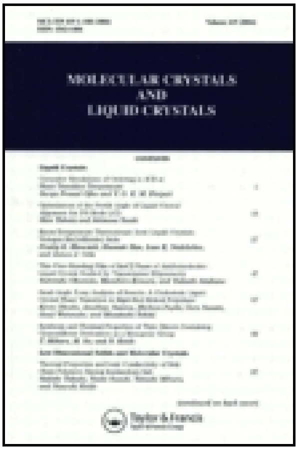

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On Thermotropic Liquid Crystalline Polymers Combined with Low Molecular Weight Mesogens

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ON THERMOTROPIC LIQUID CRYSTALLINE POLYMERS COMBINED WITH LOW MOLECULAR WEIGHT MESOGENS

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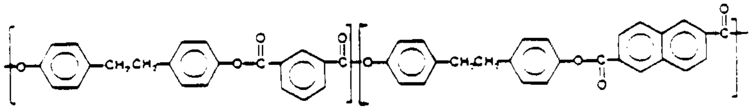
The phase behavior for each of two linear thermotropic liquid crystalline polyesters with a corresponding low molecular weight liquid crystal of similar structure have been investigated. Two distinct types of phase diagrams have been obtained for binary mixtures of a polymer, one containing an in-chain azoxybenzene moiety mixed with para-azoxyanisole and one containing a naphthalene unit mixed with a dimethylester liquid crystal. These phase diagrams were studied by DSC, polarized light microscopy and x-ray diffraction. From this understanding of the physical mixtures a transesterification reaction incorporating the bifunctional low molecular weight liquid crystal by a solid-state reaction into the naphthalene-containing polyester was undertaken. This reaction may be viewed as a potential new processing technique for polymers. The thermal stability of an interreacted blend was shown to be superior to that of either individual component by thermogravimetric analysis. Thus, the potential new processing technique features a lower melting, lower viscosity blend followed by the incorporation of the dimethylester liquid crystal into the polyester main chain producing a more rigid, more stable polymer backbone.

INTRODUCTION

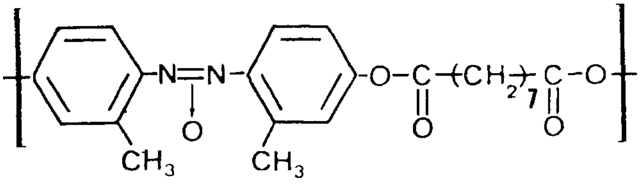
Thermotropic liquid crystalline polymers (TLCP) are now synthesized by step reaction polymerization with a wide range of rigid mesogenic and flexible spacer groups. This investigation considers phase studies of two major types of nematic TLCP that have been received from two research teams[1,2].

One type of nematic TLCP incorporates a 2,6 substituted naphthalene moiety. The general properties of this type of TLCP have been described by Calundann and Jaffe[3]. This study concerns specifically BPE/I/N20,



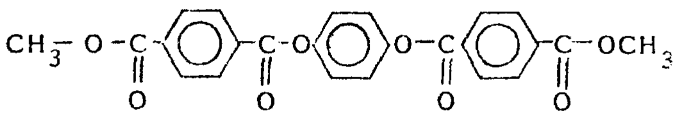
where the designation represents the monomers bisphenol E diacetate, isophthalic acid, and 2,6 naphthalene dicarboxylic acid respectively. The "N20" refers to 20% acid equivalent of the naphthalene moiety. This polymer exhibits superior mechanical properties and its rheology and melt temperature are suitable for industrial processing.

The seond type of nematic TLCP consists of a regular alternating rigid mesogenic and a hydrocarbon flexible spacer group. The specific length of the flexible spacer is 7 carbon atoms, and the mesogen is 4,4' azoxy 2,2'-methylbenzene. It has been described as exhibiting ordinary nematic order[4]. It is designated AZA9,



This type of TLCP exhibits phase transitions differing from those of its low molecular weight homologs such as the 4,4' alkoxy azoxybenzenes. The crystal-nematic transition (T_{K-N}) heat is generally much lower and the nematic-isotropic transition (T_{N-I}) heat larger and much broader. These differences can be attributed to the low degree of crystallinity, molecular weight distribution, small crystallite size, and crystalline defects typical of semicrystalline polymers. The broad nematic-isotropic transition narrows with increasing molecular weight[5] and decreasing molecular weight distribution[6]. The ratio of the entropy change at T_{N-I} to the total entropy change from crystal to isotropic state has been shown to provide a thermodynamic measure of order in the nematic phase[7]. This ratio for low molecular weight liquid crystals (LMWLC) is typically 0.02±1 and for TLCP after extrapolation to 100% crystallinity range from 0.08 to 0.20. These values suggest that the order near the nematic-isotropic transition is generally more than in LMWLC.

