

# Comparison of the Properties of Thermotropic Liquid Crystalline Copolyesters Containing Different Dissymmetrical Units

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## Synopsis

The effect of dissymmetrical units on the properties of thermotropic liquid crystalline copolyesters based on hydroxybenzoic acid (HBA), terephthalic acid (TPA), and poly(ethylene terephthalate) (PET) units was examined. The dissymmetrical units employed included 2,7-dihydroxynaphthalene (2,7-DHN), 1,4-dihydroxynaphthalene (1,4-DHN), and bromo-hydroquinone (Br-HQ). All of these polymers exhibited turbid melts. The flexible PET units lower the melting and/or stick temperature, and between 10 to 20 mol % is a critical level to achieve values in the range of 250°C or lower. The copolyesters based on 2,7-DHN have the highest glass transition temperatures and maintain stiffness to the highest temperatures. The properties of each series of copolyesters are discussed in terms of the efficiency of molecular packing. The effects of chemical and physical inhomogeneity are emphasized.

## INTRODUCTION

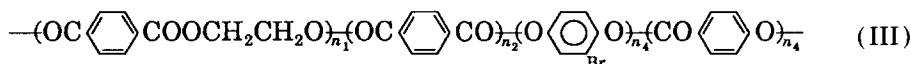
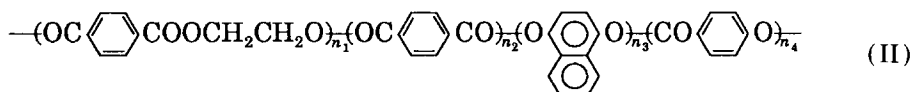
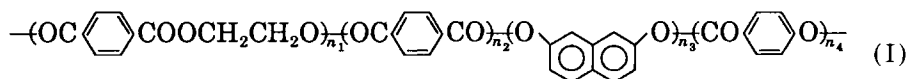
It has been widely recognized that rigid polymer chains which lead to liquid crystalline order may result in materials with excellent mechanical stiffness and strength. A few polymers of this type are now commercially available including lyotropic aramids, viz. poly(*p*-phenylene terephthalamide), and thermotropic aromatic copolyesters. The application of thermotropic polyesters as high-strength-high-modulus materials, in fibers or thermoplastics, requires reasonable melt-processing temperatures; hence, high melting points characteristic of wholly aromatic polymers must be reduced below the temperature where thermal degradation occurs. Strategies for lowering the melting temperature of rigid chain polymers include introduction of rigid unsymmetrical units or flexible spacer groups into the chain.<sup>1-4</sup> Thermotropic polyesters have been prepared using transesterification reactions with low molecular weight poly(ethylene terephthalate) (PET) as a means of introducing flexible spacer units into the chain for this purpose.<sup>5,6</sup>

In an earlier investigation of the preparation and properties of a series of thermotropic liquid crystalline copolyesters,<sup>7</sup> we used *p*-hydroxybenzoic acid (HBA) and terephthalic acid (TPA) as mesogenic monomers, poly(ethylene terephthalate) (PET) units to give a flexible linkage, and 1,4-dihydroxynaphthalene (1,4-DHN) as a dissymmetrical monomer. The proportions of these

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monomers were varied as a means of manipulating processing temperature, morphology, and properties. Here we describe the preparation and properties of a series of thermotropic liquid crystalline (LC) copolyesters having different dissymmetrical units in the polymer chain. A series of copolyesters based on HBA, TPA, PET, and containing either 1,4-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, or bromohydroquinone (Br-HQ) as dissymmetrical monomers were prepared and characterized for their thermotropic liquid crystalline properties.

The main objective of the present investigation was to examine how the structure of the dissymmetrical unit affects the properties of thermotropic LC-copolyesters. The repeat units of the polymers prepared for this study can be represented by the following:



## EXPERIMENTAL

*p*-Acetoxybenzoic acid ( $T_m = 195^\circ\text{C}$ ), 2,7-diacetoxynaphthalene ( $T_m = 130^\circ\text{C}$ ), 1,4-diacetoxynaphthalene ( $T_m = 135^\circ\text{C}$ ), and 2-bromo-1,4-diacetoxybenzene ( $T_m = 77^\circ\text{C}$ ) were prepared using the acetylation reaction procedure described in our earlier paper.<sup>7</sup> Terephthalic acid, TPA, and poly(ethylene terephthalate) with an inherent viscosity of 0.36 dL/g were obtained from industrial sources and used without further purification. Sodium acetate was reagent grade.

