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Preparation and Characterization of Poly(ethylene/Trimethylene Terephthalate) Copolyesters

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ABSTRACT

Random copolyesters were prepared from dimethyl terephthalate, ethylene glycol (EG), and propane-1,3-diol (PrG) by melt-polycondensation techniques, using varying amounts of EG and PrG. Compositions have been established by proton NMR spectroscopy. Intrinsic viscosity and number-average molecular weight were measured. Thermal properties have been studied by differential thermal analysis. Melting and degradation temperatures and thermodynamic parameters are discussed in terms of structural differences, particularly the effect of composition and chain flexibility.

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INTRODUCTION

In general, copolyesters are of great commercial importance in the field of molding plastics and fibers [1]. 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 glycol 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 a change of composition [2-13]. In the present investigation we describe the preparation and characterization of copolyesters derived from dimethyl terephthalate, ethylene glycol, and propane-1,3-diol in varying proportions.

EXPERIMENTAL METHODS

Dimethyl terephthalate (DMT), obtained from Koch-Light Laboratories, England, was purified by recrystallization (mp 141°C). Ethylene glycol (EG) (LR, BDH, bp 51°C/0.8 mmHg), propane-1,3-diol (PrG) (LR, BDH, bp 84.5°C/10 mmHg), and o-chlorophenol (SISCO, bp 173-176°C) were distilled and used. Trifluoroacetic acid (TFA) (LR, BDH, Spectroscopic grade) was used for recording proton NMR spectra.

All the copolyesters were prepared by melt polycondensation, and the preparation of 43.8 mol% EG in the copolyester is described. The polymerization reactor was a 150-mL flask fitted with a special polymerization head containing an N_2 inlet, a leakproof stirrer, and a condensate collector with an air-locked vacuum system.

0.18 mol of DMT, 0.095 mol of EG, 0.095 mol of PrG, 0.006 g of antimony trioxide, and 0.025 g of zinc acetate were charged into the flask. The system was purged with nitrogen for 15 min and lowered into a constant temperature bath maintained at 170°C and stirred continuously throughout the reaction. After 3 h, methanol evolution ceased and the pressure was reduced to 1 mmHg and the bath temperature was gradually raised to 270°C and maintained for 3 h with stirring. The bath was then removed, and the polymer was dissolved in o-chlorophenol by reflux and precipitated in an excess quantity of ice-cold ethanol, filtered, and dried in vacuum. The polymer was further purified by reprecipitation and employed for characterization.

The intrinsic viscosity, $[\eta]$, of all the copolyesters was measured in o-chlorophenol at 30 ± 0.1°C. The number-average molecular weights ($\overline{M}_n$) were determined in a Knauer (Berlin) vapor pressure osmometer at 120°C in o-chlorophenol. The ^{1}H-NMR spectra were recorded with a Perkin-Elmer R-32 (90 MHz) spectrometer employing hexamethyldisiloxane as the internal standard.

A TA 2000 Mettler DTA system differential thermal analyzer was used to measure the melting temperature (T_m), decomposition temperature (T_d), heat of fusion (ΔH_f), and entropy of fusion (ΔS_f). Samples of 5-10 mg powder were sealed in aluminum sample pans and run at 10°/min. The heats of fusion, ΔH_f, of the copolyesters were determined by comparing the area under the endothermic peak to the standard indium endotherm [14, 15].

RESULTS AND DISCUSSION

All the copolyesters were colorless and soluble in organic solvents like N,N-dimethylformamide, N,N-dimethylacetamide, o-chlorophenol, chloroform, and TFA. Methanol, ethanol, and n-hexane act as good nonsolvents. Table 1 gives the intrinsic viscosity and $\overline{M}_n$ for all the copolyesters. 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 in o-chlorophenol. The feed composition and the composition obtained from ^{1}H-NMR [16] are listed in Table 1, and the difference between the two is due to the loss of some volatile scission products [6, 17].

When the copolymers were heated at a rate of 10/min in a DTA cell, it was found that a sharp endotherm occurred around 180-240°C depending upon the comonomers content (EG and PrG) in the copolymer (Table 2). This endotherm was attributed to the melting of the copolyester, and the corresponding temperature is the melting temperature of the copolyester. As the PrG content increases, the copolyester becomes more amorphous and hence there is no melting temperature for copolyesters A1 and A2. The copolyester becomes completely amorphous when the composition of PrG reaches 60 mol%. When the composition of PrG reaches 100 mol%, the polymer becomes crystalline again. The melting temperature-composition relations for this component follow an independent curve, so that a eutectic-type minimum results at the intersection of the two curves [6, 18-20]. This is a typical behavior of random copolyesters (copolymers) when they are studied over the complete range of compositions.

The copolyesters were further heated to decomposition in a DTA cell at a rate of 10°/min. It was found that an exotherm occurred from 200 to 260°C depending upon the EG and PrG content in the copolymer (Table 2). This exotherm was attributed to the decomposition of the copolyester, and the corresponding temperature is the decomposition temperature of the copolyester (T_d).

The thermodynamic parameters ΔH_f and ΔS_f for all the copolyesters were given in Table 2. All these values are in good agreement with the composition relationship of the copolymers; i.e., it

TABLE 1. Composition, Intrinsic Viscosity, and Molecular Weight of the Copolyesters

Polymer	Feed composition (mol%) EG	Feed composition (mol%) PrG	NMR composition (mol%) EG	NMR composition (mol%) PrG	$[\eta]$ (dL/g)	$\overline{M}_n$
PPrT	0	100.0	0	100.0	0.40	5941
A2	12.5	87.5	22.3	77.7	0.09	1490
A1	25.0	75.0	29.0	71.0	0.11	1612
A	50.0	50.0	43.8	56.2	0.18	3052
A3	75.0	25.0	74.7	25.3	0.12	1750
A4	87.5	12.5	83.5	16.5	0.15	2010
PET	100.0	0	100.0	0	0.20	3303

TABLE 2. Thermal Properties of Copolyesters

Polymer	PrG content (mol%)	T_m (°C)	T_d (°C)	ΔH_f[b] (cal/g)	ΔS_f[b] (cal/(deg·mol))
PET	0	246.0	263.0	11.92	9.63
A4	16.5	238.2	252.1	18.82	7.07
A3	25.3	237.0	256.1	15.35	5.78
A	56.2	186.7	266.1	12.07	5.04
A1	71.0	-	205.2	-	-
A2	77.7	-	204.7	-	-
PPrT	100.0	225.2	240.0	-	-

[a] PET = Poly(ethylene terephthalate); PPrT = poly(propylene terephthalate).

[b] In SI units, 1 cal = 4.184 J.

forms eutectic-type curves with composition. The ΔS_f value of PET is found to be 9.63 cal/(deg·mol) which is in good agreement with the value reported by Smith and Dole [21] (10.20 cal/(deg·mol)).

In conclusion, the copolyesters are crystalline up to 60 mol% PrG content and any further increase of PrG content results in an amorphous copolyester. At 100 mol%, PrG (PPrT) again becomes a crystalline copolyester.

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