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Preparation and Study of Some Copolyesters*

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ABSTRACT

Terephthalate unsaturated copolyesters with ethylene glycol and 2-butene-1,4-diol, with ethylene glycol and 2-butyne-1,4-diol, with ethylene glycol and diethylene glycol, and with 2-butyne-1,4-diol were synthesized by trans-esterification reactions. Proton nuclear magnetic resonance spectroscopy was used to elucidate the structures of the copolyesters. The intrinsic viscosities of the copolyesters were measured in *o*-chlorophenol at 30°C. The number-average molecular weights of these copolyesters were determined by using a vapor pressure osmometer. The thermal behaviors of the copolyesters were studied by differential thermal analysis and are discussed in terms of structural differences.

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INTRODUCTION

Unsaturated copolyesters, also called polyester resins, are based on macromolecules with a polyester backbone in which both a saturated acid and an unsaturated acid are condensed with a dihydric alcohol [1]. Birley et al. [2] prepared unsaturated polyesters by employing a two-stage processes: in the first step terephthalic acid was reacted with propylene glycol to form poly(propylene terephthalate) prepolymer which was then reacted with maleic anhydride to give the unsaturated polyester in the second step. The products were characterized [3-5]. We find no published systematic study regarding the preparation and characterization of terephthalate unsaturated copolyesters by condensing a saturated acid, a saturated diol, and an unsaturated diol. We have investigated the preparation and characterization of terephthalate unsaturated copolyesters using the unsaturated diols 2-butene-1,4-diol and 2-butyne-1,4-diol.

EXPERIMENTAL

Reagents and Materials

Dimethyl terephthalate (DMT), obtained from Koch-Light Laboratories Ltd., England, was purified by recrystallization (mp 141°C). Ethylene glycol (LR BDH, bp 198°C), 2-butene-1,4-diol (LR BDH, bp 132°C at 16 mmHg), 2-butyne-1,4-diol (LR BDH, bp 140°C at 10 mmHg), diethylene glycol (LR BDH, bp 245°C), and o-chlorophenol (SISCO, bp 173-176°C) were distilled by standard procedures before use.

Preparation of Unsaturated Copolyesters

The reaction conditions for the preparation of unsaturated copolyesters are listed in Table 1. All the copolyesters were prepared by melt polycondensation. The preparation of DMT/EG/BD1 unsaturated copolyester is described. The polymerization reactor was a 150-mL flask fitted with a special polymerization head containing a leakproof stirrer, a valved nitrogen inlet, and a condensate collector with an air-locked vacuum system. 0.18 mol DMT, 0.09 mol EG, 0.09 mol BD1, 0.025 g zinc acetate, and 0.006 g antimony trioxide were charged into the flask and the system was purged with nitrogen for 15 min and lowered into a constant temperature bath maintained at 175°C and stirred continuously throughout the reaction. Methanol evolution ceased in 3 h, the bath temperature was raised to 275°C, and the pressure was reduced to 1 mmHg and maintained for 3 h. The bath was then removed and the polymer was dissolved in o-chlorophenol and

TABLE 1. Reaction Conditions for Copolyester Preparation^a

Polymer	Feed composition (mol)			Reaction conditions			
				First stage		Second stage (1 mmHg)	
	DMT	EG	X	h	°C	h	°C
D	0.18	0.09	0.09	3.0	175	3.0	275
E	0.18	0.09	0.09	3.5	170	3.0	270
F	0.18	0.09	0.09	3.0	140	3.0	160
G	0.18	-	0.18	3.0	140	3.0	165

^aX = BD1 for D, DEG for E, BD2 for F, and BD2 for G copolyesters, respectively.

precipitated in an excess quantity of ice-cold ethanol, filtered, and dried in vacuum. The polymer was purified by reprecipitation and used for characterization.

Characterization of Copolyesters

The ¹H-NMR spectra were recorded with a Perkin-Elmer R-32 (90 MHz) spectrometer operating at room temperature. Samples for analysis were prepared by dissolving about 0.1 g polymer in 0.5 mL tri-fluoroacetic acid (TFA). The viscosity measurements for all the copolyesters were made in o-chlorophenol at 30 ± 0.1°C in an Ubbelohde viscometer with sinter having a solvent flow time of 274 s. The number-average molecular weight (\bar{M}_n) for all the copolyesters were determined in a Knauer (Berlin) vapor pressure osmometer at 120°C in o-chlorophenol. A TA 2000 Mettler DTA system differential thermal analyzer was used to measure the melting temperature (T_m), heat of fusion (ΔH_f), and entropy of fusion (ΔS_f). Samples of 5-10 mg powder were sealed in an aluminum sample pan and run at 10°/min. The heats of fusion of these copolyesters were determined by comparing the area under the endothermic peak to the area of a standard indium endothermic peak [6, 7].

RESULTS AND DISCUSSION

The unsaturated copolyesters are brownish in color and soluble in organic solvents like chloroform, *o*-chlorophenol, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, and TFA. From the proton NMR spectra of unsaturated copolyesters, the structure of the copolyesters can be visualized. The chemical shifts of various protons present in the polymer relative to HMDS (hexamethyldisiloxane) are shown in Table 2.

Table 3 gives the intrinsic viscosities and number-average molecular weights of the copolyesters. The intrinsic $[\eta]$ viscosity values range from 0.08 to 0.30 dL/g depending upon the comonomer present in the polymer. The molecular weights range from 2000 to 5000. As the intrinsic viscosity increases, the molecular weight also increases in a regular fashion. The low molecular weight is due to degradation during isolation of the polymers. The intrinsic viscosity and the molecular weight of the copolyester prepared without using solvent for isolation is three times higher than the polymer with solvent employed in the preparation.

The thermal properties of the unsaturated copolyesters (the melting temperature, the enthalpy of fusion or heat of fusion, and the entropy of fusion) are given in Table 3. When the unsaturated copolyesters were heated at a rate of 10°/min in a DTA cell, it was found

TABLE 2


Polyester	Unit	Chemical shift, δ ppm
D, E, F, and G		7.85
D, E, and F	$-\text{OCH}_2-\text{CH}_2\text{O}-$	4.50
D	$-\text{OCH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{O}-$	5.70
D	$-\text{OCH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{O}-$	4.70
E	$-\text{OCH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2\text{O}-$	3.90
F and G	$-\text{OCH}_2-\text{C}\equiv\text{C}-\text{CH}_2\text{O}-$	4.72

TABLE 3. Intrinsic Viscosity, Molecular Weight, and Thermal Properties of Copolyesters

Polymer	$[\eta]$, dL/g	\bar{M}_n	T_m , °C	ΔH_f , cal/g	ΔS_f , cal/(deg·mol)
D	0.26	4777	103.0	1.54	2.87
E	0.30	5122	90.0	0.83	1.77
F	0.08	1964	123.0	5.15	8.04
G	0.13	2506	198.0	2.28	2.21

that a sharp endotherm occurred around 90–198°C depending upon the comonomer structure of the copolyesters (Table 3). This endotherm is attributed to the melting of the copolyesters, and the corresponding temperature is the melting temperature of the copolyester (T_m). The presence of flexible ether linkage and alkyl groups in the backbone of DEG lowers the melting temperature of copolyester E (Table 3). The property that has been most extensively investigated in relation to the chemical structure of copolyesters is the melting temperature. Structural elements of unsaturated copolyesters that affect the properties include structure and ratio of acid and glycol components, molecular weight, molecular weight distribution of various repeating units, and type of unsaturation. Further investigations on these copolyesters are in progress.

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