Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 19 Dec 2006.

To cite this article: Mark T. De Meuse & Michael Jaffe (1988): Model System for Liquid Crystal Polymer Blends, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 157:1, 535-566

To link to this article: http://dx.doi.org/10.1080/00268948808080255

Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt., 1988, Vol. 157, pp. 535–566
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Printed in the United States of America

MODEL SYSTEM FOR LIQUID CRYSTAL POLYMER BLENDS

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Abstract Copolymers which contain 2-hydroxy-6-naphthoic acid and p-hydroxybenzoic acid, differing only in comonomer ratios, have been used as a model system for blends in which both of the component materials are capable of forming liquid crystalline phases. The rheological behavior suggests that not all of the blends behave the same in the anisotropic melt. Solid state data which was obtained using DSC, DMTA, X-ray, and optical methods is interpreted in terms of miscibility of the component materials. Calculations, based on Windle's sequence matching calculations, have been performed to explain the observed DSC transition temperatures in the blends.

INTRODUCTION

A considerable amount of effort has been expended during the last several decades to attempt to understand the behavior of polymer mixtures. Variables such as molecular weight, temperature, and composition of the two component materials have been shown to be important in understanding the behavior present in such systems (1).

Much of the recent attention has focused on determining miscibility criteria for polymer blends. It is not necessarily true that miscible blends are required to achieve desireable properties. Certainly, in some systems what is desired is not molecular

mixing but simply adhesion between the two coexisting phases. Miscible systems do offer the advantage of tailoring ultimate properties to desired needs. As such, they offer systems where ultimate properties can be controlled. With this in mind, it is of great practical value to be able to make predictions about the expected miscibility of any polymer-polymer systems.

A major step in this direction has been made by several groups recently (2-4). Using a mean-field theory approach, it has become possible to explain why a window of miscibility exists in systems in which at least one of the components is a copolymer. This approach has been found to be extremely useful in explaining unexpected miscibility behavior in systems consisting of PPO with various halogen-substituted polystyrenes (5-8).

What these workers have done is to decompose the classical Flory χ parameter into segmental interaction parameters characteristic of the interaction between the various monomeric units. In this formalism, χ_{BLEND}, characterizing the enthalpic interactions between the two components, is given by

$$\chi_{BLEND} = xy\chi_{AC} + x(1-y)\chi_{AD} + (1-x)y\chi_{BC} + (1-x)(1-y)\chi_{BD} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD} \quad (1)$$

where the general system being described consists of copolymers designated AB and CD. The volume fraction of component A in polymer 1 is designated x and the volume fraction of component C in polymer 2 is denoted as y. This is the general expression for the mixing of any two copolymers.

The above expression for χ_{BLEND} simplifies considerably in certain situations. For example, when considering two copolymers composed of the same monomers but differing in composition, simplifies to

$$\chi_{BLEND} = (x-y)^2\chi_{AB} \quad (2)$$

This expression now contains only one χ parameter. Using the fact that as in the usual Flory-Huggins theory, a critical point in polymer mixtures corresponds to

$$\chi_{BLEND} = \chi_S \tag{3}$$

where

$$\chi_S = \frac{1}{2}\left(\frac{1}{\sqrt{N_1}} + \frac{1}{\sqrt{N_2}}\right)^2 \tag{4}$$

The degrees of polymerization of the two component materials are N_1 and N_2 . It should be possible to systematically examine copolymers differing in composition and determine when phase separation occurs. Such an analysis should allow a determination of χ_{AB} .

It should be noted that Equation (2) implies that in the limit of infinite molecular weight, the copolymers composed of the same monomers but differing only in the comonomer ratio will be miscible only when x=y. Finite molecular weight of the polymers allows nonzero composition differences to be tolerated and still have a miscible system. Analyses of such systems have been very limited in the literature (9).

The present investigation will consider such a preliminary analysis of thermotropic liquid crystalline polymers which form nematic phases in the molten state. These polymers can be processed when molten and as such can form highly oriented specimens. Due to their rodlike molecular conformation, the above formalism may not be applicable to such systems. As such, the present work is a very stringent test of the theoretical framework.

By analogy with small molecule nematics, where the type of liquid crystal formed is used as a test for miscibility, it might be expected that all polymer molecules that form nematic phases would be miscible (10). This is in contrast to the ideas expressed in Equation (1) which indicates that certain copolymers will be immiscible with each other. The present work will suggest which of these ideas is applicable to the liquid crystal polymer blend systems.

A related study has recently been reported by Ciferri et al (11) using the system cellulose acetate and (hydroxypropyl) cellulose dissolved in N,N-dimethylacetamide (DMAc). The two polymers exhibit similar conformations, thereby eliminating gross entropic differences which are known to lead

to phase separation in rigid rod/random coil systems (12,13). Both of the polymers also exist in anisotropic phases above a certain critical concentration. It is found that when the ternary systems are examined, two anisotropic phases exist above the critical volume fraction. Each of the stable anisotropic phases contain pure polymer. The authors conclude that compatibility between polymers forming similar mesophases may not be often observed, in contrast to the case of low molecular weight liquid crystals.

The liquid crystal polymers of interest to the present investigation are insoluble in most common solvents and their solubility in any solvent is limited to fractions of a percent. Therefore, a miscibility criterion for systems which form mesophases in the melt had to be established. The classical test is lack of phase separation in the melt leading to no light scattering from phase boundaries and thus no appearance of cloudiness. This test is generally used for isotropic melts and is ruled out for the liquid crystal polymers because of their opacity due to the intense scattering from the domains.

Another criteria which has been used to determine miscibility of systems in the melt is the rheology of the blends as a function of composition compared to the rheology of the component materials. Due to the fact that the morphology of a two phase system changes with processing conditions, it is expected that the viscosity of miscible systems will change in some way intermediate to the component materials whereas two phase systems will show deviations from such behavior. Evidence for such behavior has indeed been observed for such two phase systems as polyethylene-polypropylene (14), polycarbonate-acrylonitrile butadiene styrene copolymer and polycarbonate-polypropylene, and polystyrene-polyethylene and polystyrene-polypropylene (15). On the other hand, systematic variation between the viscosity of the component materials has been observed for such miscible systems as poly(phenylene oxide)-high impact polystyrene (16), polycarbonate-poly(methyl-methacrylate) (15), and cis 1,4 polyisoprene-natural rubber (17).

The purpose of the present investigation is to extend the above studies to blend systems consisting

of two components each of which is capable of forming a liquid crystal phase in the melt. Section II contains a summary of experimental procedures. The melt viscosity is summarized in Section III. Sections IV and V contain characterization details of the solid state structure which is present in the blends. Section VI is devoted to a theoretical interpretation of the solid state results. Finally, Section VII contains the summary and conclusions.

EXPERIMENTAL PROCEDURE

The samples used in this study consist of copolymers containing p-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) in the mole fraction ratios 30/70, 58/42, and 75/25. When referring to these samples, the mole fraction of HBA will always appear first. Degrees of polymerization for these samples are about 100 to 150. These polymers are believed to be essentially random copolymers, with a relatively narrow molecular weight distribution.

