Block Copolymers of Styrene Containing Oligomeric Esters of Terephthalic Acids

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ABSTRACT: A new generation of block copolymers were synthesized starting with depolymerized PET by glycolysis with some oligomeric diols. α,ω-Dihydroxy poly(dimethyl siloxane)s, hexylene glycol, poly(ethylene oxide)glycols, and ethylene glycol were used as diols. The dihydroxy-terminated depolymerization products containing a terephthalyl group and oligomeric diols were used to prepare a diradicalic macroinitiator (MI). These MIs were used to polymerize the styrene monomer. The new block copolymers obtained were characterized by physical and chemical methods and mechanical and thermal analyses. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 648–653, 2000

Key words: block copolymer; macroinitiator; poly(ethylene terephthalate); poly(dimethyl siloxane); hexylene glycol; poly(ethylene oxide); ethylene glycol

INTRODUCTION

Macroperoxidic[1–3] and macroazo[4–6] initiators are useful to prepare block copolymers via free radical polymerization. A variety of these types of initiation-containing poly(ethylene oxide) (PEO) and poly(dimethyl siloxane) (PDMS) units were reported recently.[2–6] Because PEO has a high hydrophilicity, flexibility, and ion absorbability, while PDMS has high chain flexibility, hydrophobicity, thermal and UV stability, a wide variety of property variations and possibilities arose for using this method. This work deals with the synthesis of a macroperoxidic initiator having PEO or PDMS units starting with depolymerized PET.

Poly(ethylene terephthalate) (PET) can be depolymerized by using dihydroxy compounds to obtain oligomeric diols containing terephthalyl moeity.[7–9] These type of oligomeric diols were used to synthesize polyurethane coating materials,[7] water-reducible alkyd resin,[8] and block copolymers of polyacrylonitrile, vinyl acetate, and polyacrylamide.[9]

In this study, PET were depolymerized by glycolysis with a thermal treatment method into monomeric PET units containing oligomeric diols by using α,ω-dihydroxy poly(dimethyl siloxane) (PDMS), hexylene glycol (HG), poly(ethylene oxide) glycol 10,000 (PEG 10,000, PEO), and ethylene glycol (EG). These dihydroxy-terminated depolymerization products of poly(ethylene terephthalate) (DHTD PET) were used to prepare for styrene-containing copolymers by using a stepwise procedure.[2,3] The copolymers obtained were characterized by physical and chemical methods and by mechanical and thermal analyses.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate) (PET) (from SASA Turkey), with molecular weights of 20,000 g/mol, was used as purchased. Ethylene glycol (EG) (from Petkim, Petrochemical Company, Izmit, Turkey), hexylene glycol (HG) and poly(ethylene

oxide) glycols (PEG 10,000, PEG 20,000) (from the Union Carbide Company) were used after drying *in vacuo* at 70°C for 3 h. The molecular weights of PEG 10,000 and PEG 20,000 were 10,000 and 20,000 g/mol, respectively.

α,ω-Dihydroxy poly(dimethyl siloxane) (PDMS) was a product of Goldschmidt Chemical Corporation (Essen, Germany). Tegomer H-Si 2111, with molecular weights of 950 $\pm$ 80 g/mol, were dried at 30°C in a vacuum oven for 48 h before use. Isophorone diisocyanate (IPDI) was a product of Fluka A.G. (Buchs, Switzerland), and used without purification. The purity determined by isocyanate analysis was 95.1%. t-Butyl hydroperoxide (t-BHP) (from Fluka A.G.) was distilled under reduced pressure. The peroxide content was found equal to 91.7%. It was used after drying over anhydrous magnesium sulfate. Dibutyltin dilaurate (T-12) (from Fluka A.G.) was used as catalyst. Styrene (from PETKIM, Petrochemical Company, Izmit, Turkey) was made free of inhibitor by treating with 10% aqueous sodium hydroxide. It was washed with water several times, and after drying overnight with anhydrous calcium chloride, it was fractionally distilled in a vacuum. Solvents used were products of Merck A.G. (Darmstadt, Germany), and they were carefully dried over molecular sieves (Linde Type 5A) (from the Davison Chemical Company), followed by fractional distillation.

Analyses

Isocyanate and peroxygen analyses were performed by using standard methods.[10,11] Infrared (IR) spectra were recorded on a JASCO FTIR-5300 Fourier transform infrared spectrometer.

^{1}H-NMR spectra were obtained for the CDCl$_3$ solution on a Bruker AC (200 MHz). ^{1}H-NMR spectra of the siloxane-containing sample was obtained without the TMS-containing CDCl$_3$ solution.

