Polymer Bulletin 20, 525–530 (1988)

Polymer Bulletin

Dependence of properties of liquid crystalline aromatic copolyesters on monomer sequence-copolyesters derived from terephthalic acid, 2,7-naphthalenediol and p-hydroxybenzoic acid

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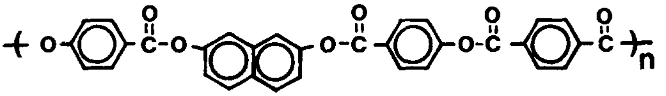
Summary

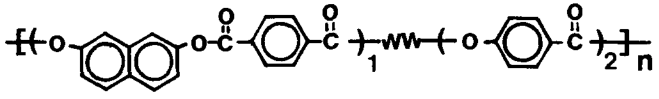
An aromatic copolyester with the ordered sequence of terephthalic acid (TA)-p-hydroxybenzoic acid (HB)-2,7-naphthalenediol (ND)-p-hydroxybenzoic acid (HB) was prepared and its properties were compared with those of the corresponding random copolyester having the same overall monomer composition. Thermal and crystallizing properties of the two polymers are quite different. The former exhibits significantly higher glass transition and melting temperatures than the latter. The former's degree of crystallinity also is much higher than the latter's. Both polymers are thermotropic and form nematic melts.

Introduction

One(1) of our recent papers describes synthesis of two aromatic copolyesters from isophthalic acid, hydroquinone and p-hydroxybenzoic acid. They had the same overall monomer composition, but one was a random copolyester while the other was of ordered sequence. They exhibited significant differences in thermal transition and crystalline properties. As a part of our continuing effort to understand further the importance of comonomer sequence in controlling the properties of aromatic copolyesters, we prepared a copolyester 1 of an ordered sequence and compared its properties with those of a random copolyester 2 having the same overall composition.



1 (ordered)



2 (random)

The copolyester 1 was synthesized by reacting 2,7-naphthalene bis(4-hydroxybenzoate) with terephthalic acid at a low temperature in $SOCl_2$/pyridine mixture and the random copolyester 2 by melt polymerization of 2,7-diacetoxynaphthalene, terephthalic acid and 4-acetoxybenzoic acid in the mole ratio of 1:1:2.

Experimental

Synthesis of 2,7-Naphthylene bis(4-hydroxybenzoate), 5

Benzyl-p-carboxyphenylcarbonate 3 was synthesized from p-hydroxybenzoic acid and benzylchloroformate following the literature method(2). This compound 3(16.32 g, 6.0×10^{-2} mol) was dissolved in $SOCl_2$ and the solution was refluxed for 4 hours, after which the excess $SOCl_2$ was removed by distillation at room temperature under vacuum. The acid chloride formed was used directly in the next step. The acid chloride was dissolved in 30 ml of dry THF, to which added dropwise was a solution of 2,7-naphthalenediol(3.20 g, 2.0×10^{-2} mol) in 40 ml of dry pyridine. The mixture was stirred at room temperature for 30 hours and was poured into acidified cold water. The precipitate of the compound 4 was washed with H_2O and recrystallized from toluene. Yield(8.56 g) was 64%, m.p. 140 °C.

Anal. Found C 71.83%, H 4.17%: Calcd. C 71.86%, H 4.19%.

H-NMR spectrum(DMSO-d_6); δ 5.4(s, 4 H, Ar-CH_2-O), δ 7.4-8.5(m, 24 H, 2,7-naphthalene, 1,4-Ar).

IR spectrum(KBr); $>C=O$ stretching at 1760 cm^{-1} and aromatic $>C=C<$ stretching at 1615 cm^{-1}.

The compound 4(5.0 g, 7.5×10^{-3} mol) was dissolved in 120 ml of THF and was subjected to hydrogenolysis using 5% Pd/C catalyst and H_2 gas(32 psi). After 2 hrs. of reaction, the mixture was filtered collecting the filtrate, which was then evaporated to dryness. The solid residue was dissolved in 1 M NaOH. The product 5 was obtained as white precipitate by acidifying the solution with 1 M HCl. The crude product was recrystallized from an acetone/water mixture(v/v=1/1). Yield(1.56 g) was 52%, m.p. 234 °C.

Anal. Found C 71.95%, H 3.98%; Calcd. C 72.00%, H 4.00%.

H-NMR spectrum (DMSO-d_6); δ 6.8-8.2(m, 14 H, 2,7-naphthalene, 1,4-Ar), δ 10.5(brs, 1 H, OH).

IR spectrum (KBr); O-H stretching at 3400 cm^{-1}, $>C=O$ stretching at 1715 cm^{-1} and aromatic $>C=C<$ stretching at 1615 cm^{-1}.

