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Liquid Crystalline Properties of the Copolyesters Prepared from Resorcinol, *p*-Hydroxybenzoic Acid, and Terephthalic Acid

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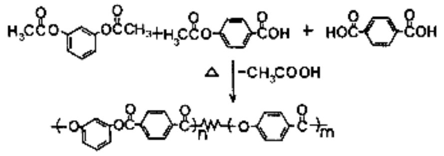
ABSTRACT: A series of aromatic copolyesters was prepared in melts from 1,3-diacetoxybenzene, terephthalic acid and *p*-acetoxybenzoic acid, and the copolyesters' liquid crystalline and other properties were investigated. The compositions containing more than 65 mol% the *p*-oxybenzoyl (POB) unit exhibited thermotropic behavior, whereas those with less than 40 mol% the POB structure were not thermotropic. The copolyesters with an intermediate level (50–60 mol%) of POB units showed an interesting, shear flow induced formation of mesophases. The possibility of compositional heterogeneity in the copolyesters was demonstrated by collecting and characterizing insoluble fractions.

KEY WORDS Aromatic Copolyesters / Resorcinol / Terephthalic Acid / *p*-Hydroxybenzoic Acid / Liquid Crystalline / Compositional Heterogeneity / Shear Induction /

The structure–property relationships of thermotropic aromatic copolyesters are of commercial and academic interest. A few thermotropic aromatic copolyesters of commercial importance are presently available on the market, and they are known to have many distinctive properties such as high modulus, very low mold shrinkage, low melt viscosity, etc. It has been rather well established, both theoretically and experimentally, that a rigid rodlike structure is a prerequisite for a polymer to be liquid crystalline.[1–3] Two representative rigid rodlike polyesters, poly(*p*-oxybenzoate) and poly(*p*-phenyleneterephthalate) are expected to be thermotropic. They, however, have to be structurally modified to make melt processable. Inclusion of unsymmetric substituents on the phenyl rings, modification to include flexible spacers or kinky units in the main chain, and copolymerizations are the most frequently employed approaches to structurally modify these two polyesters, lowering their melting points and rendering them melting processable.[4,5] There are quite a few articles by us,[4–11] and others,[3,12–19] that describe how those modifications change the liquid crystalline and other properties of the resulting polyesters.

In this study we prepared a series of copolyesters consisting of terephthalic acid (TPA), *p*-hydroxybenzoic acid (POB), and resorcinol (RES) units. The last moiety was included to create a kinky structure. The copolyesters were prepared by melt transesterification polymerization from terephthalic acid (TPA), 1,3-diacetoxybenzene (RD), and *p*-acetoxybenzoic acid (ABA).



The mol% of the POB moiety, *m*, in the copolyesters was varied: 0%, 16%, 31%, 53%, 63%, 70%, 79%, and 86%. The polymers' thermal, rheological and liquid crystalline properties were studied. Each copolyester is named mR-RES X; *m* denotes melt polymerization, R random copolyester, RES resorcinol as a bent monomer and X mol% of POB unit contained in the copolyester. For example, mR-RES 70 contains 70 mol% of *p*-oxybenzoyl structure in the chain. A preliminary report was presented earlier.[20]

EXPERIMENTAL

Materials

p-Hydroxybenzoic acid, resorcinol, and terephthalic acid used were of reagent grade. *p*-Hydroxybenzoic acid and resorcinol were acetylated in excess boiling acetic anhydride solutions for 4 h[21] and were purified by recrystallization from acetic acid and by vacuum distillation. The purity was checked by TLC, NMR, and IR spectroscopy. Other chemicals were of reagent grade and used without further purification.

Polymerization

The copolyesters were prepared in melts from RD, TPA, and ABA. The composition of the copolyesters was varied by changing the mol fraction of ABA. The molar ratio of RD to TPA was kept constant at unity. A typical polymerization method used for the preparation of mR-RES 70 is as follows: In a 2 gallon autoclave equipped with a condenser, an agitator, a nitrogen purge line and torque (kW) measuring and recording devices, 215.52 g (1.11 mol) of resorcinol diacetate, 339.93 g (2.22 mol) of *p*-acetoxybenzoic acid, 184.55 g (1.11 mol) of terephthalic acid and 30 ml of acetic anhydride were charged. The reactor was purged with dry nitrogen to expel oxygen.

