The Solution Structure of Liquid-Crystal Polymers with Small Liquid-Crystal Thermoset Maleimides and Nadimides[1]

R. P. Hjelm,[2,3] E. P. Douglas,[4] and B. C. Benicewicz[4]

The solution structure of the deuterated liquid-crystal polyamide polymer (LCP) poly(*p*-phenylene-2-nitroterephthalamide), alone and mixed with small, rodlike, amide, liquid-crystal molecules (LCT) in *N*-methyl-2-pyrrolidinone (NMP), is studied using small-angle neutron scattering. Measurements were made as a function of LCP concentration using different LCTs mixed at 20 and 40 wt% relative to LCP. Our motivation for studying this system comes from a need to connect solution structure with film morphology in processing these materials for high-performance molecular composites. Our analysis shows that the LCP in NMP forms large domain-like structures. The presence of LCT breaks up the LCP domains into smaller structures, some of which are filamentous LCP-LCT aggregates. This result suggests that the simple entropic description of the solution behavior of mixtures of long and short rods is not adequate in describing systems of this type.

KEY WORDS: composites; liquid crystals; neutron scattering; solution structure.

1. INTRODUCTION

Our understanding of the phase behavior and structure of solutions of long and short rigid rodlike molecules in a quasispherical solvent comes largely from the work of Abe and Flory [1], who described these systems in terms of interactions between rodlike molecules governed totally by excluded-volume effects. A complex phase behavior is predicted by this theory.

According to this description (Fig. 1), at low solute concentrations an isotropic solution is formed. At sufficiently high volume fraction a biphase results, consisting of an anisotropic (nematic) phase rich in long rods and an isotropic phase rich in short rods. This effect is driven by the entropy of packing the long rods. At higher concentrations of solute, different combinations of isotropic and anisotropic phases rich in small and large component are predicted by the theory (Fig. 1) [1].

In real systems, however, there are often attractive interactions between the solute molecules and between the solvent and solute. Further, the polymers are better described as semirigid rods [2]. Thus the question arises as to how the phase behavior and solution structure of real systems might correspond to the theoretical predictions.

We have become interested in this problem as a result of our recent work on the realization of molecular composites [3]. These materials are
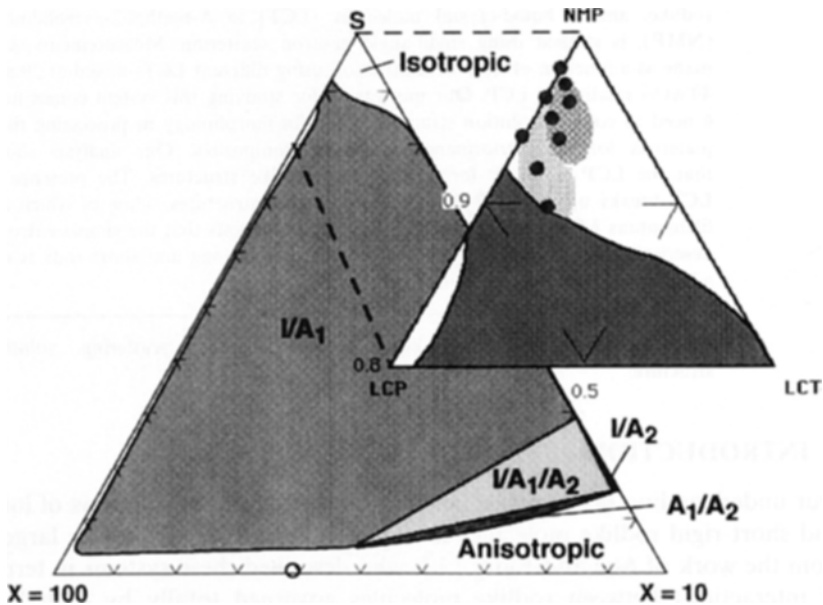
Fig. 1.   Calculated phase diagram for a mixture of long ($n = 100$) and short ($n = 10$) rigid-rod polymers. Phase diagram was calculated in Ref. 1. Here I refers to isotropic phases. A1 and A2 refer to, respectively, long ($X = 100$) and short ($X = 10$) rod-rich anisotropic (nematic) phases. The solvent is represented by S. The points on the map sampled in this study are shown by solid circles on the expanded solvent corner of the map (upper right). The light and dark regions around the points correspond to domain-like and dispersed solution structure, respectively. The open circle shows sample described in our earlier work on film microphase morphology [2]. The axes are in units of volume fraction.