Preparation of Polymers

The random copolyester was obtained by melt polymerization from 2,7-diacetoxynaphthalene, terephthalic acid and p-acetoxybenzoic acid in the feed mole ratio of 1:1:2. Detailed polymerization method is described in the previous article (3).

In contrast with the random copolymer, the copolymer with an ordered sequence was prepared by a low temperature solution polymerization method. Terephthalic acid (2.08 g, 1.25×10^{-2} mol) was dissolved in a cold mixture of 25 ml of pyridine and 2.0 ml $SOCl_2$. The bisphenol compound 5(5.00 g, 1.25×10^{-2} mol) dissolved separately in 25 ml of pyridine was added to the terephthalic acid solution with vigorous stirring. The mixture was stirred for 24 hours at 80 °C and poured into methanol. The precipitate was thoroughly washed with boiling methanol and dried. Yield(3.78 g) was 57%.

Anal. Found C 72.54%, H 3.39%, Calcd. C 72.45%, H 3.40%.

H-NMR spectrum(CF_3COOD+$CDCl_3$); δ 6.8-8.6(m, 18 H, 2,7-naphthalene, 1,4-Ar).

IR spectrum(KBr); $>C=O$ stretching at 1750 cm^{-1} and aromatic $>C=C<$ stretching at 1615 cm^{-1}.

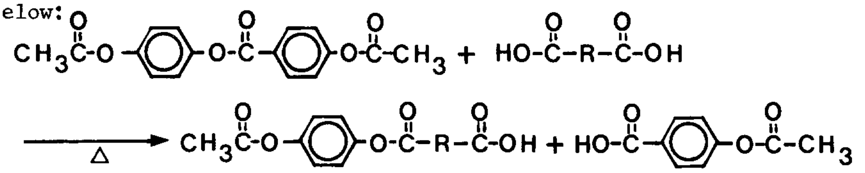
Characterization of Polymers

Elemental analyses were performed by the Analytical Laboratory of the Korea Institute of Chemical Technology. Inherent viscosities of the copolymers were measured at 25 °C by using 0.1 g/dL solution in a pentafluorophenol/p-chlorophenol/chloroform=30/30/40(v/v/v) mixture. The thermal behavior was studied under a N_2 atmosphere on a duPont 910 DSC and a Perkin-Elmer TGS-2 at a heating rate of 10°C/min. The optical texture and thermal behavior of the melts also were examined on a hot-stage (Mettler FP-2) attached to a polarizing microscope (Leitz, Ortholux).

The degree of crystallinity was approximately estimated from the crystalline and the amorphous reflection areas in the wide angle x-ray diffractogram (4) obtained on a JEOL JDX-8D instrument using nickel-filtered Cu-K_α radiation. The scan speed was 4°/min. Quenched samples for x-ray analyses were prepared by immersing the polymer melts in a dry-ice/ acetone bath. Annealing was conducted in a vacuum oven (1 torr) preheated to a desired temperature, and followed by slow cooling to room temperature(ca. 10°C/min) in the oven.

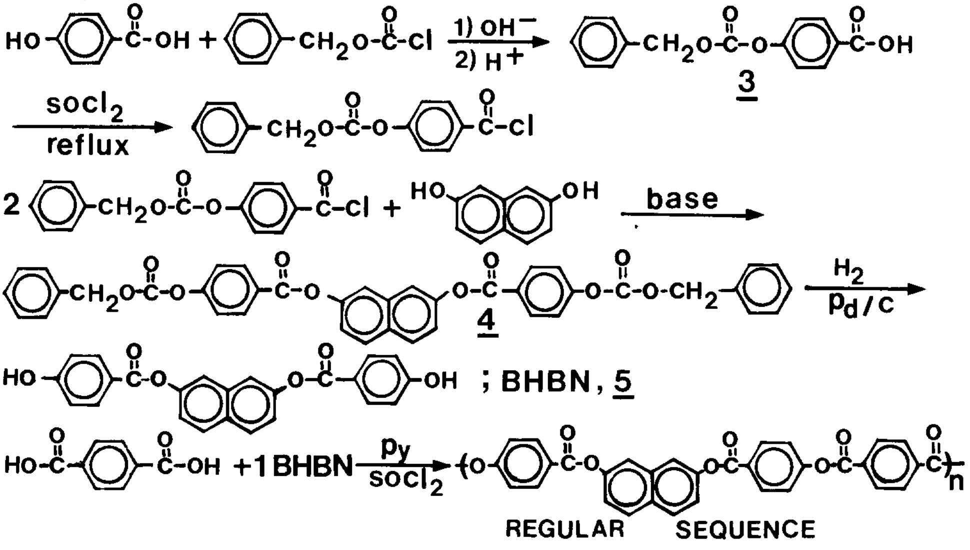
Results and Discussion

There are several reports(2,5,6) that copolyesters having an ordered, regular sequence are significantly different in physical properties than those of random copolyester having the same overall composition. They employed high temperature melt polymerization method with monomers having predesigned comonomer sequence. Under this condition, we, however, can expect occurrence of monomer sequence randomization to an unneglectable extent due to the transesterification in early stage between, for example, a dyad, ester type diol and a dicarboxylic acid. One example of such side reaction is given below:



Similar type interchain reactions also should occur during polymerization between ester bonds of a growing polymer chain and carboxylic chain end of

Synthetic Scheme



another chain. In fact, one recent report describes that such side reactions occur and randomize the sequence (5).

The synthetic method utilized in the preparation of 1, however ensures that the monomer sequence in the resulting copolymer is regular in the order of p-hydroxybenzoic acid(HB)-2,7-naphthalenediol (ND)-p-hydroxybenzoic acid (HB)-terephthalic acid (TA). In order to prepare 1, we first had to synthesize 2,7-bis(4-hydroxybenzoyloxy) naphthalene (BHBN, 5) via the sequence shown in the synthetic scheme.

The direct polycondensation at a low temperature of diol and diacid promoted by $SOCl_2$ and pyridine was earlier reported by Higashi et al. (7). The reaction condition employed in such synthetic method excludes any possibility of sequence randomization during polymerization. On the other hand, the usual melt polymerization method was employed for the synthesis of the random copolyester 2. The mixture of 2,7-diacetoxynaphthalene, terephthalic acid and p-acetoxybenzoic acid in the mole ratio of 1:1:2 was heated to 220°C and then temperature was slowly increased to the final reaction temperature while slowly reducing the pressure. Acetic acid was continuously removed during polymerization.

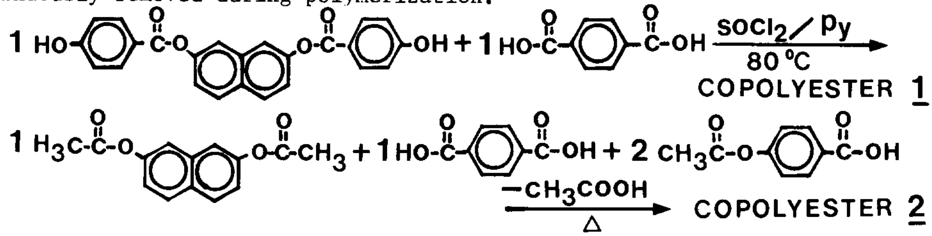


Table 1 summarizes the properties of the two polymers 1 and 2 before and after annealing. The glass transition temperature, Tg, of 1 is only marginally higher than that of 2, while the melting temperature, T_m, of the former is much higher than that of the latter. The former's T_m is 272°C and the latter's is only 191°C. The ordered monomer sequence of 1 definitely favors more efficient molecular packing than the random sequence of 2, which in turn, results in higher T_m.

Figure 1 shows DSC thermograms of the copolyesters before and after annealing. The copolyester 1 was annealed at 235°C and 2 at 270°C for 3 hours. Comparison of the thermograms indicates that, especially before annealing, the copolyester 1 has much higher crystallinity than the latter. The thermogram of 1 clearly reveals a crystallization exotherm at 200°C followed by an endotherm probably for a crystal-to-crystal transition. The first endo-

Table 1. Comparison of the properties of copolyesters 1 and 2

Polymer	Ta, °C	η_{inh}	Tg, °C	T_{k-k}, °C	T_m, °C	D.C., %	Liquid Crystallinity
Before							
annealing 1		0.61	116	225	272	24	nematic
2		0.73	106	-	191	10	nematic
After							
annealing 1	235	ins	116	-	273	38	nematic
2	170	ins	113	181	195	16	nematic