The purpose of this investigation is to study the change in transition behavior for two major types of TLCP and upon the addition of similar LMWLC diluents. The AZA9 polymer was blended with para-azoxyanisole and BPE/I/N20 with a dimethylester liquid crystal (DMELC).



This LMWLC exhibits polymorphism including smectic B, smectic A, and nematic forms. Note that the DMELC is bifunctional with the potential for transesterification with BPE/I/N20. Phase diagrams were constructed across the entire compositional range for both systems and the miscibility rules of Demus and Sackmann were considered[8].

EXPERIMENTAL

Phase transitions were determined by differential scanning calorimetry (Perkin Elmer, DSC-2) equipped with a thermal analysis data station and by a polarizing microscope (Zeiss) equipped with a variable temperature programmer (Valley Forge). All DSC measurements were taken at heating rates of 10°/min. The peak maxima correspond well with microscope observations for the T_{N-I} and T_{K-N} transitions.

X-ray diffraction patterns were obtained with a Statton camera using Ni filtered CuKα radiation. A standard flat-film photographic technique was used at a sample to film distance of 51.55 mm. The Statton camera is equipped with an in-house heating cell monitored by a Mettler thermocouple.

Thermogravimetric analyses were performed with a Perkin Elmer TGS-2 equipped with a System 4 Microprocessor controller.

The binary mixtures for phase diagram studies were prepared for the AZA9/PAA system by freeze drying at 10^{-3} Torr from 1,1,2,2 tetrachloroethane and by melt mixing directly in the DSC pan. For the BPE/I/N20-DMELC system the physical mixtures were prepared by heating for 4 hours at 80° in a 60/40 phenol -1,1,2,2 tetrachloroethane polyester solvent followed by coprecipitation into methanol. The coprecipitate was filtered, rinsed with warm methanol, and refluxed in methanol an additional 5 hours. The coprecipitate was again rinsed with warm methanol and dried in vacuo at 100°C for 48 hours.

PAA, BPE/I/N20, and DMELC were used as control samples of blending procedures. The freeze-drying technique removed impurities from PAA, increasing its total heat of transition. The coprecipitation technique for preparing blends lowers the total heat of transition in BPE/I/N20 but the transition temperature remained the same. This indicates that only the degree of crystallinity was altered. DMELC remained relatively the same in total heat of transition and the formation of smectic modifications remained unaltered as evidenced by polarized light microscopy.

RESULTS

The transition temperatures for the TLCP and LMWLC used in this study are listed in Table I.

TABLE I Phase Transitions for Pure Components

Component	Phase Transitions (°C)
AZA9	K 107 N 144 I
BPE/I/N20	K 282 N
PAA	K 118 N 134 I
DMELC	K 233 S 248 N

The nematic-isotropic transition was not observed on heating for BPE/I/N20 or DMELC being intervened by the onset of thermal degradation. The DMELC exhibits a transition to the smectic B phase at ~233°C as evidenced by a mosaic texture which persisted to 240°C. The smectic B transforms to a Schlieren texture indicative of the nematic state at 254°C. It has been observed that smectic B phases are often followed by smectic A and it is presumed that a smectic A modification is intermediate between the smectic B and nematic phases[8].

Table II is a summary of the x-ray diffraction data for DMELC at the temperatures indicated.

TABLE II X-Ray Diffraction Peaks of DMELC

	25°C	255°C	265°C
X-Ray d-spacings (Å)	24.0 (str)	24.0 (str)	3.9 (v wk)
	11.9 (wk)	11.9 (wk)	3.1 (wk)
	7.9 (wk)	8.0 (wk	2.5 (v wk)
	4.6 (v str)	5.4 (str)	
	3.9 (v wk)	3.9 (v str)	
	3.4 (v wk)	3.1 (wk)	
	3.1 (v wk)		

DMELC is a rigid molecular of ~25Å in length and the d-spacing of 24Å indicates both a layered structure in the crystal and smectic modifications. The d-spacings at 12Å and 8Å are attributed to higher order reflections. The d-spacings at 4.6Å in the crystal and 5.4Å at 255°C are attributable to lateral distances between rigid molecules in the layers. The higher angle reflections are thought to be intramolecular distances in the aromatic structure. DSC indicates that the phase transition to the nematic state is complete at 250°C and a Schlieren texture forms at 254°C. However, x-ray diffraction reveals a layered structure persisting to 263°C which is evidence for a cybotactic nematic-phase[10]. This phenomenon is important when considering miscibility with BPE/I/N20.