predicted to have greatly enhanced mechanical properties [4], but there is presently little information to validate this notion. Approaches to produce stable molecular composites are limited by immiscibility between the reinforcement and matrix components [5]. To circumvent this problem, we proposed using liquid-crystal polymers (LCP) as the reinforcing component, with structurally similar liquid-crystal thermosets as the matrix. The two components should have better miscibility than systems used in earlier work [5] and therefore should approach the ideal molecularly dispersed state more readily. Our initial studies on birefringent films [3], indicated by the open circle in the mixed nematic part of the phase map (Fig. 1), showed enhanced miscibility, as indicated by weak segregation of components into two randomly interpenetrating phases having a characteristic size of 8 nm [3]. These appeared to be equilibrium structures, as they did not change with extensive annealing of the films. A comparison of theoretical predictions with the experimental behavior of these systems as they are
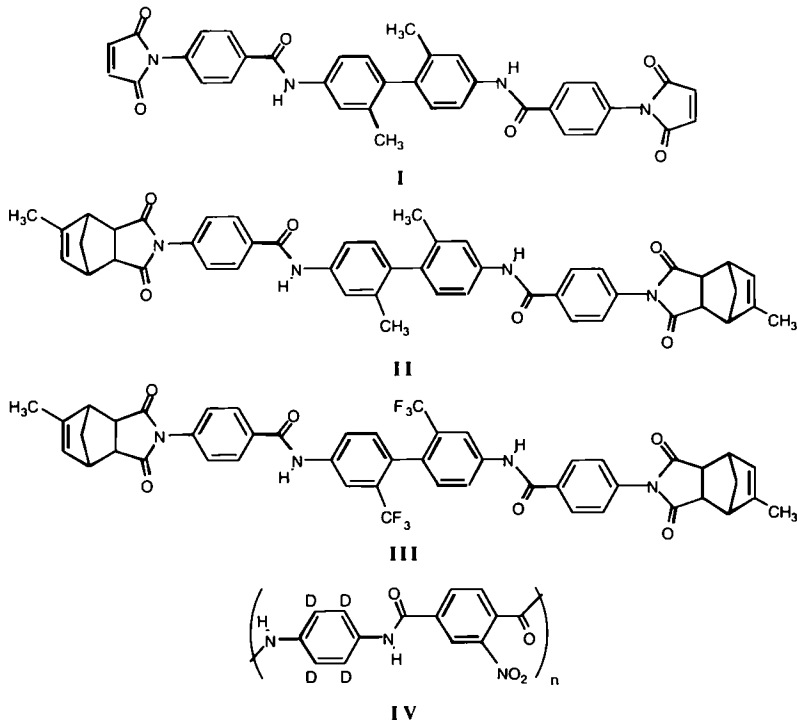
Fig. 2. Liquid-crystal thermosets and liquid-crystal polymer used in this study. Liquid-crystal thermosets: I, 2,2'-dimethylbiphenyl bismaleimide amide; II, 2,2'-dimethylbiphenyl bis(methylnadimide) amide; III, 2,2'-bis(trifluoromethyl)biphenyl bis(methylnadimide) amide. Liquid-crystal polymer: IV, poly(p-phenylene-2-nitroterephthalamide).

processed by drying from solution is important in developing concepts for the nanoscale engineering of these systems.