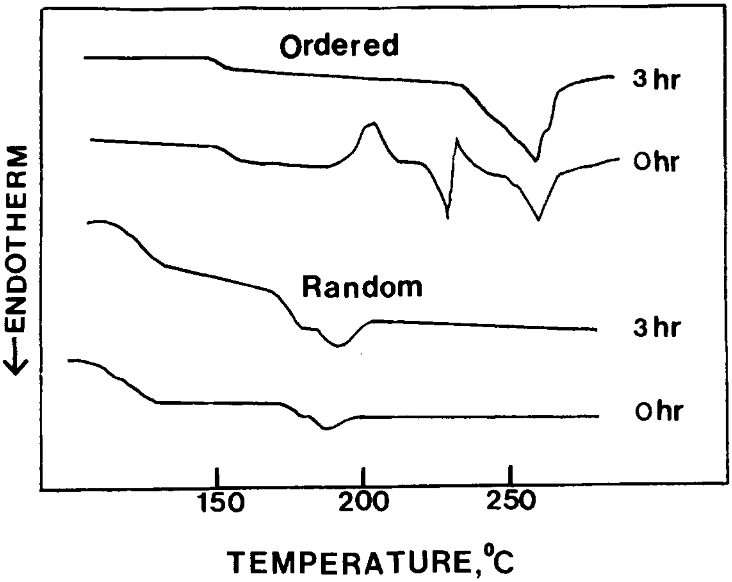


Figure 1. DSC thermograms of polymers 1 and 2 before and after annealing. The lower curves are the thermograms of untreated samples and the upper ones are the corresponding thermograms of annealed polymers.

thermic transition is directly connected to a subsequent exothermic peak at 225°C of the second crystallization process, which then is followed by the final endothermic crystal-to-mesophase transition at 272°C. On the contrary, the thermogram of 2 does not reveal any comparable exothermic crystallization peak(s) implying that 2 is not able to undergo crystallization during DSC scanning. Annealing certainly increases the degree of crystallinity as observed in the growth of the area of melting peaks. The DSC curve of the annealed 1 does not show the lower temperature T_{k-k} endotherm at 225°C present in the DSC curve of the original sample. This is due to the destruction of the lower temperature polymorph during annealing at 235°C that is higher than the T_{k-k}. It is also possible that T_{k-k} corresponds simply to a premelting temperature.

Figure 2 compares the wide angle x-ray diffractograms of 1 and 2 before and after heat-treatment. The copolyester 1 exhibits relatively sharp and strong diffractions at 2θ of 19°(4.7Å), 20°(4.2Å), 25°(3.7Å), a medium diffraction at 2θ at. 32°(2.9Å) and weak diffractions at 2θ of 15°(6.0Å) and 30°(3.1Å). The copolyester 2, however, exhibits a broad diffraction centered at 2θ of 20°(4.5Å). We can see the sensitive dependence of x-ray diffraction patterns on the monomer sequence (8). A rough estimate of the degree of crystallinity of the polymers was made from the area of crystalline and amorphous diffraction following Ruland method (4) and the results are included in Table 1. One can see that the degree of crystallinity is much higher for 1, which is consistent with the thermal behavior described earlier. Another point to be noted is that the extent of increase in crystallinity by annealing is much higher for 1 than 2, indicating again that the former having a regular monomer sequence is much easier to crystallize than the latter having a random sequence.

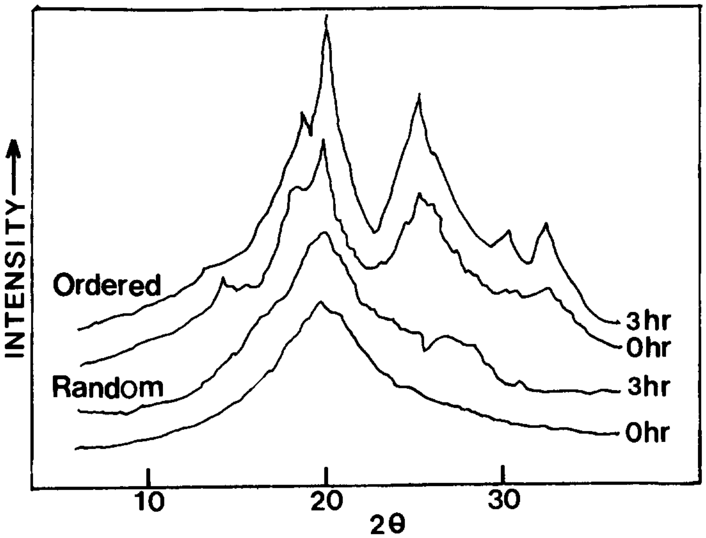


Figure 2. Wide angle x-ray diffractograms of polymers 1 and 2 before and after annealing.

Both polymers form thermotropic liquid crystal phases as judged from the optical texture observed through a polarizing microscope. Their melts exhibited typical nematic texture of threaded Schlieren or polished marble type. Results of further work describing the properties of the similar copolyesters derived from other isomeric naphthalenediols and having an ordered sequence of comonomers will soon be reported in detail. The properties of the corresponding random copolyesters are described in our previous paper (3).

Acknowledgement

Authors greatly acknowledge the support of this work by Asan Foundation. J.-H. Chang wishes to thank the Korea Science and Engineering Foundation for the support.

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Accepted October 15, 1988 S