Preparation and Properties of a Series of Thermotropic Liquid Crystalline Copolyesters

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Synopsis

A series of thermotropic liquid crystalline copolyesters were prepared by melt polymerization using p-hydroxybenzoic acid (HBA) and terephthalic acid (TPA) as mesogenic monomers, poly(ethylene terephthalate) (PET) to give a flexible linkage, and 1,4-dihydroxynaphthalene (1,4-DHN) as a dissymmetrical monomer. The composition of these monomers was varied as a means of manipulating processing temperature, morphology, and properties. Copolyesters with inherent viscosities near 0.7 that were melt processible in the temperature range of 200–300°C were obtained. The glass transition, thermal degradation, and melting temperatures, and crystal size all increased with increasing mesogenic unit content. The heterogeneous structure consisting of a PET-rich phase and a phase rich in mesogenic units was observed by SEM after chemical etching and by X-ray diffraction analysis. Highly anisotropic melts were observed indicating the presence of a nematic mesophase. The thermotropic LC copolyesters exhibit unusually well developed and highly oriented fibrillar structure at the neck area when injection molded. The orientation developed during processing is very similar to those of short-fiber-filled polymer composites. The LC copolyesters commonly have three relaxations in the temperature range of −100–200°C. By dynamic mechanical thermal analysis at 10 Hz, the relaxation temperatures were found to increase with increasing content of mesogenic units and of 1,4-DHN. For the temperature range of 25–120°C, the storage modulus of one of the members of this series were compared with Vectra (Celanese) and with Eastman PHB80, which have almost the same mesogenic contents. This new copolyester maintained its modulus until 80°C, while the modulus of Vectra decreased in two steps: a small depression at 40°C and then a large reduction at 85°C. PHB80 shows a large single transition at 50°C.

INTRODUCTION

Liquid crystalline, LC, polymers may have mesogenic units in the main chain or as side chains. In the former, mesophase formation is due to rigid aromatic components along the polymer backbone.[1,2] In general, polymers composed wholly of rigid backbone units such as poly(p-phenylene terephthalate) or poly(p-benzamide), which are recognized for their very high rigidity and strength,[3,4] melt at very high temperatures or decompose before melting. Polymers like this must be processed from solution which in addition to introducing such complications as solvent removal precludes convenient forming techniques like injection molding.

Recently, thermotropic liquid crystalline polymers having mesogenic units along the main chain have attracted attention as a result of their good mechanical properties and ease of processing.[5,6] To obtain a useful thermotropic

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polymer, careful attention must be given to monomer composition. To reduce the melting point of the intractable homopolymer, monomers must be introduced that disrupt the order or regularity of the backbone. Processing temperature can be lowered by copolymerizing the rigid backbone moieties with controlled amounts of a moiety having flexible linkages and/or dissymmetrical units having bulky side groups or kinks.

Hamb[7,8] found that copolyesters could be prepared by the reaction of poly(ethylene terephthalate) (PET) with 4,4-isopropylidene diphenol diacetate and an equimolar amount of terephthalic acid. At the beginning of the reaction, it was observed that the initial high viscosity rapidly decreased and a clear melt resulted. Continued heating under vacuum resulted in a highly viscous melt. The proposed mechanism was an initial acidolysis of the PET followed by condensation of the carboxylic and acetate end groups to form high molecular weight polymers. In an attempt to enhance the properties of PET, Jackson and Kuhfuss[9] used a similar approach to prepare a series of copolyesters of PET and hydroxybenzoic acid (HBA). They reported that melts of copolyesters having more than 30 mol % HBA exhibited liquid crystalline character. High moduli ($\sim$ 12 GPa) were observed for specimens injection-molded from these materials. Since their introduction, numerous reports describing the properties, processing, and characterization of these materials have appeared.[10,11]

Demartino[12] prepared a series of thermotropic liquid crystalline polyesters based on hydroxybenzoic acid (HBA), 2,6-dihydroxynaphthalene (2,6-DHN), and terephthalic acid (TPA), containing small amounts of either bisphenol A, 2,7-dihydroxy naphthalene (2,7-DHN) or PET units as comonomers. The latter three monomers were investigated as a means of lowering the spinning temperature of the base polymer without sacrificing properties. The copolyesters containing 2.5–5 mol % PET units retained full properties of the base polymer at spinning temperatures 60–80°C below the control.

This paper deals with the synthesis and characterization of a series of thermotropic liquid crystalline copolyesters based on various combinations of poly(ethylene terephthalate) (PET), p-hydroxybenzoic acid (HBA), terephthalic acid (TPA), and 1,4-dihydroxy naphthalene (1,4-DHN) units. This series of materials, prepared by the scheme described by Hamb,[7] permits further examination of the trade-off between high mechanical performance and melt processibility.

EXPERIMENTAL

p-Acetoxybenzoic acid was obtained by refluxing 400 g of HBA, 800 mL of acetic anhydride, and 0.4 g sodium acetate for 2 h. Upon cooling, the white solid was filtered and recrystallized from fresh acetic anhydride. Its melting point was found to be 195°C. 1,4-DHN was prepared in the same manner to give a white solid with melting point of 135°C. TPA and PET with an inherent viscosity of 0.36 dL/g [PET (0.36 IV)] were obtained from industrial sources and used without further purification. Sodium acetate was Fisher reagent grade.

All polymers were prepared in the same manner, utilizing an ester interchange reaction. PET (0.36 IV), TPA, 1,4-DHN, and HBA in the desired proportions plus 0.17 wt % sodium acetate were added to a 250 mL three-neck, round-

bottom flask, equipped with a mechanical stirrer, an argon inlet, and a distillation head/condenser. The reaction system was evacuated and purged with argon four times. The flask was placed in a bath and heated at 250°C for 40 min under a steady flow of argon. The argon flow was halted and a vacuum connection attached after which the temperature was raised to 290°C while reducing the pressure slowly to 45 mm Hg over a 10-min period and then holding the vacuum for 1.5 h. After this reaction period, the vessel temperature was raised to 300–310°C for 30 min under vacuum. Subsequently, the vacuum was released, argon flow returned, and the flask was cooled and the resulting polymer was recovered. The various materials prepared in this way are identified in Table I.

Inherent viscosities were measured at 25°C in trifluoroacetic acid at a polymer concentration of 0.1 g/100 mL. Thermal behavior of as-polymerized samples was examined using a Perkin-Elmer DSC-7 differential scanning calorimeter and a Perkin-Elmer TGA-7 thermal gravimetric analyzer. Initial or first DSC scans were run at 40°C/min to the upper temperature limit where the sample was held isothermally for 30 s before cooling at 40°C/min. A second scan was then made at 10°C/min. All TGA runs were made at 40°C/min. The optical texture was observed using a polarized microscope with a hot stage. The samples were also examined using a Jeol 35C SEM scannings electron microscope at 25 kV after gold sputtering. Infrared spectroscopy was performed using a Digilab FTS-15/90 FTIR spectrometer. Absorption spectra were obtained by melt pressing or solution casting thin films on KBr Pellets. A CS-183 Mini-Max molder was used to make tensile bars (length = 0.314 in. and radius = 0.063 in.) for mechanical testing. X-ray diffraction patterns were obtained by using a diffractometer whose source of radiation was copper with a nickel filter. For LC-0, LC-1, Eastman PHB80, Vectra (a commercial product from Hoechst-Celanese), and PHB60 films compression-molded at 260°C were used. A film of LC-1 was molded at 280°C and as-cast films of LC-2 and LC-4 were also used for X-ray diffraction. Apparent crystal size was calculated using the well-known Scherrer equation from the measured breadth of the X-ray reflections at half maximum. For the compression-molded films, densities were measured at 25°C using a density gradient column based on aqueous solutions of calcium

TABLE I
Description of LC Copolyester Series

Designation	Composition (mol %) PET/TPA/1,4-DHN/HBA	Content of mesogenic monomers	Inherent viscosity[a]	Density[b] (g/cm^3)
LC-0	0/10/10/80	90	—	—
LC-1	10/10/10/70	80	—	1.415
LC-2	20/10/10/60	70	0.71	1.402
LC-3	30/10/10/50	60	0.72	1.397
LC-4	40/10/10/40	50	0.73	1.395
LC-5	10/20/20/50	70	—	1.394
LC-6	25/5/5/65	70	0.69	1.395

[a] Measured at 25°C at C = 0.1 g/100 mL using trifluoroacetic acid as solvent. Units = 100 mL/g.
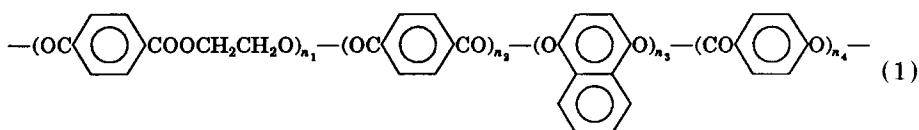
[b] Measured at 25°C using a density gradient column based on calcium nitrate solutions.

nitrate. A Polymer Laboratories DMTA dynamic mechanical thermal analyzer was used to measure dynamic mechanical thermal properties for samples with dimensions 3 × 12.5 × 14 mm.
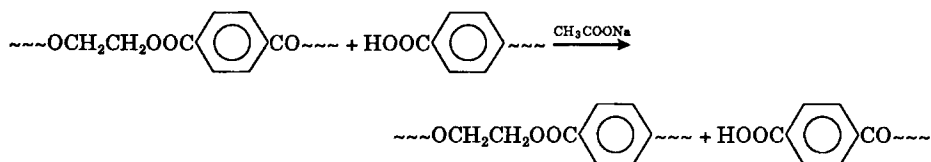
RESULTS AND DISCUSSION

Polymer Preparation

The copolyesters based on PET have sufficient chain flexibility, asymmetric moiety, or a varied mixture of moieties to allow them to melt at or below 300°C. However, these polymers do exhibit the characteristic melt turbidity and fibrous behavior of solidified materials obtained from a flow-oriented nematic mesophase. The series of thermotropic liquid crystalline copolyesters, containing various composition of HBA, TPA, PET, and 1,4-DHN prepared here by melt polymerization can be represented by the following generalized structure:

$$-(OC\text{–}C_6H_4\text{–}COOCH_2CH_2O)_{n_1}-(OC\text{–}C_6H_4\text{–}CO)_{n_2}-(O\text{–}C_6H_4\text{–}O)_{n_3}-(CO\text{–}C_6H_4\text{–}O)_{n_4}- \quad (1)$$

The expected reaction mechanism involves a two-step process to form the following copolyesters:

Acidolysis of PET by PHB/TPA:

$$\sim\sim\sim OCH_2CH_2OOC\text{–}C_6H_4\text{–}CO\sim\sim\sim + HOOC\text{–}C_6H_4\sim\sim\sim \xrightarrow{CH_3COONa}$$

$$\sim\sim\sim OCH_2CH_2OOC\text{–}C_6H_4\sim\sim\sim + HOOC\text{–}C_6H_4\text{–}CO\sim\sim\sim$$

Condensation of the carboxy-terminated and acetate-terminated segments including the self-condensation of HBA to form the high molecular weight copolyesters:

$$\sim\sim\sim COOH + CH_3COO\sim\sim\sim \longrightarrow \sim\sim\sim CO\sim\sim\sim + CH_3COOH$$
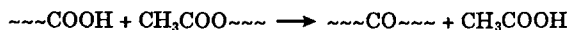
The latter reaction is driven by the removal of volatile acetic acid under vacuum.

