

Rheological Behaviors of Bisphenol Series Thermotropic Liquid Crystalline Wholly Aromatic Copolyesters

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SYNOPSIS

Rheological experiments were performed on a series of thermotropic liquid crystalline aromatic copolyesters based on terephthalic acid (TPA), isophthalic acid (IPA), *p*-hydroxybenzoic acid (HBA), and a family of bisphenols. The anisotropic melts behaved as non-Newtonian fluids in a shear elongation flow. The non-Newtonian exponents of the melts decreased with increasing the linearity of the bisphenol bridge group, and decreased with increasing the optical anisotropy in the liquid crystalline phase. The cross-section morphologies along the longitudinal direction of the extrudates were surveyed by scanning electronic microscopy (SEM) and discussed with melt-flow rate distributions. The extrudates exhibited skin-core microstructures and oriented fibril structures. The die swells of the extrudates decreased sharply to negligible levels when shear stress was above 1000 Pa.

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INTRODUCTION

Thermotropic liquid crystalline polymers (TLCPs) are receiving more and more attention in both academic and industry fields due to their chemical and physical properties as well as to their potential to produce high performance materials.¹⁻³ To make TLCPs processable, the polymers are usually modified in several ways, such as by copolymerization of different mesogenic monomers and incorporation into a main chain of flexible spacers, bulky side groups, kinks, or crankshafts.⁴⁻⁶ Among these structure-modification approaches, kinks or crankshafts seem to be an effective and feasible way based on copolymerization, which has been chosen for several commercialized TLCPs. *Para*-substituted bisphenols, which is a kind of kink, when used in a limited amount, can change the molecular packing, reduce the melting point of the polymer, and produce liquid crystalline phase or mesophase behavior, with most of mechanical properties retained.^{3,7} Rheological

characterization, on the other hand, is a bridge between polymerization and application of TLCPs. It has been shown that elongation flow is more effective than is shear flow in producing molecular orientation.⁸ The development of orientation in the elongation flow is independent of the rate of elongation.⁹ The so-called skin-core morphologies were reported in the extrudates of a copolymer of ethylene terephthalate (ETP) and *p*-hydroxybenzoic acid (HBA) and in injection-molding specimens of a copolymer of naphthalene diacetate, terephthalic acid (TPA), and HBA.¹⁰⁻¹² Some other melt-deformation phenomena were also observed for specific TLCP systems, such as thixotropy and contraction of the extrudate.^{13,14} Despite those studies, the rheology of TLCPs is not completely known, nor are the papers existing in the literature considered exhaustive.

The purpose of the present investigation was to rheologically characterize a series of thermotropic liquid crystalline wholly aromatic copolyesters. The copolyester family was prepared based on TPA, isophthalic acid (IPA), HBA and one of the following bisphenol monomers: 4,4-dihydroxydiphenyl (BP), 4,4-dihydroxydiphenyl methane (BPM), 4,4-dihydroxydiphenyl propane (BPA), or 4,4-dihydroxydiphenyl sulfone (SDP). The mol ratio of HBA/

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bisphenol/TPA/IPA is 60/20/14/6. The correspondent copolyesters were then termed TIHBP, TIHBPM, TIHBPA, and TIHSDP, respectively. In previous studies, it was shown that the copolyester family exhibited broad nematic mesophase temperature ranges without showing transitions to the isotropic phase. The early stage of the mesophase formation was a one-dimension heterogeneous nucleation. The morphological structures of the copolyesters were studied under different external conditions by various methods.¹⁵

EXPERIMENTAL

The materials were cut in the form of chips and dried carefully in an oven at 120°C under vacuum for 48 h to prevent hydrolytic chain scission. The rheological measurements were carried out using a self-assembled capillary rheometer, which was equipped with 1 and 2 mm-diameter capillaries having a length-to-diameter ratio of 20. The temperature range was 25–500°C with a control precision of 0.50°C. Each copolyester was extruded at a temperature of 35°C above its melting point, which was 331.0, 285.8, 310.0, and 291.9°C for TIHBP, TIHBPM, TIHBPA, and TIHSDP, respectively.¹⁶ The melt-flow behaviors were investigated by extruding the melts at different shear rates and the calculations were performed using a computer program. Die-swell values were measured on the specimens after their solidification. The swelling effect was evaluated as the recoverable strain (S):

$$S = (d - D)/D \quad (1)$$

where d is the diameter of the extrudate, and D , the diameter of the die. The microstructures and the internal profiles of the extrudates were examined using a scanning electron microscope (SMDX-1). The samples had been immersed in acetone for 24 h to remove oligomers and impurities before they were cut and deposited with evaporated gold.