All the polymers were prepared according to the melt polymerization procedure described previously.<sup>7</sup> Inherent viscosities were measured at  $25^\circ\text{C}$  in trifluoroacetic acid at a polymer concentration of 0.1 g/100 mL. Densities of compression molded films were measured at  $25^\circ\text{C}$  using a density gradient column based on aqueous solutions of calcium nitrate. The films were pressed at  $260^\circ\text{C}$  or  $290^\circ\text{C}$  (for the polymers designated I-1 and II-1) using a force of 10 tons. The sample designations, compositions, densities, and inherent viscosities are shown in Table I. Thermal behavior of the as-polymerized samples was examined using a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of  $20^\circ\text{C}/\text{min}$  in the initial scan followed by quenching, and then heating and cooling at  $10^\circ\text{C}/\text{min}$  in second scans. A Perkin-Elmer TGA-7 thermogravimetric analyzer was used to monitor mass loss at a heating rate of  $20^\circ\text{C}/\text{min}$ . A Polymer Laboratories DMTA was used to measure dynamic mechanical thermal properties of molded samples with dimensions of about  $3 \times 12.5 \times 14$  mm at a heating rate of  $2^\circ\text{C}/\text{min}$ .

TABLE I  
Description of Thermotropic Copolyester Series

Sample designation	Composition (mole fraction)	Inherent viscosity <sup>a</sup> (100 mL/g)	Density (g/cm <sup>3</sup> )	V <sub>o</sub> <sup>b</sup> (cm <sup>3</sup> )	V <sup>c</sup> /V <sub>o</sub>
PET/TPA/2,7-DHN/HBA					
I-1	0.1/0.1/0.1/0.7	—	1.401	0.647	1.103
I-2	0.2/0.1/0.1/0.6	0.69	1.394	0.649	1.105
PET/TPA/1,4-DHN/HBA					
II-1	0.1/0.1/0.1/0.7	—	1.415	0.647	1.092
II-2	0.2/0.1/0.1/0.6	0.71	1.402	0.649	1.099
II-3	0.1/0.2/0.2/0.5	—	1.394	0.649	1.105
PET/TPA/Br-HQ/HBA					
III-1	0.2/0.1/0.1/0.6	0.76	1.432	0.629	1.110

<sup>a</sup> Measured at 25°C at C = 0.1 g/100 mL using trifluoroacetic acid as solvent.

<sup>b</sup> V<sub>o</sub> = volume occupied by molecules calculated by Sugden method.<sup>8</sup>

<sup>c</sup> Specific volume = V = 1/measured density.

## RESULTS AND DISCUSSION

### Viscosity

Inherent viscosities were measured for representative samples based on each dissymmetrical monomer. The results, shown in Table I, indicate that good molecular weights were achieved in each case. For the fixed reaction conditions used, the inherent viscosities are in the order: Br-HQ > 1,4-DHN > 2,7-DHN. This may reflect differences in chemical reactivities of these monomers caused by either electronic or steric effects.

The morphological texture of all the samples described in Table I indicate a nematic mesophase over a broad temperature range apparent from the birefringent turbid melts observed using crossed polarizers.<sup>7</sup> Melt viscosities of these copolyesters seem to be remarkably dependent on the kind and content of the dissymmetrical units. The relationship between the structure and the rheological properties of these copolyesters is being investigated more thoroughly and will be reported in a future paper.

### Thermal Characterization

Figure 1 shows initial DSC scans of the copolyesters obtained at a rate of 20°C/min while Figure 2 shows second scans run at 10°C/min. The latter eliminate previous thermal history effects and, therefore, more nearly reflect indigenous characteristics of the polymers. The thermograms are complex and difficult to interpret unambiguously. There seem to be multiple melting transitions as reported previously for other copolyesters having liquid crystalline characteristics; however, each melting peak is rather small.

