Preparation and characterization of poly(ethylene/tetramethylene terephthalate) copolyesters

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Random copolyesters were prepared from dimethyl terephthalate (DMT), ethylene glycol (EG) and butane1,4-diol (BD) by melt-polycondensation techniques, using varying amounts of EG and BD. Compositions have been established by ^1H n.m.r. spectroscopy. Intrinsic viscosity and number average molecular weight ($\bar{M}_n$) were measured. Thermal properties have been studied by differential thermal analysis. Melting and crystallization temperatures and thermodynamic parameters are discussed in terms of structural differences, particularly the effect of composition and chain flexibility. The degree of crystallinity from differential thermal analysis, i.r. and wide angle X-ray scattering (WAXS) are discussed.

Keywords Melt polycondensation; ester-exchange; melting temperature; percent crystallinity; heat of fusion; entropy of fusion

INTRODUCTION

The structure–property relationships of the copolyesters of a mixture of two glycols and a dicarboxylic acid are used in the synthesis of polymers with specific properties. In the synthesis of these polymers, an excess of glycols is used in the ester-exchange reaction and then removed during the polycondensation reaction to form a high molecular weight polymer. The thermal and physical properties of copolymers, however, vary with change of composition[1]. The preparation and properties of poly(methylene terephthalates)[2] and a detailed investigations on the copolyesters of tetramethylene terephthalate–tetramethylene sebacate and tetramethylene terephthalate–tetramethylene oxide were made[3–6]. Here, we report on the preparation and characterization of copolyesters derived from dimethyl terephthalate (DMT), ethylene glycol (EG) and butane-1,4-diol (BD) in varying proportions.

EXPERIMENTAL

Dimethyl terephthalate (DMT), obtained from Koch-Light Laboratories Ltd., England, was purified by recrystallization (m.p. 141°C). Ethylene glycol (EG) (LR, BDH, b.p. 51°C/0.8 mm Hg), butane-1,4-diol (BD) (LR, BDH, b.p. 90°C/0.1 mm Hg) and *o*-chlorophenol (SISCO, b.p. 173°–176°C) were distilled and used. Trifluoroacetic acid (TFA) (LR, BDH, spectroscopic grade) was used for recording ^1H n.m.r. spectra.

All the copolyesters were prepared by melt polycondensation and the preparation of 45.3 mole % EG in the polyester is described. The polymerization reactor is a 150 ml flask fitted with a special polymerization head containing a N_2 inlet, a leak proof stirrer and a condensate collector with an air-locked vacuum system.

15.5 g (0.08 mole) DMT, 5.5 g (0.095 mole) EG, 8.1 g (0.095 mole) BD, 0.025 g zinc acetate and 0.006 g antimony trioxide are charged into the flask and the system was purged with nitrogen for 15 min and lowered into a constant temperature bath maintained at 165°C and stirred continuously throughout the reaction. After 3 h, methanol evolution ceased and the bath temperature was raised to 275°C and the pressure was reduced to 1 mm Hg and maintained for 3 h. The bath was then removed and the polymer was dissolved in *o*-chlorophenol and precipitated in an excess quantity of ethanol, filtered and dried in vacuum. The polymer was purified by reprecipitation and used for characterization.

The intrinsic viscosity, $[\eta]$, of all the copolyesters were measured in *o*-chlorophenol at 30° ±0.1°C. The number average molecular weights ($\bar{M}_n$) were determined in a Knauer, (Berlin) vapour pressure osmometer at 120°C. The i.r. spectra (KBr pellet) of polymers were taken in a Perkin Elmer i.r. model 283 spectrometer. The ^1H n.m.r. spectra were recorded with a Varian XL 100 spectrometer (100 MHz) employing TMS as an internal standard. Wide angle X-ray scattering (WAXS) patterns were recorded in the reflection mode using a Philips diffractometer. A copper target in conjunction with a Ni–Kβ filter was used for all the X-ray experiments.