M_n and M_w values of block copolymers were calculated from gel permeation chromatographic (GPC) methods according to standard polystyrene calibration using a Knauer M64 instrument, and tetrahydrofuran (THF) served as eluent at 25°C. The flow rate was 1 mL/min.

DSC thermograms were obtained by using Perkin-Elmer DSC-6 instrument; the heating rate was 10°C/min under a nitrogen atmosphere.

Stress–strain tests were done by use of a Lloyd Mechanical Tester, Model LS 500 at room temperature, with a constant crosshead speed of 2 mm/min. Polymeric films were prepared from so-

lutions of the toluene and methylene chloride (50/50, v/v) mixture. Dried film was used for mechanical testing.

Molecular weights of copolymers were determined by the viscometric method. Specific viscosities of copolymers were measured in toluene. The following viscosity–molecular weight relationships were used, depending on the middle group of copolymers[12,13]: $[\eta] = 1.1 \times 10^{-4} \, M_n^{0.725}$, at 30°C, used for PDMS containing samples[2]; $[\eta] = 4.4 \times 10^{-5} \, M_n^{0.65}$, at 25°C, used for PEO containing samples.[3]

PROCEDURE

Preparation of Oligomeric Esters of Terephthalic Acid

The depolymerization experiments were carried out in a Dean-Stark apparatus by glycolysis in the presence of titanium tetra isopropylate as a catalyst under a nitrogen atmosphere at 200°C for 4–6 h, depending on the type of oligomeric diols. The molar ratio of oligomeric diols to PET was held at 2.1 n, where n is the repeating unit number of PET. The hydroxylated oligomers obtained were purified.

Preparation of Macroinitiators

The dihydroxy-terminated depolymerization products of poly(ethylene terephthalate) (DHTD PET) were reacted with isophorone diisocyanate (IPDI) to obtain diisocyanate-terminated depolymerized poly(ethylene terephthalate) (DITD PET) in the first step. This reaction was carried out in dichloro ethane solution at 60°C under a blanket of dry nitrogen for 80 h. The molar ratio of IPDI to DHTD PET was held at 3 to prevent chain extension. The isocyanate contents of the end-capped products were determined by end-group titration of isocyanates. The calculated molecular weights are given in Table I. After the isolation from the unreacted IPDI, DITD PET was reacted with *t-butyl* hydroperoxide in methylene chloride by using a T-12 catalyst. The reaction was carried out

Table I   Characteristics of Macroinitiators

MI No.	Isocyanate Weight (%)	M_n[a] (g/mol)	Peroxide Weight (%)	M_n[b] (g/mol)
PET Si	2.4 ± 0.05	3500 ± 75	1.77	3615
PET HG	11.05	760	6.8	940
PET PG (PEG 10,000)	0.24	35,150	0.18	35,350
PET EG	4.7 ± 0.10	1785 ± 40	3.04	2108
PG 20,000	0.41	20,490	0.31	20,650

[a] Calculated from isocyanate content.
[b] Calculated from peroxide content.

under a nitrogen atmosphere at room temperature in the dark for 200 h. The molar ratio of *t-butyl* hydroperoxide to urethane (—OOH/—NCO) was approximately 3, to prevent undesired chain extension. The resulting products were isolated by precipitating in petroleum ether; they were filtered and dried in vacuum at room temperature, and used as macroinitiators for the polymerization of styrene. The structural formula of macroinitiators can be represented as follows:

MI
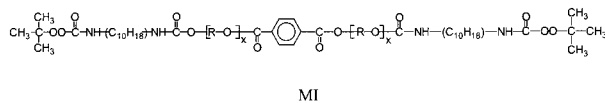
The molecular weights of the products were calculated from peroxide analysis. The results were collected in Table I.

Synthesis and Characterization of Copolymers

These macroinitiators (MI) were used to prepare block copolymers of styrene. Weighed amounts of MIs were dissolved in predetermined amounts of styrene. Toluene was added to mixture as the polymerization solvent. The mixtures in Pyrex® tubes were deggased on the vacuum line, then immersed in thermostatically controlled baths (80°C), and the polymerization was carried out for 120 h. The solid products were dissolved in toluene and then precipitated in methanol and then filtered and dried in vacuum 30°C for 24 h.