The sample designations, compositions, densities and inherent viscosities (IV) are shown in Table I. The highest IV values were obtained when strenuous precautions were taken to eliminate effects of air and moisture on the reaction. LC copolyesters with IV near 0.7 were obtained. However, IV measurements could not be made for LC-0, LC-1, and LC-5, which contain below 10 mol % of PET units, because these materials were not soluble in trifluoroacetic acid. The LC copolyesters become more dense with increasing mesogenic unit content.

FTIR spectra of the various LC copolyesters (see Table I) are shown in Figure 1. The methylene group absorption band at 1460 cm^{-1} and the PET crystal band at 1340 cm^{-1} of LC copolyesters increase as more PET units were used in polymerization. The crystallinity difference between solution cast film samples and as-polymerized samples of LC-2 and LC-4 is evident by comparing
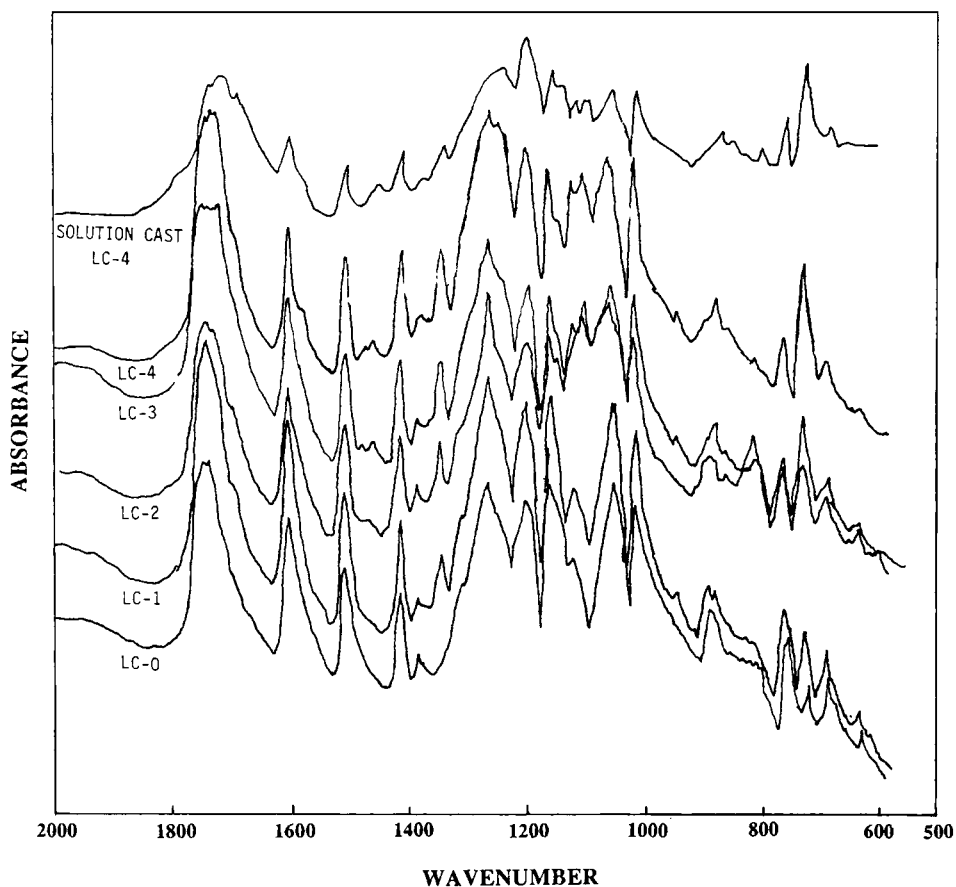
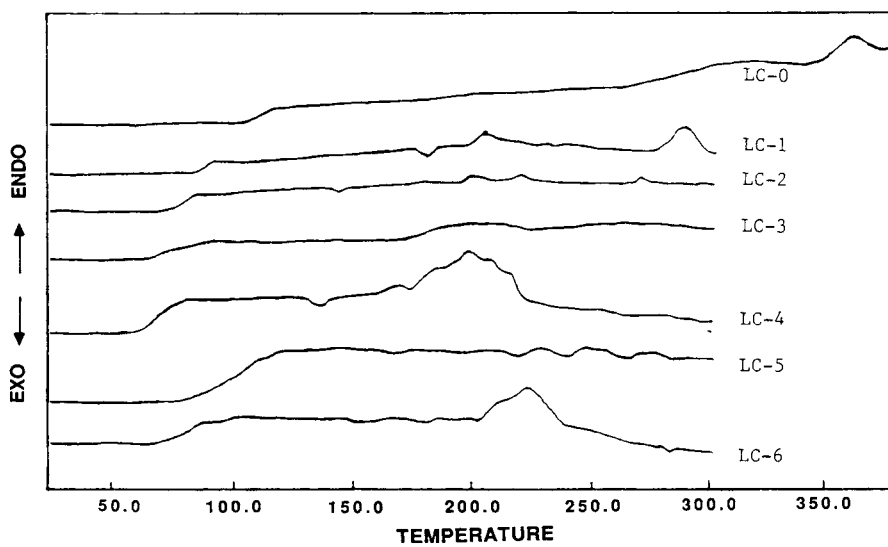Fig. 1.   FTIR Spectra of the LC copolyesters shown in Table I.

Fig. 2.   DSC thermograms for the LC copolyesters. First scans at 40°C/min.
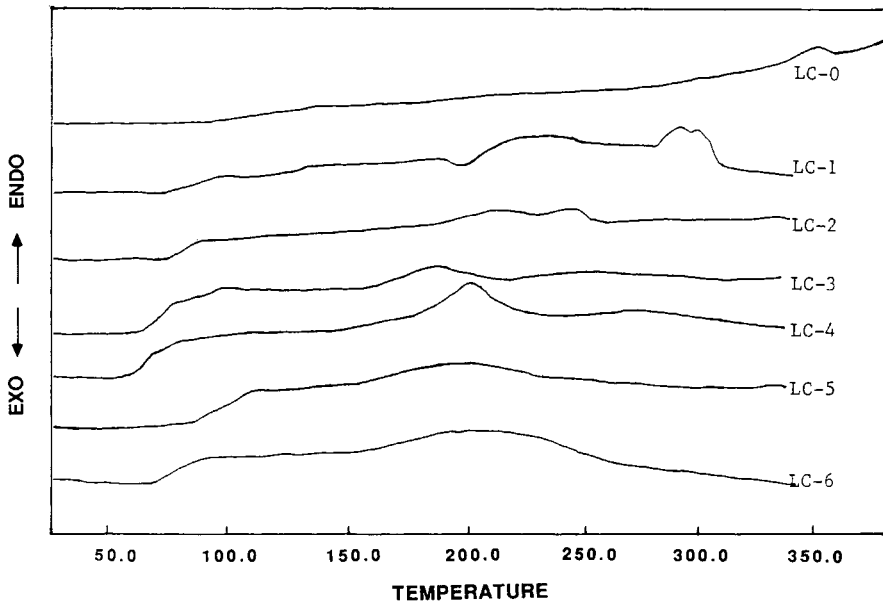
Fig. 3.   DSC thermograms for the LC copolyesters. Second scans 10°C/min.
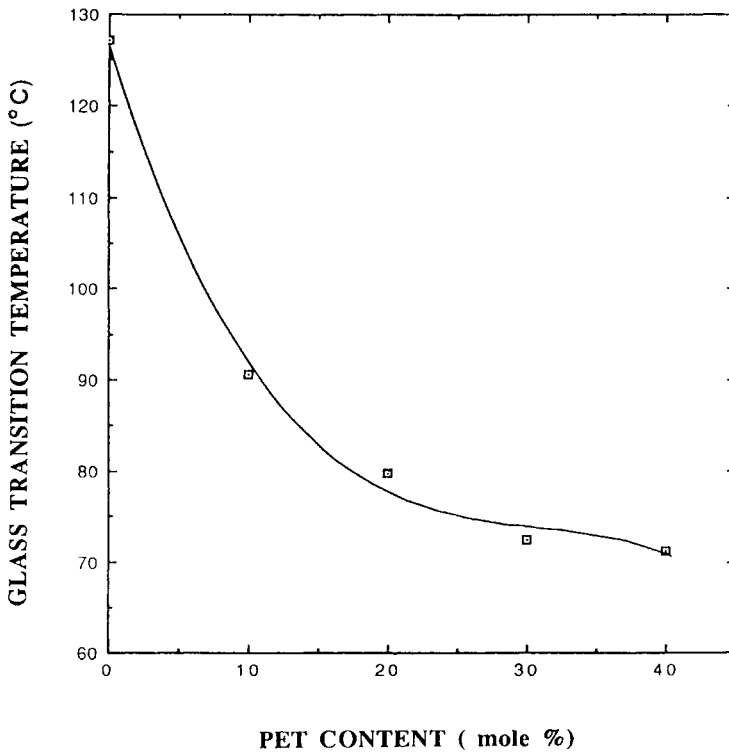