The melt birefringence measurements were performed with a depolarized light intensity analyzer (DLI-2), which was composed mainly of program temperature control sets, light sources, a pair of polarizers, a sample holder, a cooling water system, and a light transmittance recorder. The polymer powder was placed between two microscope cover glasses with a sample thickness around 30 μm . The system was calibrated with a hydroquinone standard and a quartz compensator of known birefringence for both temperature and birefringence accuracy. The

samples were also measured at a temperature of 35°C above their melting points.

RESULTS AND DISCUSSION

The melt birefringences of the copolyesters were compared based on the measurements of melt depolarization ratio (R) as in eq. (2).

$$R = I_{\text{cp}}/I_{\text{pp}} \times 100\% \quad (2)$$

where I_{cp} and I_{pp} represented the light intensities under crossed polarizers and parallel polarizers, respectively. The ratio R , as listed in Table I, represented the percent of anisotropic light transmittance among the total light transmittance through a melt mesophase. The optical anisotropy in the liquid crystalline phase came from the local orientation of the molecular domains. The results in Table I show that $R_{\text{TIHBPA}} < R_{\text{TIHSDP}} < R_{\text{TIHBPM}} < R_{\text{TIHBP}}$. The increasing trend in anisotropy was due to the increase of linearity of the bridge group in the bisphenols. A linear rigid-chain structure has been proved more favorable for the formation of a liquid crystalline phase.³

The bisphenol series copolyesters displayed pronounced shear thinning even in the low shear stress region, as illustrated in Figure 1. The melt also showed viscosity fluctuations suggesting melt structural changes during the shear process, which were often observed for mesophase melts in low shear stress regions.¹⁷

$$\tau_w = \dot{\gamma}^n \quad (3)$$

Equation (3) is the power-law model used to express the relationship between shear stress τ_w and shear rate $\dot{\gamma}$, where n is the power-law exponent of a fluid. When $n = 1$, the fluid was a Newtonian fluid; otherwise, the fluid was a non-Newtonian fluid. It can be seen from the melt-flow curves, as in Figure 2, that there were good linear relationships between shear stress $\log \tau_w$ and shear rate $\log \dot{\gamma}$. The exponent

Table I Melt Depolarization Ratios of the Bisphenol Series Copolyesters

Sample	TIHBP	TIHBPM	TIHBPA	TIHSDP
I_{cp}	9.00	7.00	0.50	2.00
I_{pp}	14.00	14.00	5.00	12.00
R (%)	64.30	50.00	10.00	16.67

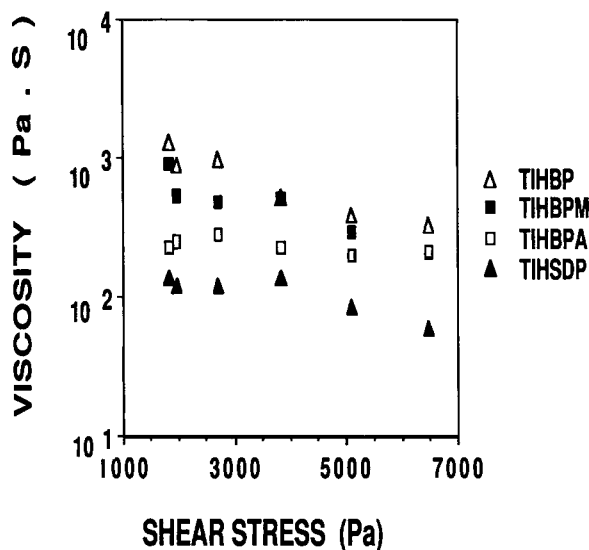


Figure 1 The effect of shear on melt viscosities of the bisphenol series copolyesters.

n , which was related to the rigidity and the stereo effect of molecular chains, was obtained from the slope of each straight line as listed in Table II.

All the n in Table 2 were below 1 and thus indicated that the melts of this series of copolyesters behaved as non-Newtonian fluids. It was interesting that the non-Newtonian exponents of the copolyesters decreased in a trend of $n_{\text{TIHBPA}} < n_{\text{TIHSDP}} < n_{\text{TIHBPM}} < n_{\text{TIHBP}}$, which was in agreement with the increase of linearity of the bridge group in the bisphenols. Since it is known that the optical an-