In this work, we study the solution structure in N-methyl-2-pyrrolidinone (NMP) of the deuterated polyamide LCP, poly(p-phenylene-2-nitroterephthalamide), alone and in mixtures with any one of three liquid-crystal thermosets, shown in Fig. 2, by small-angle neutron scattering (SANS). The use of SANS allows study of nanostructure over length scales from 1 to 50 nm. The solution compositions studied, indicated by the filled circles in Fig. 1, should form isotropic solutions according to the theories for rigid [1] and semiflexible [2] hard-core interacting rods.

2. MEASUREMENTS

2.1. Samples

The deuterated LCP and the three thermosets used in this study (Fig. 2) were prepared as previously described [3, 6]. Solutions of LCP in NMP were prepared at different concentrations [expressed as (g of LCP)/(100 ml NMP) = w/v %] of 3, 5, and 9 w/v %, and contained 100/0, 80/20, and 60/40 w/w % LCP/LCT.

2.2. Procedure

SANS was done on the SANS instruments at the Los Alamos Neutron Scattering Center (LQD) [7] and at the National Center for Cold Neutron Scattering Research at the National Institutes of Standards and Technology (NG7SANS). All measurements were done at room temperature (22°C). Scattering data were reduced to differential scattering cross section per gram of LCP, $I(Q)$ $(m^2 \cdot g^{-1})$, as a function of momentum transfer, $Q = 4\pi/\lambda \sin \theta$, where 2θ is the scattering angle and λ is the neutron wavelength. The methods of data reduction for the pulsed-source instrument (LQD) are outlined elsewhere [8, 9].

3. RESULTS

The solutions of LCP in NMP and the ternary mixtures of LCP, LCT, and NMP were yellow for the 3 w/v % LCP mixtures to light brown for the 5 w/v % LCP mixtures to dark brown for the 9 w/v % LCP mixtures. There was no sign of turbidity in the samples. All samples were observed to be isotropic by polarized optical microscopy. The 3 w/v % samples were viscous. Viscosity increased with increasing concentration. The 9 w/v % solutions were highly viscous and could not be poured.
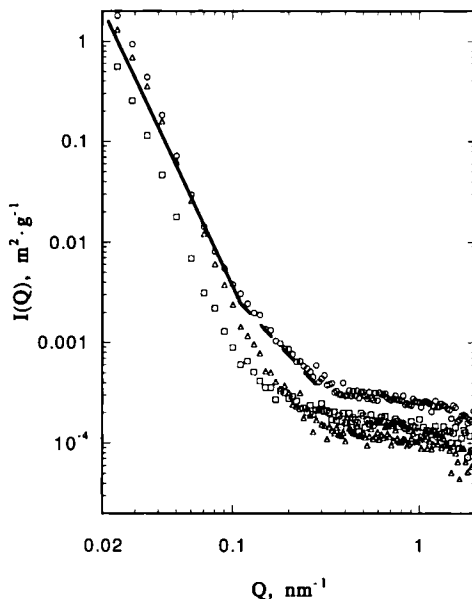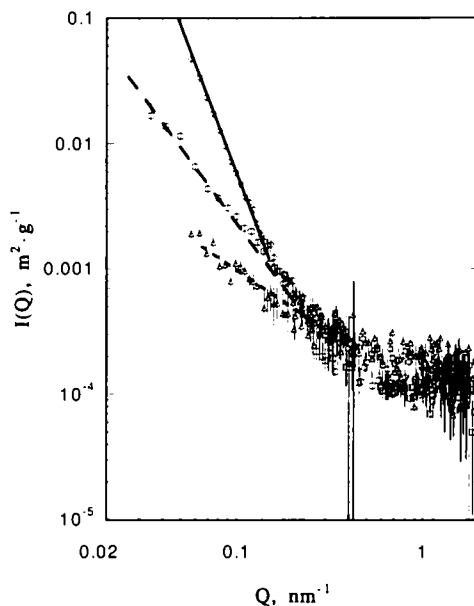
Fig. 3. Small-angle neutron scattering from
9 w/v% LCP and LCP–LCT solutions in NMP.
○, LCP only; □, LCP with LCT II, 80/20 w/w%
LCP/LCT; △, LCP with LCT II, 60/40 w/w%
LCP/LCT. Lines indicate scattering law behavior:
—. Q^{-4}; - -. Q^{-2}.

