 3. FTIR spectrum of poly(methylene terephthalate); KBr disc.

str.) (1740 cm^{-1} [14]). DP = 5365; Mn = 9,400-11,600 (assuming repeating unit weight as 178 corresponding to $C_9H_6O_4$). DP's were determined from end groups as follows: The area for the end group CH_3 was divided by 18 (3 x 3 x 2 assuming two end groups for each chain) to obtain the area per proton (or per end group). This area was divided into the area for the main chain CH_2 (previously divided by two) to give the number of repeating units (n) which is DP. Another value for DP was obtained by carrying out the same type of calculation using the area of the CH_2 of the end group. The area for the aromatic portion of the main chain could also be used for other determinations.

(b) From Dichloromethane

Procedure similar to (a) using triethylamine (3.7 mL, 2.7 g, 0.27 mol), terephthalic acid (2.2 g, 0.013 mol), DMF (15 mL), dichloromethane (4.2 mL, 5.6 g, 0.067 mol). Heated at 120°C for 5 days. Yield, 0.78 g, 33%; yield of triethylammonium chloride salt by removal of solvent from filtrate and washings, 2.2 g. (55%); T_m = 246-250°C; DP = 160-193; M_n = 28,500-33,800. DSC studies showed a gradual decomposition beginning at 375°C.

Synthesis of Poly(ethylene terephthalate) (PET)

(a) From 1,2-Dibromoethane

Triethylamine (2.9 mL, 2.1 g, 0.021 mol) was added dropwise from a syringe to terephthalic acid (1.7 g, 0.011 mol). DMF (12 mL) was added and the mixture was stirred for 0.5 hours. 1,2-Dibromoethane (0.91 mL, 2.26 g, 0.013 mol) was added with a syringe. The solution was stirred under argon and heated by a sand bath at 100-110°C for 28 hours, during which time a precipitate formed. The mixture was allowed to cool to room temperature and the precipitate was collected by filtration, washed with anhydrous methanol, and dried *in vacuo* for 16 hours to obtain 1.3 g, 62% yield. On evaportion of the combined filtrate and washings, a 75% yield of triethylammonium bromide was obtained. ^{1}H NMR of PET δ, ppm, $CDCl_3$/trifluoroacetic acid-d) (Figure 4): 1.38 [t, CH_3