A TA 2000 d.t.a. system differential thermal analyser was used to measure the melting temperatures (T_m), crystallization temperature (T_c), heat of fusion (ΔH_f), per cent crystallinity (X_c) and other thermodynamic parameters. Samples of 5–10 mg powder were quenched in liquid nitrogen and scaled in aluminium sample pans and run at 10°/min. The heat of fusion, ΔH_f, of the copolyesters were determined by comparing the area under the endothermic peak to the area of standard indium endotherm[7,8]. The per cent crystallinity, X_c, of the copolyesters was calculated by the following equation[8,9]:

$$\%X_c = \frac{\Delta H_f(\mathrm{EG}.M_1) + (\mathrm{BD}.M_2)}{\Delta H^\circ_f(\mathrm{EG}.M_1)} \times 100 \qquad (1)$$

where EG = mole % of ethylene terephthalate in the copolymer; M_1 = molecular weight of ethylene terephthalate repeat unit (192); BD = mole % of butylene terephthalate in the copolymer; M_2 = molecular weight of butylene terephthalate repeat unit (220) and ΔH°_f = the heat of fusion per gram of repeat unit of poly(ethylene terephthalate) (PET) (32.2 cal g^{-1}).

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RESULTS AND DISCUSSION

All the copolyesters were colourless and soluble in organic solvents like *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, *o*-chlorophenol, chloroform and TFA. Methanol, ethanol and n-hexane are good non-solvents. The intrinsic viscosity and $\bar{M}_n$ for all the copolyesters are collected in *Table 1*. As the intrinsic viscosity increases the molecular weight also increases in a regular fashion. The low molecular weight is due to the degradation during isolation. The intrinsic viscosity of the copolyester prepared without using solvent is three times higher than the polymer where solvent is employed in the preparation. The feed composition and the composition obtained from ^{1}H n.m.r.[10] are in *Table 1* and the difference between the two is due to the loss of some volatile scission products[11].

The *FT*i.r. studies of amorphous poly(butylene terephthalate) (PBT) and crystalline PBT were recently reported by Holland-Moritz and Siesler[12]. The i.r. spectrum of PBT was taken, and then the PBT was heated to 260°C. It was cooled to room temperature (10°/min) and the i.r. spectrum of this heat treated PBT resembles that of crystalline PBT[12]. This clearly shows that the crystallinity of PBT increases after the heat treatment. The characteristic change from semicrystalline to crystalline is accompanied by a significant increase in 1460/1455 cm^{-1} [$\delta(CH_2)$] and the 917 cm^{-1} [skeletal/$\gamma(CH_2)$] absorption bands which are characteristic of a near *gauche–trans–gauche* conformation of the aliphatic segments in the crystalline α-phase[13] and a decrease of relatively broad absorption bands at about 1472 cm^{-1} and 960 cm^{-1}. The i.r. spectrum of PET[14,15] shows the following characteristic absorptions. These are 1370 cm^{-1} (–CH_2–wagging *gauche*), 1340 cm^{-1} (–CH_2–*trans* wagging), 970 cm^{-1} (C–O *trans* stretching), 870 cm^{-1} (–CH_2–*gauche* rocking) and 840 cm^{-1} (–CH_2–*trans* rocking). Incorporation of BD in the copolyester leads to a significant change in the 937 cm^{-1} and 960 cm^{-1} regions. These bands are assigned to –CH_2–trans (937 cm^{-1}) and –CH_2–*gauche* (960 cm^{-1}) bond rotations. The characteristic changes in infra-red absorption bands for the different copolyesters and the two homopolyesters PET and PBT are listed in *Table 2*.

The wide angle X-ray diffractogram for the homopolymers and the copolymers are shown in *Figure 1*. X-ray determination of crystallinity in PET was studied by Bosley[16] and the peak at the diffraction angle of 17° is assigned for 010 plane, the peak at the diffraction angle of 23° is for 110 plane and the peak at the diffraction angle of 26° is for 100 plane[17,18]. This is observed in the copolyesters and also in the homopolyester PET and PBT. This clearly shows that the polymer prepared is semicrystalline. The incorporation of BD content in the copolyester affects the peak at the diffraction angle 26° due to the change in crystallinity. Increase in BD content results in the conversion of the singlet peak at 26° to a doublet (*Figure 1*).