The SANS from LCP solutions at 9, 5, and 3 w/v% in NMP alone
and with 80/20 and 60/40 w/w% LCP/LCT II (Fig. 2) are shown in
Figs. 3–5, respectively, and illustrate the general features of the LCP–LCT
solutions. The other solutions studied showed the same general features;
thus they are omitted for clarity.

The 9 w/v% solution of LCP is characterized by a steep decline in
intensity at low Q, following the approximate power law $I \propto Q^{-4}$. There
appears to be a crossover to $I \propto Q^{-2}$ for $0.09 \leqslant Q \leqslant 0.3$ nm^{-1}, until the
scattering becomes flat due to incoherent scattering above $Q = 0.3$ nm^{-1}.
All mixtures containing 9 w/v% LCP with the different LCTs in 80/20 and
60/40 w/w% proportions show the same basic shape of the scattering curve
with $I \propto Q^{-4}$ for $Q < 0.1$ nm^{-1}, although none show the $I \propto Q^{-2}$
behavior of the 9 w/v% LCP solution at intermediate Q.

The 5 w/v% solution of LCP shows the same steep decline, $I \propto Q^{-4}$,
for $Q < 0.15$ nm^{-1} (Fig. 4) as the 9 w/v% LCP solutions. The 5 w/v%
LCP–LCT solutions, on the other hand, show very different behavior. In
all but one of the measured ternary mixtures the scattering intensity goes

as Q^{-1} for $Q < 0.4$ nm^{-1}, as illustrated for one of these in Fig. 4. The exception is the 80/20 w/w% mixture with LCT II (Fig. 4). In this case the scattering for $Q < 0.2$ nm^{-1} goes approximately as Q^{-2}. This latter mixture was measured both on NG7SANS and on LQD with the identical result.

The 3 w/v% LCP solution shows significantly different scattering from the more concentrated solutions in that the low-Q scattering shows Q^{-3} dependence (Fig. 5). The 3 w/v% LCP mixtures with LCT (Fig. 5) show scattering that is identical to that observed with the majority of the 5 w/v% LCP/LCT solutions for $Q > 0.05$ nm^{-1} (Fig. 4). However, there is a crossover to a Q^{-3} dependence at lower Q (Fig. 5) that could have been missed in the measurements of the 5 w/v% solutions, which access only for $Q > 0.05$ nm^{-1} (Fig. 4).

4. DISCUSSION

The form of the scattering curves for the more concentrated LCP solutions is indicative of domain-like structure. This is inferred from the
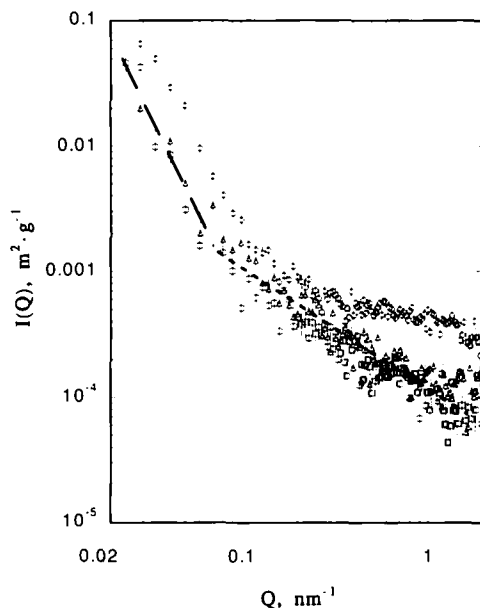
Fig. 5. Small-angle neutron scattering from 3 w v% LCP and LCP LCT solutions in NMP. Symbols are the same as for Fig. 3. Lines indicate scattering law behavior: , Q^{-3}; ---, Q^{-1}.