The phase diagram for BPE/I/N20 - DMELC (Figure 1) indicates miscibility in the nematic state. The hatched area represents the region of thermal degradation as evidenced by thermogravimetric analysis and DSC. The crystal-smectic transition (●) of DMELC remains constant across the entire compositional phase diagram indicating that the smectic phase of DMELC is phase separated from the semicrystalline polymer. This was verified by microscope observations as well as x-ray diffraction.

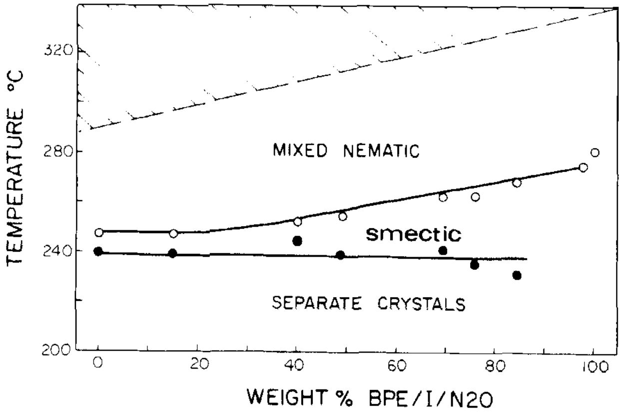


FIGURE 1 Phase Diagram BPE/I/N20 - DMELC

The phase diagram (see Figure 1) exhibits eutectic-type behavior above 40% polymer as evidenced by the depression of the transition into the mixed nematic phase. X-ray diffraction at temperatures just below the nematic transition give d-spacings characteristics of pure BPE/I/N20 crystals. Compositions above 50% polymer showed a fan-shape texture for DMELC which was not observed in pure DMELC. The temperature range of this smectic A modification increased slightly with increasing polymer concentration. Sample DSC thermograms for this region are given in Figure 2. The higher temperature peak represents the transition into an ordinary nematic phase. X-ray diffraction patterns taken above this transition gave no evidence of cybotatic groups.

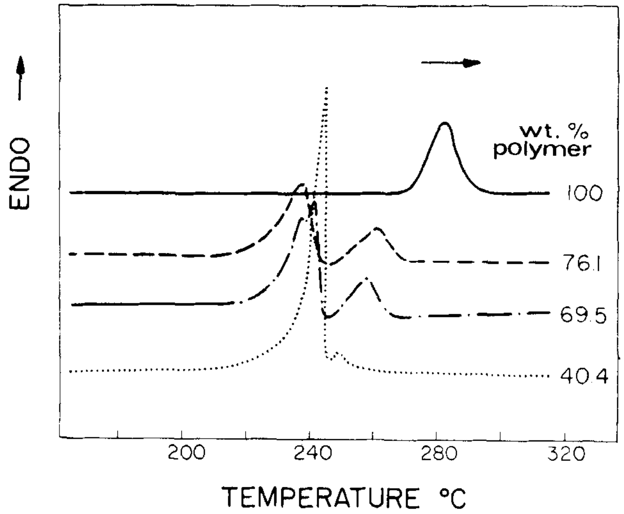


FIGURE 2 DSC Thermograms of BPE/I/N20 Blends with DMELC

The phase behavior of the BPE/I/N20 binary systems indicates a nematic phase that is partially miscible with the cybotactic nematic phase of DMELC. The 14.6 wt.% blend shows phase transitions similar to those of pure DMELC. Optical microscopy shows a transition to a smectic B phase separate from the BPE/I/N20. Upon further heating, the BPE/I/N20 and smectic B modification of DMELC simultaneously form a mixed nematic phase which appears miscible. Thus, at low polymer concentration the nematic phase of BPE/I/N20 and cybotactic nematic phase of DMELC comesophase.

This investigation represents an evaluation for a new concept for the processing of thermotropic polyesters. Historically polyesters are generally processed at low molecular weight (<10,000) followed by post-treatment in the solid-state at temperatures where transesterification can increase the molecular weight[11]. For a TLCP the melt temperature is often near that for significant thermal and/or oxidative degradation. The eutectic type of phase diagram with a bifunctional LMWLC thus provides a method to significantly decrease the transition temperature, to decrease viscosity, and to subsequently incorporate the LMWLC dimethylester into the polyester backbone by transesterification.