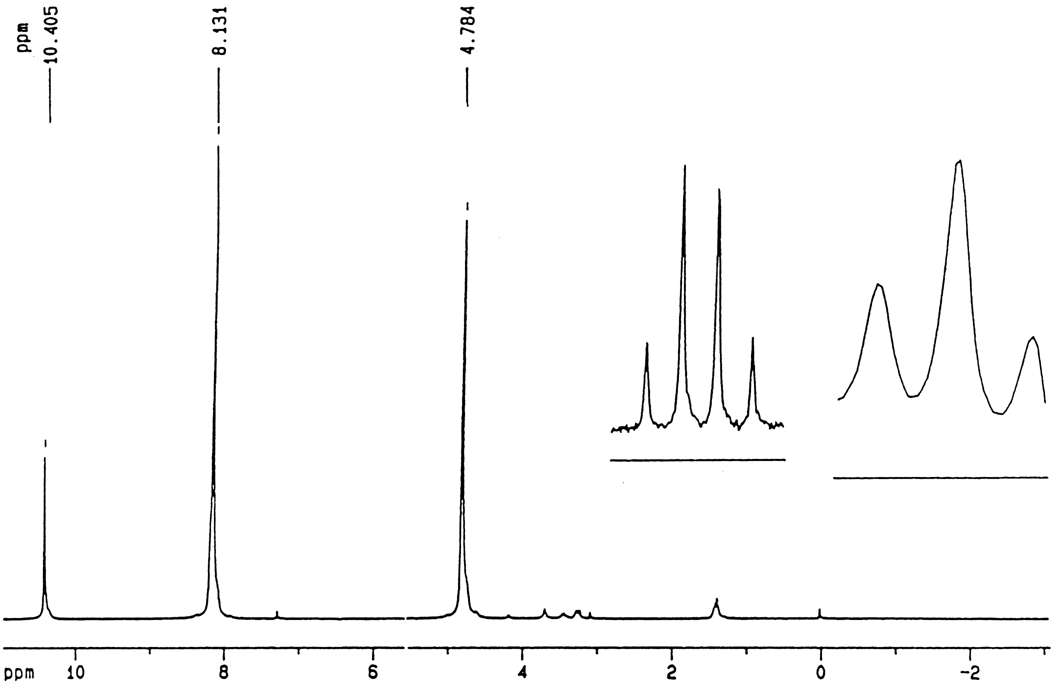


Figure 4. ^{1}H NMR spectrum of poly(ethylene terephthalate) in TFA/$CDCl_3$ synthesized by triethylamine-promoted polymerization of terephthalic acid and 1,2-dibromoethane.

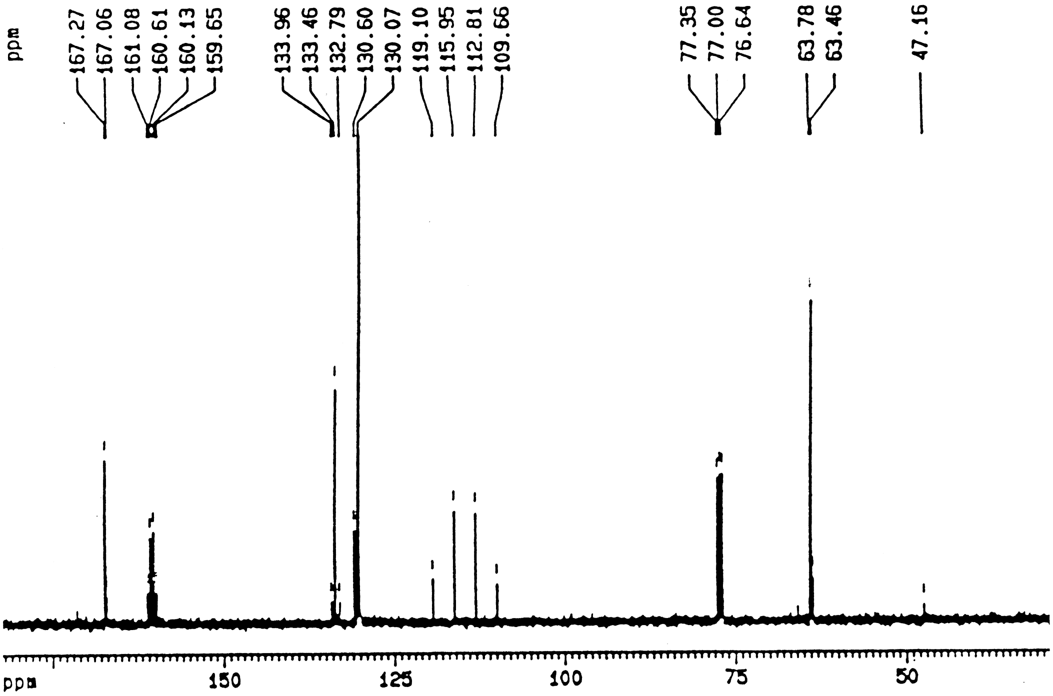


Figure 5. ^{13}C NMR spectrum of poly(ethylene terephthalate) in TFA/CDCl$_3$ synthesized by triethylamine-promoted polymerization of terephthalic acid and 1.2-dibromoethane.