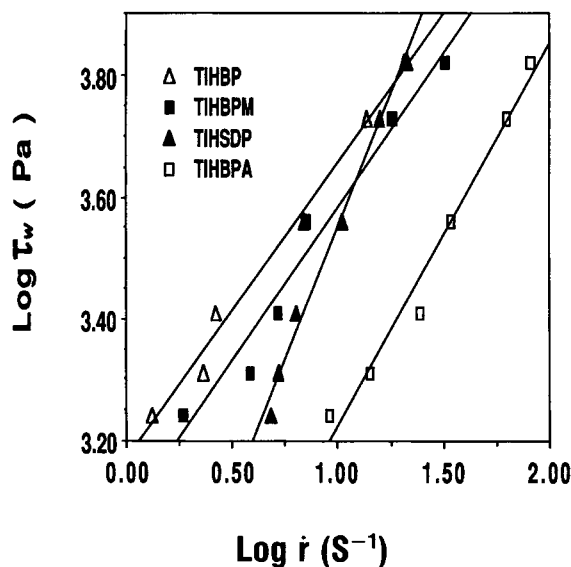


Figure 2 Melt-flow curves of the bisphenol series copolyesters.

Table II Power-law Exponents of the Bisphenol Series Copolyesters

Sample	TIHBP	TIHBPM	TIHBPA	TIHSDP
n	0.4837	0.5039	0.8252	0.6252

isotropy in a mesophase increased with increasing linearity in the molecular chain, this meant that the non-Newtonian exponents decreased with increasing the optical anisotropy in the mesophase.

With the non-Newtonian exponents, it then became possible to investigate the melt flow during extrusion of the copolyesters. According to polymer rheology,¹⁸ the melt-flow velocity V_r and the mean velocity \bar{V} at the die exit are given as the following:

$$V_r = -(G/2K)^{1/n}n/(n+1)R^{(n+1)/n} \times [1 - (r/R)^{(n+1)/n}] \quad (4)$$

$$\bar{V} = -(G/2K)^{1/n}n/(3n+1)R^{(n+1)/n} \quad (5)$$

where G is the pressure gradient in a die, K , the constant for a fluid, R , the radius of the die, and n , the non-Newtonian exponent.

Theoretically, the fluid velocity at the surface of die should be zero, whereas that at the center of die should be the maximum. In the case of the pressure-driven flow in a die, however, the velocity profile of the melt after the die exit was flat. This fact meant that in the regions near the surface of die (where $V_r < \bar{V}$) the melt was stretched along the flow direction and that in the central regions (where $V_r > \bar{V}$) the melt was compressed along the flow direction. By dividing \bar{V} by V_r , Ide and Ophir derived eq. (6),⁸ from which the melt-flow rate distribution curves were plotted as in Figure 3:

$$\bar{V}/V_r = [(n+1)/(3n+1)] \times \{1/[1 - (r/R)^{1/n+1}]\} \quad (6)$$

Supposing that the skin layer came from the stretched fluid and the core layer from the compressed fluid, a boundary between skin and core regions should exist at a critical radius r_c , where $V_r = \bar{V}$. Then, eq. (7) could be inferred at the critical radius. The rates of skin over core in the extrudates of the bisphenol series copolyesters were calculated as listed in Table III.

$$r_c/R = [2n/(3n+1)]^{n/(n+1)} \quad (7)$$

The rates of skin over core increased with the decrease of the non-Newtonian exponents. In fact, due

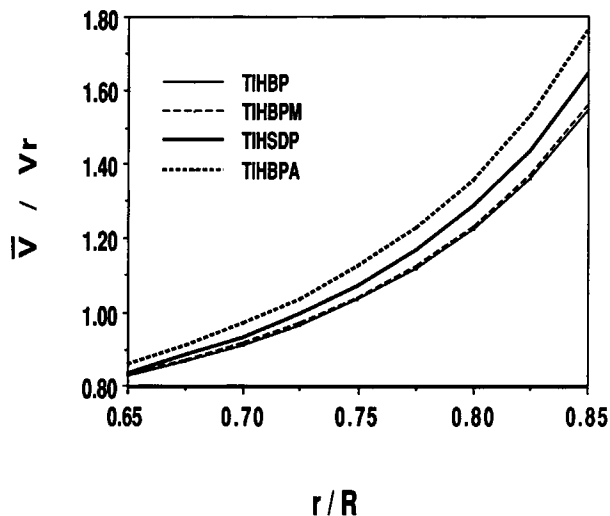


Figure 3 Flow-rate distributions of the bisphenol series copolyesters during melt extrusion.

to the complexity and variety of the flow process, there were some differences between the calculated skin/core rates and the observed rates in the extrudates. Meanwhile, the boundary between skin and core regions was not always distinguishable.