PET CONTENT (mole %)

Fig. 4.   The glass transition temperatures as a function of content of PET units for the LC copolyesters.
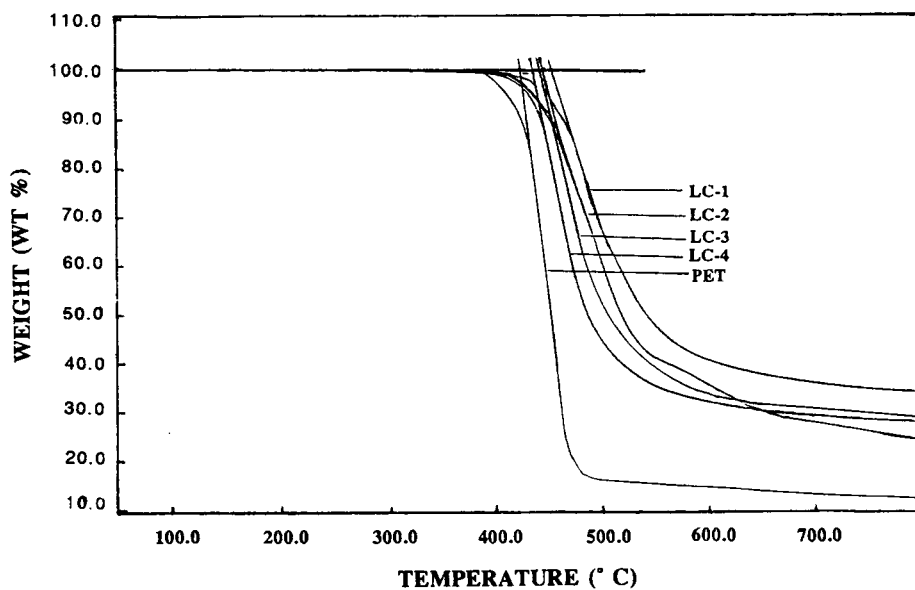
Fig. 5. TGA curves for selected LC copolyesters and PET. Heating rate = 40°C/min.

the sharpness of certain bands in Figure 1. The spectrum of solution cast samples have more broadened peaks indicating amorphous character.

Thermal Characterization

Differential scanning calorimetry was used to obtain information about the thermal transitions of these materials. Selected DSC scans are shown in Figures
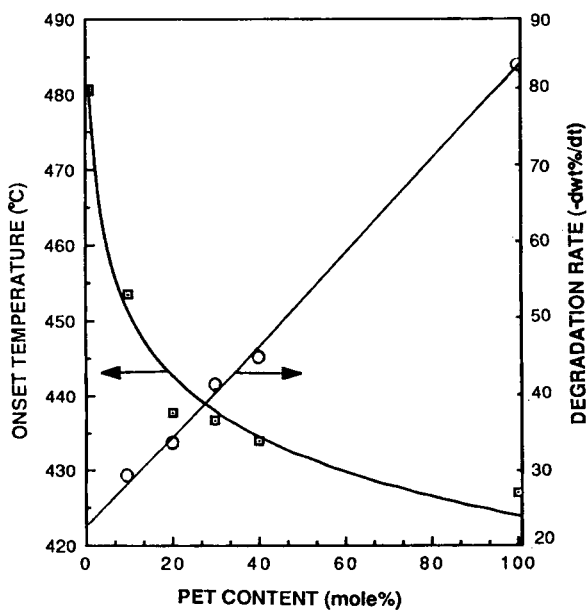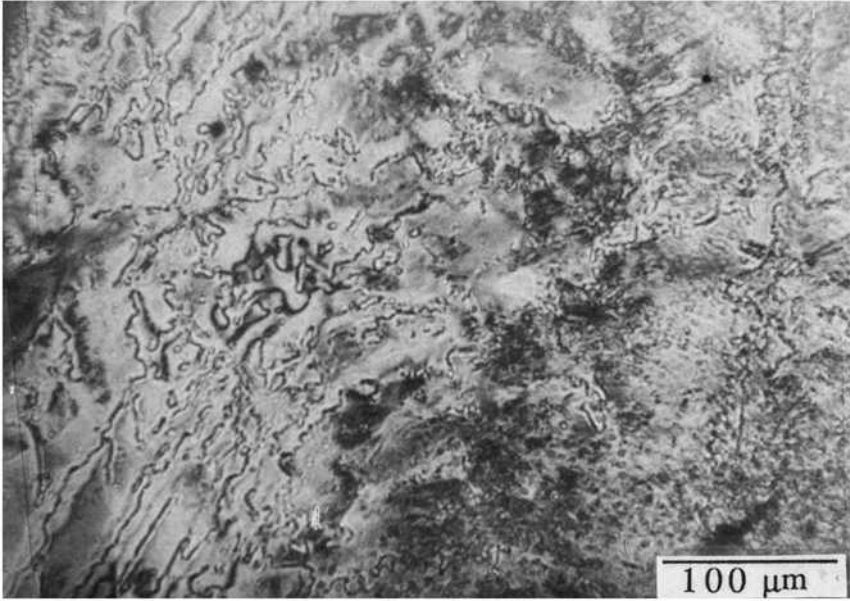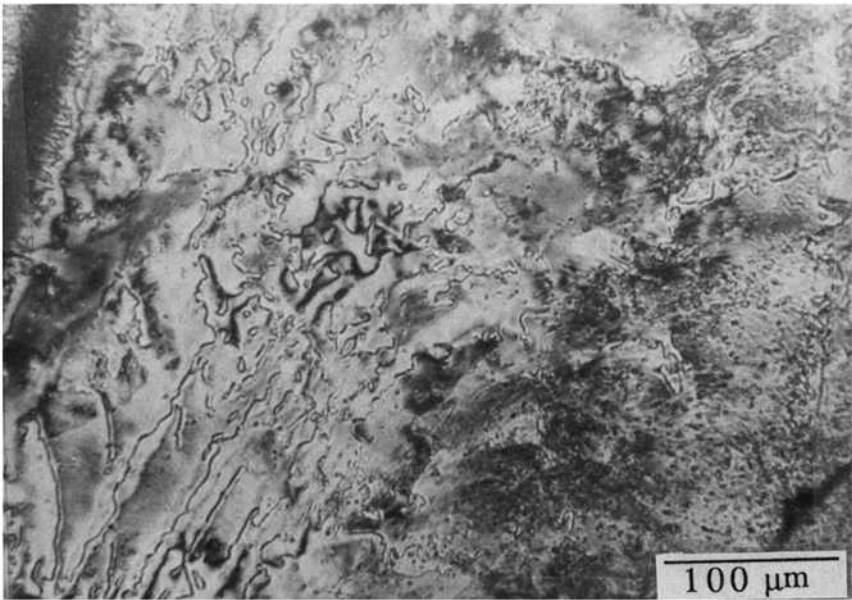

Fig. 6. The thermal degradation onset temperature (left) and degradation rate (right) as a function of PET content for the LC copolyesters series.
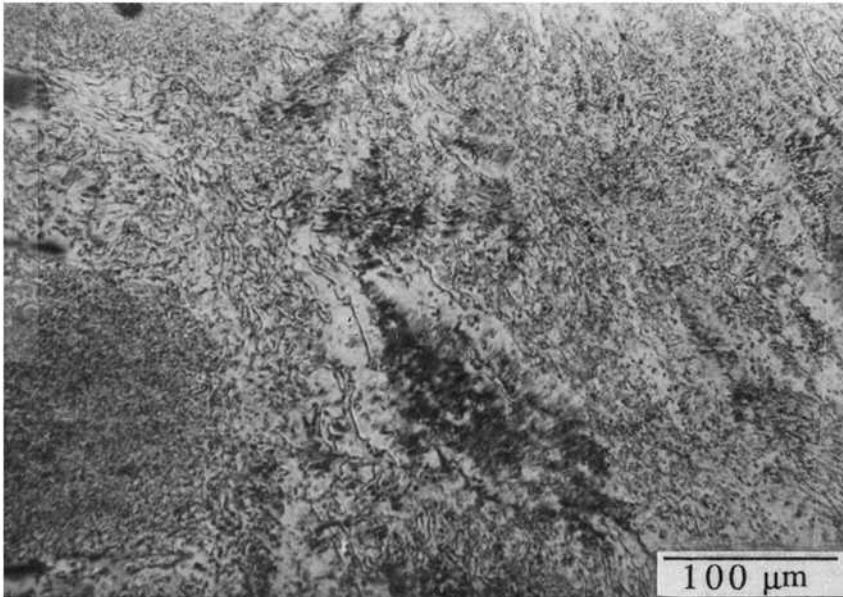
(a)

(b)

Fig. 7. Optical photomicrographs of LC-2 film viewed between crossed polarizers at various temperatures (°C): (a) 320; (b) 300; (c) 280; (d) 260.

2 and 3. Generally, the transition peaks are very weak and broad. Glass transition temperatures for this series of polymers are approximately defined by the content of PET units in the structure as shown in Figure 4.