The polymerization was conducted in two stages. In the first stage of reaction with nitrogen purging, the temperature of the mixture was raised to 200°C over an hour and then it was further raised to 240°C in a 50 min with continued nitrogen purging. The temperature of the reaction mixture was maintained at 240°C until most of the acetic acid was evolved. Throughout this operation stirring was maintained at 200 rpm. In the second stage, a vacuum was applied, reducing the pressure gradually from one atmosphere to 0.1 Torr while the temperature of the mixture was raised from 240°C to 295°C. The stirring rate was reduced to 50 rpm. The extent of the reaction was followed by observing readings on the torque meter (Figure 1). At the end of the polymerization, the polymer formed was extruded into water and cut into chips. A large scale polymerization (40 kg/Batch) also was conducted, following the same procedure, for the preparation of mR-RES 70.

Characterization

Melting points of the monomers and intermediates were measured on a DSC (Perkin-Elmer, DSC-2) or on a Fisher-Johns melting point apparatus. Elemental analysis was performed by the Analytical Service Department of the Korea Research Institute of Chemical Technology. To determine the compositions of the copolyesters, the polymers were hydrolyzed by combining about 50 mg of polymer with 6 g of KOH and 50 ml of ethanol in a 250 ml round bottom flask. The mixture was refluxed for 30 h with stirring. The hydrolyzed products were acidified with 12 M HCl to a pH of 4. The mixture was evaporated to dryness and the residue extracted 3 times with 20 ml of methanol. The total volume was adjusted to 100 ml. The sample was analyzed by high pressure liquid chromatography using a Water's Associate Model-244 HPLC equipped with a UV detector (254 nm) and a Lichrosorb RP-18 $10^1+10^2+10^3$ column. As an elution solvent, a water–methanol (7 : 3 by volume) mixture acidified with 1% acetic acid was used. The volume of sample solution injected was 5 μl and the flow rate of eluent solvent was 1.0

ml min^{-1}.

Solution viscosities of the polymers were measured at 30°C by a Cannon-Ubbelohde viscometer using a *p*-chlorophenol–2,3,4,5,6-pentafluorophenol–chloroform (3 : 3 : 4 by volume) mixture. The concentration of the solution was 0.1 g/100 ml.

$\bar{M}_n$ and $\bar{M}_w$ were measured on a Water's GPC Model-I equipped with a Styragel $10^1+10^2+10^3$ column and differential refractometer detector using polystyrene as a standard. The polymers were dissolved in *o*-chlorophenol–chloroform (1 : 4 by volume) at a concentration of 0.25 wt% and were eluted at room temperature by the same solvent at a rate of 1.0 ml min^{-1}.

Microscopic observations were made on a Leitz Ortholux polarizing microscope equipped with a Mettler FP-5 hot stage. Thermal analyses were performed on a DSC-2 (Perkin-Elmer) instrument at a heating rate of 10°C min^{-1}. The polymers' thermal stability was studied under nitrogen atmosphere on a TGA (Perkin-Elmer TGS-2) at a heating rate of 20°C min^{-1}. Crystalline properties were examined by X-ray diffractometry (D-Max IIIB, Rigaku) using a Ni-filtered Cu-K_α source.

The homogeneity of selected compositions was studied by dissolving the polymers in *o*-chlorophenol at 3 wt% concentration. These solutions were examined on a polarizing light microscope with polars crossed. The undissolved particles were separated by a high speed (3000 rpm) centrifuge and analyzed by NMR spectroscopy, X-ray diffractometry and monomer composition analysis.

The viscoelastic properties were studied on a rheometer, RDS-7700 (Rheometrics Co.).