of $^{+}$HN(CH$_2$CH$_3$)$_3$ end group, J=7.2 Hz], 3.34 [q, CH$_2$ of $^{+}$HN(CH$_2$CH$_3$)$_3$ end group, J=7.2 Hz], 4.78 (s, CH$_2$CH$_2$), 8.13 (s, Ar). ^{13}C-NMR (δ, ppm) (Figure 5: 47.16 (CH$_2$CH$_2$), 130.1-134.0 (Ar), 167 (C=O). IR (wavenumbers, cm^{-1}, KBr pellet) (Figure 6): 1724 (C=O str.) (1724-1729 cm^{-1}) [17-19]). DP = 27; Mn = 5,200 (assuming repeating unit weight as 192 corresponding to $C_{10}H_8O_4$). DSC studies showed a sharp endotherm at 250°C followed by a gradual endotherm beginning at 305°C, the first being T$_m$ and the latter the start of decomposition.

(b) From 1,2-Dichloroethane

Procedure similar to (a) using triethylamine (2.2 mL, 1.6 g., 0.016 mol), terephthalic acid (2.0 g, 0.0072 mol), DMF (12 mL), 1,2-dichloroethane (1.0 mL, 1.3 g, 0.015 mol). Heated at 110°C for 4 days. Yield 0.92 g, 58%; Mn = 12,000.

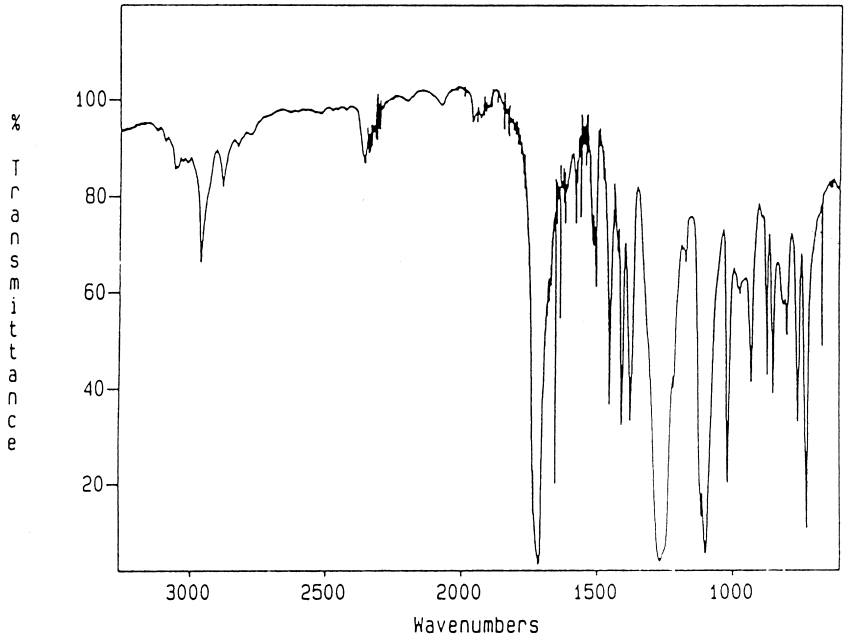


Figure 6. FTIR spectrum of poly(ethylene terephthalate); KBr disc.

Syntheses of Poly(ethylene-co-methylene terephthalate) Copolymers: Example of General Procedure with 50/50 Mol% Synthesis

Triethylamine (2.2 mL, 1.6 g, 0.016 mol) was added dropwise from a syringe to terephthalic acid (1.3 g, 0.0078 mol). DMF (25 mL) was added and the mixture was stirred for 0.5 hours. Dibromomethane (0.27 mL, 0.67 g, 0.0039 mol) and 1,2-dibromoethane (0.33 mL, 0.72 g, 0.0039 mol) were added using syringes. The solution was stirred and heated by a sand bath at 140°C for 23 hours during which time a precipitate formed. The mixture was cooled slowly to room temperature and the precipitate was collected by centrifugation, washed with methanol (until no more color was removed), and dried by heating *in vacuo* for 16 hours to obtain 1.10 g, 81% yield. The calculation of relative amounts of methylene and ethylene units in the copolymer product was as follows. The CH_2 and CH_2CH_2 signal areas at 6.35-6.36 and 4.78 (, respectively (Figure 7); the reference peak at 7.27 (is for chloroform) were divided by 2 and 4, respectively to correspond with area per proton or grouping. These areas were then divided by the sum of the methylene and ethylene areas to give the relative mole fractions which when multiplied by 100 gave 43% and 57% of CH_2 and