When the copolymers were heated at a rate of 10°C/min in a d.t.a. cell, it was found that a sharp endotherm occurred around 170°–246°C depending upon the EG and BD content in the copolymer (*Table 3*). This endotherm was attributed to the melting of the copolyester and the corresponding temperature is the melting temperature of the copolyester (T_m). When the melt was cooled at a rate of 10°C/min from 10°C above the melting temperature to room temperature, a sharp exotherm occurred due to the crystallization of the polymer (*Table 3*). This temperature is the crystallization temperature (T_c) of the copolyester. The melting temperature–composition relations for this component follow an independent curve, so that an eutectic type minimum results at the intersection of the two curves[19–21]. This is typical behaviour of random copolymers when studied over the complete range of compositions.

Table 1 Compositions, intrinsic viscosity and molecular weight of the copolyesters

Polymer	Feed composition (mole %) EG	BD	N.m.r. composition (mole %) EG	BD	[η] (dl/g)	$\bar{M}_n$
PBT	0	100.0	0	100.0	0.19	2129
B2	12.5	87.5	5.4	94.6	0.27	2329
B1	25.0	75.0	14.6	85.4	0.33	3720
B	50.0	50.0	45.3	54.7	0.19	3140
B3	75.0	25.0	67.1	32.9	0.41	5988
B4	87.5	12.5	82.1	17.9	0.35	3951
PET	100.0	0	100.0	0	0.20	3303

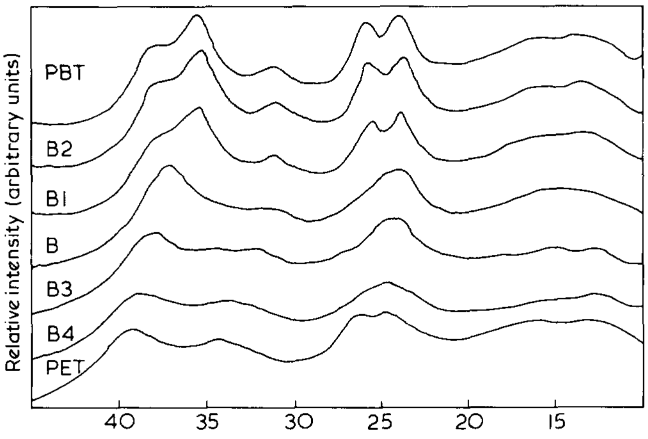

Figure 1 Wide angle X-ray scattering (WAXS) for polymers PBT, B2, B1, B, B3, B4 and PET

Table 2 Changes in the i.r. absorption of copolyesters

Polymer	1385 cm^{-1}	1340 cm^{-1}	1000–900 cm^{-1}	900–800 cm^{-1}
PBT	Small	Very small	triplet (910, 930, 960)	Very sharp band at 870
B2	Small	Very small	triplet (915, 935, 960)	Very sharp band at 870
B1	Very small	Very small	triplet (910, 930, 960)	Very sharp band at 870
B	Very small	Formation of a well defined peak	doublet (930, 966)	Very sharp band at 870
B3	Very small	Formation of a well defined peak	doublet (940, 970)	Very sharp band at 870
B4	Shifted to 1370 cm^{-1}	Formation of a well defined peak	doublet (945, 970)	Very sharp band at 870
PET	Shifted to 1370 cm^{-1}	Formation of a well defined peak	singlet (965)	Very sharp band at 870

When the polymers were reheated after crystallization at a rate of 10°C/min, multiple melting endotherms were observed on all d.t.a. curves, and the peak temperature of the major endothermic peak was taken as the T_m. The T_m values for PBT are similar to those reported by Smith[2] (221°C) and by Shulken[22] (223°C) by d.t.a., Conix[23] (230°C) by dilatometry, and Ward *et al.*[24] (232°C) by dynamic mechanical methods. The different results obtained can be ascribed to the different methods used for their evaluation.