RESULTS AND DISCUSSION

Melt Viscosity Change During Polymerization

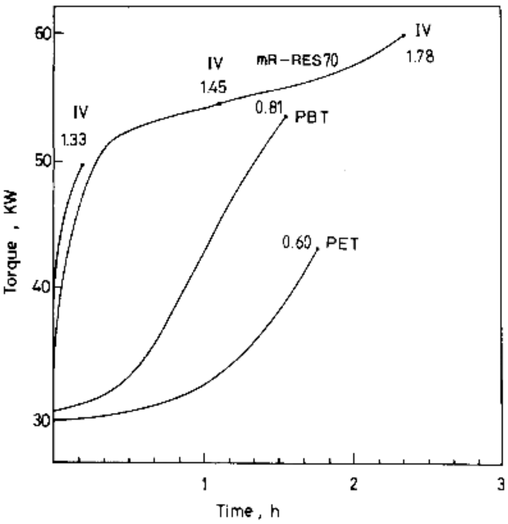


Figure 1. Torque of the agitator in the polymerization reactor *vs.* polymerization time. The numbers indicate the inherent viscosity values at the points indicated. ABA content, 70 mol%; Batch size, 40 kg batch^{-1}; PET, poly(ethylene terephthalate); PBT, poly(butylene terephthalate).

According to Figure 1, the torque encountered by the reactor stirrer in the polymerization of the LC forming composition, an indicator of melt viscosity, initially increases rapidly, but the rate of increase abruptly diminishes after a certain period of polymerization time. The initial rate of viscosity increase is much higher than those observed for isotropic polyesters such as poly(ethylene terephthalate) and poly(butylene terephthalate). The isotropic compositions, however, exhibited a continued exponential increase in melt viscosity with reaction time. We believe that such a difference arises from the relatively rigid nature of LC compositions. Initially, the increase in molecular weight or in chain length of rigid molecules causes a sharp increase in melt viscosity when compared to flexible, isotropic polymers. Then, as the length of the rigid chains continues to grow and reaches a threshold value, the polymer becomes able to form a homogeneous nematic phase. As is well known, the melt viscosity of a nematic state is very shear sensitive and susceptible to shear-thinning. This should result in a diminished rate of increase in the melt viscosity or torque experienced by the stirrer in the

Table I. Properties of copolyesters

Polymer	ABA/mol%		η_{inh}	T_g	T_m	L.C.	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
	Feed	Actual	dl g^{-1}	°C	°C			
mR-RES 0	0.0	0.0	1.00	157	297	No	35,000	5.7
mR-RES 16	18.2	16.0	0.76	157	289	No	Not measured	
mR-RES 31	33.3	31.0	0.76	144	269	No	31,000	6.1
mR-RES 53	50.0	53.4	0.68	142	—	By shear	39,000	6.7
mR-RES 63	60.1	63.1	0.71	142	—	By shear	Not measured	
mR-RES 70	66.7	69.6	1.21	127	—	Yes	57,000	6.5
mR-RES 79	75.0	78.9	1.68	120	—	Yes	Insoluble	
mR-RES 86	82.4	85.5	1.55	161	—	Yes	Insoluble	
mR-RES 100	100		0.45	329	—	—	Insoluble	

latter part of polymerization. On the other hand, the melt viscosity of isotropic polymers is very well known to increase with molecular weight and is much less sensitive on shear. This point will be discussed later.

General Properties, Glass and Melting Transitions and Liquid Crystallinity

The compositions, inherent viscosities, thermal transition temperatures, liquid crystallinity and molecular weights of the polymers are listed in Table I. According to the composition analysis results given in Table I, actual copolymer compositions are fairly close to those of the feed. In general, with the exception of the first two copolymers, mR-RES 16 and mR-RES 21, the copolyesters contain slightly greater levels of *p*-oxybenzoyl (POB) unit than the feeds. Probably a greater loss of terephthalic acid and 1,3-diacetoxybenzene during polymerization causes this. Elemental analyses, however, did not provide firm conclusion for the copolymer compositions, due to the virtual independence of C and H content on composition.