Figure 4 shows the morphology of the longitudinal cross section of an extrudate, where a distinct layer structure was found. The skin layer near the surface experienced mainly elongation flow, which led to a highly oriented and dense structure. The subskin experienced shear and elongation flow that caused a oriented fiber structure. The core regions under the skin regions showed little fibrils and much lower orientation, which may be caused by a compressed and transversal flow. Some traces of a transversal flow could also be found in the core regions.

Considering the effect of stretching or elongation, the melts of the bisphenol copolyesters were then extruded under an constant external drawing force. Figure 5 shows the extrudate profiles of the bisphenol series copolyesters, all of which exhibited oriented fibril structures. These structures indicated that the anisotropic melts in the mesophase were easily oriented during elongation processing and thus provided the basis for high-strength materials.

Table III The Rates of Skin over Core in the Extrudates at the Critical Radius

Sample	TIHBP	TIHBPM	TIHBPA	TIHSDP
r_c/R	0.7385	0.7364	0.7137	0.7259
Rate (%)	35.41	35.80	40.12	37.76

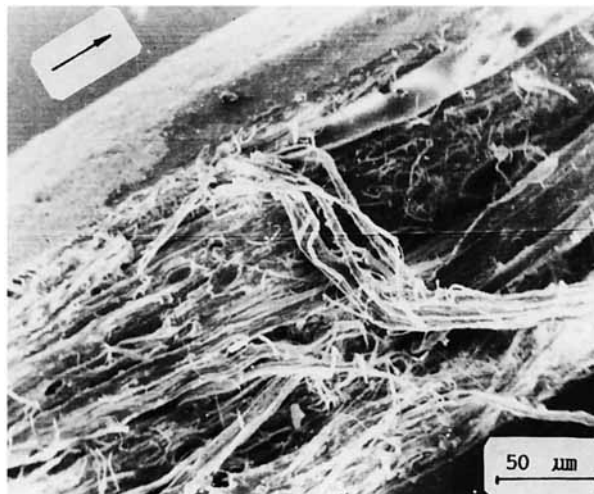


Figure 4 SEM photograph of the longitudinal cross section of an extrudate, TIHBP copolyester sample.

The fibrils of the TIHBP copolyester seemed to be more uniform and oriented than those of the other copolyesters, which was believed to have originated from the highest melt birefringence as measured in Table I. The highest degree of local domain orientation in the mesophase made it easy for TIHBP copolyester to obtain a more uniform and oriented structure than that of the others when a foreign force was applied. The defects on the profiles of the extrudates, such as cavities and droplets, indicated that the melts experienced an incomplete flow.

The effect of the extrudate die swells can be seen in Figure 6, where the die swells decreased sharply to low levels and remained constant when the shear stress was up to 1000 Pa. The phenomenon might implicate that shear strain must reach a threshold value in order to change locally ordered domains, which could have different orientation axes, into a highly oriented chain structure along the shear direction. Such a chain orientation structure once formed was not easy to relax in an extrusion process due to the rigid molecular backbones.

CONCLUSION

The melt depolarization ratio, which measured the melt birefringence in a mesophase, indicated that the optical anisotropy in the mesophase increased with increasing linearity of the bridge group in the bisphenols. The experimental results for the copolyesters showed that the melts were shear-sensitive even in low shear stress regions and behaved as non-Newtonian fluids. The non-Newtonian exponents