The polymers containing 2,7-DHN have a prominent glass transition temperature that is somewhat higher than that for the polymers based on 1,4-DHN or Br-HQ. However, the melting temperature and/or the so-called stick tem-

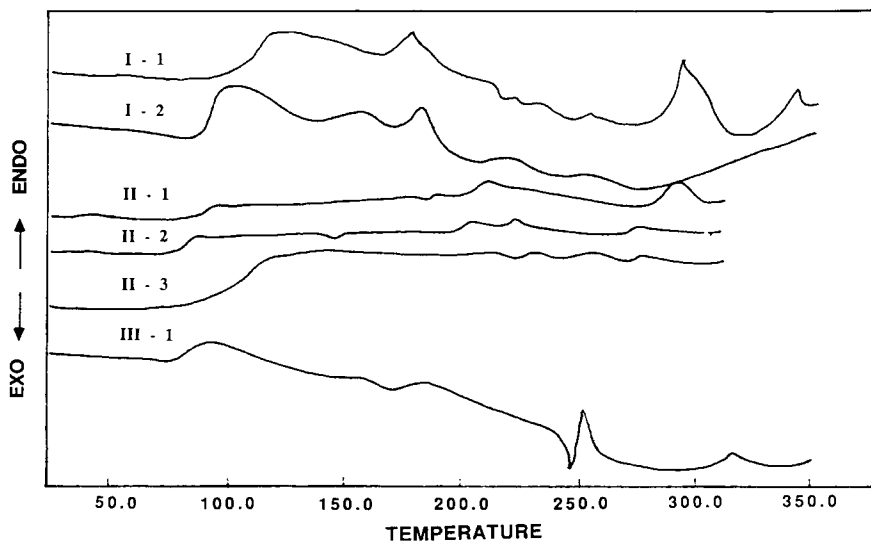


Fig. 1. DSC thermograms for the thermotropic liquid crystalline copolyesters containing different dissymmetrical units. First scans at  $20^{\circ}\text{C}/\text{min}$ .

perature mainly depend on the ratio of flexible PET units to rigid mesogenic units. By increasing the PET content from 10 to 20 mol %, the melting and/or stick temperature is decreased from near  $300^{\circ}\text{C}$  to below  $250^{\circ}\text{C}$ . Beyond 20 mol % of PET, these temperatures remain near  $200^{\circ}\text{C}$  to  $250^{\circ}\text{C}$ . As a result of this investigation, it is concluded that between 10 and 20 mol % of PET units

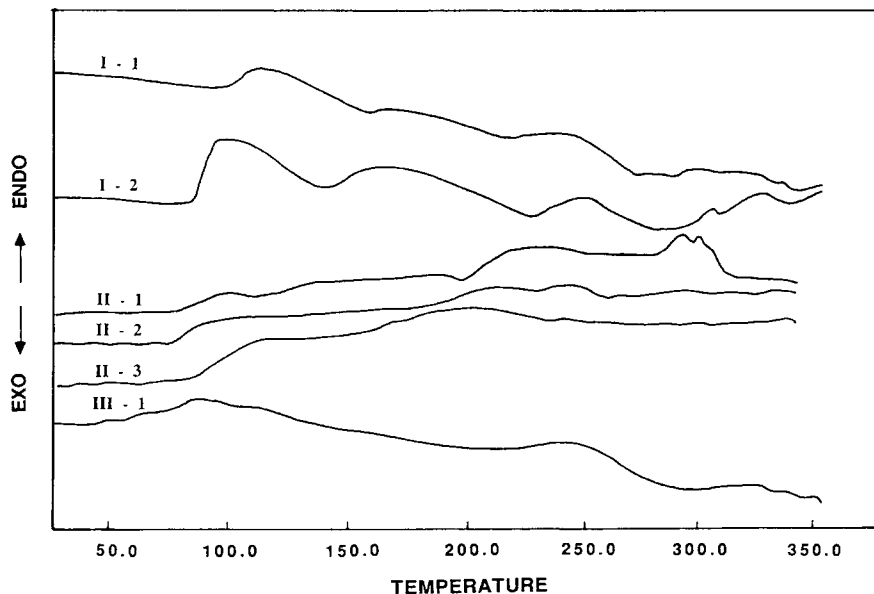


Fig. 2. DSC thermograms for the thermotropic liquid crystalline copolyesters containing different dissymmetrical units. Second runs at  $10^{\circ}\text{C}/\text{min}$  after quenching.

is a critical level for achieving melting and/or stick temperatures, which may be regarded as the minimum temperature for melt processing, below 250°C.