The reaction of DMELC with BPE/I/N20 was investigated by thermogravimetric analysis and DSC. To demonstrate the reaction, the 76 wt.% blend was chosen since it is high polymer content and the crystal-nematic transition was depressed 20°C for the physical blend with DMELC. Figure 3 illustrates the thermogravimetric analysis of the two pure components, the 76% physical blend, and the 76% blend reacted for 5 hours at 220°C in vacuo. The physical blend exhibits degradation characteristic of pure components while the reacted blend exhibits similar weight loss to that of BPE/I/N20 but with superior thermal stability. The reaction takes place at the end groups of the BPE/I/N20 and/or randomly along the chain as illustrated in Figure 4. Note that the reaction temperature of 220°C is in the solid physical blend. As the reaction proceeds between DMELC and BPE/I/N20, the crystal-smectic transition systematically disappears by change in area since there are no units in the system remaining which can organize smectic layers. Indeed the reaction can actually be monitored by the disappearance of the crystal-smectic phase transition characteristic of DMELC. The melting point of the 76% blend increased to 281°C after reacting for 5 hours and to 284°C after 7 hours. A more detailed investigation of the new liquid crystal polyester formed in the reaction and its physical characterization will be presented later.

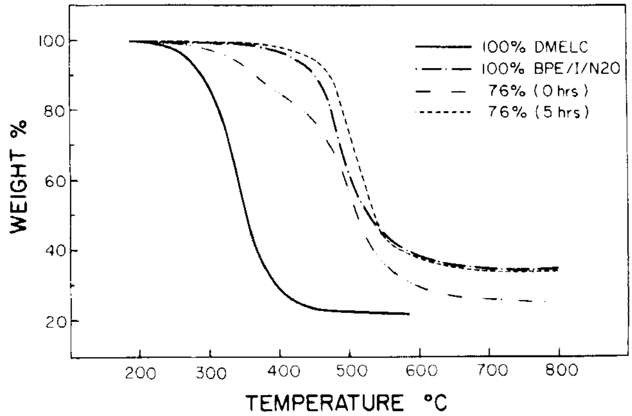


FIGURE 3 Thermogravimetric Analysis BPE/I/N20-DMELC

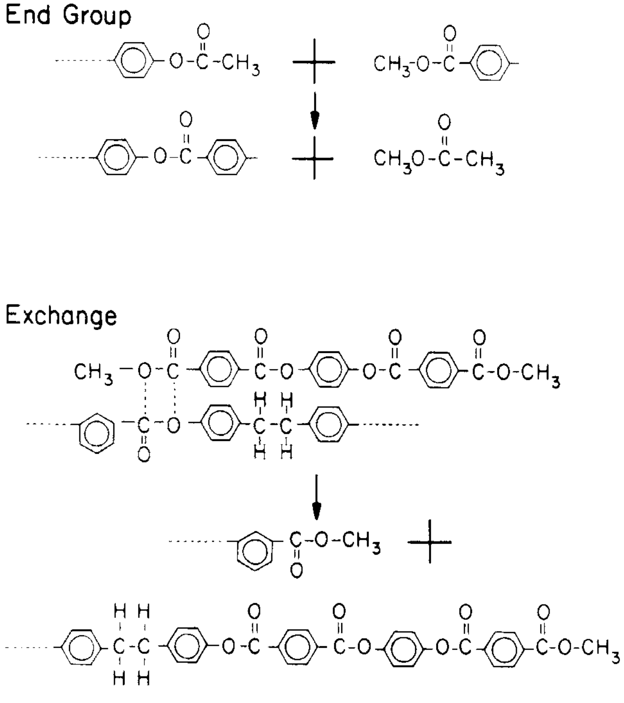


FIGURE 4 Reactions of BPE/I/N20-DMELC

The binary phase diagram for the AZA9/PAA system (Figure 5) indicates mutual miscibility in both the nematic and isotropic phases over the entire range of composition. This criterion is the basis of the miscibility rules[8] confirming the nematic order present in the AZA9 mesophase. The transition temperatures T_{N-I} (■) and T_{K-N} (●) remain constant across the entire phase diagram. This indicates that co-crystallization is likely in the solid state. X-ray diffraction patterns were taken for pure components and the 52 wt.% blend at room temperature. Several d-spacings in the blend were not present in either pure component.

