Extrusion, Fiber Formation, and Characterization of Thermotropic Liquid Crystalline Copolyesters

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ABSTRACT: The flow behavior and the effect of the spinning conditions on the fiber properties and structure of the copolyesters, i.e., samples of copoly(p-hydroxybenzoate–bisphenol A terephthalate), were investigated. The experimental results indicated that the apparent viscosity was affected significantly by shear rate, melt temperature, and p-hydroxybenzoate unit content; and the copolyester melts exhibit highly shear thinning behavior. The fiber modulus increase with the increase in extrusion temperature and draw-down ratio, and the tensile properties could be improved when a high spin draw ratio was used. High birefringence, indicating the presence of mesophase, was observed on a hot-stage polarizing microscope. Scanning electron microscopy revealed that the fibers spun at relatively high temperature had a well-developed, highly oriented fibrillar structure. The fibers spun at low temperatures, however, were poorly oriented and nonfibrillar in character. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1389–1397, 1997

Key words: liquid crystalline copolyesters; extrusion; fiber; oriented structure

INTRODUCTION

Thermotropic aromatic liquid crystalline (LC) polyesters have been investigated and developed as injection-modable, high-performance engineering resins and materials for high strength and high modulus fibers and films. The motivation in this area is based on a unique mixture of intrinsic material properties, such as low melt viscosity, very little mold shrinkage, low thermal expansion coefficient, and excellent mechanical properties, combined with easy and cost-efficient processing techniques.[1] Thermotropic polyesters can be converted into high-strength, high-modulus fibers using conventional melt-spinning equipment. The macroscopic orientation of the domains of the thermotropic melt is easily achieved in a shear flow and/or elongational flow field, and the chain orientation develops very rapidly with increasing draw-down ratios. This unique feature makes LC polyesters the best prospects for high-performance fibers. In particular, with respect to the spinning process, thermotropic LC polymers have clear advantages over the earlier developed lyotropic LC polymers, such as the aromatic polyamides and heterocyclic polybenzoxazoles, which have to be processed from corrosive and aggressive solvents.[2–4]

In recent years, many aromatic polyesters capable of forming anisotropic melts have been described.[5,6] Among thermotropic copolyesters, those based on p-hydroxybenzoic acid (PHBA) are especially attractive. However, the processing and technological applications of this class of polymers have been rarely reported. Some of the problems associated with the study of these systems arise from their high melting points and low solubility in most solvents. For example, the copolyesters containing only a 1,4-phenylene unit, such as Xydar[R], exhibiting unique thermal and mechanical properties, are insoluble in all available solvents,

Table I   Composition, η Values, and Thermal Properties of Copolyesters

Samples	PHBA–BPA–TPA (mol ratio)	PHBA Content (mol %)	η^a (dL/g)	T_g (°C)	T_m (°C)	T_d (°C)
P_1	1 : 2 : 2	20	0.603	180	285	428
P_2	1 : 1 : 1	33.3	0.560	177	280	430
P_3	2 : 1 : 1	50	0.522	188	305	425

^{a} Measured for solutions in p-chlorophenol at 45°C.

and their processing temperature are about 400°C; hence, these polymers are very difficult to be further processed using conventional equipment. The wholly aromatic copolyester from p-acetoxybenzoic acid (PHBA), terephthalic acid (TPA), and acetoxybisphenol A (BPA), called copoly(PHBA–BPA–TPA), is a new type of aromatic copolyester that has an obvious character of the thermotropic liquid crystal.[7–11] Because these three kinds of monomer-forming polymers are produced on a large scale, the copolyester may have the potential to be developed into a new kind of high-technique material, and its synthesis and characterization will have special meaning for future applications. In this article, we report on the preparation and characterization of fibers from copoly(PHBA–BPA–TPA), and the effect of hot drawing on the properties and structure of thermotropic copolyesters fibers has been investigated.

