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Terephthalate Copolyesters of Ethylene Glycol and Propane-1,3-Diol

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SUMMARY

Terephthalate copolyesters of ethylene glycol and propane-1,3-diol of various compositions were prepared by trans-esterification of poly(ethylene terephthalate) (PET) with propane-1,3-diol [PrG(1,3)]. The compositions of the copolyesters were determined by ^{1}H NMR. The melting and crystallization temperatures were measured by differential thermal analysis (DTA). Intrinsic viscosities were measured in orthochlorophenol at 30°C.

INTRODUCTION

In our previous paper (BALAKRISHNAN et al, 1981), we described the preparation and characterization of the copolyesters of PET with butane-1,4-diol. WIENER, 1967 prepared a polyester by treating dimethyl terephthalate (DMT) with excess 2-methyl-2-phenyl-1,3-propanediol and ethylene glycol (EG) and studied the fiber properties. PETER et al, 1971 prepared a highly crystalline PET/butane-1,4-diol and PET/propane-1,3-diol [PrG(1,3)] copolyesters. But, there is no systematic study published in scientific paper regarding PET/PrG(1,3) copolyesters. In this paper we are reporting the preparation and characterization of PET/PrG(1,3) copolyester.

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EXPERIMENTAL

Reagents and Materials:

PET ($\bar{M}_n \simeq 20{,}000$, Indian Organic Chemicals Ltd., Madras) was purified as given below. It was dissolved in trifluoroacetic acid (TFA), reprecipitated in methanol, filtered, dried and used. TFA (LR, BDH) was used for recording ^{1}H NMR spectra . Propane-1,3-diol (LR, BDH b.p. 213-214°C) and orthochlorophenol (SISCO, b.p.173-176°C) were distilled by standard procedures and used.

Preparation of the copolyesters:

Random copolyesters of PET with PrG(1,3) were prepared in different molar ratios, the mole ratio of PrG(1,3) being 10,25,50,60 and 75. The polymerization reactor was a 100 ml round bottomed flask fitted with a head containing a leak-proof stirrer, a valved nitrogen inlet and a condensate collector with air locked vacuum system.

After charging 10g (0.052 m) of PET and 10g(0.131 m) of PrG(1,3) to the flask, the system was purged with purified nitrogen and placed in a molten eutectic sodium salt bath (210°C) stirring the contents under nitrogen for 3 hours. After this initial fragmentation any accumulated condensate was removed and the nitrogen valve was closed. Vacuum was then applied slowly over 3-5 minutes interval. The process of molecular weight build up by the combination of the end groups (JACKSON, KUHFUSS, 1976)of terephthalic acid, ethylene glycol and PrG(1,3) was allowed to occur for 4 hours at 270°C. Care was taken to see that the stirring was continuous and the atmospheric leak into the system was avoided. The polymer melt was then cooled under a steady stream of nitrogen and the polymer in the vessel was refluxed in orthochlorophenol (175°C) for about four hours so as to dissolve the contents.

The solution was filtered into a cooled, vigorously stirred excess quantity of ethanol. The precipitated polymer was filtered, dried in vacuum and used.

Characterization of the copolyesters:

Proton Nuclear Magnetic Resonance Spectroscopy:

The NMR spectra were recorded with a Perkin Elmer - R32 (90 MHz) spectrometer operating at room temperature. Samples for analysis were prepared by dissolving 0.1 g of the copolyester in 0.5 ml of TFA.

Viscosity measurements:

The viscosity measurements were made in orthochlorophenol ($O-ClC_6H_4OH$) at 30 ± 0.1°C in an Ubbelohde viscometer with sinter having a solvent flow-time of 274 seconds. Extrapolation methods (HUGGINS, 1942 and KRAEMER, 1938) were used for evaluating the intrinsic viscosities.

IR Spectroscopy:

The infrared spectra of the copolyesters were recorded in Beckman IR-20 in chloroform.

Thermal measurements:

A TA-2000 Mettler DTA system differential thermal analyser was used for investigating the thermal properties of the copolyester (BALAKRISHNAN et al, 1981).