An assessment of the thermal degradation characteristics of the copolyesters was made by TGA. The temperature for the onset of thermal degradation did not depend on which aromatic dissymmetrical unit was used to form the copolyester. For example, the samples I-2, II-2, and III-1 in Table I have identical compositions except for the type of dissymmetrical unit and each has an onset temperature for thermal degradation near 415°C at a heating rate of 20°C.

### Dynamic Mechanical Behavior

The storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss factor ( $\tan \delta$ ) for the copolyesters obtained at 10 Hz are shown in Figures 3, 4, and 5. Selected major transitions obtained from DMTA curves at 3, 10, and 30 Hz are listed in Table II. Each copolyester exhibits a low temperature relaxation peak. For this discussion, the primary focus will be on the more major events above room

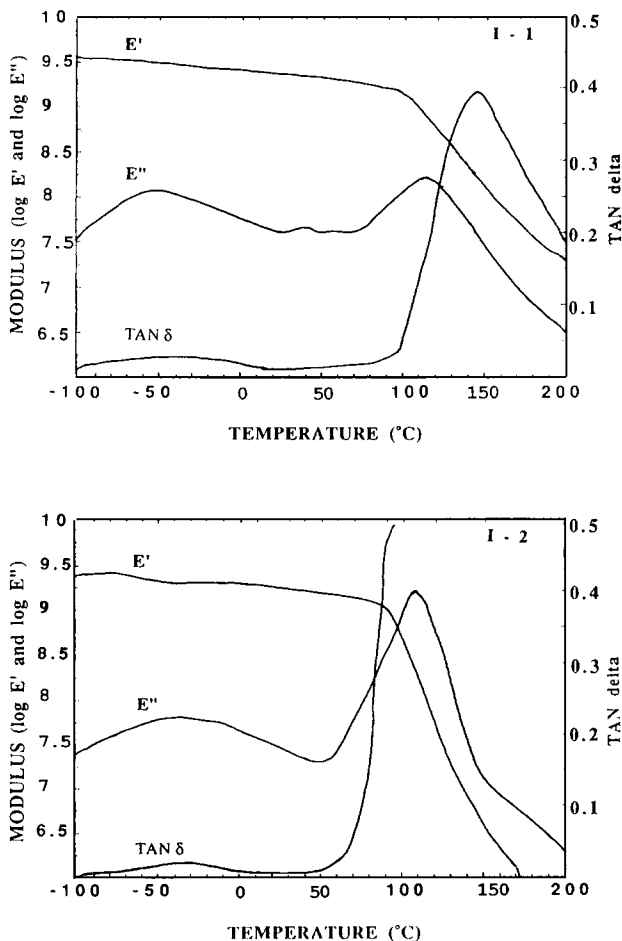


Fig. 3. Dynamic mechanical thermal analysis curves at 10 Hz for copolyesters I-1 and I-2 having 2,7-DHN units.

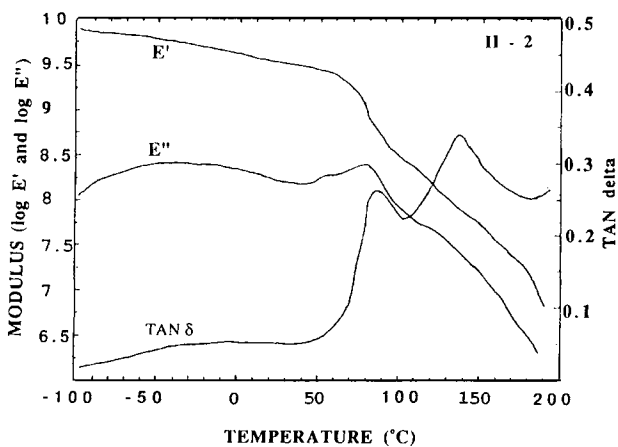
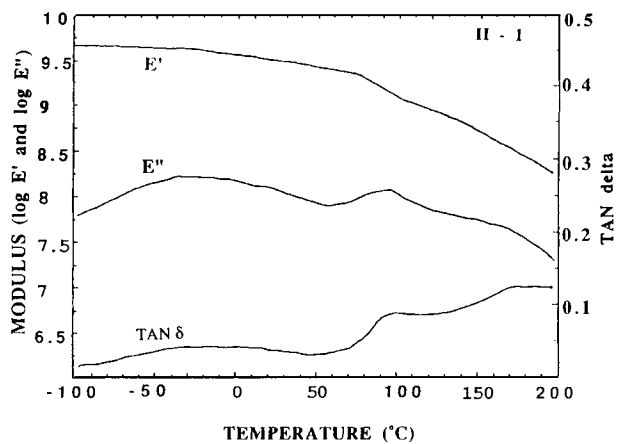