The blends were produced via a melt blending procedure. The equipment which was used was a Haake-Buchler Rheocord. The sample size was 70.0 grams which was determined by the density of the sample. Standard mixing conditions were to melt blend the samples for five minutes using a rotor speed of 40 RPM at a particular temperature. The samples were, then, given two minutes at 5 RPM followed by programming the rotor speed to 100 RPM in a two minute period. The speed is, then, instantaneously lowered back down to 5 RPM in 2 minutes. This is followed by two minutes at 5 RPM to determine whether the ramp test has affected the sample in any way. Since the copolymers used in this work are capable of undergoing hydrolytic degradation, drying before any melting process is required. The samples in the present study were dried overnight at 120 C prior to testing.

The X-ray diffraction work which is reported was performed on strands of both the neat materials and the blends. Meridonal scans were performed using a focused beam on a high resolution Huber diffractometer, utilizing $CuK\alpha$ radiation on a high intensity rotating anode. The beam, focused at the sample position, was about 1x1 mm in size. A θ-2θ coupling was performed using the total reflection

of a glass slide. A step scan was performed in transmission mode from 5 degrees to 60 degrees (2θ) with 0.1 step size for a period of 60 seconds and for expanded scans from 8 degrees to 16 degrees (2θ), the stepping time is 120 seconds per step. Experiments were also carried out on one set of samples to study if diffraction patterns are sample dependent.

The DSC results which are presented were obtained using a DuPont 1090 DSC. All experiments were run in a nitrogen atmosphere using a heating rate of 20 C/min, unless otherwise noted.

RHEOLOGY RESULTS

One of the suggestions for what might happen when blends of different aromatic copolyesters are made is that a chemical reaction might occur and produce a single polymer with composition intermediate to the starting materials. Specific catalysts have been defined for promoting such reactions (18). The possibility of such reaction occurring had to be investigated.

What was done was to provide the blends with a constant mixing speed and monitor the torque as a function of mixing time. If a chemical reaction is not occurring, once the torque reaches a steady value, it will not deviate from this value with increased time. If instead, the suggested ester exchange reaction does occur, the torque generated will change as the two copolymers react and eventually attain some constant value which corresponds to the new composition sample.

Figure 1 contains the results of the suggested experiment for a 50/50 blend of HBA/HNA 58/42 and HBA/HNA 75/25. As can clearly be seen, the torque value remains essentially constant on the timescale of this experiment, which is considerably longer than the time required to perform the mixing experiments referred to later. The suggestion, then, is that chemical reaction is not a significant factor in the present experiments.

Having demonstrated that chemical reaction is not a major factor in the present blends, it is possible to show that the Haake-Buchler equipment can be used to obtain rheology data. As demonstrated by Goodrich and Porter (19) and Blyler and Daane (20), such mixing equipment can

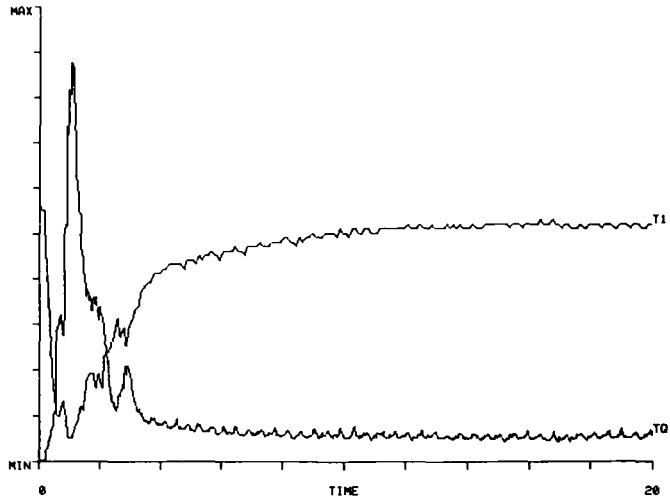

FIGURE 1. Torque vs. mixing time data for HBA/HNA blend

be used to gather the same rheological information as is obtained via more traditional capillary rheometer methods. They have shown that the following relation is applicable to torque and rotor speed data

$$M = K \cdot C(n)\, S^{n} \qquad (5)$$

In this relation, M is the torque, K is the consistency index familiar from viscosity-shear rate relationships, S is the rotor speed, and n is the power-law index, also familiar from viscosity versus shear rate plots. From equation (5), it can be seen that a log-log plot of torque versus rotor speed should yield a straight line with intercept given by log (K·C(n)) and slope given by n, the power-law index.

The method outlined above presents an alternative to traditional capillary rheology as a means of obtaining useful rheological information. Before presenting data on the blends, evidence will be presented to confirm that the two methods measure the same information.

To achieve this goal, samples which contain 58 mole percent HBA were dried overnight. One set of samples was run in duplicate on the Haake Rheocord

using the previously described method of programming the rotor speed and measuring the torque which is subsequently generated. Another set of samples was run in duplicate on a Sieglaff-McKelvey capillary rheometer. The torque versus rotor speed data was analyzed using relation (5) given previously. The capillary rheometer data was analyzed using the relation

$$\eta = K\dot{\gamma}^{n-1} \tag{6}$$

In this relationship, the viscosity is η , $\dot{\gamma}$ is the shear rate, K is the consistency index, and n is the power-law index.

The results of the two sets of experiments are listed in Table I. Analysis of both sets of data yielded correlation coefficients of 0.99 or better, proving that the data corresponds to the indicated relation. The excellent agreement between the power-law values measured by the two methods indicates that complementary information is being obtained.

TABLE I Comparison of capillary rheology and torque rheometer results

Method	Prefactor	Power-Law Index
Haake	$K \cdot C(n) = 16.2 \pm 4.5$	0.47 ± 0.03
Sieglaff	$K = 2.79 \pm 0.10 \times 10^4$	0.46 ± 0.01

Having shown that the Haake equipment measures the same parameters as capillary rheology equipment, it is possible to use the equipment to obtain rheological information on the blends. The power-law values which are obtained for the component materials as well as the blends for HBA/HNA 58/42 and HBA/HNA 75/25 are listed in Table II. The values obtained are the average of two runs. There does not seem to be any significant difference between the values obtained for the component materials and the blends.

TABLE II Power-law values for blends of HBA/HNA 58/42 and HBA/HNA 75/25

Weight % HBA/HNA 75/25	Power-law Index
0	0.47 ± 0.03
25	0.44 ± 0.02
50	0.45 ± 0.03
75	0.44 ± 0.01
100	0.48 ± 0.01

Compiled in Table III are the apparent viscosities which are generated by the various samples at constant torque (shear stress) of 50 meter-grams. The apparent viscosities are calculated by dividing the torque by the rotor speed analogously to the way that one calculates viscosities by dividing shear stress by shear rate. Since torque is directly proportional to shear stress and rotor speed is directly proportional to shear rate, the calculated values are related to the real viscosities by some undefined constants. Hence, the values are termed apparent viscosities. It is important to

TABLE III Apparent viscosities for blends of HBA/HNA 58/42 and HBA/HNA 75/25

Weight % HBA/HNA 75/25	Apparent viscosity
0	4.5 ± 2.0
25	7.3 ± 1.2
50	14.2 ± 1.4
75	22.0 ± 5.0
100	35.6 ± 2.0

use the apparent viscosities at constant torque rather than at constant rotor speed. The reason for this is because it is torque (shear stress) rather than rotor speed (shear rate) which is continuous across phase boundaries.

