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Synthesis and properties of aromatic copolyesters with different monomer sequences

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Summary

A random aromatic copolyester was prepared from 1:1:1 molar ratio of p-hydroxybenzoic acid, hydroquinone and isophthalic acid. The properties of the polymer were compared with those of the polymer prepared from 4-hydroxyphenyl-4'-hydroxybenzoate and isophthalic acid. These two copolyesters have different monomer sequences, but the same overall compositions. It was found that the latter exhibits much higher melting point and also higher degree of crystallinity than the former. Moreover, their crystal structures seem to be quite different. Both of them are thermotropic.

Introduction

The monomer sequence is a very important factor in controlling the properties of copolymers. There are few studies reporting on the structure-property relationship of copolyesters that have different monomer sequences but of the same overall monomer compositions. While we were studying the properties of a series of thermotropic aromatic copolyesters(1-3), we made the interesting observation of a very strong dependence on monomer sequence of the crystal structure and thermal properties.

In this study, the sturctural characteristics of a random copolyester (sR-IPA 50) prepared from 1:1:1 molar ratio of p-hydroxybenzoic acid(HBA), hydroquinone(HQ) and isophthalic acid(IPA) are compared with those of the polymer(sO-IPA 50) prepared from 4-hydroxyphenyl-4'-hydroxybenzoate and IPA. Since the dimeric diol monomer, 4-hydroxyphenyl-4'-hydroxybenzoate, is not symmetrical, the resulting polymer does not have a strictly ordered monomer sequence. The carboxylate can be reversed and, therefore, three different triad sequence of HQ-IPA-HBA, HQ-IPA-HQ, and HBA-IPA-HBA can be considered. But IPA is every third unit and no two or more consecutive HBA units appear along the chain. A solution polymerzation method(4-6) was adopted to synthesize the copolyesters either with a defined order of monomer sequence (refer to the synthetic scheme shown below) or a random monomer sequence.

The crystalline structure of the copolyesters prepared were examined by X-ray diffractometry and thermal properties by differential scanning calorimetry(DSC).

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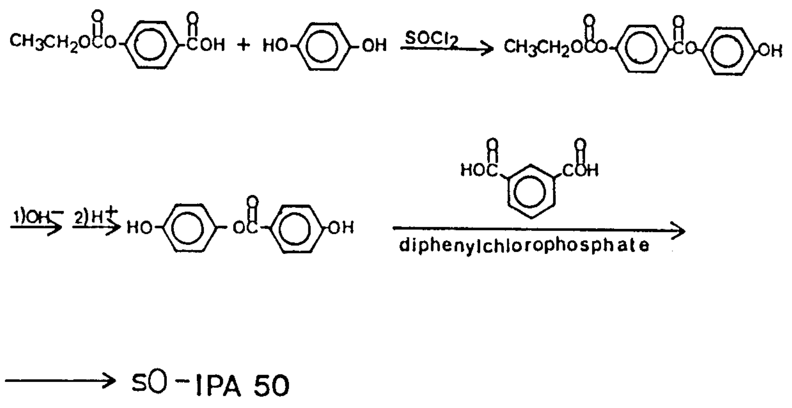

Experimental Section

Synthesis of 4-Hydroxyphenyl-4'-carbethoxybenzoate(7)

A 4-neck flask was purged with N_2, into which thionyl chloride(18.24 ml, 0.250mole) was charged and cooled to 0℃-5℃ with stirring. Pyridine (80.13 ml, 1.00 mole) was added dropwise and the mixture was held at 0-5℃ for 30 minutes. p-Carbethoxybenzoic acid(50.04 g, 0.24 mole) dissolved in 150ml pyridine was added dropwise into the pyridine/thionyl chloride mixture over a period of 60 minutes. In a different flask hydroquinone(79.28 g, 0.72 mole) was dissolved in 200 ml of pyridine and 300 ml of 1,2-dichloroethane. To this solution at room temperature was added dropwise the above prepared p-carbethoxybenzoic acid solution in the thionyl chloride/pyridine mixture. The mixture was allowed to stand overnight. It then was evaporated to dryness in a rotatory evaporator and washed with distilled water and afterwards with a dilute $NaHCO_3$ solution. Finally, the product was washed with distilled water several times. The resulting product was recrystallized from a water/acetone mixed solvent (yield, 66 % ; melting point, 134.5℃).

Synthesis of 4-Hydroxyphenyl-4'-hydroxybenzoate

The above prepared 4-hydroxyphenyl-4'-carbethoxybenzoate(75.05 g, 0.25 mole) was dissolved in 700 ml of dimethylformamide. A separately prepared NaOH solution(20.0 g dissolved in 200 ml of water) was added to the above solution over a period of 3 hours at room temperature. The reaction was allowed to continue at this temperature for 1 hour. Then the reaction mixture was acidified with 1 M HCl and the crude product was collected on a filter. The product was washed with distilled water and recrystallized from an ethanol/water mixture (yield, 31%; melting point, 282.5℃)(8). Elemental Analysis, Caculated; C,68.57; H,4.03 %. Observed; C,68.63; H,4.10 %.