The value of the solution viscosities measured in a *p*-chlorophenol–2,3,4,5,6-pentalfuorophenol–chloroform (3 : 3 : 4 by volume) solution ranges from about 0.5 to 1.7. The $\bar{M}_w$ values ranged from 31000 to 57000. The polydispersity indices were about 6—6.5. Glass transition temperature slowly diminished with POB content and showed minimum at 79 mol%. Afterward, it increased sharply.

The copolyesters with less than 70 mol% POB formed isotropic phases upon melting, judging by the textures of polymer melts observed through a polarizing microscope. The copolyesters containing 53 and 63 mol% POB, *i.e.*, mR-RES 53 and mR-RES 63, however, were observed to form nematic textures under high shear. The compositions containing up to 31 mol% of the POB unit were crystalline and exhibited melting endotherms on DSC thermograms. The DSC melting peaks of the copolyesters containing 53 to 70 mol% POB, however, were very small even after prolonged heat-treatment (at 200 or 220 or 240°C). This implies that these copolyesters are essentially amorphous in nature. X-Ray diffraction studies of the copolyesters further supported these DSC observations. Compositions with POB content higher than 79 mol% are crystalline after annealing at 200°C for 15 h, but their melting transition temperatures could not be observed on a DSC due to their thermal decomposition before reaching T_m. Figure 2 shows a typical amorphous X-ray diffraction pattern of the mR-RES 70 copolyester.

Figure 3 shows an optical texture observed for the shear-induced liquid crystalline phase for mR-RES 53. This picture was taken at 280°C after shearing the polymer melt between a glass slide and cover slip. This texture grad-

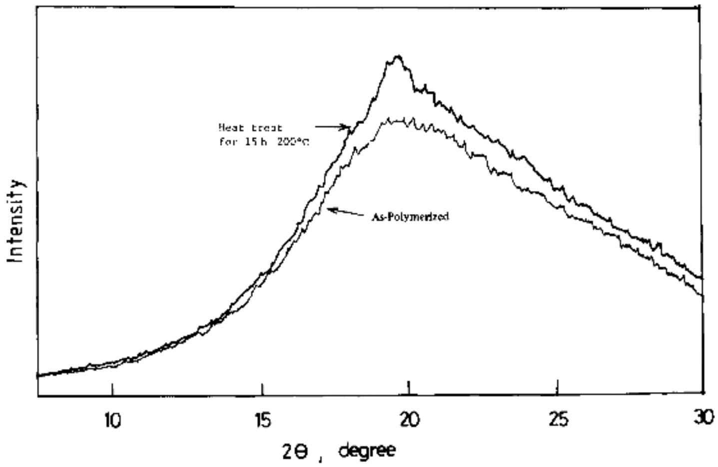


Figure 2. X-Ray diffractogram of mR-RES 70: X-ray source; Cu-K_α Ni-filtered radiation; slit, DS 1°, RS 0.15°, S.S. 1°; voltage, current, 35 kV, 15 mA; scan speed, 1°C min^{-1}.

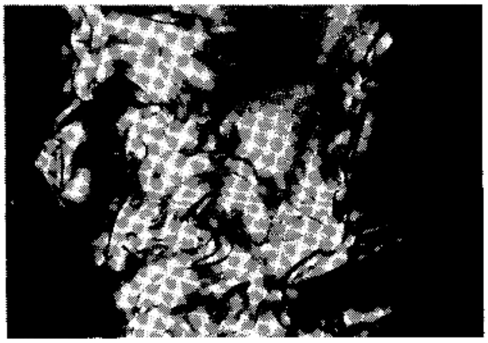


Figure 3. Photomicrograph of shear-induced liquid crystalline phase of mR-RES 53 taken on a cross polarizing microscope at 280°C (magnification 80×).