The values compiled in Table III are also plotted in Figure 2 and compared to the predictions of the logarithmic rule of mixtures for the apparent viscosities. The straight line is defined by

$$\ln \eta_{BL} = w_1 \ln \eta_1 + w_2 \ln \eta_2 \qquad (7)$$

where η_{BL} is the viscosity which is generated by the blend, the w's are the weight fractions of the two component materials in the blend, and η_1 and η_2 are the viscosities of the respective component materials. Equation (7) is the blending law generally associated with the rheology of compatible systems (21).

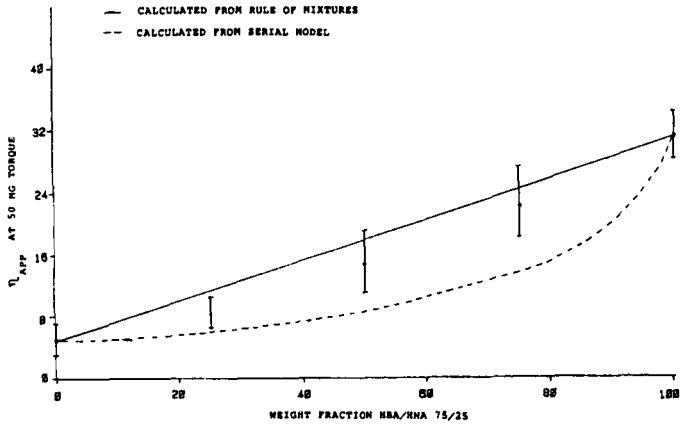

FIGURE 2. Apparent viscosities of blends of HBA/HNA 58/42 and HBA/HNA 75/25

Also plotted in Figure 2 are the predictions from

$$\frac{1}{\eta_{BL}} = \frac{w_1}{\eta_1} + \frac{w_2}{\eta_2} \qquad (8)$$

This last equation is the relationship that is expected between the viscosity which is generated by the blend and the viscosity generated by the

component materials if the two component materials are completely immiscible.

Figure 2 demonstrates that the viscosities of the HBA/HNA 58/42 + HBA/HNA 75/25 blends are fitted very well by the logarithmic rule of mixtures. As suggested above, this result indicates that these blends are miscible in all proportions in the nematic melt.

A different type of rheological behavior is observed with the HBA/HNA 30/70 + HBA/HNA 75/25 blends. The calculated power-law values are displayed in Table IV. Once again, the values are all averages of two separate experiments. The values of the apparent viscosities at a constant torque of 50 m-grams are plotted in Figure 3 versus wt. percent HBA/HNA 75/25 in the blend. The monotonic increase that was observed for the 58/42 + 75/25 blends is not observed here. Instead, the torque seems to pass through a maximum for the blend which contains 25 percent HBA/HNA 75/25 and a minimum for the blend which contains 50 percent HBA/HNA 75/25. Also plotted in Figure 3 are the predictions from Eq. (7), indicative of a miscible blend and the predictions of Eq. (8).

TABLE IV Power-law values for blends of HBA/HNA 30/70 and HBA/HNA 75/25

Weight % HBA/HNA 75/25	Power-law Index
0	0.55 ± 0.04
25	0.37 ± 0.01
50	0.46 ± 0.06
75	0.41 ± 0.03
100	0.45 ± 0.05

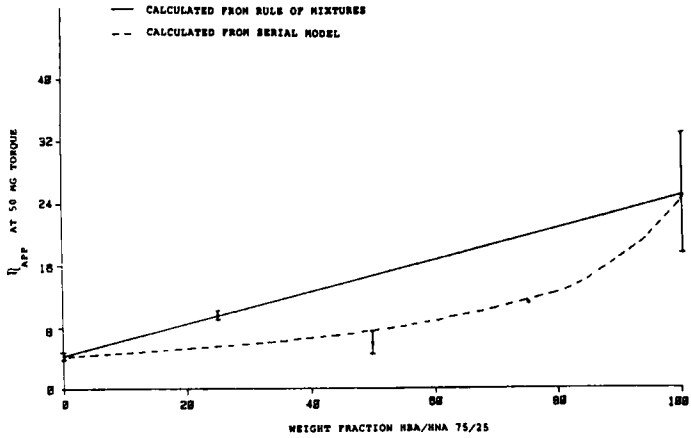

FIGURE 3. Apparent viscosities of blends of HBA/HNA 30/70 and HBA/HNA 75/25

What this data indicates is that the rheological response for the sets of blends is different. Blends of the two copolymers which are close in average composition have a rheological response characteristic of miscible systems. As the difference in HBA content increases, the rheological response is characteristic of immiscible systems. This is to be contrasted with the behavior expected of small molecule liquid crystals where all nematics are expected to form miscible mixtures. Attention is now turned to the solid-state characterization of these blends.

X-RAY RESULTS

In a paper by Gutierrez et al (22), X-ray diffraction patterns were shown of random arrangements of HBA/HNA along the polymer chain. Model calculations were also given as a function of composition variation of HBA/HNA. Those results show that significant change can only occur in the first and second meridonal peaks as a function of HNA concentration. No significant change is observed in the strong third peak. As a result of these observations, the present examination will focus on the changes in the first two peaks to

determine if the polymers are indeed blended at the molecular level.

Figure 4 shows the X-ray flat plate picture of the first set of samples consisting of HBA/HNA 58/42, HBA/HNA 75/25, and a 50/50 blend of these two component materials.

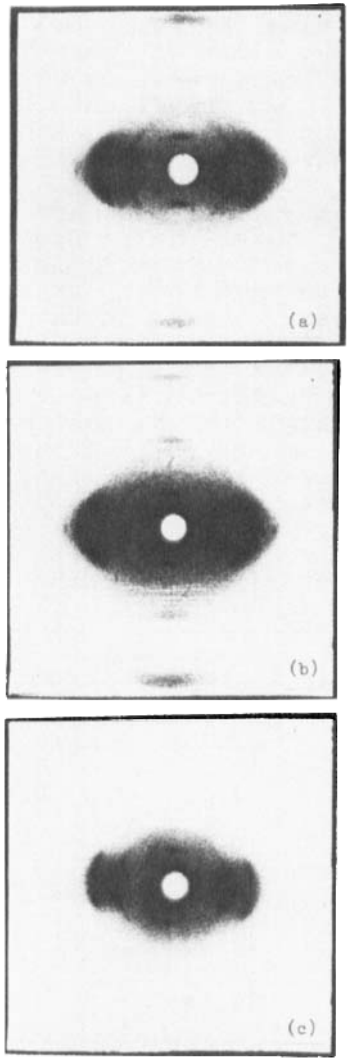

FIGURE 4. Flat plate x-ray pictures of (a) HBA/HNA 58/42 (b) 50/50 blend of HBA/HNA 58/42 and HBA/HNA 75/25 and (c) HBA/HNA 75/25

The fibers are in the vertical position with respect to the picture. These figure indicate that the diffraction patterns are essentially the same and are consistent with the previous results. It is clear from these pictures that detailed diffractrograms are needed to determine the expected differences in the meridonal peaks.