EXPERIMENTAL

Preparation of Copolyester Samples

The wholly aromatic copolyesters from PHBA, TPA, and BPA which have an obvious character of the thermotropic liquid crystal,[9–11] were synthesized in our laboratories.[7,8] The composition, inherent viscosity, and transition temperatures of the copolyesters are listed in Table I. The polymers in pellet form were vacuum dried overnight

at 120°C in order to avoid hydrolytic chain scission at high temperature. Inherent viscosities were determined at 45°C by use of a Ubbelohde viscometer and 0.1 g dL solutions in p-chlorophenol.

Melt Extrusion and Spinning

Extrusion and fiber spinning were carried out in an Instron 3211 capillary rheometer. Fibers were spun from the nematic melt at temperatures of 305, 320, and 330°C, respectively. The length of the capillary was 20 mm and the L/D ratio of 40. The fiber was collected with wind-up equipment placed 1.0 m from the bottom of the spinneret. The spin-draw ratio, V_f/V_o, was determined by measuring the decrease in the cross-sectional diameter of the fiber by microscopy using the relation $V_f/V_o = (D_o/D_f)$,[2] where V_f/V_o is the take-up velocity/average extrusion velocity, and D_o/D_f is the diameter of the die orifice/diameter of fiber at roller.[12]

Fibers were heat treated under vacuum in a glass tube, which was connected to a nitrogen tank. The treatment temperatures are approximately 10–15°C below the melting points of the fiber. Nitrogen gas was introduced into the tube for 1 h before heating was begun.
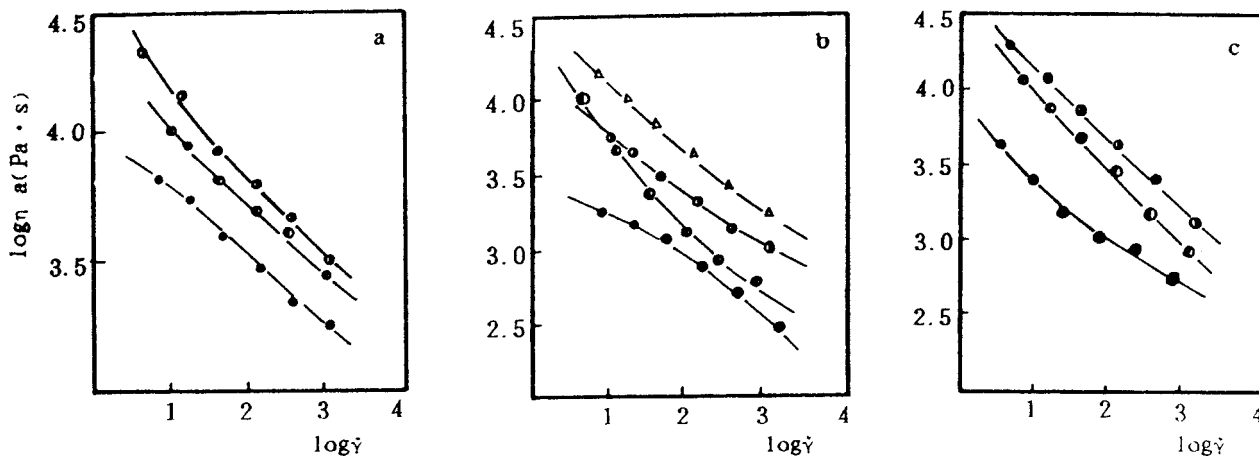
Measurements

Tensile Drawing and Mechanical Testing

The stress–strain curve was measured with an Instron model 1130 by use of a strain rate of 0.5

Table II   Flow Activation Energies ΔE_η (kJ/mol) at Constant Shear Rate $\dot\gamma$ (s^{-1}) of Copolyesters

Samples	ΔE_η (kJ/mol)		
	$10\ s^{-1}$	$100\ s^{-1}$	$1000\ s^{-1}$
P_1	205.1	175.0	109.4
P_2	172.3	141.8	105.3
P_3	121.4	106.0	74.5

Figure 1 Apparent melt viscosity η_a versus shear rate $\dot{\gamma}$ plot for copolyesters (a) P_1, (b) P_2, and (c) P_3 as a function of temperature: ($\triangle$) 295°C; ($\mathbf{\ominus}$) 305°C; ($\mathbf{\oplus}$) 320°C; ($\bullet$) 330°C.

mm min with single fibers of 20 mm in length. The initial modulus M_o was the average of six values calculated from stress–strain curves. Cross-sectional areas were determined with UNION HM-4 microscope.

