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Preparation and Study of Terephthalate Copolyester of Ethylene Glycol and Butane-1,4-diol

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SUMMARY

Random terephthalate copolyesters of ethylene glycol and butane-1,4-diol of various compositions were prepared by trans-esterification of poly(ethylene terephthalate) (PET) with butane-1,4-diol (BD). Proton nuclear magnetic resonance spectroscopy (NMR) was used to elucidate the structure and compositions of copolyesters. The thermal behaviour of the copolyesters were investigated by differential thermal analysis (DTA). Intrinsic viscosities were measured in ortho-chlorophenol at 30°C.

INTRODUCTION

Polymeric materials consisting of more than one component (copolymer) are of great commercial importance (ELIAS, 1975) in the fields of moulding of plastics and fibers. These materials are often stronger and tougher than one component systems. JACKSON and KUHFUSS, 1976, first reported the formation of copolyesters of polyethylene terephalate and p-hydroxybenzoic acid. The structure - property relationships of the copolyesters of two glycols and

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a dicarboxylic acid are understood fairly well and are used widely in the synthesis of polymers with specific properties. In the synthesis of these polymers an excess of glycols was used in the ester - exchange reaction to form a high-molecular-weight polymer. The thermal and physical properties of a copolymer, however, vary with change of composition (EDGAR and HILL, 1952). YAMADERA and MURANO, 1967, developed a technique for quantitatively measuring the composition and sequence distribution in copolyesters of PET by proton NMR spectroscopy. Though there are a few patents in the literature regarding the preparation of PET/BD copolyesters (YOSHIMASA, et al, CA, 81, p 38095 v), we find no systematic study published as papers. We have undertaken to investigate the preparation, characterization and the use of these copolyesters.

EXPERIMENTAL

Reagents and Materials:

PET ($\bar{M}n \simeq 20{,}000$, Indian Organic Chemicals Ltd., Madras) was purified by dissolving in trifluoroacetic acid (TFA), reprecipitated in methanol, filtered, dried and used. TFA (LR, BDH) was used for recording NMR spectra. Butane-1,4-diol (LR, BDH, b.p.227-230°C) and orthochlorophenol (SISCO, b.p. 173-176°C) were distilled and used.

Preparation of the copolyesters:

Random copolyesters of PET with BD were prepared in different molar ratios, the mole ratio of

BD being 25, 40, 50, 60, 75 etc. 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 adding 10 g (0.052 M) of PET and 10 g (0.111 M) of BD to the flask, the system was dried at 100°C for 30 minutes under vacuum with stirring in order to prevent any possible hydrolysis. Subsequently the vessel was purged with purified nitrogen and was placed in a molten eutectic sodium salt bath (220°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 butane-1,4-diol was allowed to occur for 4 hours. Care was taken to see that the stirring was continuous and atmospheric leak into the system was avoided. The polymer melt was then cooled under a steady stream of nitrogen and the stirrer was slowly lifted out of the melt. The head along with the stirrer was removed and the vessel was fitted with an upright condenser with $CaCl_2$ drying tube at the top. The polymer in the vessel was refluxed in chloroform (65-70°C) for about four hours so as to dissolve the contents. The solution was filtered into a cooled, vigorously stirred excess quantity of n-hexane. The precipitated polymer was filtered and dried in vacuum.

Characterization of the copolyesters:

Proton Nuclear Magnetic Resonance Spectroscopy:

The NMR spectra were recorded with a Perkin Elmer (90 MHz) spectrometer, operating at room temperature. Samples for analysis were prepared by dissolving about 0.1 g of the copolyester in 0.5 ml TFA. The areas of the various resonance peaks were determined by integration of the appropriate regions of the spectra.

Viscosity measurements:

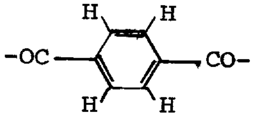
The viscosity measurements were made in orthochlorophenol at 30 ± 0.1°C in an Ubbelohde viscometer with sinter having a solvent flow-time of 274 seconds. Extrapolation methods of HUGGINS, 1942 and KRAEMER, 1938, were used for evaluating the intrinsic viscosities.

Thermal measurements:

A TA - 2000 Mettler DTA system differential thermal analyser was used for investigating the thermal properties of the copolyesters. Samples of 5-10 mg of the powdered polymer were sealed in aluminium pans and crimped empty pan was used as reference and placed in the DTA cell. Nitrogen was used as a purge gas. A heating rate of 10°/min and a chart speed of 10 mm/min were used for all the heating and cooling operations. The chart temperature of the instrument was periodically corrected by a calibration curve constructed by measuring the melting temperatures of lead, tin, indium and benzoic acid. The melting and crystallization temperatures were determined by comparison with the calibration curve.

RESULTS AND DISCUSSION

The chemical shifts of the various protons in the polymer relative to HMDS (Hexamethyl disiloxane) are shown below.

		Chemical shift (ppm)
(i)	$-O-CH_2-CH_2-O-$	4.25
(ii)		7.88
(iii)	$-O-CH_2-(-CH_2-CH_2-)-CH_2-O-$	4.55
	$-CH_2-CH_2-$	1.75

The mole fraction of the butane-1,4-diol in the copolyester was calculated from the NMR peak integrations by means of the equation

$$\text{Mole fraction of BD} = \frac{C}{A + B + C}$$

Where A is the integration height of phenyl proton, B is the integration height of $-OCH_2$ glycol protons and C is the integration height of BD protons. Mole fraction of PET = 1 - mole fraction of BD. The feed compositions and the compositions of PET and BD from the NMR are given in TABLE 1.

TABLE 1

Composition of PET/BD copolyesters and intrinsic viscosities

Polymer sample	Feed composition mole percent		NMR composition mole percent		$[\eta]$ in $O-ClC_6H_4OH$ dl/g
	PET	BD	PET	BD	
P1	75	25	79.0	21.0	0.1065
P2	60	40	71.8	28.2	0.1120
P3	50	50	55.6	44.4	0.0665
P4	40	60	51.3	48.7	0.0590
P5	25	75	48.6	51.4	0.0215

The difference between the monomer feed ratio and the composition by NMR may be due to the loss of some volatile scission products of PET (GO, 1973). Further, the variations of NMR compositions showed that the copolyesters were random copolymers and not alternating or block type.

The DTA data for the copolyesters of PET/BD in different compositions are given in TABLE 2. The melting temperature (T_m) decreases as the BD content increases with the exception in 48.7 mole percent of BD. Similarly the crystllization temperature (T_c) also decreases with the increase of BD content with the exception in 48.7 mole percent of BD. From the melting temperature it is clear that as the BD content is increased the T_m slowly decreases due to the loss of stiffness in the PET units.

TABLE 2

Thermal properties of PET/BD copolyesters

Polymer sample	mole percent of BD	Peak Temperature (°C)		
		T_m	T_c	T_m*
P1	21.0	159.3	126.3	164.8
P2	28.2	155.8	124.8	157.8
P3	44.4	126.3	91.9	130.5
P4	48.7	131.8	102.8	133.3
P5	51.4	89.4	65.1	81.9

T_m - Melting temperature; T_c - Crystallization temperature and T_m* - Melt - Crystallized T_m

TABLE 1 gives the intrinsic viscosity $[\eta]$ for the copolyesters in orthochlorophenol at 30 ± 0.1°C. The values of $[\eta]$ ranges from 0.1120 to 0.0215. That is it decreases with increase of BD content with the exception for P2. Further work is in progress.

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