Figure 5 contains the meridonal scans for HBA/HNA 58/42 at two different positions of the same fiber. The second position is about 1 cm away from the first position. In this figure, relative intensity is plotted versus 2θ . Three peaks were observed in both samples at approximately the same positions of 12.1° , 30.2° , and 43.5° . Expanded scans of the first peak are shown in Figure 6. Curves (1) and (2) are taken from the same fiber at about 1 cm apart and curve (3) is taken from another fiber of the same batch. The 2θ spacings are listed in Table V. Based on the results which are taken from Figures 5 and 6, it can be concluded that there are no significant differences in the diffraction patterns taken from different parts of a fiber sample of the same batch. No significant change in the peak width was observed. These results indicate that the fiber samples are essentially homogeneous.

TABLE V Peak position and widths (2θ) for HBA/HNA 58/42

Peak	2θ	ω
1	12.15	0.66
2	12.11	0.70
3	12.09	0.68
ave	12.12	0.68
1	30.23	1.35
2	30.20	1.37
ave	30.22	1.36
1	43.64	1.28
2	43.51	1.21
ave	43.58	1.25

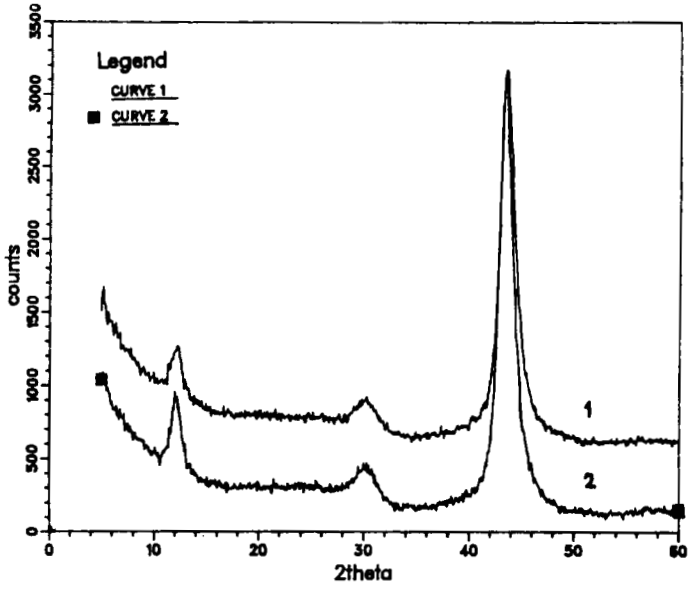

FIGURE 5. X-ray diffraction patterns of HBA/HNA 58/42 taken at two positions

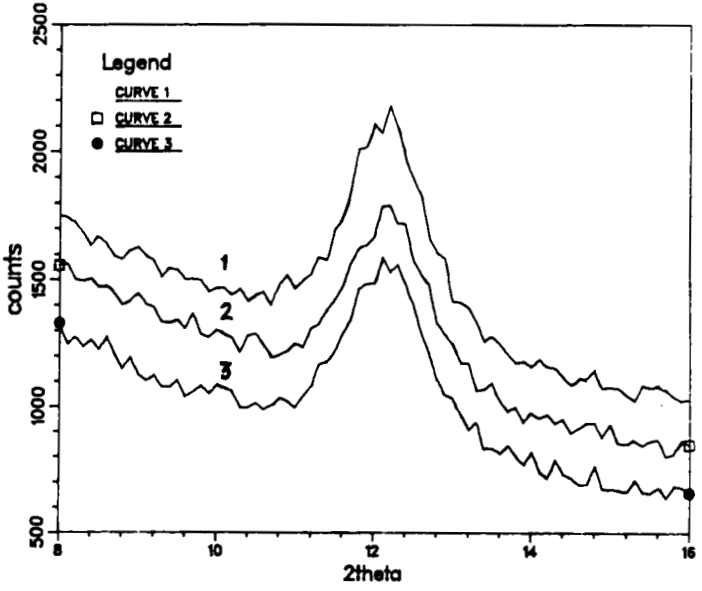

FIGURE 6. Expanded scan of the first peak of HBA/HNA 58/42

Figure 7 contains the meridonal scans for HBA/HNA 75/25. The peak positions were found to be about 13.26° , 28.62° , and 43.64° . An expanded scan of the first peak is shown in Figure 8. This peak position occurs about 1.25 degrees higher than the HBA/HNA 58/42 peak. This result indicates that if the 50/50 mixture of HBA/HNA 58/42 and HBA/HNA 75/25 is not molecularly mixed or blended, there will be two peaks separated by about 1.25 degrees.

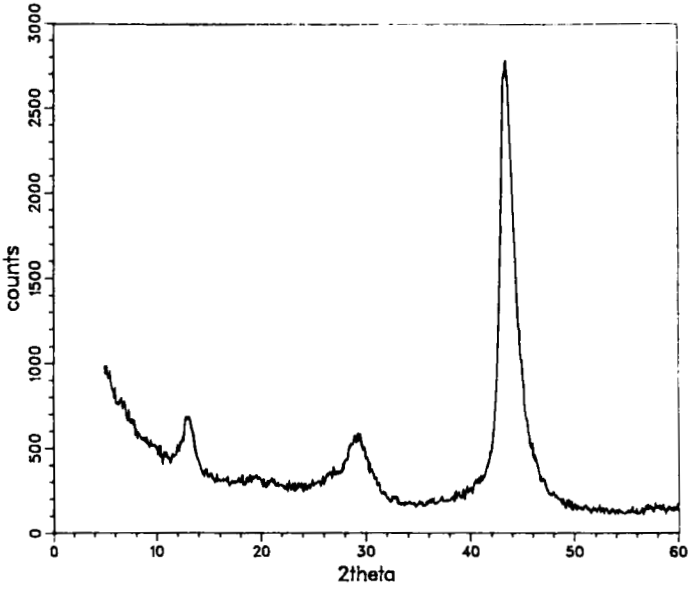

FIGURE 7. X-ray diffraction pattern of HBA/HNA 75/25

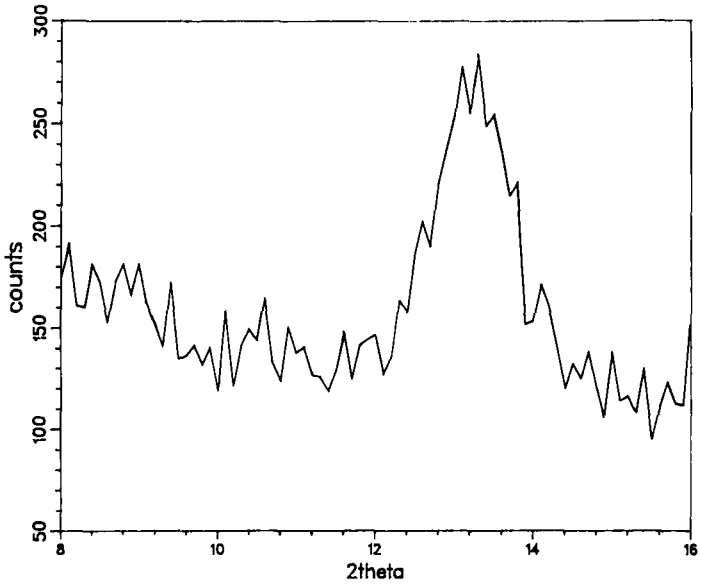

FIGURE 8. Expanded scan of HBA/HNA 75/25

To ensure that this is correct and not due to instrumental errors, two fibers, one from HBA/HNA 58/42 and the other from HBA/HNA 75/25 were placed next to each other in the diffractometer and the resultant scans are shown in Figures 9 and 10. There are clearly two overlapping peaks in the first region. The expanded scan shows that the peaks are separated by about 1 degree, as expected. It is also significant that there are no clear signs of overlapping peaks in the second and third region. This clearly shows that the first peak is the correct one to monitor the changes in HBA/HNA compositions/ or molecular blending.