Hot-Stage Optical Microscopy

A Mettler FP5 microhot stage equipped with a polarizing microscope (Leitz, Ortholux) was employed to examine the texture of samples with temperature.

Scanning Electron Microscopy

A scanning electron microscope Model Hitachi-S520 was used to investigate the morphology or structure of the fibers. The scanning electron microscopy (SEM) study was done on either surface-peeled or fractured samples. The Scott method of peel-back was applied to expose the sample's interior.[13]

RESULTS AND DISCUSSION

Melt Rheological Properties

The apparent viscosities of the copolyesters as a function of the shear rate and as a function of the chain composition at different temperatures were determined as shown in Figure 1. The apparent viscosities are influenced strongly by the shear rate and melt temperature, indicating obvious nonNewtonian behavior of these copolyesters. It can be seen that the viscosity decreases remark-

ably as the temperature increases. Contrary to ordinary thermoplastic polyesters, the highly shear-thinning behavior for the LC copolyester melts was observed in the present experiment. In the microscopic view point, it may be attributed to the orientation of rigid macromolecular chains of the copolyesters in mesomorphic state. During the process of flow, the oriented molecules slide smoothly over each other, dissipating less energy than random and entangled molecules. The other interesting aspect is the relationship between the flow property and the composition of copolyesters. It is clear that the higher the PHBA unit content, the higher the shear thinning effect.

Figure 1 shows that the viscosity of the copolyester melts decreases with increasing temperature. To measure the sensitivity of viscosity to temperature, the flow activation energy ΔE_η is deduced by plotting log η_a against $1/T$ and using the Andrade equation, as follows:

$$\eta_a = A \exp(\Delta E_\eta / RT)$$

where A is a constant, and R is the gas constant. The data are listed Table II. The ΔE_η data indicate that the flow activation energies are higher than those of some thermoplastic polyester melts (for PET, ΔE_η = 54 to 84 kJ/mol). Moreover, the values of ΔE_η are rapidly decreasing when both of the shear rate γ and temperature are increasing. This can be explained also as a result of rigidity of molecular chains. Macromolecules in the nematic state are readily oriented under the action of a shear stress, and the orientation can increase the activation energy of the flowing process.

Table III   Structural Viscosity Index (SVI) of Copoly(PHB–BPA–TPA) Melts

| Samples | T (°C) | SVI | | |
		$100 \ s^{-1}$	$500 \ s^{-1}$	$1000 \ s^{-1}$
P_1	305	2.70	1.14	0.79
P_1	330	2.18	0.93	0.64
P_2	305	3.03	1.26	0.87
P_2	330	2.91	1.20	0.82
P_3	305	3.98	1.64	1.11
P_3	330	3.11	1.28	0.87

The spinnability of the copolyester melts is correlated with the structural viscosity index $\Delta\eta$, which indicates the degree of structurization of polymer melts. Lower values of $\Delta\eta$ are indicative of better spinnability. The parameter $\Delta\eta$ can be defined from the following equation[14,15]:

$$\Delta\eta = -(d \log \eta_a / d\gamma^{1/2}) * 10^2.$$

The results are listed in Table III. The experimental data indicate that a good spinnability of the copolyester melts can be attained at the high temperature and shear rate for the sample with the low content of PHBA unit.