(c)
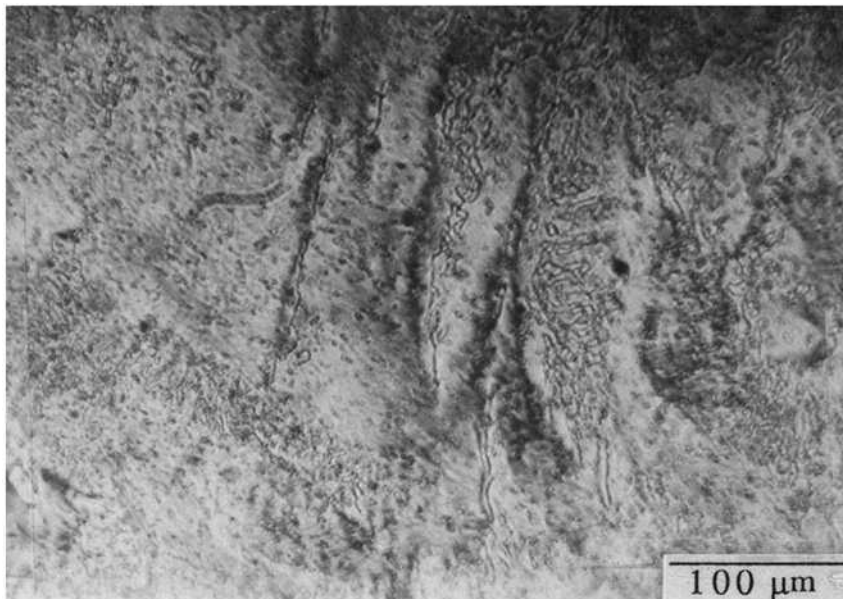
(d)

Fig. 7. (*Continued from the previous page.*)

Although these LC-copolyesters contain several comonomers, it is reasonable to simplify the discussion of the melting transitions by considering only the relative amounts of PET and HBA since these are the major variables in this series. Economy et al.[13] found that the pure *p*-oxybenzoyl polymer (PHB) has

a high-temperature melting point in the range of 325–360°C. In our highest HBA content polymer (LC-0) which has no PET units, the broad high temperature transition seen in Figures 2 and 3 has properties similar to the pure PHB melting point. It is speculated that this endotherm is due to melting of a pure HBA phase. With increasing PET content, the endotherm moves to lower temperatures because of classical copolymer melting point depression for LC-0 through LC-2. This is an example of the PET diluent effect as seen in the polymer series LC-0 through LC-2.

The lower temperature endotherms for LC-3 and LC-4 may be due to PET crystallinity and may be indicative of some chemical heterogeneity leading to a PET-rich phase. If so, the melting point of the PET phase is depressed from that for pure PET to 197°C for LC-4 caused by the diluent effect of the other comonomers. Evidence for such behavior is seen in all the copolyesters containing PET units.

Along with the major endotherms, there are a few small and broad endotherm peaks which varied with composition of the LC-copolyesters as seen in Figures 2 and 3. Noel[14] has suggested that multiple melting transitions are due to: (a) interconvertable forms of polymer, which differ only in degree of crystal size and perfection, (b) fundamental differences in crystal morphology, for example, folded-chain crystals and partially extended chain crystals, (c) true polymorphism, and (d) solid–mesophase and mesophase–mesophase transitions. A detailed assignment of these multiple melting transitions for these LC copolyesters will not be attempted. The multiple transitions observed are no doubt due to the complex nature of the copolyesters comprised of four monomers. However, the DSC results do suggest that crystallinity from both HBA- and PET-rich phases may be present.

In order to eliminate all previous thermal history, each sample was heated in the DSC to a temperature well past its highest melting endotherm and held there (see Fig. 2 for limits) before cooling to room temperature. Subsequent heating and cooling scans were then performed at a rate of 10°C/min. The melting peaks were extremely broad and appeared to involve several overlapping contributions. Some first scan melting peaks were not separated in the second scan (see Fig. 3). The trends in the position of peaks with composition were almost the same as those in first scans.

An assessment of the thermal degradation characteristics of the copolyesters was made by TGA. As shown in Figures 5 and 6, the onset temperature for thermal degradation and the degradation rate of these polymers seem to be dependent only on the ethylene terephthalate (ET) content or PET units in the LC copolyester. The thermal degradation rate increases linearly with the content of PET units, as the onset temperature decreases. Evidently the early stages of thermal degradation involve aliphatic portions of these copolyesters. LC-1 which contains a low content of PET units has a high onset temperature for degradation at 453.5°C and a relatively low degradation rate at 29.3 wt %/min.

The so-called "stick" temperature may be used to estimate the melt processing temperature range. This is the lowest temperature at which a filament is formed by probing and removing a pin from the molten material. This temperature was found to be in the temperature range of 210–250°C for LC-2–LC-4 and LC-6. The melt processing temperature of LC-1 is about 315°C, which
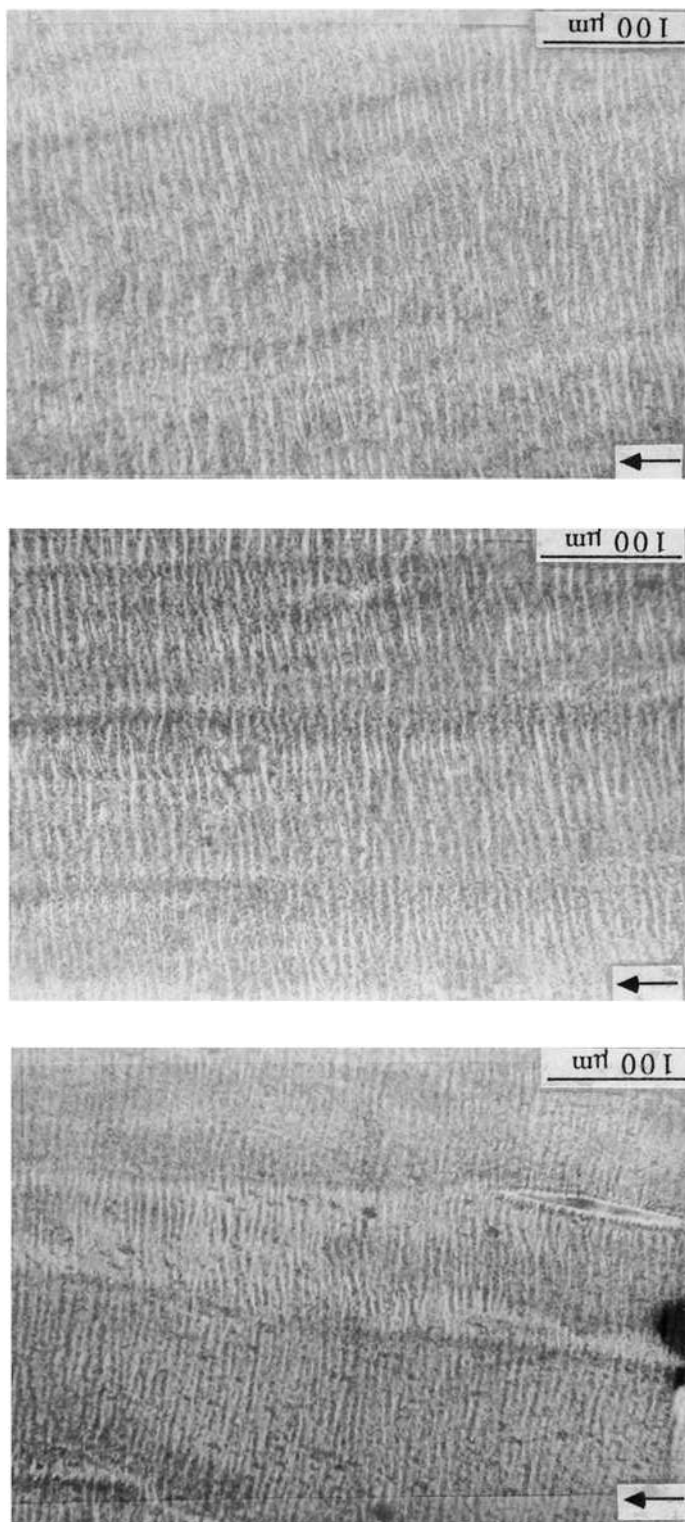
Fig. 8.   Optical photomicrographs for LC-2 viewed between crossed polarizers. The material was heated to (a) 260, (b) 280, and (c) 300°C on a glass plate and rubbed by a glass rod and then cooled to room temperature. Rubbing direction is shown by arrows.

compares with 320°C for the commercial Vectra product from Hoechst-Celanese and 350°C for Eastman PHB 80. Based on these thermal data, the current LC copolyesters appear to be melt processibile at relatively low temperatures.

Optical Microscopy Studies

The morphological texture of a typical LC copolyester prepared here, LC-2, was studied as a function of temperature using a hot stage mounted on a polarizing optical microscope. Photomicrographs taken at different temperatures during the heating experiment are shown in Figure 7. LC-2 exhibits a nematic mesophase in the broad temperature range of 260°C up to at least 340°C, apparent from the high birefringence under crossed polarizers. The domains remained clearly discernible and fused in the surrounding mesophase with increasing temperature. A threaded texture of the nematic phase of the LC copolyester increased with increasing temperature [from Fig. 7(d) to Fig. 7(a)]. The melt viscosity decreased noticeably with formation of the threaded texture. The mesophase supercooled without the reformation of the crystal aggregates (domains) on cooling to ambient temperature.

When the polymer melt was sheared on a glass plate by rubbing with a glass rod at different temperatures, the melt exhibited a fine ordered texture of bands perpendicular to the shearing direction (Fig. 8). This band structure developed from the low melt viscosity mesophase at 260, 280, and 300°C. The bands were clearly discernible in the supercooled solid state, and their breadth increased slightly with an increase of the temperature at which the shearing was done. Zachariades and Logan reported that the Eastman PHB80 has band structures perpendicular to the shear direction.[15] Ordered bands perpendicular to the shear direction is an optical effect observed also with low molecular weight nematic liquid crystals in the presence of electric and magnetic field or under conditions of mechanical stress. Although various explanations for the formation of band structure have been suggested, the nature of this phenomenon is poorly understood.[15]

Structure and Density

Over the last decade, there has been a considerable interest in the development of polymers with ultra high tensile modulus and strength. In principle, this has been achieved by preparing anisotropic morphologies of oriented and extended molecular chains through processing of flexible and rigid chain polymers. For liquid crystalline polymers, the ordered melt is easily oriented to give a high strength material. While injection molding of flexible chain polymers leads, under similar molding conditions, to anisotropic materials caused by molecular orientation, the level of anisotropy is never of the magnitude observed for mesophase systems. Therefore, to examine the orientation phenomenon of the thermotropic LC copolyesters during typical melt processing, we prepared samples under similar conditions using a Mini-Max molder.