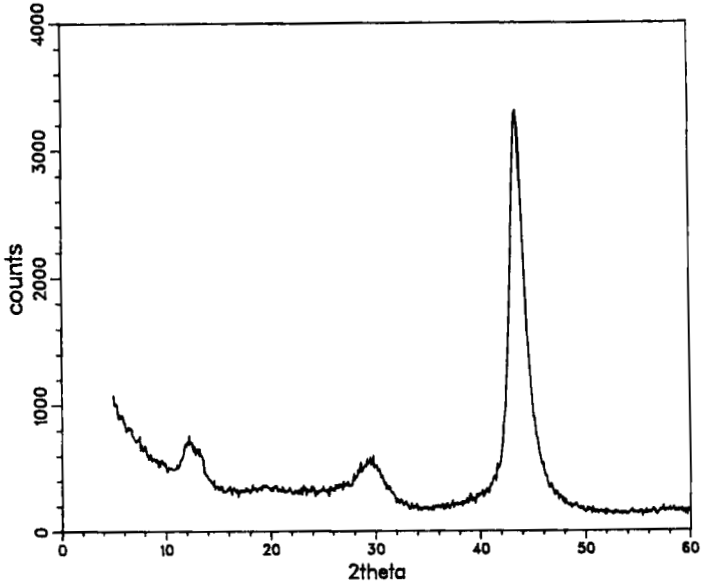

FIGURE 9. X-ray diffraction pattern of physically mixed HBA/HNA 58/42 and HBA/HNA 75/25

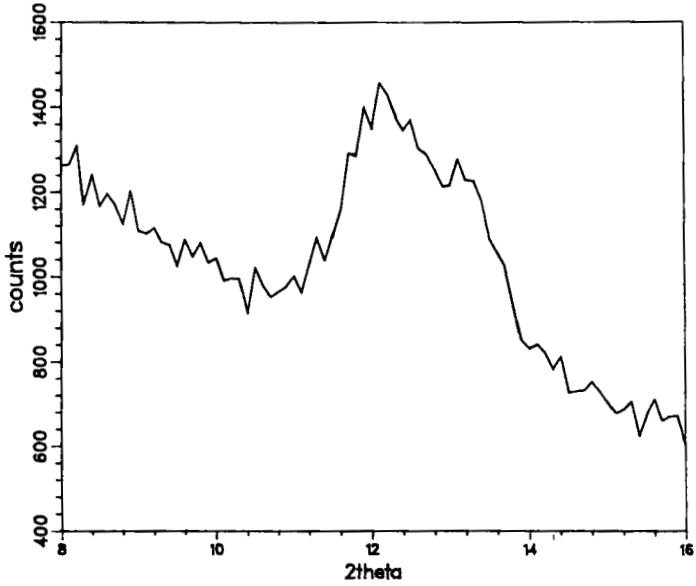

FIGURE 10. Expanded scan of physically mixed HBA/HNA 58/42 and HBA/HNA 75/25

Figures 11 and 12 are the resultant diffraction patterns of the 50/50 blend of HBA/HNA 58/42 and HBA/HNA 75/25. To ensure the reproducibility, two expanded scans were performed on different parts of the fiber sample as shown in curve 12. It should be noted from the width of these peaks that there is no indication of two overlapping peaks as observed in the physical mixture case. Also, it is to be noted that the position of the first peak at 12.98° corresponds to a scattering distance of 6.82 Å . If chemical reaction had occurred in the blend, a copolymer of composition HBA/HNA 67/33 would have been produced. Previous work suggests a scattering distance of about 6.99 Å for the first peak of this copolymer. The difference between this and the observed position is outside of experimental error and provides further evidence that chemical reaction is not a dominant feature in these blends.

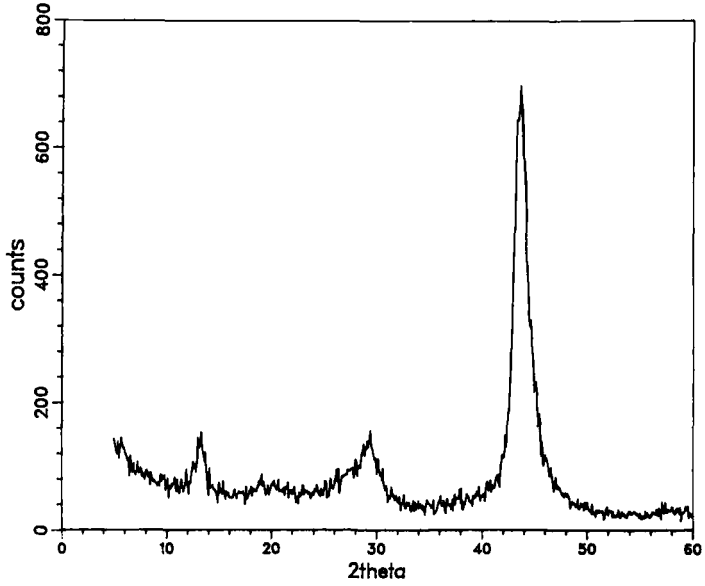

FIGURE 11. X-ray diffraction pattern of 50/50 blend of HBA/HNA 58/42 and HBA/HNA 75/25

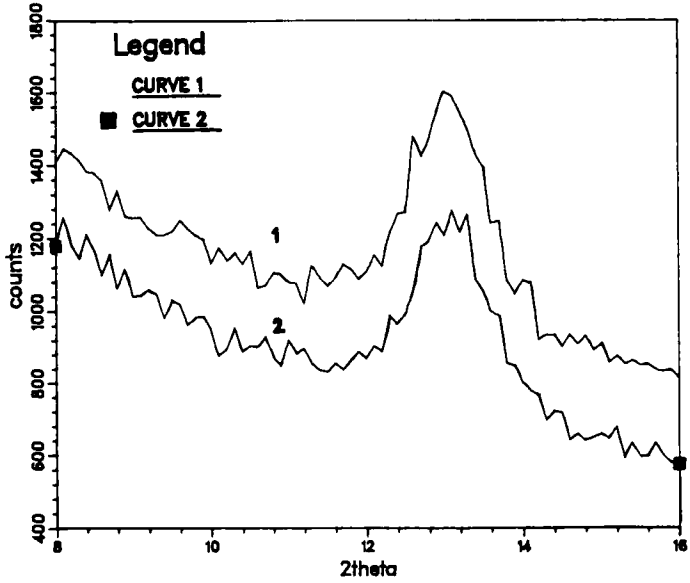

FIGURE 12. Expanded scan of 50/50 blend of HBA/HNA 58/42 and HBA/HNA 75/25

The results for the second set of samples are plotted in Figure 13. Intensity in arbitrary units is plotted on the y-axis while 2Θ appears on the x-axis. The respective scans are for HBA/HNA 30/70, HBA/HNA 75/25, a physical mixture of HBA/HNA 30/70 and HBA/HNA 75/25 and a 50/50 blend of the two component materials. Expanded scans of the regions of the first peak from 8° to 16° is shown in Figure 14. There are also some rather small shifts in the second and third peaks, however rather small.