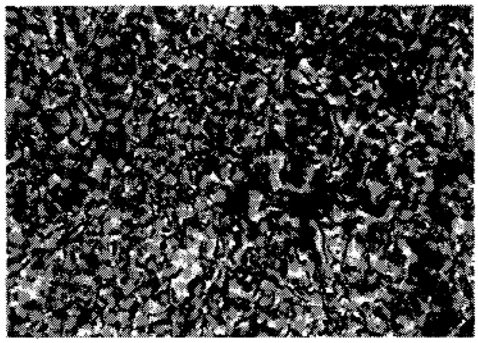


Figure 4. Photomicrograph taken at 290°C of the optical texture observed for the melt of mR-RES 70 (80×).

ually disappeared when shearing was stopped and disappeared completely in 15 min. This clearly indicates the shear induced formation of the anisotropic phase. A similar phenomenon was observed for mR-RES 63. mR-RES 70 and those containing higher levels of ABA structure were able to form nematic phases in quiescent melts (Figure 4).

Analysis of the Insoluble Copolymers

When mR-RES 70 was dissolved in *o*-chlorophenol, insoluble, swollen particles were observed. The amount of insolubles was 4.6% by weight. The insoluble particles, collected by centrifugation from the solution, were found to be highly crystalline (Figure 5), while the bulk polymer was nearly amorphous (Figure 2). The insoluble particles contained a higher level of POB unit (88.5 mol%) than the bulk polymer (69.6 mol%). Moreover, the X-ray diffraction pattern of the insolubles was very similar to that of poly(*p*-oxybenzoate) (PPOB), but with an additional peak at a 2θ of 16° (Figure 5).

The melting point of the insoluble portion determined by DSC was 298°C. This demonstrates that even the insoluble polymer portion is not a homopolymer of *p*-hydroxybenzoic acid. The insoluble polymers probably

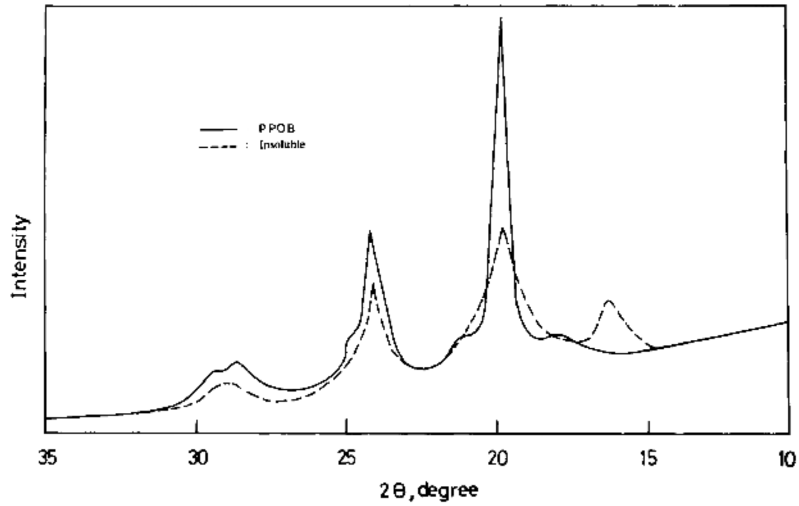


Figure 5. X-Ray diffractogram of insoluble particles collected from mR-RES 70.

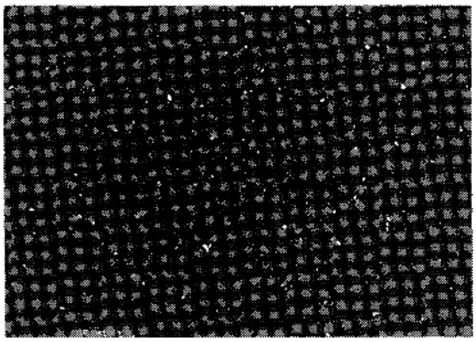


Figure 6. Photomicrograph of the *O*-chlorophenol solution of mR-RES 70 taken with crossed polars. Concentration of the solution was 3% (magnification 80×).

consist primarily of short blocks of POB units along the chains. We believe that there is no possibility of the formation of poly(*p*-oxybenzoate) homopolymer or copolymers containing long blocks of poly(*p*-oxybenzoate) structure in light of the fact that this copolymer is completely soluble in a mixed solvent of an *o*-chlorophenol/chloroform while poly(*p*-oxybenzoate) is not. A 3% solution of mR-RES 70 in *o*-chlorophenol was examined on a polarizing microscope. Figure 6 shows an optical photomicrograph obtained from the *o*-chlorophenol solution. Small, individual and segregated, birefringent particles are evident. These observations further support our contention that this copolyester is not truly homogeneous in composition.