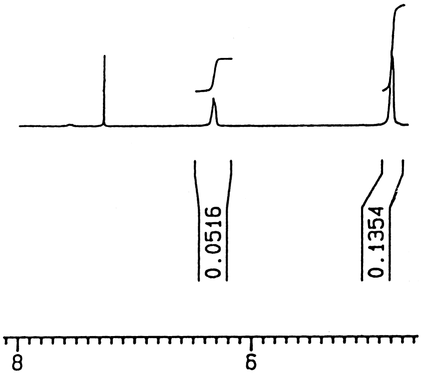


Figure 7. Partial ^{1}H NMR spectrum of poly(ethylene-co-methylene terephthalate) in TFA/$CDCl_3$ synthesized by triethylamine-promoted polymerization of terephthalic acid and 1,2-dibromoethane (50%)/dibro-momethane (50%) showing integrations of CH_2CH_2 and CH_2 peaks.

CH_2CH_2 units, respectively incorporated into the copolymer. Data for the other copolymers are in Table 1.

RESULTS AND DISCUSSION

Data on the polymers synthesized are in Table 1. Feed ratios are in terms of ratios of moles of dihaloalkane whereas, polymer product ratios are in terms of relative polymer weights.

Comparisons of Bromo with Chloro Feedstocks

In the syntheses of PMT using dibromomethane or dichloromethane, although the yield of PMT with dichloromethane was lower (33% vs. 58%) even though the reaction time with the chloro reactant was much longer (5 days vs. 24 hours), M_n (28,500-33,800 vs. 5,700) and T_m (246-250°C vs. 230°C) were significantly higher.

In the case of the PET syntheses with 1,2-dichloroethane, a longer reaction period of 4 days was also required as compared with 28 hours for the bromo analog. The yields from the chloro and bromo ethanes are nearly the same (58% vs. 62% for chloro and bromo, respectively) but for PET from the chloro is again higher than that from the bromo starting material (12,000 vs. 5,200).

TABLE 1. Data on Poly(ethylene-co-methylene terephthalates)

Feed Ratio[a] (Et/Me)	**Prod. Ratio (PET/PMT)**	**Yield, g (%)**	**M_n**	**T_m (°C)**
0/100	**0/100**	**0.811 (58)**	**5,700**	**254**
25/75	**37/63**	**0.593 (47)**	**6,000**	**170**
50/50	**57/43**	**1.10 (81)**	**11,600**	**154**
75/25	**84/16**	**0.932 (63)**	**15,200**	**210**
90/10	**92/8**	**0.983 (66)**	**20,500**	**215**
100/0	**100/0**	**1.30 (62)**	**5,200**	**250**

[a](CH_2CH_2/ CH_2) ratio.

Feed Ratio of Dibromomethane/1,2-Dibromoethane vs. Product Ratio (Ethylene/methylene) Correlation

In the competition between dibromomethane (DBM) and 1,2-dibromoethane (DBE) for incorporation into the copolymer, the latter is slightly more reactive (Table 1). This order of reactivity is constant at various feed ratios as shown by a good linear correlation between the feed (as mole fractions) and the product composition (PMT/PET) (Figure 8). This correlation is useful in deciding what feed ratio to use for a particular desired product composition. Since the difference in reactivities between DMB and DBE are small, the concentration of DBE relative to DBM does not decrease very much with time, thus maintaining the linear relationship. Although such correlations are common with alkenes in free radical/addition polymerizations; no related types of studies with step-reaction polymerizations are readily available for comparison to our knowledge.