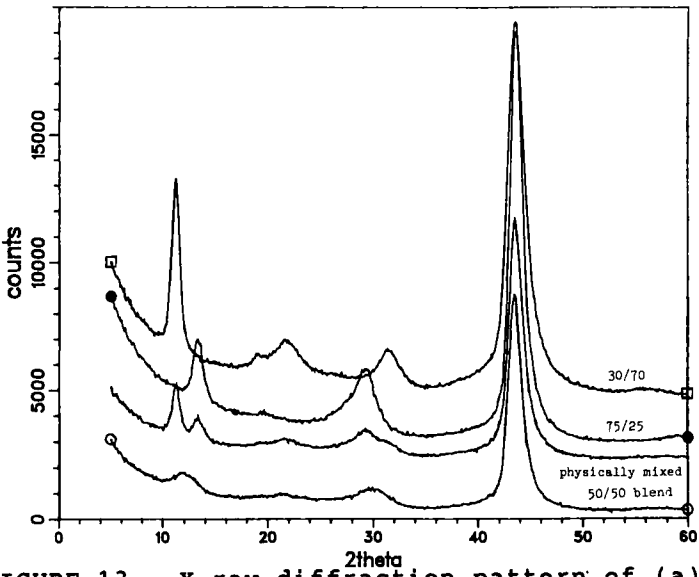

FIGURE 13. X-ray diffraction pattern of (a) HBA/HNA 30/70 (b) HBA/HNA 75/25 (c) physically mixed and (d) 50/50 blend of (a) and (b)

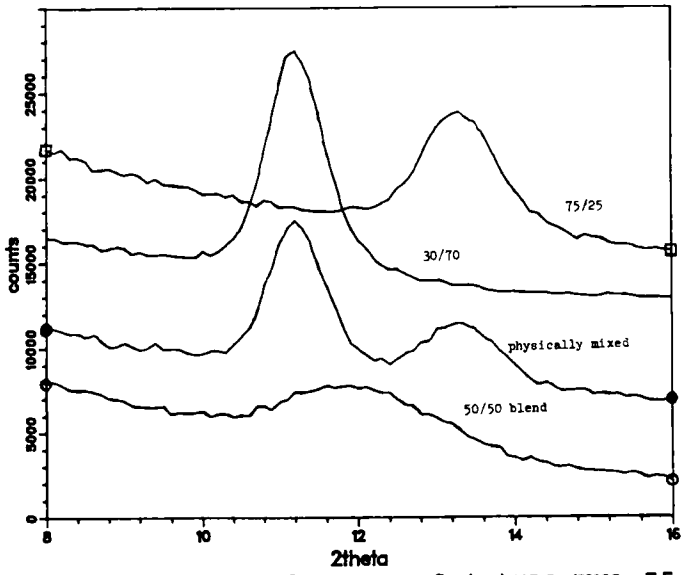

FIGURE 14. Expanded scans of (a)HBA/HNA 75/25 (b) HBA/HNA 30/70 (c) blend of HBA/HNA 75/25 and HBA/HNA 30/70 and (d) physical mixture of HBA/HNA 30/70 and HBA/HNA 75/25

Both Figure 13 and 14 clearly show that there are two peaks in the physically mixed fiber, one which corresponds to HBA/HNA 75/25 and the other to HBA/HNA 30/70. The peak positions are listed in Table VI. Clearly, if the blends are completely immiscible, there will be two peaks observed as shown in Figure 14. The blend shows the existence of only a single peak centered at about 12.1 degrees. By examining the width of the peak, it is seen to encompass both of the component materials. It can be concluded that the polymers are molecularly mixed and form a different matrix from either of the component materials.

TABLE VI Peak positions for blends of HBA/HNA 30/70 and HBA/HNA 75/25

Peak	75/25 2θ	30/70 2θ	50/50 blend 2θ	Mixture 2θ
1	13.16	11.17	12.10	[11.16]
				[13.28]
		19.10		
		21.78		21.64
2	28.88	31.51	29.89	29.12
				31.51
3	43.67	43.68	43.56	43.62

DSC RESULTS

As another method of probing the solid state structure which is present in the blends, DSC studies were performed on the component materials as well as the blends. After having mixed the samples as described previously, they were ground into a fine powder using a Wiley mill. The component materials were treated in a similar manner in order to guarantee similar thermal histories.

DSC scans for HBA/HNA 58/42 and HBA/HNA 75/25 are displayed in Figure 15. The typical small endotherm attributed to the crystal to nematic transition is observed. The irregular baseline is another common feature associated with these scans. It has been observed previously (23) that the

endothermic peak temperature is highly dependent on the composition of the copolymer.

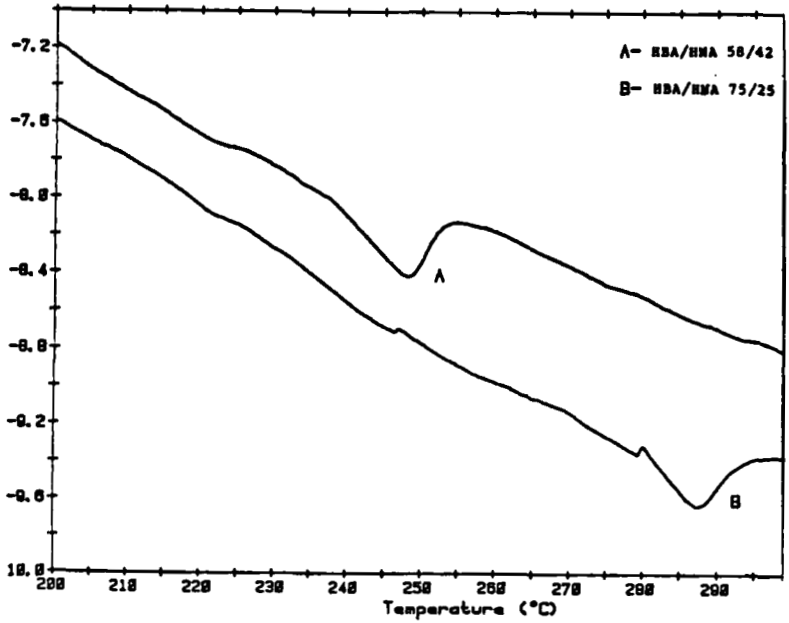

FIGURE 15. DSC scans of HBA/HNA 58/42 and HBA/HNA 75/25

The transition temperatures for the three blends consisting of different ratios of HBA/HNA 58/42 and HBA/HNA 75/25 are displayed in Figure 16. This data was generated under the same conditions as for the component materials. It should be noted that the 50/50 blend displays a transition at about the same temperature as the HBA/HNA 58/42 sample. Surprisingly, the blend which contains 75 weight percent HBA/HNA 58/42 displays a transition which is lower in temperature than the neat 58/42 sample.