Fig. 4. Dynamic mechanical thermal analysis curves at 10 Hz for copolyesters II-1 and II-2 having 1,4-DHN units.

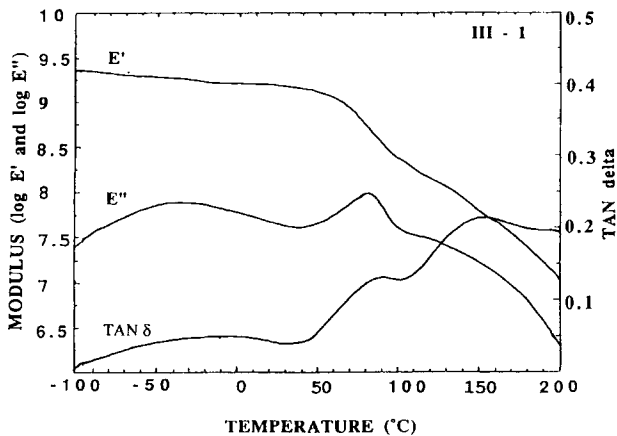


Fig. 5. Dynamic mechanical thermal analysis curves at 10 Hz for copolyester III-1 having Br-HQ.

TABLE II  
Major Transitions of Thermotropic Copolyesters by DMTA

Sample designation	Peak	Temperature of $E''$ peaks ( $^{\circ}\text{C}$ )			Temperature of onset of $E'$ decline ( $^{\circ}\text{C}$ )
		3 Hz	10 Hz	30 Hz	10 Hz
I-1	low	-48	-43	-34	
	high	105	108	111	102
I-2	low	-55	-46	-36	
	high	89	91	94	85
II-1	low	-38	-32	-22	
	high	86	90	94	80
II-2	low	-47	-39	-29	
	high	77	78	81	70
III-1	low	-43	-36	-27	
	high	76	78	80	65

temperature that can be associated with glass transitions. In each series of polymers shown in Table I, an increase in the concentration of PET units, at the expense of HBA units, results in a lowering of these main transition temperatures and a more precipitous drop in storage modulus above the transition (compare the two polymers in Fig. 3 or the two polymers in Fig. 4). The extent to which the storage modulus decreases beyond the glass transition temperature depends on several factors including the degree of crystalline order in the material and the properties of the mesophase. It is reasonable that introduction of more PET units would both lower the transition temperature and reduce the modulus at higher temperatures. Generally, the storage modulus at room temperature decreases with increased content of PET units.

The DMTA data can also be used to assess the effects of the dissymmetrical monomer unit by making comparisons at constant contents of PET and HBA units, and the following conclusions can be reached. The copolyesters based on 2,7-DHN (series I) appear to have a single glass transition temperature; whereas, those based on 1,4-DHN (series II) or Br-HQ (series III) seem to have two high temperature transitions (see  $\tan \delta$  curves in Figs. 4 and 5). The latter may reflect a degree of chemical heterogeneity that can lead to two separate phases as noted for other similar copolyesters made using transesterification reactions of PET.<sup>7</sup> The glass transition temperatures observed for the 2,7-DHN based polymers are higher than the lowest of the two glass transitions observed for the polymers based on 1,4-DHN or Br-HQ, and consequently polymers based on the former maintain a high storage modulus to higher temperatures (see Table II). The temperatures at which the storage modulus begins to decline sharply for polymers based on 1,4-DHN and Br-HQ are essentially the same. After the onset temperature for the decrease in the storage modulus, the rate of modulus loss with temperature is greatest for polymers based on 2,7-DHN followed by those based on 1,4-DHN while those based on Br-HQ show the least rate of decline. At room temperature, the storage moduli of the copolyesters based on 2,7-DHN and Br-HQ are about the same; however, values for copolyesters based on 1,4-DHN are significantly higher than these. Many of the trends mentioned above can be traced to the apparent tendency for 2,7-