Highly oriented polymers form microfibrillar morphologies in the solid state. Recently, it has been shown that the solid state of thermotropic copolyesters can best be described in terms of a hierarchical model composed of various fibrillar units (oriented fiber–macrofibril–fibril–microfibril). Similar structures
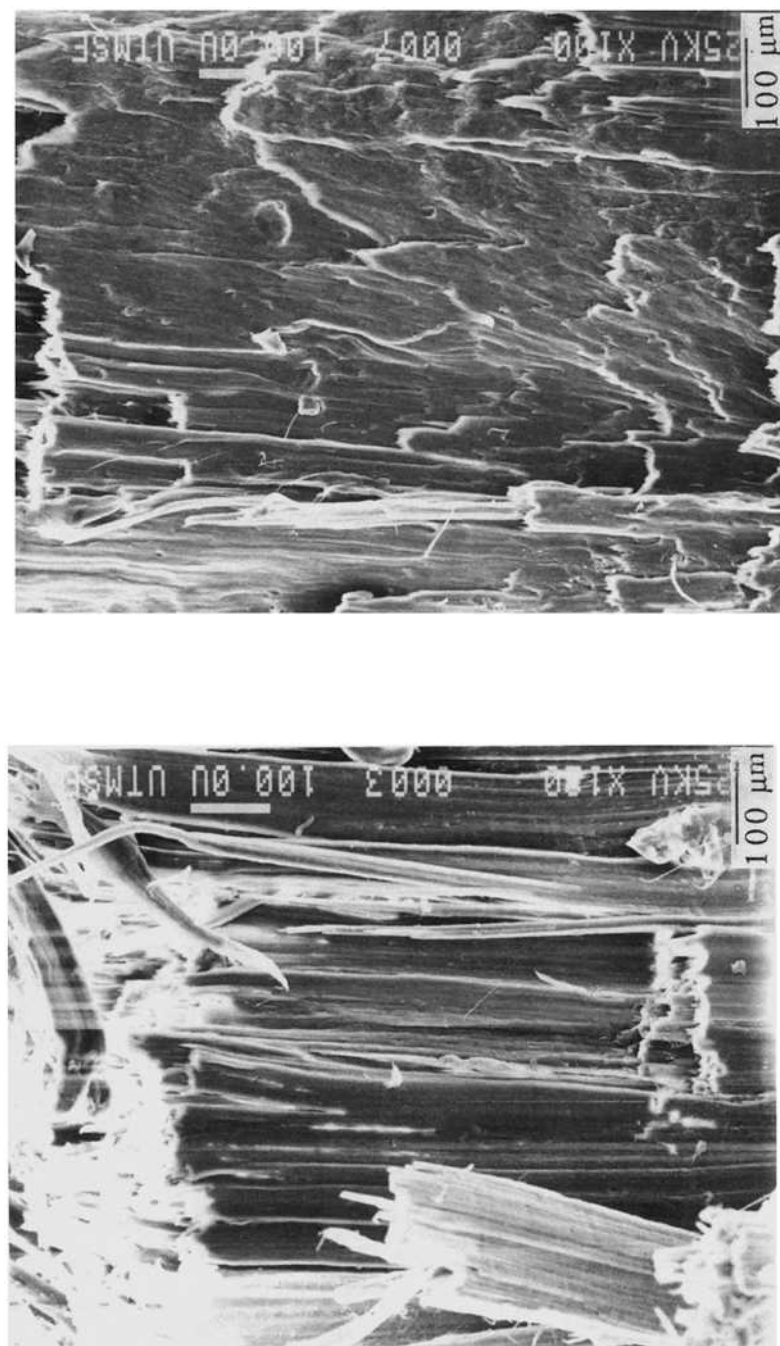
Fig. 9. SEM photomicrograph of the longitudinal fracture surface from the neck region of specimens prepared from LC-2 (a) and PHB60 (b) using the Mini-Max molder at 285°C.

(a)

(b)

(c)

Fig. 10. SEM photomicrographs of the cross sectional fracture surface neck region of samples of LC-2 (a), PHB60 (b), and PET (c) prepared in a Mini-Max molder at 285°C.

have been noted in aramids[16] and high modulus polyethylene.[17] SEM photomicrographs of LC-2, PHB60, and PET prepared in a Mini-Max molder are shown in Figures 9 and 10. Figure 9 shows longitudinal fracture surfaces of LC-2 and PHB60, while Figure 10 shows the cross sectional fracture surfaces of LC-2, PHB60, and PET. LC-2 has the most highly oriented and smooth fibrillar structure, whereas pure PET has a poorly oriented morphology. The PHB60 also consists of highly oriented and smooth fibrils, but it appears to be less ordered than the LC-2 material. It was found that molded samples made from PET, a flexible chain polymer, exhibit morphologies quite different than those made from PHB60 and the LC-2, although it has been reported that the PET has a fibrillar structure when subjected to extensive spinning and draw-down.[18]

Cuculo and Chen[11] reported that numerous fibrils split apart when PHB60 fibers spun at relatively high temperature were treated with a ultrasonic dismembrator. We also found that numerous fibrils split apart when we dipped a molded LC-2 sample into liquid nitrogen for a short time and then fractured it.

According to Sauer et al.,[19] the shape and parallel arrangement of rodlike molecules gives rise to very efficient packing in the molten state. The thermotropic LC copolyesters LC-2 and PHB60 chain were found to have a higher packing density than PET, while the LC-2 has a higher packing density than
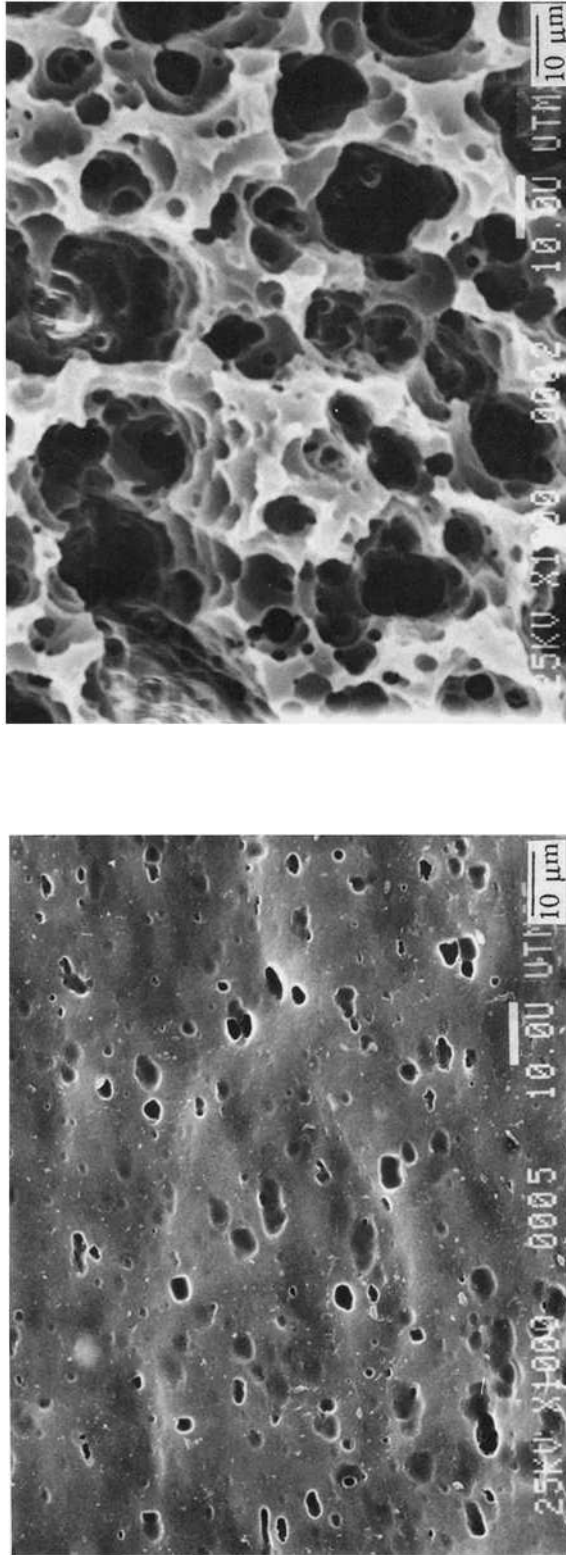
Fig. 11. SEM photomicrographs of LC-2 film etched with 70 wt % ethylamine aqueous solution for (a) 4 and (b) 18 h at 25°C.
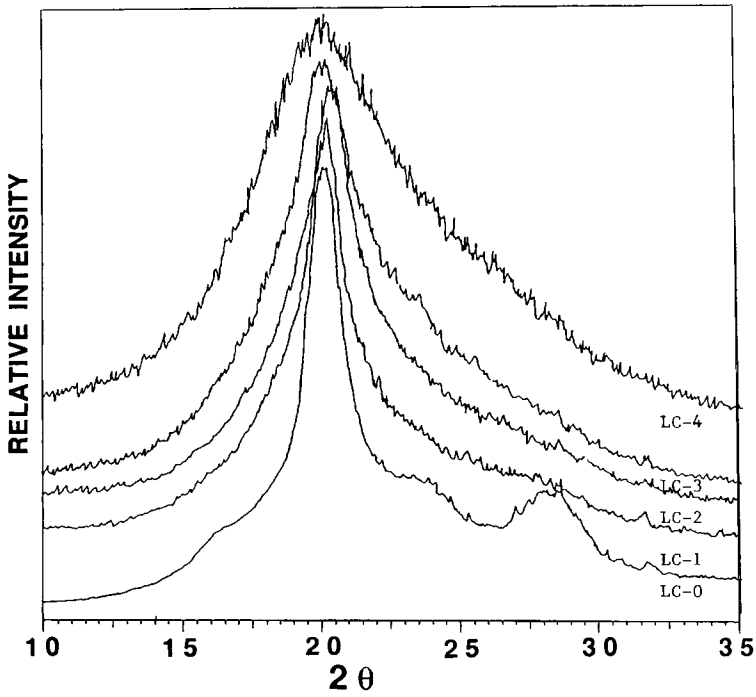
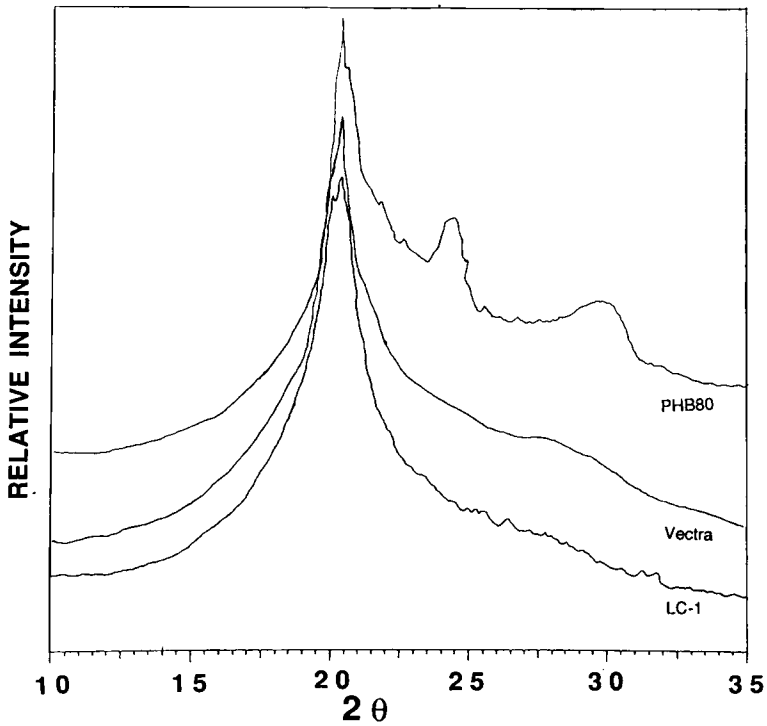Fig. 12.   X-ray diffraction patterns for films of LC-1–LC-4 made by compression molding.