Fiber Tensile Properties

Figure 2 shows typical stress–strain curves of the fibers. The LC fibers have high modulus and low elongation at break. In the course of a tensile break, the fibers undergo an elastic deformation and break at an elongation of only 2–4%. No apparent plastic deformation occurs during the tensile break. In present studies, fibers were spun at three temperatures in the range of 305 to 330°C, taking the spin draw ratio as a variable. Figures 3 and 4 show the dependence of the initial modulus M_o upon the spin drawn ratio V_f/V_o at each temperature. The modulus increases appreciably with V_f/V_o in the region of low drawn ratios, with only a relatively small increase in the modulus for further drawing. Spin drawing is probably necessary in order to optimize fiber properties even in the LC spinning process. Although there is considerable scatter, the data are adequately represented by two curves. The initial moduli are lower for the spinning temperature of 305°C, closer to the melting point T_m, and increase rather slowly with spin draw ratio. However, for spinning temperatures of 320 and 330°C, the initial moduli are

Figure 2 Stress–strain relationships of monofilaments: $V_f/V_o = 189$; 320°C.
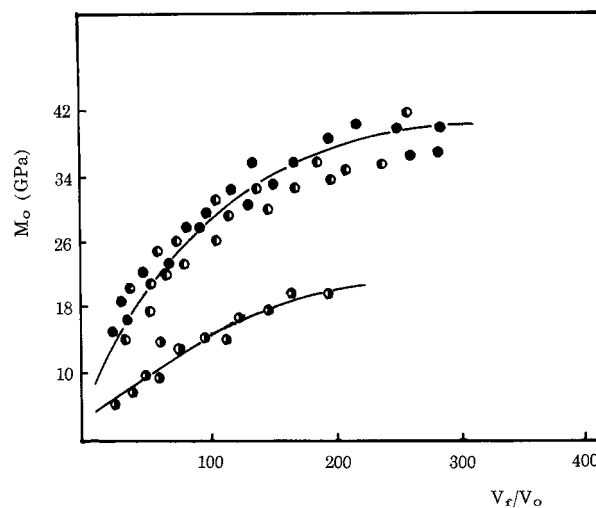
Figure 3 The initial modulus plotted as a function of spin draw ratio for P_2 fibers spun at the following temperatures: (◑) 305°C; (◐) 320°C; (●) 330°C.
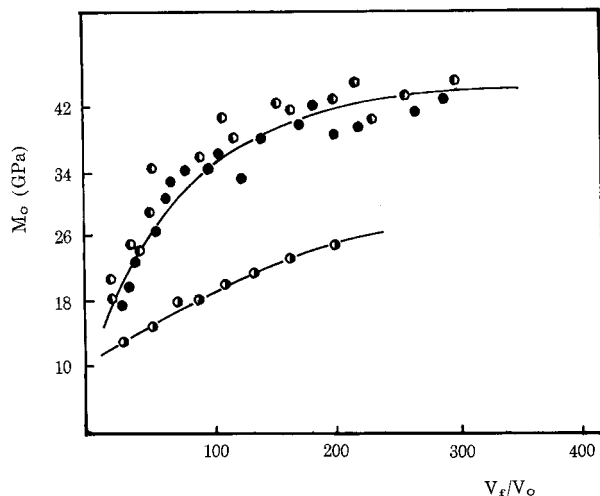
Figure 4 The initial modulus plotted as a function of spin draw ratio for P_3 fibers spun at the following temperatures: (◐) 305°C; (◑) 320°C; (●) 330°C.

Table IV **Effect of Extrusion Temperature on Initial Modulus (GPa) of As-Spun Fibers of Copolyesters**

Samples[a]	Extrusion Temperature (°C)		
	305	320	330
P_1	10.3	25.6	30.8
P_2	14.7	30.6	38.7
P_3	21.2	38.2	42.3

[a] V_f/V_o for P_1 is 208.2; V_f/V_o for P_2 is 192.0; V_f/V_o for P_3 is 198.6.

higher and increase more rapidly with spin drawn ratio up to V_f/V_o of about 100; above the spin drawn ratio, the increase is more gradual. These results can be explained as follows. At very low spin drawn ratios, the fiber has low orientation and low modulus. There are many entanglements. The initial modulus increases with increasing spin drawn ratio due to the development of better orientation. The improvement in M_o becomes slower at a spin drawn ratio of 100. These are due to the fact the chains are now nearly fully extended and parallel, and the number of entanglements is reduced. The V_f/V_o values necessary to obtain high values of the modulus are relatively large compared to those necessary for rigid liquid crystal polymers.[16–18]