Table 3 Melting and crystallization temperature of copolyesters

Polymer	T_m (°C)	T_c (°C)	Second heating T_m (°C) T_{m_I}	 $T_{m_{II}}$
PBT	213.0	183.0	191.0	213.0
B2	215.0	185.0	201.0	214.5
B1	212.5	181.0	194.5	208.0
B	184.0	151.5	172.5	184.0
B3	178.0	122.0	162.0	177.5
B4	211.5	161.5	195.0	211.0
PET	246.0	194.0	220.0	246.0

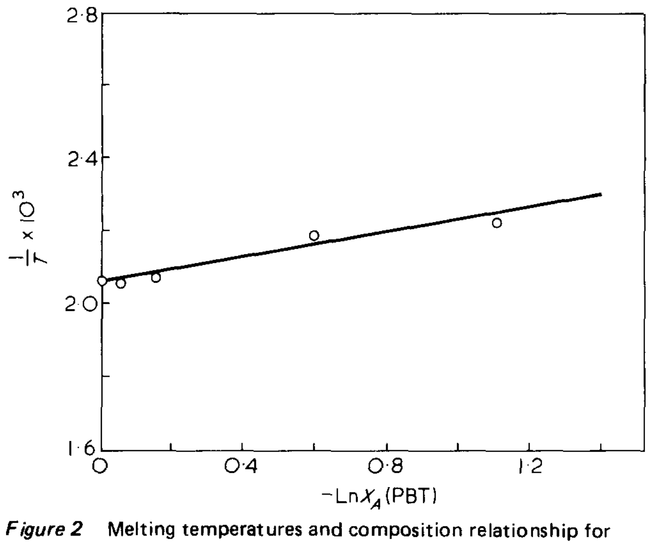

Figure 2 Melting temperatures and composition relationship for the copolyesters of PBT (verification of Flory's equation)

It can be seen from *Table 3* that the polymers have essentially the same T_m irrespective of their thermal history. The decrease in T_m with increasing BD content in the copolymer is in agreement with the theory of equilibrium melting of random copolymers[25]. This theory predicts a depression in T_m caused by the non-crystallizing units according to the equation:

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{R}{\Delta H_f^\circ} \ln X_A \tag{2}$$

where T_m = the melting temperature of the copolymer; T_m° = the melting temperature of the homopolymer; ΔH_f° = the heat of fusion per repeat unit of the homopolymer, and X_A = the mole fraction of crystallizable units. The melting point depression is dependent on the heat of fusion per mole of the crystallizing unit and on the sequence propagation probability p, which it is suggested in random copolymers can be identified with X_A[25]. The melting temperature and the mole fraction have been plotted according to the above equation (2). From the slope of the line, a value of 11 466 cal. mol^{-1} is obtained for the heat of fusion of PBT which is significantly larger than the value of 7600 cal. mol^{-1} obtained by Conix and Van Kerpel[23] from the polymeric diluent method and 7500 cal. mol^{-1} calculated theoretically by Kirshenbaum[26]. The values of ΔH_f determined from an analysis of copolymer melting always differ by varying amounts from the values obtained by other methods[27]. There is an apparent discrepancy which resides in either the experimental methods or the subsequent analysis. From d.t.a. studies the ΔH_f was found to be 3746 cal. mol^{-1} for PBT. This is lower than that predicted by the Flory equation. Using the Flory equation the T_m° calculated from the $\frac{1}{T_m}$ vs. $-\ln X_A$ plot (*Figure 2*) was in good agreement with the d.t.a. T_m of PBT and PET. (T_m for PET by the Flory equation 242.5°C; by d.t.a. 246.0°C and for PBT by Flory equation 213.6°C and by d.t.a. 213.0°C). The per cent crystallinity of the copolyesters vary from 23 to 64 depending upon the composition of copolyester (for B2: 64.2%; B1: 51.3%; B: 33.2%; B3:30.2% and B4: 22.8%).

The thermodynamic parameters ΔH_f, ΔH_c, ΔS_f and ΔS_c for all the copolyesters are listed in *Table 4*. All these values are in good agreement with the composition relationship of copolymers; i.e., it forms eutectic type curves with composition. The ΔS_f values of PBT and PET are found to be 17.30 cal. deg^{-1} mol^{-1} and 9.63 cal. deg^{-1} mol^{-1} respectively which is in agreement with the value reported by Conix and Van Kerpel[23] 15.10 cal. deg^{-1} mol^{-1} for PBT and for PET it is 10.20 cal. deg^{-1} mol^{-1} reported by Smith and Dole[28]. The ΔS_f values of the copolyesters are in between the PBT and PET and are presented in *Table 4*. ΔH_{f_1}, ΔH_{f_2}, ΔS_{f_1}, ΔS_{f_2} are the enthalpy and entropy of fusion for the first and second melting endotherms (*Table 4*).