Mechanisms

Based on previous studies [10, 12] of mechanisms for this type of reaction, the following can be considered (Schemes 1 and 2).

Terephthalic acid is initially monodeprotonated by triethylamine to form triethylammonium and terephthalate anion (3) which undergoes an S_N2 reaction at the methylene carbon of 1.2-dibromoethane to displace bromide ion (Scheme

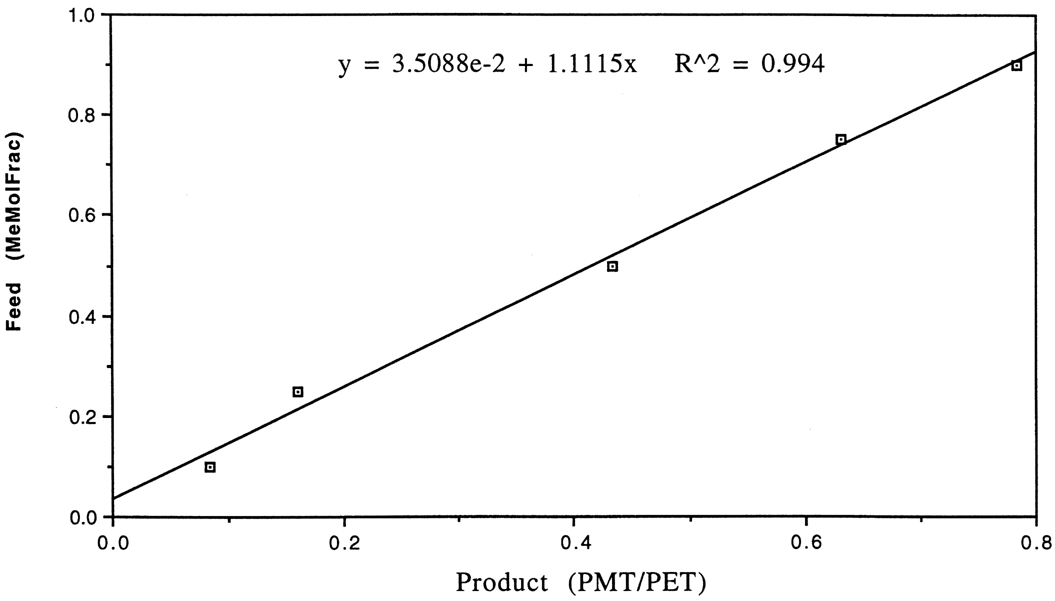
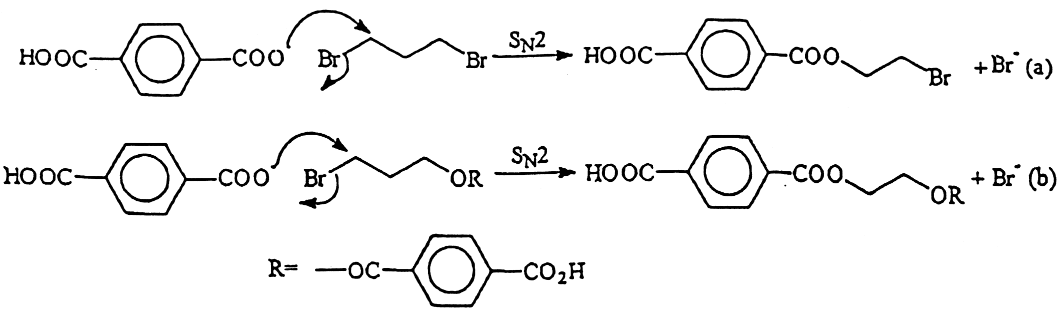