The initial modulus of as-spun fibers as a function of spinning temperature are shown in Table IV. P_1 fibers were obtained at a V_f/V_o of 208.2, whereas fibers from P_2 and P_3 were spun at V_f/V_o of 192 and 198.6, respectively. It is seen that the initial moduli of P_1, P_2 and P_3 increase with spinning temperature. The fiber spun at

305°C has a lower value of initial modulus than that spun at 320°C based on the same denier. The increase of the modulus with temperature can be correlated with the easier orientation of the domains due to the lower viscosity. Furthermore, at this temperature, the relaxation times of the LCP samples are very high, however, thus preventing the disorientation of the macromolecules. The load-holding ability of the bent chains is appreciably smaller than that of the extended chains, although not only extended chains but also bent chains in noncrystalline regions make a contribution to load-holding, owing to the high level of chain rigidity. Thus, the fiber P_3 containing fewer BPA units has a relatively high modulus at a given spin drawn ratio, compared with the fibers P_1 and P_2.

Table V shows the effect of heat treatment on initial modulus of the fibers P_3 spun at 320°C with respect to time at 290°C. Heat treatment causes the initial modulus M_o to increase from about 41.2 to 73.9 GPa at a high spin drawn ratio of 201.6; the M_o also increases, but to a lesser extent at a low drawn ratio of 49.5. Fibers with good orientation have a higher modulus after heat treatment than those with poor orientation. The improvement may result from increases in molecular weight and crystallinity without loss of molecular orientation.
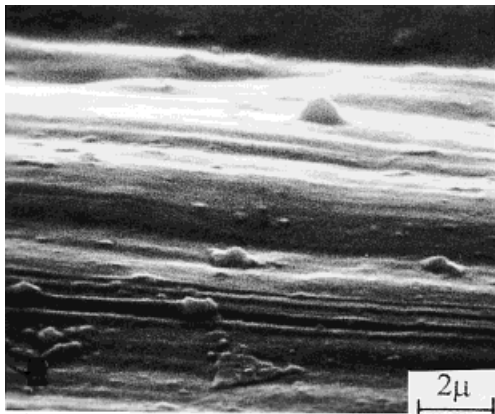
Table V **Initial Modulus (GPa) of Heat-Treated P_3 Fibers as Spun at 320°C**

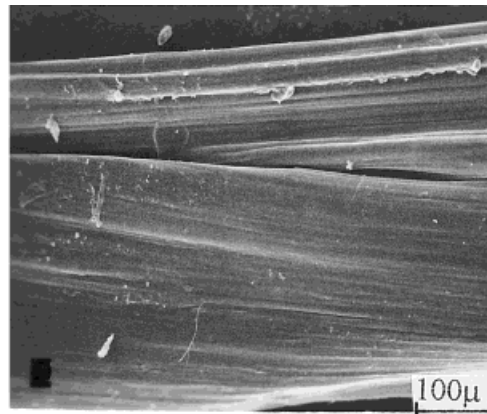| Drawn Ratio (V_f/V_o)	Heat Treatment Time (h)[a]			
	0	2	6	12
49.5	26.2	28.0	31.4	36.3
201.6	41.2	56.5	68.6	73.9