RESULTS AND DISCUSSION

Eight copolymers of styrene were synthesized from the five type of macroinitiators (MI) given in Table I. In this study, different types of MIs were prepared by using depolymerized PET with some oligomeric diols, such as PET Si (by using PDMS),

PET HG (by using hexylene glycol), PET PG (by using PEG 10,000), and PET EG (by using EG). PEG 20,000 was used to prepare a macroinitiator (PG 20,000) to compare the results with PET PG. The difference in these two MIs is only the PET group in the middle of the PET PG. Table I contains the characteristics of the macroinitiators in different preparation steps. The molecular weights of isocyanate end products (DITD PET) obtained in the first step of the MI preparation are higher than expected. This shows that DITD PET contains more than two oligomeric diols and more than one terephthalyl groups like chain extension. In the peroxide step, the expected molecular weights were consistent with the theoretical
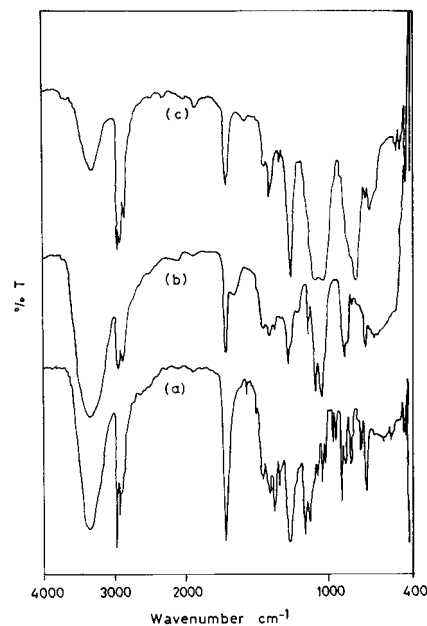

Figure 1   FTIR spectra of dihydroxy terminated depolymerization products of poly(ethylene terephthalate) (DHTD PET) by using (a) hexylene glycol, (b) ethylene glycol, (c) α,ω-dihydroxy poly(dimethyl siloxane).
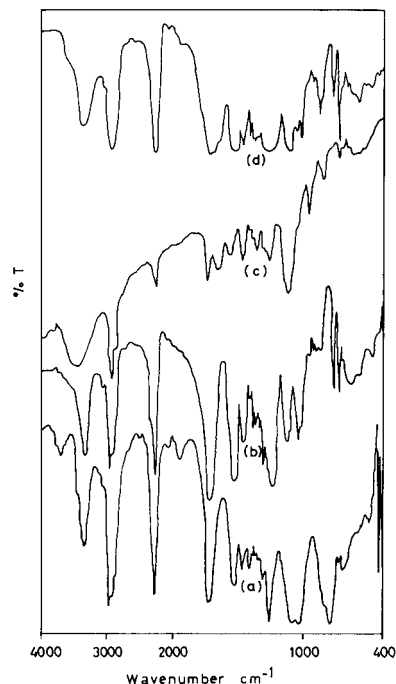
Figure 2 FTIR spectra of diisocyanate terminated depolymerization products of poly(ethylene terephthalate) (DITD PET) by using (a) α,ω-dihydroxy poly(dimethyl siloxane), (b) ethylene glycol, (c) poly(ethylene oxide)glycol 10,000, (d) hexylene glycol.

ones. These MIs were used as starting material for the synthesis of ABA type styrene (A block) containing block copolymers.
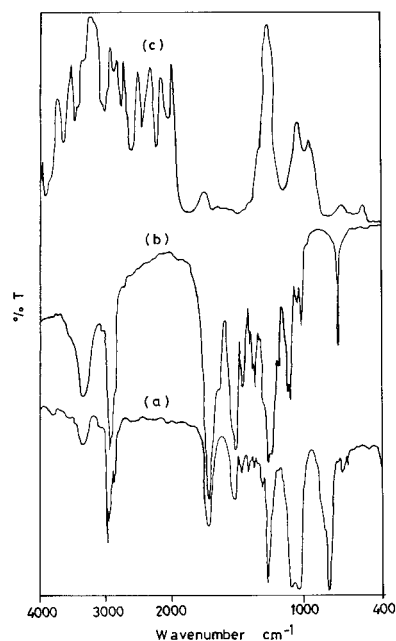

Figure 3 FTIR spectra of macroinitiators (a) PET Si, (b) PET HG, (c) PET PG.
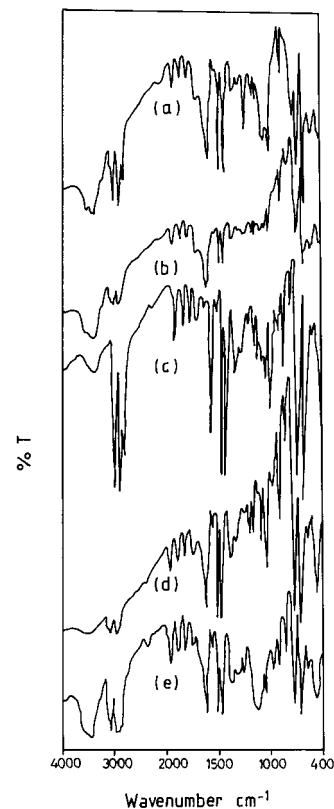
Figure 4 FTIR spectra of (a) Cop. No. 2, (b) Cop. No. 4, (c) Cop. No. 5, (d) Cop. No. 7, (e) Cop. No. 8.