RESULTS AND DISCUSSION

From the NMR spectra of the copolyesters the chemical shifts of various protons in the polymer relative to HMDS (Hexamethyldisiloxane) are shown below:

Chemical shifts (δ ppm)

(i)

8.28

	Chemical shifts (δ ppm)
(ii) $-O-CH_2-CH_2-O-$	4.95
(iii) $-O-CH_2-(CH_2)-CH_2-O-$	4.85
$-(CH_2)-$	1.70

The mole fraction of propane-1,3-diol in the copolyester was calculated from the integration values by means of the equation:

$$\text{Mole fraction of PrG(1,3)} = \frac{A/2}{A/2 + B/8 + C/4}$$

where A is the integration height for the methylene (CH_2) protons in PrG(1,3), B is the integration height for the $-OCH_2$ protons of both ethylene glycol and propane-1,3-diol and C is the integration height for the phenyl protons. Mole fraction of PET = 1 - mole fraction of PrG(1,3). The feed compositions and the NMR compositions of EG and PrG(1,3) units are given in TABLE 1.

TABLE 1

Composition of PET/PrG(1,3) copolyesters and Intrinsic Viscosities

Polymer Samples	Feed Compositions mole percents		NMR Compositions mole percents		$[\eta]$ in $O-ClC_6H_4OH$ dl/g
	PET	PrG(1,3)	EG unit	PrG unit	
Q1	90	10	83.7	16.3	0.1053
Q2	75	25	73.4	26.6	0.1360
Q3	50	50	62.8	37.2	0.0830
Q4	40	60	47.3	52.7	0.0800
Q5	25	75	56.5	43.5	0.0790

The variation of NMR compositions showed that the copolyesters were random copolymers and not alternating or block type. The difference between the monomer feed ratio and the

NMR composition may be due to the loss of some volatile products of PET (GO, 1973).

The IR spectra of these copolyesters (Q1, Q2, Q3 Q4 and Q5) showed a strong absorption at 1710-1720 cm^{-1} indicating the presence of ester carbonyl in the polymer. The $-OCH_2$ function exhibits an absorption at 1100 to 1180 cm^{-1}. A weak absorption around 1570 cm^{-1} proved the presence of p-substituted aromatic nucleus in the polymer chain.

TABLE 1 gives the intrinsic viscosity of the copolyesters in orthochlorophenol at 30 ± 0.1°C. From the intrinsic viscosities, it is evident that as the incorporation of PrG(1,3) is increased the intrinsic viscosity decreases. This is not only due to the introduction of trimethylene group in PET but also to the decrease in molecular weight of the copolyester ($\bar{M}_n$ = 2500-5000).

The thermal properties of the copolyesters of PET/PrG(1,3) are given in TABLE 2. The melting temperature (T_m) decreases as the PrG(1,3) content increases up to 37.2 mole

<u>TABLE 2</u>

Thermal properties of PET/PrG(1,3) copolyesters

Polymer Sample	Mole percents of PrG(1,3)	Peak Temperature (°C)		
		T_m	T_c	T_m*
Q1	16.3	180.4	120.3	177.2
Q2	26.6	151.3	98.9	150.1
Q3	37.2	162.1	82.4	162.3
Q4	52.7	223.7	160.8	211.0
Q5	43.5	191.2	148.5	191.2

T_m - melting temperature; T_c - crystallization temperature and T_m* - melt-crystallized T_m

percents and forms an eutectic temperature (EDGAR and ELLERY, 1952, SONNERSKOG, 1956 and IZARD, 1952) at this composition and after that the T_m increases with composition of PrG(1,3). Similarly, for cooling operation, i.e., crystallization, the crystallization temperature (T_c) reaches a minimum at 37.2 mole percents of PrG(1,3) and then starts increasing. Further investigations on these copolyesters and PET/PrG(1,2), DMT/EG/PrG(1,3) and DMT/EG/PrG(1,2) are in progress.

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