Fig. 13.   X-ray diffraction patterns for LC-1, PHB80, and Vectra powders.

PHB60 (Table I). Based on observations of their morphology and packing densities, we can conclude that the dense close packing is directly related to the ease of formation of a fibrillar structure which leads to high tensile strength and modulus. LC-2 copolyester contains 10 mol % more mesogenic units than PHB60. The mesogenic content can be directly related morphological and packing density differences between LC-2 and PHB60.

Chemical Etching

Several authors[20,21] have utilized the technique of chemical etching to study the bulk morphology of semicrystalline PET. An etching reagent that preferentially degrades the amorphous PET regions is used, and this provides some information concerning the morphology of the remaining crystalline substrate. More recently Joseph et al.[10,22] and Hedmark et al.[23] have utilized this technique to study the morphology of PHB60. They report that PHB60 is composed of a discontinuous PET-rich phase surrounded by a PHB-rich matrix.

To obtain structural information about the LC copolyesters prepared here, the technique of chemical etching was employed, using ethylamine as the etchant

TABLE II
X-Ray Diffraction Results

Sample #	2θ (peak max)	d Spacing (Å)	Peak width at half-height	Crystal dimension[a] (Å)
Compression-molded film				
LC-1	20.2	4.40	2.24	40.0
LC-2	20.3	4.37	2.80	28.9
LC-3	19.9	4.46	4.08	19.8
LC-4	20.1	4.41	6.12	13.2
LC-2	20.3	4.37	2.80	28.9
LC-5	20.0	4.44	3.21	16.8
LC-6	20.2	4.40	2.95	27.4
	(20.1) = avg	(4.41) = avg		
PHB60	19.5	4.55	5.67	13.8
	23.5	3.79		
Solution-cast film				
LC-2	20.3	4.37	5.91	13.6
	23.1	3.85		
LC-4	19.9	4.46	7.82	10.5
	20.1	3.85		
Powder samples				
LC-0	20.0	4.45	1.82	44.2
LC-1	20.4	4.36	2.95	27.3
PHB80	20.6	4.35	2.74	28.4
Vectra	20.1	4.98	2.65	30.4
	23.1	3.85		
	26.3	3.38		

[a] Calculated using the Scherrer equation: $t = 0.9\lambda/B \cos \theta_B$ (t = crystal dimension, λ (Cu Kα X-ray) = 1.54 Å, B = peak width at half height in radian, θ_B = Bragg angle).

and SEM for observing the etched material. Etching was carried out at 25°C for 4 and 18 h.

The typical LC-2 sample etched with ethylamine displayed a Swisscheese-type morphology as seen in Figure 11. The sample etched for 4 h exhibits spherical holes of 1–4 μm (2.3 μm in average diameter) [Fig. 11(a)]. The holes grow together with increased etching time of 18 h. It is demonstrated by electron microscopy on the LC copolyester (I) that the PET-rich phase is discontinuous and is surrounded by a PHB-rich matrix. Therefore, this LC copolyester exhibits similar morphology to PHB60.

X-Ray Diffraction

Figure 12 shows X-ray diffraction patterns for five of the liquid crystal materials synthesized in this study (LC-0–LC-4). Their maximum peak positions were found to be near $2\theta = 20.12°$. This peak is similar to the peak resulting from crystallinity of PHB. Peak sharpness of these LC copolyesters increases with increasing mesogenic unit content, suggesting that chain rigidity promotes increased order in the polymer sample. The diffraction peaks are broadened due to defects formed by the presence of several different monomeric components. An estimate of the crystal size can be made from measurement of the diffraction peak widths at half maximum using the Scherrer equation. Typically,
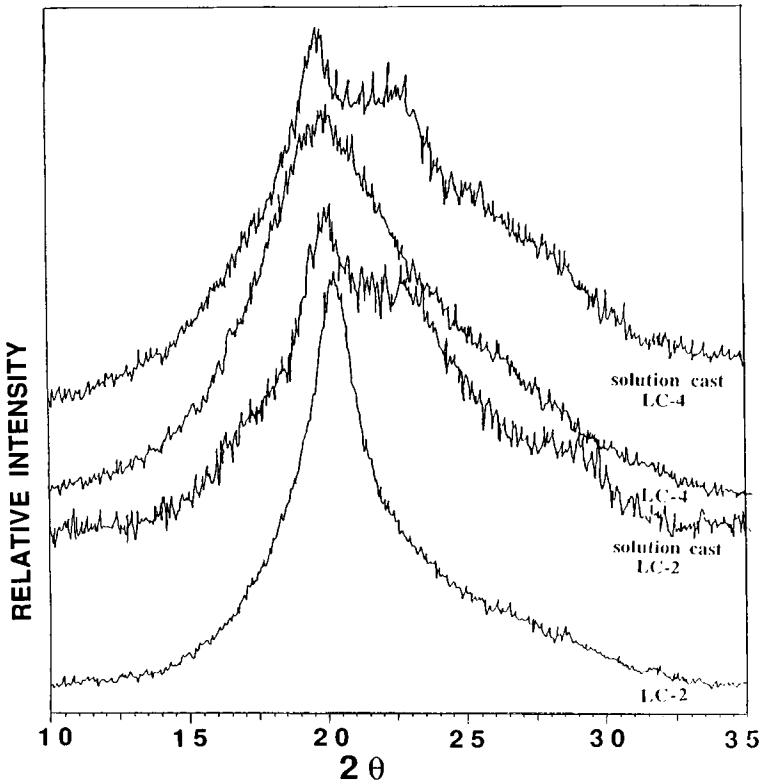

Fig. 14. X-ray diffraction patterns for LC-2 and LC-4 films made by compression molding and solution casting.
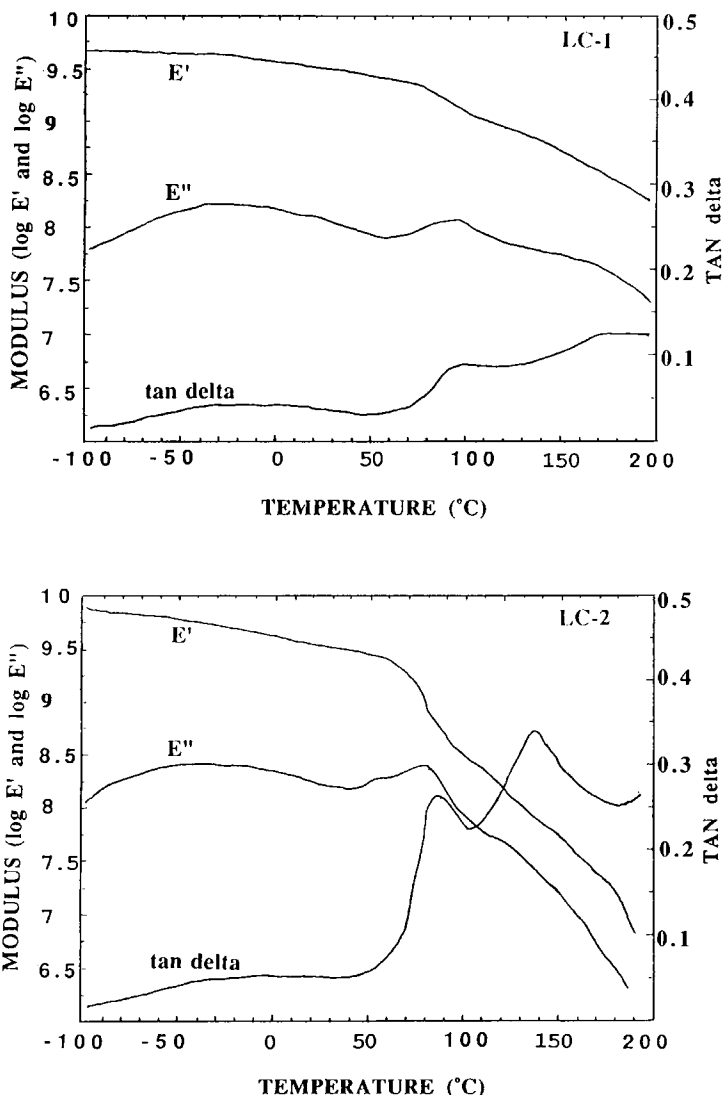
Fig. 15. Dynamic mechanical thermal analysis curves for LC-1–LC-4 at 10 Hz.

conventional polymer crystals range from 50 to 100 Å in size; however, crystal dimensions of the LC copolyesters determined using the Scherrer equation are in the range from 10 to 45 Å. Again, reduction in crystal size is attributed to the presence of dissimilar comonomeric units in the chain. From X-ray powder diffraction patterns shown in Figure 13, the crystal sizes of LC-1, PHB80, and Vectra appear to be nearly the same.