Intermediates and the products were characterized by FTIR spectroscopy. In the FTIR spectra of DHTD PET products (Fig. 1) the peaks at 3350 cm^{-1} are due to —OH groups, and at 1720 cm^{-1} are due to the carbonyl groups coming from oligomeric diols and PET, respectively. The peaks observed between 1667–2000 cm^{-1} are typical peaks of PET due to p-substitute benzenoid compounds. In Figure 1(c) the peaks at 800 cm^{-1} from Si—CH$_3$ and at 1030 cm^{-1} from Si—O are the characteristic peaks of PDMS. The —OH absorption peaks dissappeared at the end of the capping reaction with isocyanate (Fig. 2). The peak at 2280 cm^{-1} is due to the stretching vibration of —NCO, and it is the principal absorption peak for the isocyanate groups. Urethane peaks around 3440 cm^{-1} were observed due to —NH stretching in the —NH—CO— group. The disappearance of the —NCO peaks indicate the formation of MIs, which are illustrated in Figure 3. Figure 4 compares the FTIR spectra of copolymers. In these spectra, the typical peaks of PS are shown in between 1667–2000 cm^{-1} from a monosubstitute aromatic compound. The urethane peaks around 3440 cm^{-1} were observed in all copolymeric sam-
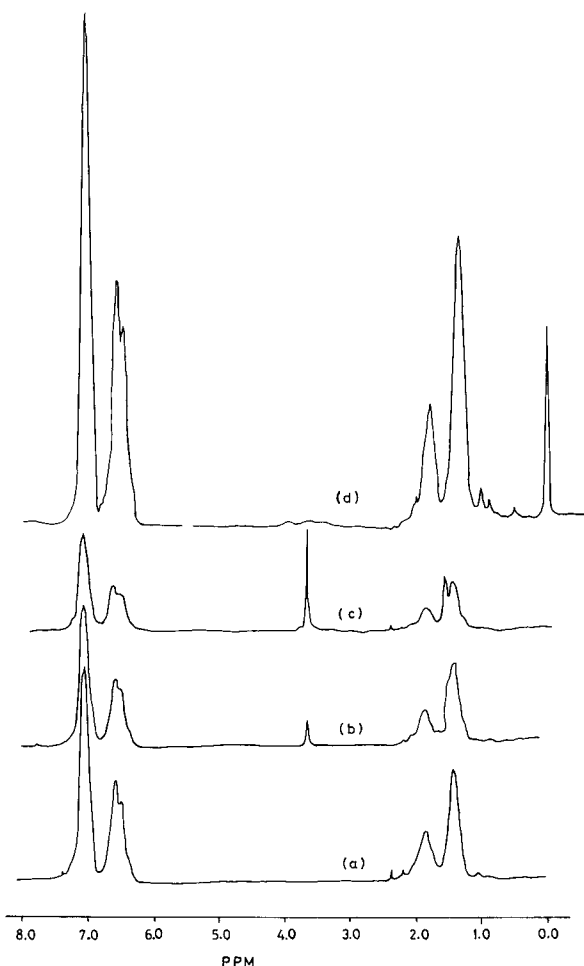
Figure 5 ¹H-NMR spectra of (a) Cop. No. 7, (b) Cop. No. 5, (c) Cop. No. 8, (d) Cop. No. 2.

ples, which indicates the incorporation of MIs into the copolymers.

In Figure 5, ¹H-NMR spectra of Cop. Nos. 2, 5, 7, and 8 are presented. As shown in the figure, the signal at 1.05 and 1.5 ppm are due to the —CH₃ groups, while those between 1.8 and 2.2 ppm are from the —CH₂ and —CH groups. The signals of phenyl protons in PS are 6.5 and 7.0 ppm. The methyl siloxy protons in siloxane segment of the Cop. No. 2 [Fig. 5(d)] were observed with the signals of 0.08 ppm. The specific signals of CH₂ protons in —CH₂O— groups of copolymer Nos. 5 and 8 [Fig. 5(b) and (c)] at 3.65 ppm came from the PEO contents in the MIs.