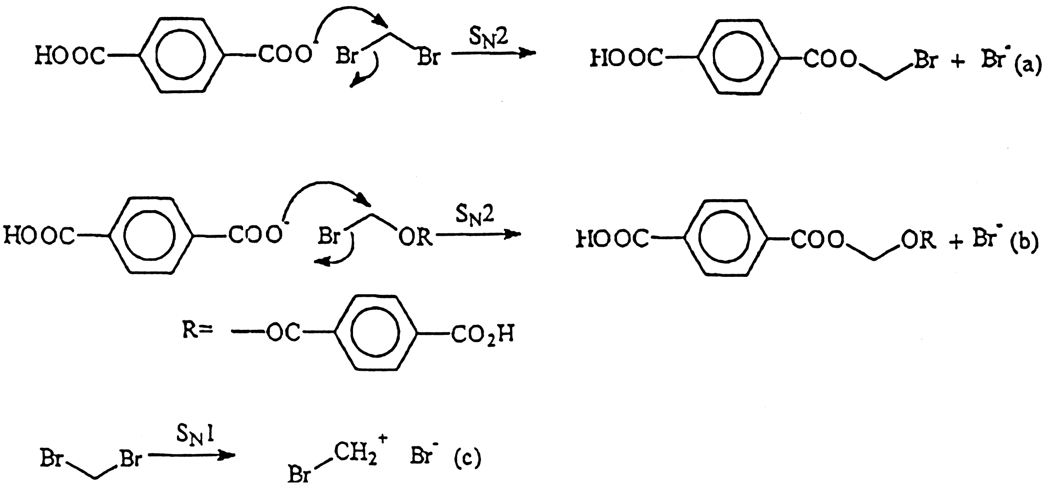
Figure 8. Feed vs. product composition in PMT/PET copolymer syntheses.

1, step a). This step is repeated by reaction of another terephthalate anion (3) with the other bromomethylene group. These steps are repeated to form PET polymer having triethylammonium end groups from reaction of the end carboxylate groups with triethylamine.

The S_N2 steps (Scheme 2) of reaction of terephthalate anion with dibromomethane leading to PMT are similar to those with 1,2-dibromoethane leading to the same type of structure and triethylammonium end groups. An S_N1 reac-



Scheme 1.



Scheme 2.

tion with rate-determining formation of a bromomethyl carbocation and bromide ion (Scheme 2) does not seem feasible since the primary bromomethyl carbocation would not be stabilized very much by the attached bromine. Nevertheless, either mechanism would lead to the same product.

It is possible that the end groups in the synthesis of PET from 1,2-dibromoethane could be -OCH_2CH_2Br (or -OCH_2CH_2OH from hydrolysis) from reaction of one bromine. However, the ^1H NMR spectrum would be expected to show two triplets from coupling and no evidence for these comparable in signal size to the triethylammonium end groups appears. It would be expected that the second bromine (as -OCH_2CH_2Br) would be more reactive than the first one (in $BrCH_2CH_2Br$) as a result of greater activation by oxygen as compared with bromine. In the corresponding case of the PMT synthesis, the analogous end group from CH_2Br_2 would be OCH_2Br. The second bromine in this case would likewise be expected to be more reactive than the first. In addition, this grouping (or its hydrolysis product, -OCH_2OH) is unstable and would not survive workup conditions. There is, of course, the possibility that some of the methylene could be lost by this pathway; this would account for the greater incorporation of ethylene into the copolymers. There is no evidence at present to exclude this possibility.

CONCLUSION

Poly(methylene terephthalate) (PMT) and poly(ethylene terephthalate) (PET) were synthesized by triethylamine-mediated reactions of dihalomethanes or 1,2-dihaloethanes respectively and terephthalic acid. Reactions with chloromethanes and -ethanes required longer reaction times and higher temperatures than with bromo analogs. Copolymers of PMT and PET were synthesized. Compositions of copolymers were determined by integration of methylene and ethylene ^{1}H NMR signals. Mn values were calculated from end group ^{1}H NMR signals. 1,2-Dibromoethane is slightly more reactive than dibromomethane in the competitive copolymer synthesis. Molar feed is linearly related to polymeric product ratios. Mechanisms are proposed for the reactions.

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