The peak positions, d spacings, and peak widths at half-height of the samples studied are listed in Table II. The peak widths of LC-2 and LC-6 copolymers, which contain the same mesogenic unit content, are the same. However, LC-5 (which has the same mesogenic unit content as LC-2 and LC-6 but a higher 1,4-DHN content) has a larger peak width than LC-2 and LC-6. This may be due to a larger decrease of the polymer chain order caused by the dissymmetrical
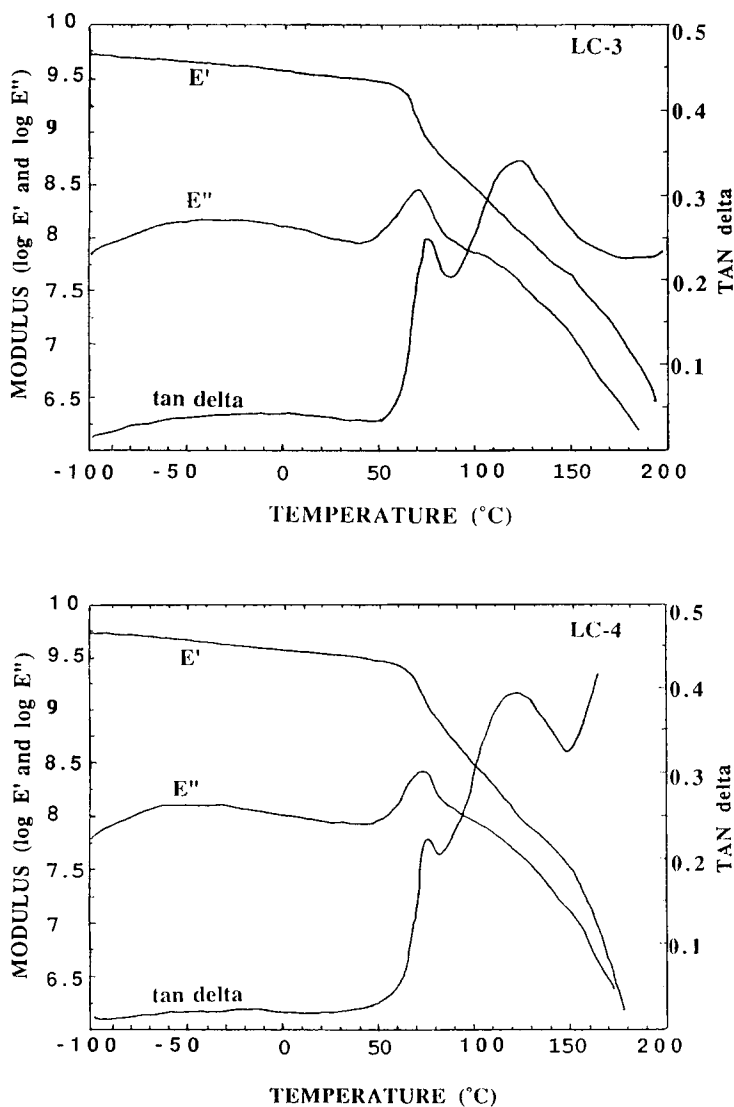
Fig. 15.   *(Continued from the previous page.)*

bulky unit 1,4-DHN relative to PET units. Jackson et al.[9] reported that the PET crystalline fraction decreased continuously as the PHB concentration increased in the PET/PHB system and that PHB60 has very little crystallinity. The PHB crystal diffraction peak at $2\theta = 19.4°$ increased as the amount of PHB incorporated into the polymer chain was increased. For the systems synthesized for this investigation, X-ray diffraction peak widths increased with increasing PET unit content. In the LC copolyesters, the peak broadening effect was very distinguishable; however, the level of crystallinity of most of these materials is small. The width of the peak for PHB60 lies between the values obtained for the LC-3 and LC-4 copolymers. From these results, we can deduce that LC-1, LC-2, and LC-3 have a more ordered structures than PHB60.

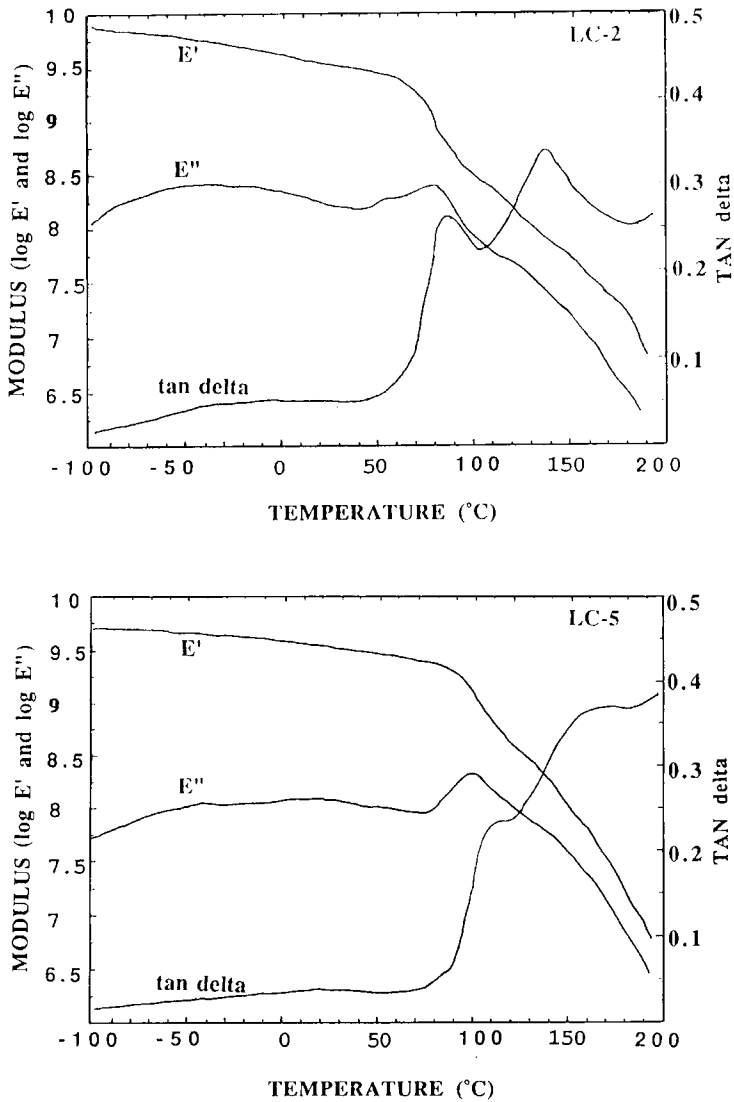Figure 14 shows X-ray diffraction patterns of solution-cast and compression-

Fig. 16.   Dynamic mechanical thermal analysis curves for LC-2, LC-5, LC-6, and PHB60 at 10 Hz.

molded films of LC-2 and LC-4 copolyesters. There are many studies regarding the chain structure of PET modified with HBA using a variety of techniques including chemical etching, ESCA, NMR, and thermal analysis. There is general agreement from these studies that the material is not perfectly random. In our examination of the chain structure of these LC copolyesters, we are able to obtain information from the X-ray diffraction patterns of the solution cast films. A peak at $2\theta = 23.1°$ (shown in Fig. 14) has been identified as a conventional PET crystal peak. For solution cast films of LC-2 and LC-4, a diffraction peak at $2\theta = 23.1°$ is apparent. This suggests that there is a PET-rich phase in these materials and that crystallization of this part occurs more readily from solution, due to the freedom of rotation and movement allowed in this envi-
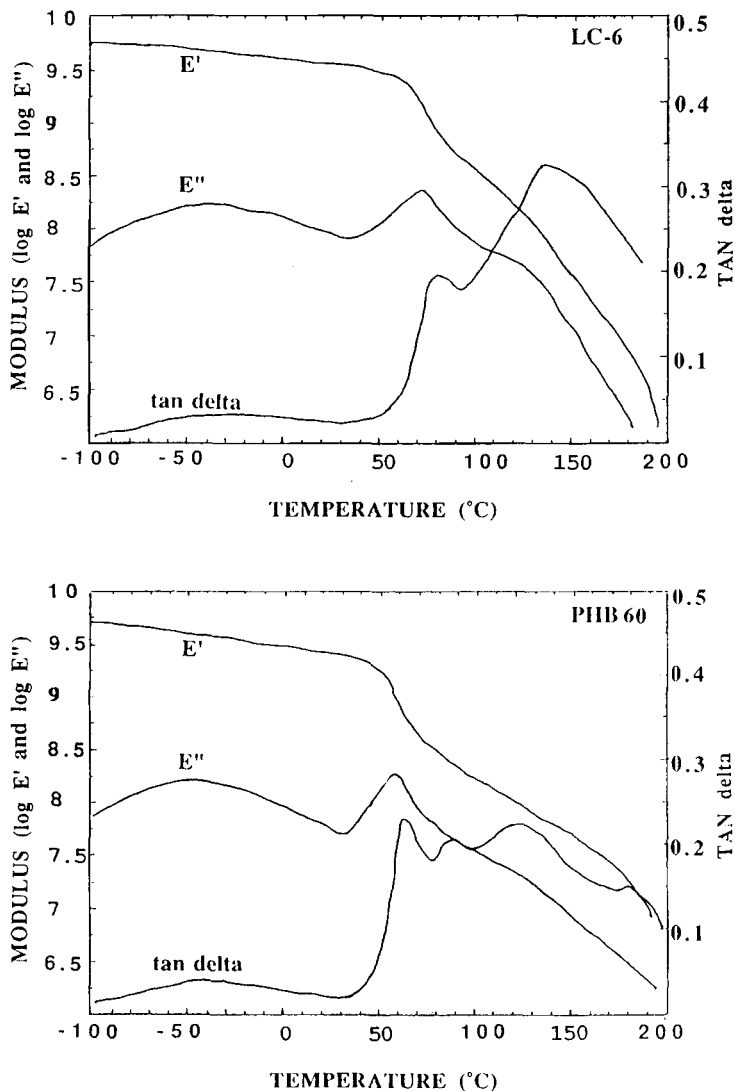
Fig. 16. (*Continued from the previous page.*)

ronment. In melt-processed films, the movement of PET-rich chain segments to form their crystal is evidently more restricted. It is concluded that the LC copolyesters synthesized here do not have a perfectly *random* sequence distribution.