Table 4 Thermodynamic parameters of copolyesters

Polymer	Mole % EG	ΔH_f	ΔH_c	ΔH_f (melt-crystd.) ΔH_{f_1}	 ΔH_{f_2}	ΔH_f (total) ($\Delta H_{f_1} + \Delta H_{f_2}$)	ΔS_f	ΔS_c	ΔS_f (melt-crystd.) ΔS_{f_1}	 ΔS_{f_2}	ΔS_f (total) ($\Delta S_{f_1} + \Delta S_{f_2}$)
PBT	0	16.87	15.07	0.99	13.16	14.15	17.30	18.13	1.05	13.67	14.72
B2	5.4	15.86	15.64	2.41	11.52	13.93	16.29	18.60	2.63	12.09	14.72
B1	14.6	14.92	14.14	1.94	10.15	12.09	15.24	17.19	2.10	11.04	13.14
B	45.3	10.34	10.48	3.55	7.06	10.61	12.61	15.19	4.73	8.41	13.14
B3	67.1	9.60	8.75	1.32	6.25	7.57	12.09	15.77	1.58	7.88	9.46
B4	82.1	7.27	7.93	2.25	5.20	7.45	7.36	10.83	2.63	5.26	7.89
PET	100.0	11.92	11.88	2.28	9.49	11.77	9.63	11.79	1.84	7.80	9.64

All ΔH_f and ΔH_c values are in cal. g^{-1}
All ΔS_f and ΔS_c values are in cal. deg^{-1} mol^{-1}

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Anomalous dielectric relaxation in poly(dimethyl siloxane) polymers

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The dielectric relaxation in poly(dimethylsiloxane) of viscosity 10^5 CSt at around the melting point is found to deviate from the existing theory. Although the position of maximum loss is insensitive to changes in temperature in the range −40°C to −54°C, the magnitude of the loss changes by about 50%.

Keywords Absorption curves; anomalous behaviour; α-relaxation; loss peak; spherullites; rotator phase

Dielectric behaviour in siloxane polymers was previously studied around room temperature[1–2] and little was known about the low temperature region above and around the glass transition where the loss peaks appear in the audio frequency region[3–5]. Studies of poly(dimethylsiloxane) fluids ranging in viscosity from 100 cSt to 10^5 cSt ($1\ \mathrm{cSt} = 10^{-6}\ \mathrm{m}^2\ \mathrm{s}^{-1}$) at room temperature were reported[6] earlier. Broad loss peaks in the audio frequency region due to micro-Brownian motion were observed in the temperature range −120°C to −100°C. However for poly(dimethylsiloxane) of viscosity 10^5 cSt which crystallizes at around −50°C, the curves in the α relaxation region are highly skewed towards the low frequencies. These features are typical of the crystalline polymers[7]. As the temperature is raised, the absorption curves move to the higher frequencies and the locus of $\log_{10}f_m$ (frequency of maximum loss) against $\frac{1}{T}k$ curves is predicted by the WLF equation[8].

As the temperature is raised near the melting point at about −50°C where poly(dimethylsiloxane) becomes opaque due to the crystallization and growth of spherulites[9], anomalous behaviour of the relaxation was observed in the temperature region −60°C to −40°C as shown in *Figure 1*. The thermal treatment of the sample was carefully controlled and the rate of cooling was maintained practically the same in all observations. A striking feature is that although the position of the loss peak is apparently insensitive to changes in temperature in the range −40°C to −54°C, the magnitude of the loss changes by about 50%.

These peaks cannot be associated with electrode difficulties. A three terminal dielectric cell, used in this study, was constructed so that the electrodes followed any contraction of the sample as the temperature was lowered. The loss peaks may not be attributed to the contaminated water vapour, since the samples of poly(dimethylsiloxane) were dried for several hours *in vacuo*

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