Experimental data on the preparation of copolymers are given in Table II. Intrinsic viscosities in toluene and average molecular weights of the block copolymers are given in Table II along with other weight averages. M_v values are between M_n and M_w values of copolymers found by GPC. Two different intrinsic viscosity–molecular weight relationships were used to calculate M_v values, because two different applications were given in the literature, depending on the siloxane or PEO containing PS block copolymers.[2,3] Polydispersities of copolymers show a variation in the range of 1.35–2.00. Molecular weights of the samples in the PET Si and PET PG series decrease with increasing MI wt % in the copolymers, depending on the yield percent.

The glass transition temperatures of the samples were determined by DSC thermograms studied above room temperature. In these block copolymers three different special groups affect the thermal characterization of the samples; terephthalyl groups are in the middle, and PS chains in the outer. EG, HG, PEG-10,000, and PDMS groups are between these two hard segments. The results of DSC thermograms are given in Table

Table II   Preparation Conditions and Some Characteristics of Block Copolymers

| Block Copolymer No. | MI No. | Initial Composition | | Yield (%) | [η] (dL/g) | $M_v \times 10^{-3}$ (g/mol) | $M_n \times 10^{-3}$ (g/mol)[a] | $M_w \times 10^{-3}$ (g/mol)[a] |
		MI (wt %)	Styrene (wt %)					
1	PET Si	10.4	89.6	85	0.422	88	68	120
2	PET Si	25.6	74.4	60	0.539	123	115	156
3	PET Si	40.2	59.8	53	—	—	—	—
4	PET HG	10.3	89.7	90	—	—	—	—
5	PET PG	10.3	89.7	88	1.65	300	201	402
6	PET PG	24.7	75.3	65	—	—	—	—
7	PET EG	10.6	89.4	90	0.65	75	61	119
8	PEG 20	24.7	75.3	58	0.78	100	65	117

[a] Obtained from GPC.

Table III   Thermal and Mechanical Characteristics of Block Copolymers

Block Cop. No.	MI No.	MI (wt %)	Strain at Break (%)	Stress at Break (MPa)	Young's Modulus (MPa)	T_g[a] (°C)	T_m[a] (°C)
1	PET Si	10.4	3	13	760	106	—
2	PET Si	25.6	2	13	1250	104	—
5	PET PG	10.3	2	14	1090	76	42
6	PET PG	24.7	1	6	750	78	40
8	PEG 20	24.9	2	13	1000	102	48
PS H—Si 2500[b]	H—Si 2500	9.1	7	16	310	70	—
PS H—Si 2500[b]	H—Si 2500	23.1	7	15	370	70	—
PS[c]	—	—	2	22	1600	100	—

[a] T_g and T_m values are due to the PS and PEO segments in the copolymers, respectively.
[b] Ref. 2.
[c] Ref. 3.

III. T_g values are from PS, because the other groups have lower molecular weights than PS chains in the copolymers. The T_m values given in the last column of Table III are from PEO contents of the samples. Block Cop. Nos. 5 and 6 have PEG 10,000, whereas Cop. No. 8 has PEG 20,000 and the last one does not have any terephthalyl group. The original T_m values of PEO blocks are about 60°C. Block copolymerization decreases the T_m value of the PEO-containing block copolymers as in the previous study.[3]

The glass transitions of PET Si-containing block copolymers are higher than those H—Si 2500 containing samples in an earlier work.[2] Terephthalyl groups in the Cop. Nos. 1 and 2 increase the T_g values companing with PS H—Si 2500 block copolymers given in that study.[2]

Stress and strain at break and Young's Modulus were determined from the stress–strain curves of block copolymeric films. The average values of these mechanical properties are given in Table III. Elongation at break of Cop. Nos. 1, 2, 5, and 6 are not so different than those of PS reference.[3] On the other hand, stress at break is low only in 24.7% PET PG containing block copolymer. The Young's Modulus of the copolymer prepared in this work are higher than those of H—Si 2500 containing block copolymers. Terephthalyl groups effect to increase the Young's modulus values of copolymers.

CONCLUSION

This kind of PET depolymerization with some oligomeric diols give a new style of block copolymers. The new block copolymers have higher T_g values, higher stress at break, and higher Young's modulus than those of the samples without having terephthalyl groups. The terephthalyl groups in the middle affect the thermal and mechanical characteristics of block copolymers containing PEO or siloxane.

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