DHN to give copolyesters that are chemically more homogeneous, and it would be interesting to explore more fully the fundamental origin of this effect. For example, the rate at which the storage modulus decreases with temperature will depend on what fraction of the material softens at the onset temperature and what fraction has a higher softening temperature. All trends cannot be explained on this basis and reflect to some degree the inherent contributions made by the structure of the dissymmetrical monomer unit on physical properties. However, it is rather difficult to unambiguously separate these from the physical effects induced by the apparent chemical effect. In any case, it is useful to know that the onset temperature for the decrease in storage modulus can be increased to about 100°C using 2,7-DHN which compares to about 80°C for other copolyesters.

### Packing Density

Table I lists the densities measured for the various copolyesters. These can only be used as indicators of molecular packing density or order when appropriate consideration is given to elemental composition. For example, the presence of the heavy bromine atom in polymers based on Br-HQ complicates simple comparisons with the other polymers in Table I. However, the consistent trend to lower density with higher levels of PET units no doubt reflects a loss in molecular packing efficiency or order. It seems fair to conclude that for fixed contents of PET and HBA units that polymer chains containing 1,4-DHN pack more efficiently than those containing 2,7-DHN. This would be consistent with higher levels of order or crystallinity that is one explanation for the less rapid decrease in storage modulus above the glass transition temperature observed for 1,4-DHN based polymers.

Detailed consideration of the elemental composition is needed for a more complete interpretation of these results especially those containing the heavy bromine atom. One approach is to compare the specific volume of the material to the volume actually occupied by the molecules. The latter can be estimated from group contribution methods such as the one developed by Sugden.<sup>8</sup> From tables of volumetric properties of the elements and various bonding arrangements, occupied volumes were estimated for each of the polymers in Table I. In the final column of Table I, the actual specific volumes, determined from the measured density, are compared to the calculated occupied volumes. The excess beyond unity is regarded as "free volume." As may be seen, the packing efficiency varies much less than the measured density itself does. The trends mentioned above are seen to be valid by this method of comparison, and, in addition, we can see that at constant PET and HBA contents, packing efficiencies for these series rank in the following order: II > I > III. Of course, the amounts of free volume rank in the reverse order.

### CONCLUSIONS

The effect of chemical structure on the properties of thermotropic liquid crystalline copolyesters was examined by incorporating three different dissymmetrical units in the polymer chain. These included 2,7-dihydroxynaphthalene (2,7-DHN) which introduces a kink into the chain, 1,4-dihydroxynaphthalene



(1,4-DHN) which has a pseudosubstituent on the aromatic ring, and bromohydroquinone (Br-HQ) which introduces a polar substituent onto the aromatic ring. The glass transition temperature ( $T_g$ ) determined by DSC and DMTA increases with increasing content of mesogenic and naphthalic units in the copolyester chain. At constant levels of PET and mesogenic units, polymers containing 2,7-DHN units appear to have a higher  $T_g$  than those based on 1,4-DHN or Br-HQ. This effect may be due to the higher stiffness of the bulky 2,7-DHN unit. The lower density of the polymers based on 2,7-DHN units supports this assumption. However, another factor is that copolymers based on 1,4-DHN and Br-HQ apparently are more chemically heterogeneous than those based on 2,7-DHN because the former polymers seem to exhibit two glass transitions, by dynamic mechanical measurements, while the latter polymer exhibits only one such transition. The reason for this may stem from differences in chemical reactivity of the three monomers; however, it is interesting to note that the copolyesters based on 2,7-DHN have slightly lower inherent viscosities than those based on the other two dissymmetrical monomers. The lower onset temperature for the decline in the storage modulus of the 1,4-DHN and Br-HQ containing copolyesters may be influenced by the presence of a PET-rich phase with a low glass transition temperature.

At constant naphthalic unit content, melting temperatures and/or stick temperatures of the copolyesters are highly dependent upon the content of PET and mesogenic units. By increasing the content of PET units in the thermotropic copolyesters from 10 to 20 mol %, the melting and/or stick temperature is reduced from near 300°C to below 250°C. Thus, between 10 and 20 mol % of PET units seems to be a critical level for achieving melt processing temperatures below 250°C.

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