[a] The temperature of heat treatment (T_a) is 290°C.
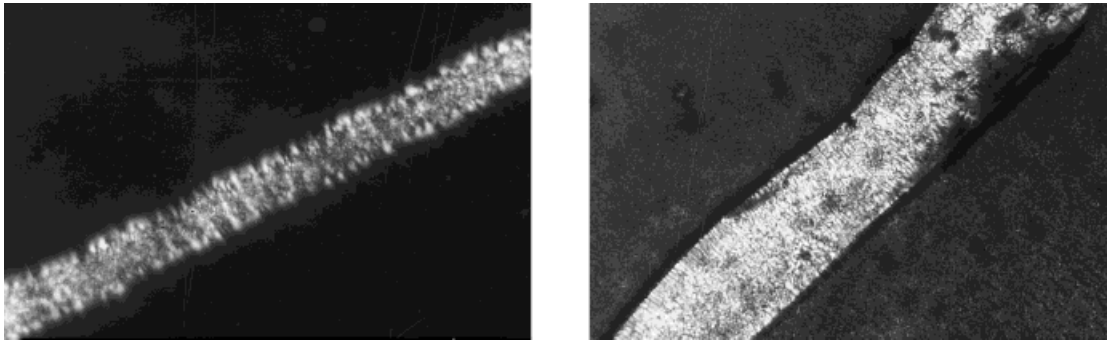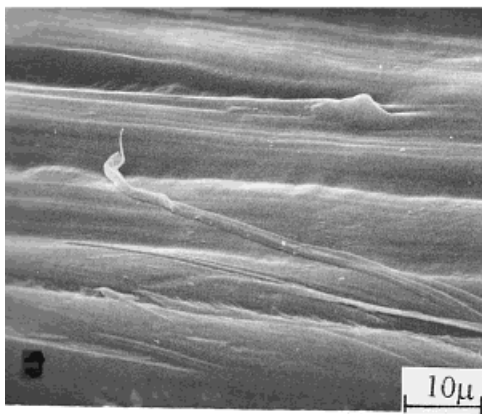
Figure 5   Optical micrographs of as-spun fibers at 330°C.
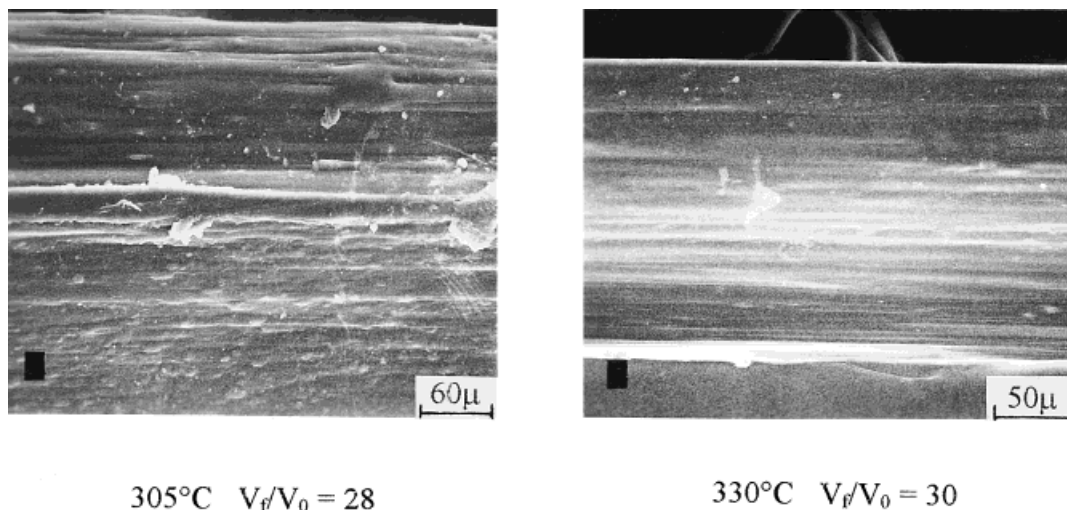

305°C $V_f/V_0 = 5$

305°C $V_f/V_0 = 67$

320°C $V_f/V_0 = 10$

320°C $V_f/V_0 = 90$

Figure 6   SEM photomicrographs of P_2 copolyester fibers spun at temperatures, and draw ratio (V_f/V_o) was indicated. The fibers were chopped parallel to the flow direction at room temperature.

305°C $V_f/V_0 = 28$ 330°C $V_f/V_0 = 30$

Figure 7 SEM photomicrographs of P_3 copolyester fibers spun at temperatures, and draw ratio (V_f/V_o) was indicated. The fibers were chopped parallel to the flow direction at room temperature.