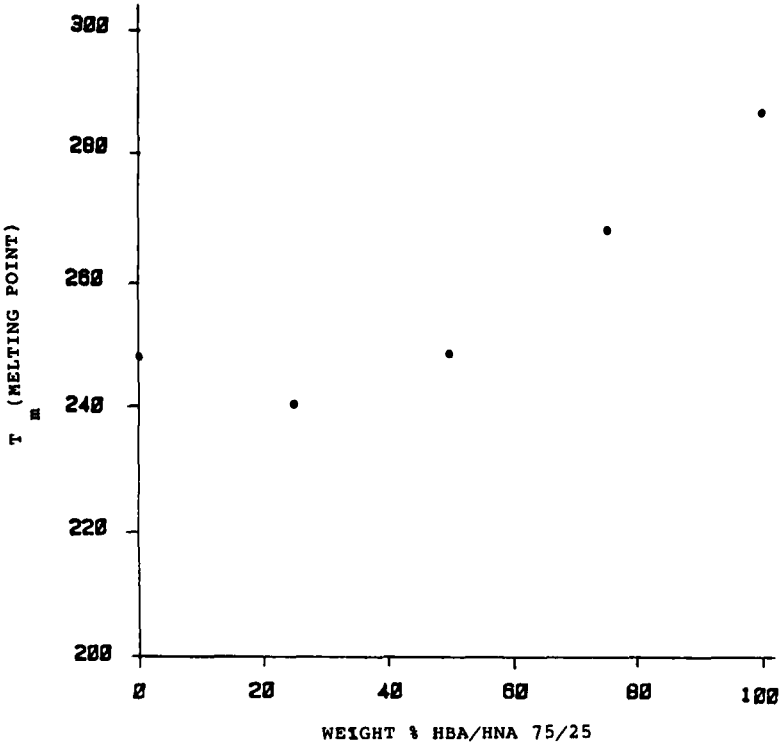

FIGURE 16. Plot of melting point vs. weight % HBA/HNA 75/25

The DSC data displayed in Figure 16 is further evidence against complete chemical reaction being a dominant feature of these blends. If the two samples in the 50/50 blend had chemically reacted to form a copolymer intermediate composition, a sample of HBA/HNA 67/33 would have been formed. Such a composition is known to have a transition temperature of about 270 C. Since the actual blend undergoes such a transition at about 250 C, chemical reaction can once again be eliminated as a dominant mechanisms.

The DSC scan for the HBA/HNA 30/70 sample is displayed in Figure 17. As noted previously (23), the sample which contains more HNA displays a higher transition temperature than the corresponding sample which contains more HBA. The reason for this observation is not presently known.

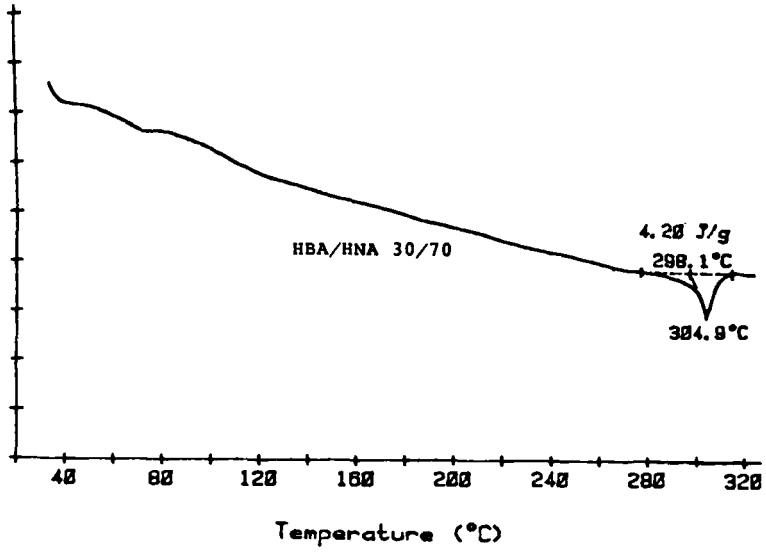

FIGURE 17. DSC scan of HBA/HNA 30/70

Figure 18 contains the DSC scans for a 50/50 blend of HBA/HNA 30/70 and HBA/HNA 75/25 as well as the component materials. All three samples display only a single transition, the temperature of which is lowest in the blend. A transition temperature of about 235 C is observed in this case. Subsequent scans on this blend verified the position of this endotherm. It should be noted that this temperature is even lower than the transition temperature of 245 C observed for the HBA/HNA sample. This composition copolymer displays the lowest transition temperature of any of the copolymers.

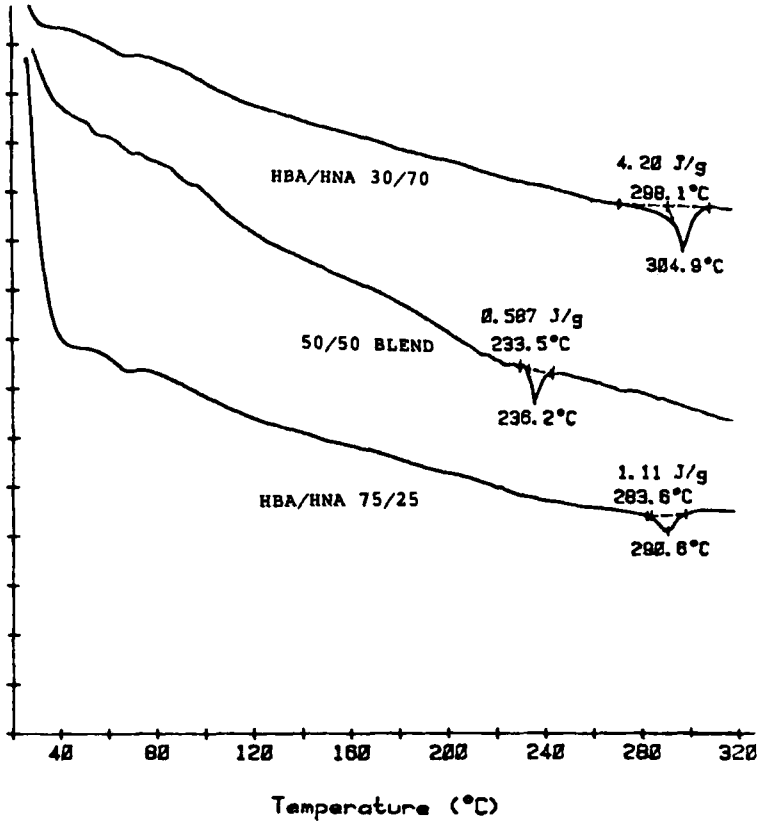

FIGURE 18. DSC scans of blends of HBA/HNA 30/70 and HBA/HNA 75/25

Summarizing the DSC results, both of the sets of blends display minima in transition temperature. The actual blend composition which displays the minimum is different for the two systems. The next section of this paper contains a possible interpretation of these DSC results.

INTERPRETATION OF DSC RESULTS

Alan Windle (24) has developed a modeling scheme for examining the solid state "order" which is present in these copolymers, specifically, and in copolymers in general. The question which is

addressed in Windle's work is, accepting the fact that the present samples are random copolymers, what is the structure within the copolymers which is responsible for the transition observed in DSC measurements ? He has developed the concept of "non-periodic layers" (NPL's), which are similar sequences of both HBA and HNA units in adjoining polymer chains. It has been shown that invoking such structures can explain the observed transition temperature dependence on copolymer composition alluded to previously. It has been found that the transition temperature correlates very well with the longest match of NPL units, the length of the primary match in Windle's terms.