Baird *et al.*[22] studied the injection molded specimen of POB/PET copolyester and found that the skin part contained a higher amount of the POB moiety than the core. They attributed this result to heterogeneous comonomer sequences in the polymer backbone. Gilkey and Caldwell[23] also reported that, when the copolyesters of *meta*- and *para*-hydroxybenzoic acids were dissolved in tetrachloroethane, they found that the copolyester with *para*-content lower than 30 mol% dissolved completely, but that insoluble particles existing for the compositions with higher levels of the *para* isomer. They reported that the insoluble particles consisted of blocks richer in POB. Our observations, together with others, imply that, when the reactivities of the comonomers are not equal, compositional heterogeneity may result from copolymerizations. In short, the copolymer with a very high content of POB unit may not be truly random in monomer sequence.

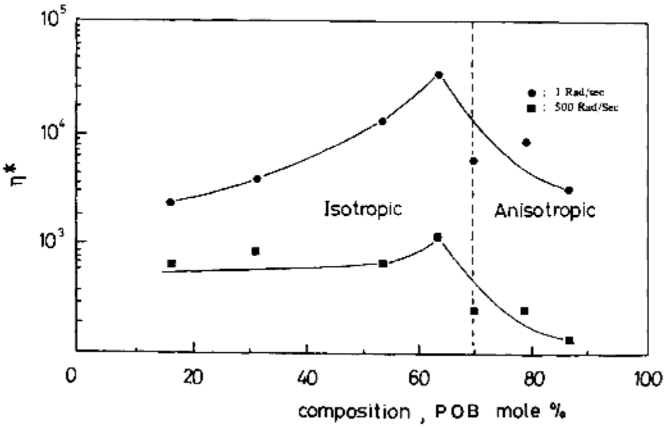


Figure 7. Dependence of complex viscosity on the composition of copolyesters. Temp, 295°C; strain, 15%; gap between disc. & plate, 0.5 mm; apparatus, RDS-7700.

Rheological Properties[24–30]

The complex viscosities of the copolyesters are presented in Figure 7. Melt viscosities of the polymers slowly increase with the content of POB and then abruptly drop at POB content higher than 63 mol%. The viscosity descending point coincides with the composition from which anisotropic melt starts to form. A similar phenomenon was reported earlier by Kuhfuss and Jackson[26] for POB/PET copolymers. Although the inherent viscosities and molecular weights of the liquid crystalline polymers were higher than those of the non-liquid crystalline ones, the complex viscosities of the former under high shear frequency were lower than those of the latter.[26–30] mR-RES 86, in spite of its high η_{inh} value, exhibits a lower complex viscosity. This may be due to the higher degree of molecular order or ease of molecular orientation in the melt of this composition than in the melts of isotropic compositions. Such a difference comes from the fact that molecular chain becomes stiffer and attains longer colinear chain segments as a higher level of POB moiety is incorporated. The experimental point for mR-RES 79 is located in the upper region from the main curve. This may be ascribed partially to its substantially higher molecular weight than others as reflected by its higher η_{inh} value.

CONCLUSIONS

The following conclusions can be drawn from this investigation: Among the series of copolyesters synthesized, only those containing more than 65 mol% of POB units are thermotropic, although those with 53 and 63 mol% are able to form mesophases under shear. The compositions having either low or high amount of POB units are crystalline. But the compositions having a medium level of the POB moiety are amorphous as judged by DSC and X-ray analyses.

The torque of the reactor agitator encountered during polymerization is highly dependent on whether the composition is mesophase-forming or not. As opposed to isotropic compositions which exhibit steady ascent in torque with reaction time, the mesophase-forming ones show an initial steep increase followed by a slower, gentle increase. There is some evidence that the copolyesters containing high overall levels (>65 mol%) of the POB unit are heterogeneous in composition.

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