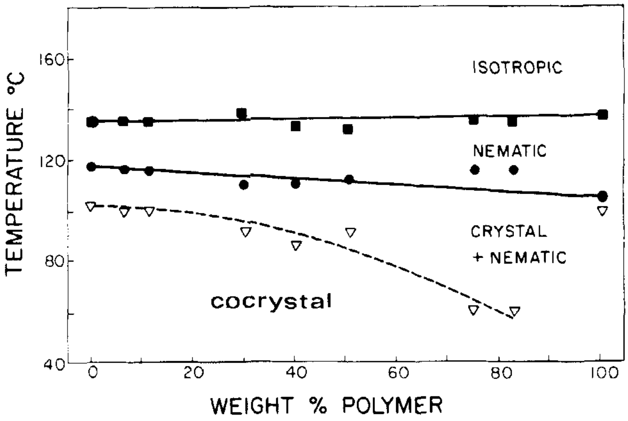


FIGURE 5 Phase Diagram AZA-9/PAA

The lower curve in Figure 5 (▽) represents the broadening of the crystal-nematic transition with increasing polymer concentration. Melt-mixed blends exhibited much broader T_{K-N} transitions whereas the freeze-drying method produced thermal transitions resembling those of pure PAA. This can be attributed to the difference in crystallization conditions, i.e., solvent grown versus melt grown crystals. Figure 6 is the DSC thermogram for the 52.6% AZA9/PAA blend prepared by freeze-drying. The temperature of the phase transitions (T_{K-N} and T_{N-I}) were not dependent upon the blending technique as observed by the formation of Schlieren textures and isotropic states by polarized light microscopy. The melt mixed blends exhibited exotherms at ~60°C which is attributed to recrystallization. The polyester is thought to suppress the crystallization of PAA upon cooling at 10°/min.

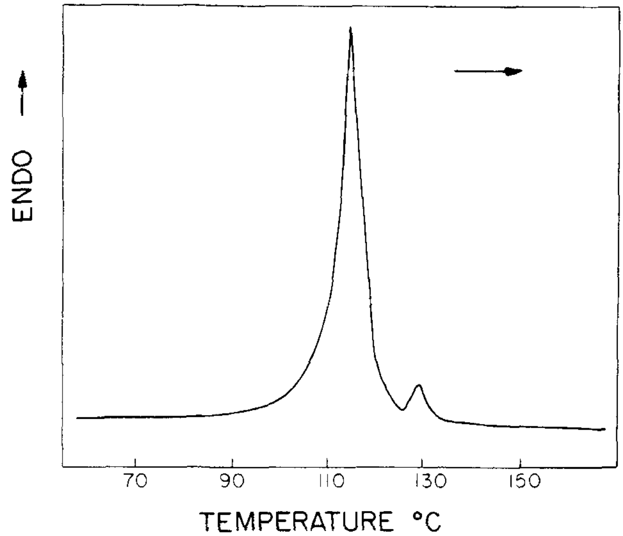


FIGURE 6 52.6% AZA-9/PAA Freeze-Dried

Table II is a summary of the calorimetric data for AZA9/PAA binary blends. PAA exhibits a much larger total heat of transition than AZA9. This dominates the transitions in binary blends. Thus, the ratio ΔH(LC-I)/H(tot) should give a relative measure of the alignment of PAA with AZA9 near the nematic-isotropic transition. ΔH(LC-I) increases as the polymer content increases and reaches a value larger than for either pure component. The ratio ΔH(LC-I)/H(tot) is approximately equal to the corresponding entropy ratio defined earlier. The ratio reaches 0.12 at 82.2 wt.%

polymer. It is interesting to note that Blumstein[12] obtained for the same polymer an equivalent ratio of 0.14 assuming ΔH(tot) for a 100% crystalline polymer. If this calorimetric method is reliable it would indicate that AZA9 has a higher degree of order than PAA near the nematic-isotropic transition and provides information without knowledge of a ΔH(tot) value for a 100% crystalline AZA9.

TABLE III Thermal Data for AZA-9/PAA Blends

% AZA-9	ΔH(tot) (cal/g)	ΔH(LC-I) (cal/g)	$\frac{\Delta H(LC\text{-}I)}{\Delta H(tot)}$
PAA	27.4	0.85	0.03
6.9	22.3	0.65	0.03
10.2	23.4	0.67	0.03
30.0	18.1	0.70	0.04
52.6	16.5	0.75	0.05
76.4	10.6	1.06	0.10
82.2	9.4	1.12	0.12
100.0	1.6	0.99	–

CONCLUSION

Two distinct types of phase diagrams have been presented for binary mixtures of TLCP in LMWLC. A new processing technique utilizing the melting point depression of a eutectic-type phase diagram was demonstrated. The technique features a lower melting, lower viscosity physical blend for melt processing followed by the solid-state transesterification of the LMWLC into the polymer backbone.

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