Polymer Preparation

A solution of isophthalic acid(16.610 g, 0.100 mole) dissolved in 100 ml of dry pyridine was placed in a 3-neck flask which had been purged with N_2. To the solution diphenylchlorophosphate(53.89 ml, 0.260 mole) and 100 ml of 1,1,2,2-tetrachloroethane were added and heated to 100℃. The reaction was allowed to proceed at this temperature for 40 minutes. In a separate flask, 4-hydroxyphenyl-4'-hydroxybenzoate(23.022 g, 0.100 mole) was dissolved in 60 ml of pyridine at room temperature and the solution was added dropwise to the above isophthalic acid solution over a period of 5 minutes. The reaction was proceeded for 3 hours at 107℃. The reaction mixture then was cooled to room temperature. The precipitate (sO-IPA 50) was collected on a filter, washed first with methanol and then with distilled water(7). The preparation procedures of the random copolyester(sR-IPA 50) and the two homopolymers, poly(p-oxybenzoate)(PHBA) and poly(p-phenyleneisophthalate)(PHI), were the same as the one described above.

Characterization

Solution viscosities were measured at 30℃ using a Cannon-Ubbelohde viscometer on a 0.1 g/100 ml solution in a p-chlorophenol/pentafluorophenol/chloroform(3:3:4 by volume) mixture. Thermal transitions were studied under a N_2 atmosphere on a DSC(Perkin-Elmer) instrument at a heating rate of 10℃/min. Optical textures of the melts or quenched melts and thermal behavior were examined on the hot-stage (Mettler FP-5) of a polarizing microscope (Leitz, Orthoplan). X-Ray analysis of the polymer samples were made at room temperature on a diffractometer (D-MAX IIIB, Rigaku) in powder form. Ni-filtered CuKα radition was employed as a radition source.

Results and Discussion

Table 1 compares the general properties of the polymers under discussion. The Tm and the degree of crystallinity of the sO-IPA 50 copolyester are significantly higher than those of the sR-IPA 50 copolyester. Both of sR-IPA 50 and sO-IPA 50 were found to be thermotropic, nematic by their schlieren textures observed on a polarizing microscope. Figure 1 shows the X-ray diffractograms of homopolymers and copolymers derived from isophthalic acid, hydroquinone and p-hydroxybenzoic acid. The diffractogram of the ordered sequence polymer(sO-IPA 50) is quite different from that of random copolymer(sR-IPA 50).

Surprisingly, the former is very similar to that of poly(oxy-1,4-benzoyl) (PHBA). The diffractogram of the random copolymer, however, is not much

Table 1. Comparison of the properties of polyesters

polyester	η (inh) dℓ/g	Tg ℃	Tm ℃	Liquid Crystallinity	Crystallinity %
sR-IPA 50	0.56	125	256	Nematic	19
sO-IPA 50	0.21	95	316	Nematic	30
PHI	0.41	-	297	No	32
PHBA	0.45	329	Decompose before melting		40

different from that of poly(p-phenyleneisophthalate)(PHI) with the exception of the weak diffraction peaks at 2θ of about 20° and 24° . These two peaks appear to be reminicence of PHBA crystal structure.

The d-spacings obtained by X-ray analysis are summerized in Table 2. It is not possible to characterize the exact crystal structure with the diffraction informations available to us. It can, however, still be pointed out that the random copolymer has a more complex X-ray diffraction pattern and its d-spacings are different from those of ordered sequence one. In particular, the ordered sequence polymer has nearly the same d-spacings as those of PHBA(see Figure 1and Table 2). The d-spacing of PHBA obtained by us are practically the same as those observed by Economy et al.(9).

It is rather surprising to find that the copolyester(sO-IPA 50) with a mixed monomer sequence of HBA-IPA-HQ, HBA-IPA-HBA and HQ-IPA-HQ appears to have the same or almost same crystal structure as PHBA which has the

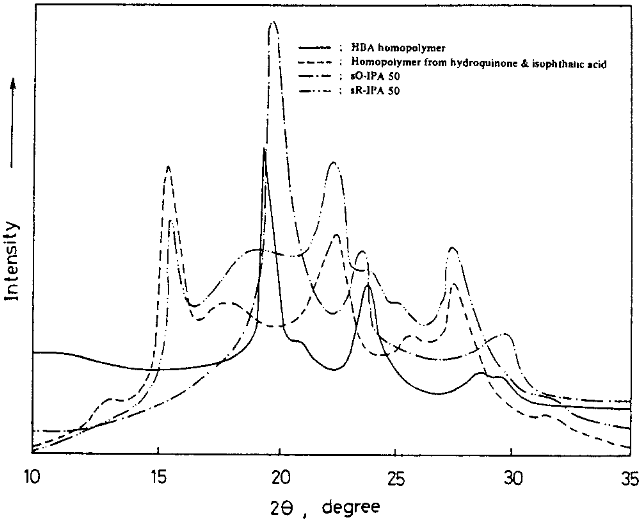

Figure 1. X-ray diffracograms of homo- and copolymers from IPA, HQ and HBA.

Table 2. d-Spacings of copolyesters

polymer	d-spacings		
	strong(Å)	medium(Å)	weak(Å)
PHBA	4.5	5.2	8.4
	3.8		2.6
	3.2		2.3
			2.1
sO-IPA 50	4.5	5.1	8.4
	3.8		2.6
	3.1		2.3
			2.1
sR-IPA 50	5.6	4.9	3.7
	3.9	4.5	3.5
		3.2	
PHI	5.6	5.0	6.8
	3.9	3.4	3.1
		3.2	

sequence of HBA-HBA-HBA. Unfortunately, we are not yet able to analyze ^{1}H- and ^{13}C- NMR spectra of the copolyesters to extract quantitative information on the monomer sequence in sR-IPA 50 and sO-IPA 50.

Acknowledgment

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