It was decided to examine whether Windle's scheme could provide insight into the observed blend transition temperature behavior. The assumption that is made in the following is that since the blends display only a single transition temperature the two component materials are miscible in the solid state. If the samples were completely immiscible, two endotherms would be observed in the DSC scans corresponding to the component materials.

Two methods of calculating the average primary match length for a given composition sample were examined. One method involves generating an array of 100 chains consisting of 50 units each with the overall ensemble having some average copolymer composition. In this model, not every polymer chain has the specified composition, but instead the entire ensemble of chains has a particular average composition. The second method of calculation involves generating two polymer chains each with the same composition but with different sequence distributions, still random however. The primary match length of two such chains is calculated and fifty such pairs of chains are generated. The average primary match length is, then, calculated by averaging the results of the fifty individual calculations.

The results of the two methods of calculation are presented in Table VII. The three compositions HBA/HNA 90/10, 70/30, and 50/50 were examined. It is expected that the compositions which contain more HNA would behave exactly the same. This table points out that for the random copolymers, the method of averaging the results does not affect the value of the average primary match length which is calculated.

Since this has been demonstrated, due to its convenience, the method of generating pairs of chains will be the method of choice in the present calculations.

TABLE VII Comparison of two methods of calculation for primary match length

Composition	Pairs of Chains	Ensemble
HBA/HNA 50/50	5.14	5.01
HBA/HNA 70/30	6.14	6.10
HBA/HNA 90/10	13.22	13.79

The primary length which is calculated for various compositions of the copolymer is displayed in Figure 19. The error bars in these calculations correspond to the 95 % confidence level. It should be noted that these calculations indicate that the primary match length decreases as the composition approaches the 50/50 range with longer primary match lengths being observed as one or the other components dominates the composition. It should also be observed that the primary match length values pass through a broad minimum which extends from about the 40/60 composition to about the 60/40 composition. It is within this composition range that the minimum in transition temperature is observed.

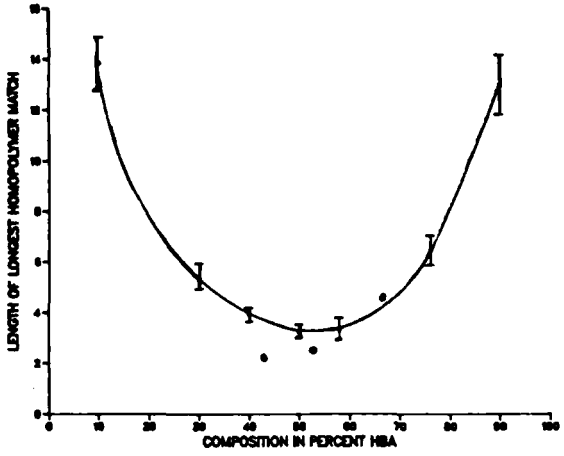

FIGURE 19. Primary match length for copolymers of HBA/HNA

Calculations for 50/50 blend samples were performed by replacing one of the chains with a chain of different composition. Thus, as an example, rather than having two chains each of which have a composition of HBA/HNA 76/24 now the system consists of one chain which has a composition of HBA/HNA 76/24 and another chain which has a composition of HBA/HNA 58/42. The average primary match length was obtained by examining sixty such pairs of chains.

Two systems of interest to the present investigation will be discussed. In the first one, chains of HBA/HNA 76/24 and HBA/HNA 58/42 were examined. This system should be very close in behavior to the experimental system consisting of HBA/HNA 75/25 and HBA/HNA 58/42. The calculated average primary match length is 5.76, which is only slightly higher than the value observed for the HBA/HNA 58/42 system. It should be remembered from a previous section that the blend displays a transition temperature only slightly higher than the neat HBA/HNA 58/42 sample. This is further suggestion that there is a definite correlation between primary match length and transition temperature.

The other system which has been examined is a 50/50 mixture of HBA/HNA 30/70 and HBA/HNA 76/24. This system should be very close in nature to the system consisting of HBA/HNA 75/25 and HBA/HNA 30/70 which has been examined experimentally. In the case of these two copolymers, a 50/50 mixture produces an average primary match length of 3.82, lower than for any of the neat copolymers. It should also be remembered that the 50/50 blend of HBA/HNA 30/70 and HBA/HNA 75/25 displayed a transition temperature that was lower than any of the neat copolymer values. This once again supports the hypothesis that there is a direct correlation between primary match length and transition temperature.

The work that has been performed thus far seems to provide a qualitative explanation for the observed DSC results. The idea that there exists a correlation between the DSC transition temperature and the primary match length is one worth pursuing. The existing data both on the neat copolymers and the blends is encouraging in this regard. The next step in the development of these model calculations is to make the scheme quantitative, rather than only qualitative in nature.

CONCLUSIONS

The present work has been an initial study of blends in which both of the components in the blend are capable of forming liquid crystalline phases. This study has focused on establishment of miscibility criteria for such systems as well as development of plausible explanations for the observed data. As such, it only serves as a beginning to understanding such systems.

The melt rheology data which was presented served two purposes. First, using that data, the issue of chemical reaction between the two copolymers was addressed and dismissed as being a dominant feature for this particular system. Second, the rheology data showed that contrary to mixtures of small molecule liquid crtystals, not all mixtures of nematic liquid crystal polymers behave the same. This result has been interpreted in terms of miscibility concepts for the mesophase.

The two characterization methods for the solid state which were presented, X-ray diffraction and DSC, provide evidence that the blends are compatible in the solid state. Specifically, the X-ray data has further supported the idea that chemical reaction is not a dominant faeture in these blend systems and has also provided some insight into the miscibility issue. The DSC scans, due to the fact that a single transition is observed, suggest that molecular mixing has occurred in the solid state.

Windle's sequence matching arguments have been applied to explain the unusual transition temperature behavior which is observed in the blends. It has been shown that qualitatively, at least, the behavior can be explained by a correlation between transition temperature and primary length. This is not to say that there are not other models which could be developed to explain such behavior. At present, the sequence matching scheme seems qualitatively correct when compared to experimental work. Further work needs to be done to make these ideas completely quantitative.

Finally, the ideas presented here have implications for the copolymer samples themselves. Since any copolymer has a certain composition distribution due to its chemical nature, it can be considered to be a blend of many different compositions. If the composition distribution is extremely wide, there are possibilites that regions

of phase separation may exist within what is generally assumed to be a homogeneous copolymer. Whether phase separation really does exist in these systems will depend on the molecular weight of the samples and the interaction between the two comonomer units. The possibility of this type of phase separation existing has definite implications for the processing of these samples.

The ideas suggested in the Introduction were that were at least two possible outcomes when blends of copolymers containing the same monomer units were made. On the one hand, recent ideas of blends containing copolymers suggests that as the difference in copolymer composition increases, immiscibility should occur. The rheology data which has been presented suggests that this may be true in these systems. The solid state data, on the other hand, suggests that the systems are all compatible and that Windle's method of treating the structures is applicable. Future work will involve exploring how the transition from one type of behavior occurs and further defining the usefulness of each of the approaches.

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