Fiber Morphology and Structure

The texture change with temperature of as-spun PHB–BPA–TPA fiber was examined under a polarizing microscope. When the as-spun fibers of P_2 and P_3 were viewed between crossed polars, unusual melting behavior was observed. Instead of forming an isotropic round droplet, the fiber remained unchanged in both shape and birefringence when temperature was increased to 305°C. High birefringence became more evident on further heating to 330°C onward (Fig. 5). Since the temperature is a critical factor in the formation of a highly oriented LC state from thermotropic polymers, it may be expected that the mechanical properties of a fiber spun from the melt of such a system may also be affected by the processing temperature. The tendency of increasing performance with increasing temperature in mechanical properties of TLCPs has also been found with other polymers.

The internal structure and orientation of the fibers were revealed by scanning electron microscopy (SEM) techniques. The inner parts of the fibers were made accessible by either using the Scott method of peel back[13] to yield longitudinal sections. Figures 6 and 7 show photomicrographs of as-spun fibers obtained at different temperatures and at different drawn down ratios, V_f/V_o. The fibers were cut or nicked near the center with a hand-held razor blade, and the upper half was peeled off. It is seen that the fibers obtained at low temperature have rough, nonuniform, poorly oriented morphology; whereas those extruded at relatively high temperatures consist of highly oriented, smooth fibrils. The average size, shape, and uniformity of fibrils are markedly dependent upon the drawn ratio. The texture formed at a low drawn ratio of 5.0 becomes less oriented and less uniform with rough surfaces as one proceeds from the surface to the center portions of the fibers. Less-deformed particles, approximately 2 or 3 μm in size, are also apparent in (Fig. 6). At a drawn ratio between 40 and 100, the fibrils become highly aligned parallel to the fibers axis, with complete transformation of the dispersed particles into fibrils.

The SEM photographs of fibers fractured after tensile testing are shown in Figure 8. The texture of the fracture surfaces of fibers spun at a high temperature consists of a uniform, axially oriented fibril structure, even when V_f/V_o is low. Fibers spun at low temperature appear to have oriented and unoriented regions in a "jelly roll" structure, and the texture becomes more uniform when the V_f/V_o ratio is increased. Figure 8 also shows higher-magnification SEM micrographs of the fractured surfaces. From these micrographs, it is clear that oriented fibrous textures develop with increases in temperature.

CONCLUSIONS

(1) Rheological measurements showed that the apparent viscosity was affected significantly by shear rate, melt temperature, and p-hydroxybenzoate unit content; and
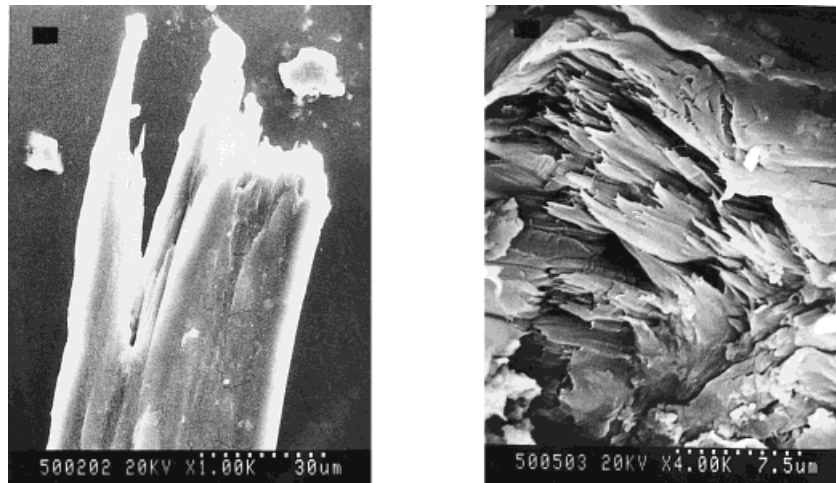
305°C $V_f/V_0 = 181$
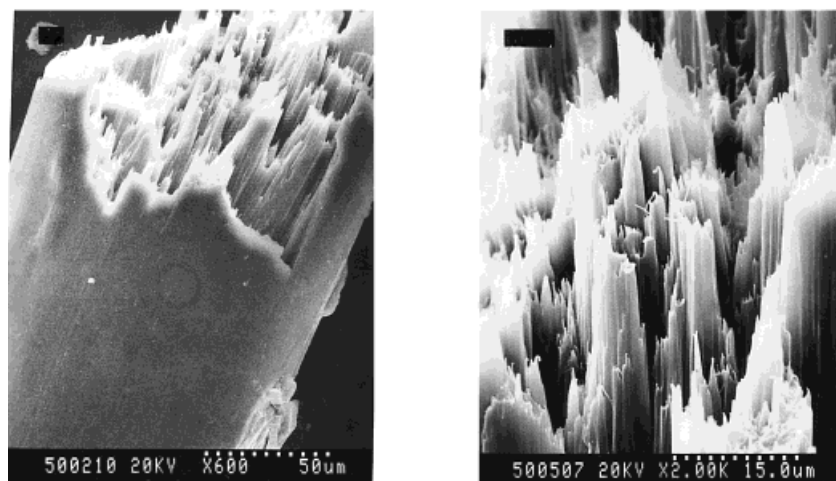
320°C $V_f/V_0 = 43$