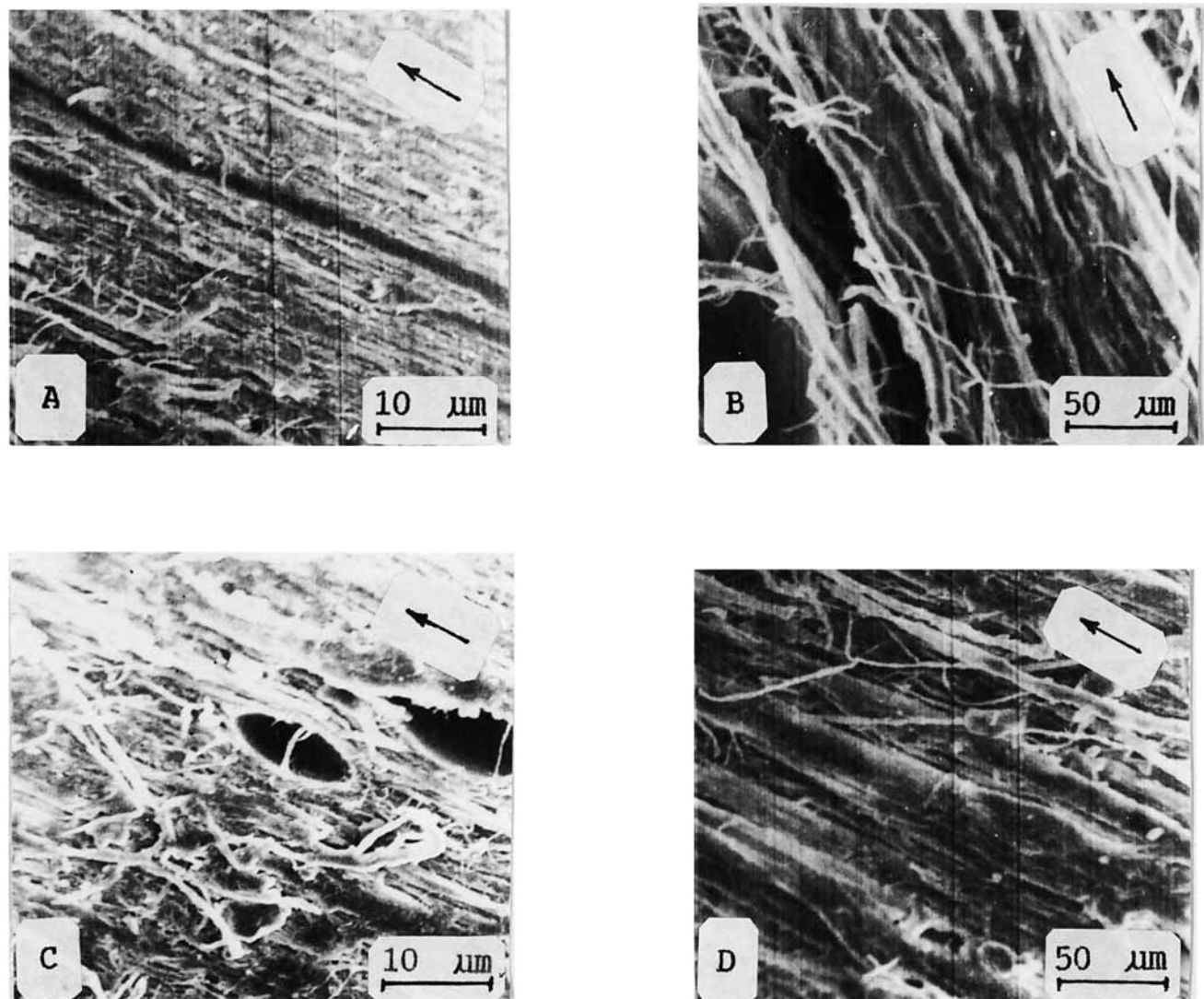


Figure 5 SEM photographs of the longitudinal cross sections of the drawn extrudates: (A) TIHBP; (B) TIHBPM; (C) TIHBPA; (D) TIHSDP.

decreased with increasing linearity of the bridge group in the bisphenols and thus decreased with increasing the optical anisotropy in the mesophase. The flow-rate distributions during extrusion of the melts indicated that the melts in the regions near the die wall were stretched and sheared while the melts in the core regions experienced mainly a compressed and transversal flow. The SEM photograph of the extrudate cross section exhibited a skin-core morphology, where the macromolecules and fibrils

in the skin regions were apparently more oriented than those in the core regions. The oriented fibril structures in the drawn extrudates implicated the potentiality of the bisphenol series copolyesters to produce high-strength materials. The die swells of the extrudates decreased to negligible levels once shear stress was above 1000 Pa, which may be related to the structural changes of the anisotropic melts in the mesophase and the rigidity of the molecular backbones.

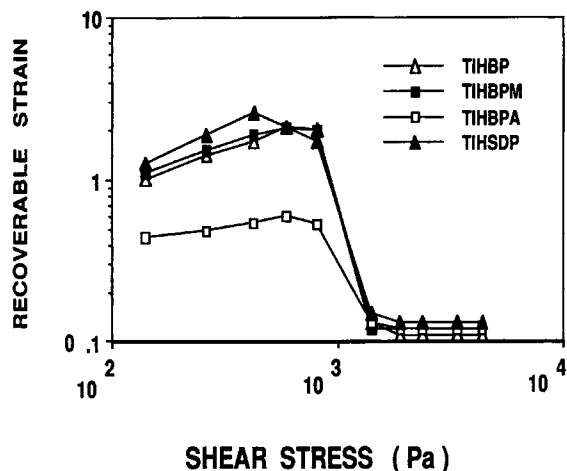


Figure 6 Die swells of the bisphenol series copolyesters during melt extrusion.

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