Dynamic Mechanical Behavior

Significant information about molecular motions of polymer chains can be obtained through the use of dynamic mechanical thermal analysis (DMTA). It has been reported that pure PET has an α-relaxation in the temperature range 80–150°C and a β-relaxation at −60°C at a frequency of 1 Hz.[24] In general, the α-relaxation peak for PET is reduced in intensity, broadens, and moves to
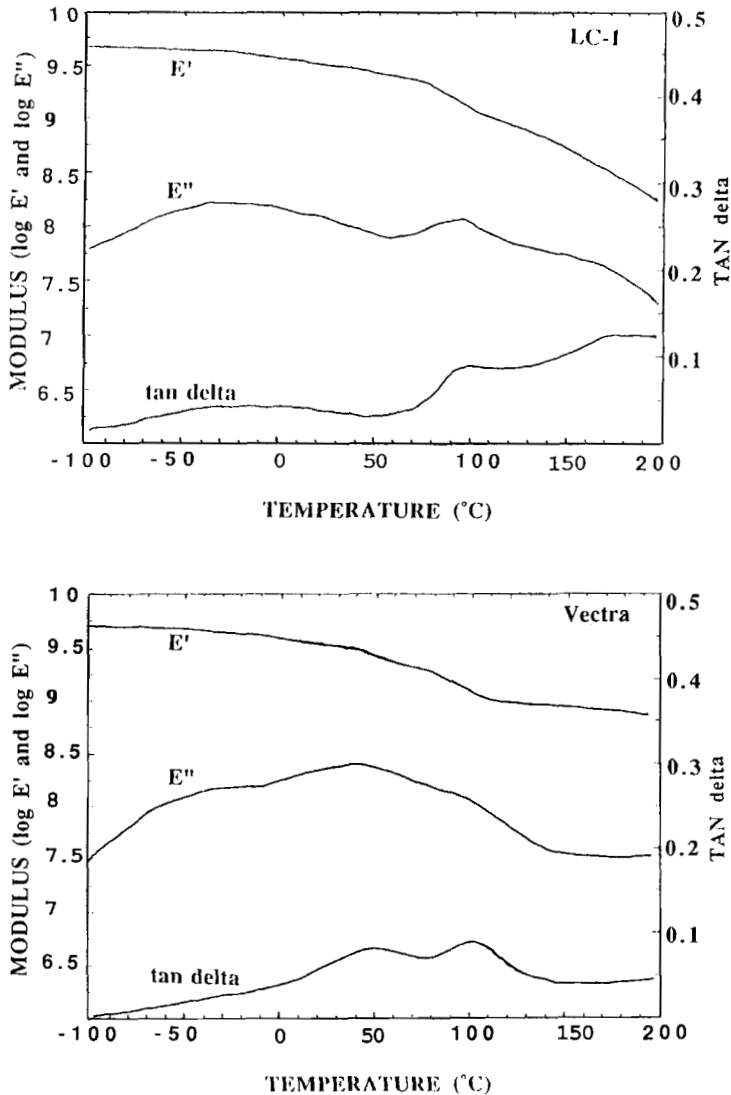
Fig. 17. Dynamic mechanical thermal analysis curves for LC-1, PHB80, and Vectra at 10 Hz.

higher temperatures with increasing crystallinity. The α-relaxation has, there-
fore, been associated with the amorphous phase, although it is strongly influ-
enced by the type and degree of crystallinity. The β-relaxation which is affected
only slightly by crystallinity is extremely broad and appears to involve several
overlapping contributions. Benson and Lewis[25] investigated the dynamic me-
chanical properties of a series of PHB/PET copolymers. They reported that
the PHB/PET 60/40 sample exhibited α-, β-, and γ-relaxation peaks at ap-
proximately 88, 62, and 45°C. For comparison, the dynamic mechanical prop-
erties of the LC copolyesters were determined as a function of temperature.
The storage modulus (E'), loss modulus (E''), and loss factor (tan δ) for the
LC copolyesters at 10 Hz are shown in Figures 15 and 16. To compare the
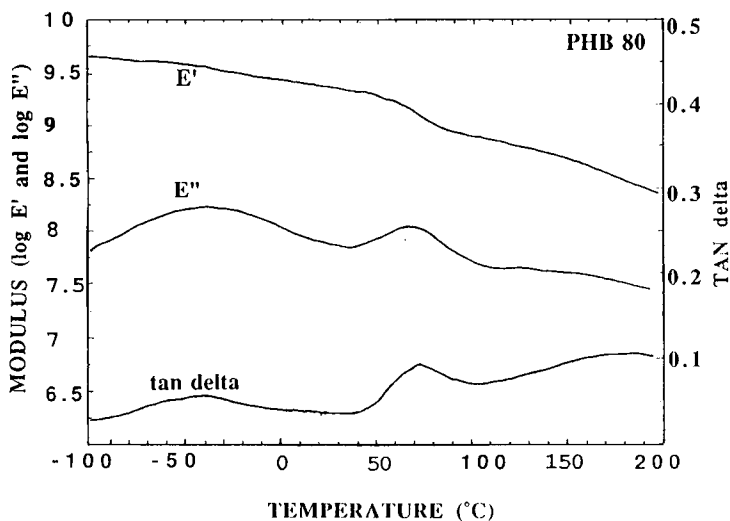behavior of the LC copolyesters synthesized in this investigation with com-

Fig. 17. (*Continued from the previous page.*)

mercial materials, the dynamic mechanical properties of Vectra (Celanese) and the two Eastman materials, PHB60 and PHB80, were also measured (see Figures 16 and 17).

In the temperature range examined several loss peaks are observed owing to the sub-T_g and T_g transitions. The LC-1 sample exhibits three relaxation peaks in Figure 15 at approximately -30, 90, and 160°C at 10 Hz based on the peak locations of the E'' curve. In the series of samples from LC-1 to LC-4, the content of mesogenic units decreases as the content of PET of units increases while the mole percentage of TPA and 1,4-DHN is held constant. The 160°C peak for LC-1 shifted to lower temperature and increased in intensity as the content of PET of units was increased. The main relaxation peak at 90°C for LC-1 was also shifted to lower temperature as PET content increased through the LC copolyester series. The peak at -40°C was affected to a much lesser extent.

The rate of decline of the storage modulus (E') with temperature after the main relaxation increased rapidly as more PET units were added. This indicated that the PET component is included primarily in the amorphous regions. Thus, it is believed that the behavior observed in this temperature range chiefly reflects the relaxation of the PET component discussed above. However, it was found that the relaxation phenomena were also dependent on the concentration of the dissymmetrical 1,4-DHN units. The 1,4-DHN content of LC-5 is higher than that of LC-2 and LC-6 while the mesogenic content is the same. This effect is clearly seen by comparing the compositions and relaxation peaks of LC-2, LC-5, and LC-6 in Figure 16. The higher relaxation temperature of LC-5 may be due to the effect of stiffness of 1,4-DHN units in the amorphous phase. The relaxation peak temperatures of all the LC copolyesters are higher than that of PHB60.

In this series of LC copolyesters, the main relaxation transition broadens, weakens in intensity, and moves to higher temperatures as the content of mesogenic units increases. This no doubt reflects the accompanying decrease

in chain flexibility and the ordering of the chain as mesogenic units replace PET units.

Figure 16 compares the LC-1, PHB80, and Vectra materials. Note that these three materials are very similar in terms of structure and content of mesogenic units. Above room temperature, Vectra has two transitions where a loss in the storage modulus is observed; a weak depression at 40°C and another strong reduction near 85°C. PHB80 has a strong depression in the storage modulus around 50°C. LC-1 synthesized for this investigation maintains its initial storage modulus very well until 80°C, where stiffness drops rapidly in comparison with Vectra. From the storage modulus data, it can be concluded that the LC-1 copolyester is an excellent material for maintaining its initial mechanical properties in the temperature range of −100–80°C.

CONCLUSIONS

A series of thermotropic copolyesters that form liquid crystalline order were synthesized by melt polymerization from poly(ethylene terephthalate) (PET), terephthalic acid (TPA), p-hydroxybenzoic acid (HBA), and 1,4-dihydroxy-naphthalene (1,4-DHN) to achieve low processing temperatures while maintaining high strength and high modulus.

Their properties are summarized as follows. LC copolyesters with an inherent viscosity of near or above 0.7 were obtained. These LC copolyesters have low melt processing temperatures. The glass transition temperature, degradation temperature, density, and crystallinity of the LC copolyesters apparently increase with increasing mesogenic unit content. The copolymer chain structure is not completely random. Highly anisotropic melts observed on a hot stage of a polarizing light microscope indicates the presence of a mesophase. The melts did not become isotropic below the temperature range where thermal decomposition becomes very severe. The thermotropic LC copolyesters exhibit unusually well developed and highly oriented fibrillar structures when microinjection-molded. Orientation development during processing are very similar to those of short fiber filled composites. The LC copolyesters have three relaxations in the temperature range of −100–200°C. The temperatures at which the storage modulus shows marked increase with increasing mesogenic unit and 1,4-DHN content. Comparing the storage moduli of LC-1, Eastman PHB80, and Celanese Vectra which have almost the same mesogenic content, the modulus of LC-1 maintains its initial value until about 80°C, while the modulus of Vectra is depressed in two steps: a small depression at 40°C and then a large reduction at 85°C. For Eastman PHB80, we saw only a large single transition at 50°C. From the storage modulus data, LC-1 compares well to Vectra and PHB80 for its maintenance of high modulus in the temperature range of 25–120°C.

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