Figure 8   SEM photomicrographs of the Instron fractured end of P_3 copolyester fibers showing fibrillar texture. Spinning conditions are indicated in the figures.

the copolyester melts exhibit highly shear thinning behavior. The flow activation energies ΔE_η are in the range of 205.1 to 74.5 kJ mol, depending on the polymer composition, with the shear rate of $10-10^3$ s^{-1}, at temperatures of 295–330°C.

(2) These liquid crystal polyesters can be easily spun at high draw ratios. Spin drawing is probably necessary in order to optimize

fiber properties, even in the LC spinning process. The fiber properties are significantly improved at higher extrusion temperature and at higher draw down ratio. Compared to those rigid liquid crystal polymers, relatively high draw ratios are needed to attain high mechanical strength for the copolyesters.

(3) SEM revealed that the fibers spun at rela-
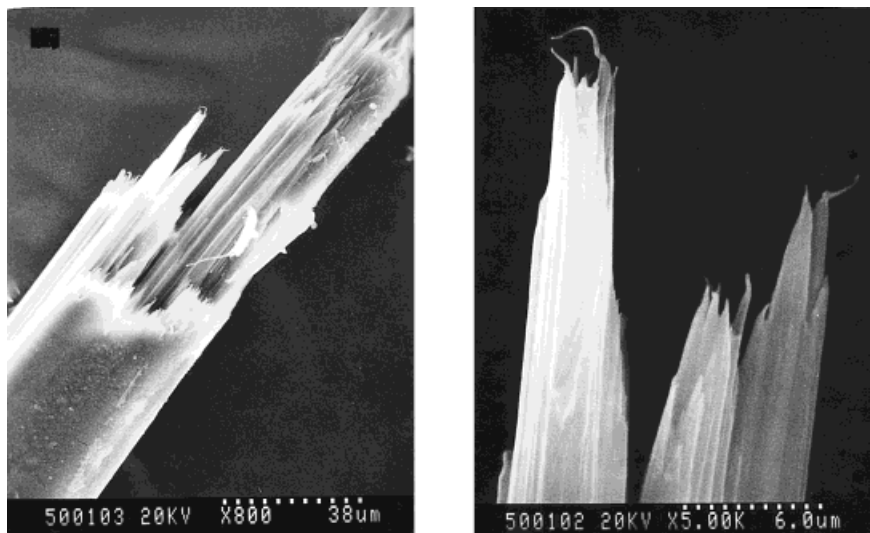
$$330°C \quad V_f/V_0 = 221$$

Figure 8 (*Continued from the previous page*)

tively high temperature had a well-developed, highly oriented fibrillar structure. The fibers spun at low temperatures, however, were poorly oriented and nonfibrillar in character.

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