Porod-law ($I \propto Q^{-4}$) scattering seen in the 9 w/v% and 5 w/v% LCP solutions (Figs. 3 and 4) interpreted as originating from smooth domain walls. The main source of contrast in these solutions is from the deuterated LCP (Fig. 2, structure IV); thus the domains correspond to LCP-rich and -depleted microphases. The characteristic size of the domains is too large to be resolved with available SANS instrumentation (>50 nm), but too small to be observed in the polarized optical microscope. The scattering from the 3 w/v% LCP solutions shows a different power law, $I \propto Q^{-3}$, which suggests some breakup of the domain-like organization into smaller, perhaps rougher-surfaced structures.

The basic features of the domain-like organization in the 9 w/v% LCP solutions are not changed by the addition of LCT at 20 or 40 w/w% relative to LCP; both the Porod-law scattering and the scattering intensities of the ternary mixtures are comparable to that of the LCP solutions (Fig. 3). However, the changes in the scattering that occur with the addition of LCT to the 5 and 3 w/v% LCP solutions (Figs. 4 and 5) imply substantial changes in the solution structure in these cases. The power-law dependence of the scattering intensity is approximately Q^{-1} in most of the

more dilute LCP/LCT solutions, suggesting a low-dimensional, filamentous structure. However, the very low-Q scattering measured from the 3 w/v% LCP/LCT solutions suggests that the structure seen in the 3 w/v% LCP solutions (Fig. 5) is still present. The structure of the solution containing 20 w/w% LCT II at 5 w/v% LCP is clearly different. The power law observed for this case (Q^{-2}) suggests a structure of higher dimensionality than in the other more dilute LCT-containing solutions. Thus, the presence of LCT in NMP solutions with LCP breaks up the domain-like structure inherent in the LCP solutions when the solute concentration is low. These results are summarized in Fig. 1.

As shown in Fig. 1, the region of the phase map explored by these measurements lies in the isotropic phase, according the prediction of rigid-rod [1] and semiflexible-rod [2] theory. These theories, as well as the interpretation of the phase behavior of rigid-rod/flexible-coil matrix blends [4], emphasize the importance of entropic effects in the organization of the rods.

Our results show that the situation is more complex for systems involving a semiflexible, associating liquid-crystal polymer and rodlike short molecules. The 9 w/v% solutions and the 5 w/v% LCP solution show the presence of large aggregates, implying a microphase-separated structure. If we assume that the domain structure observed here is due to microphase separation of LCP-rich and solvent-rich components, then the biphase region extends along the long rod axis of the phase map (Fig. 1). The 5 w/v% LCP/LCT solutions and all of the 3 w/v% solutions show behavior that suggests the mixtures in this region are not so grossly phase-separated, although there appears to be some lower-order structure present. We conclude that when interactions between the long and short rods are present the structure of the isotropic region of the phase map is richer than suggested by theories [1, 2] that do not include the enthalpy of interaction between each of the components.

ACKNOWLEDGMENTS

REFERENCES

1. A. Abe and P. J. Flory, *Macromolecules* 11:1122 (1978).
2. T. Sato, T. Shoda, and A. Teramoto, *Macromolecules* 27:164 (1994).
3. B. C. Benicewicz, E. P. Douglas, and R. P. Hjelm, in *Liquid Crystalline Polymers*, C. Carfagna, ed. (Pergamon Press, New York, 1994), p. 87.
4. W.-F. Hwang, D. R. Wiff, C. L. Benner, and T. E. Helminiak, *J. Macromol. Sci.-Phys. B* 22(2):231 (1983).
5. G. T. Pawlikowski, D. Dutta, and R. A. Weiss, *Annu. Rev. Mater. Sci.* 21:159 (1991).
6. A. E. Hoyt and B. C. Benicewicz, *J. Polymer Sci. A* 28:3403 (1990).
7. P. A. Seeger, R. P. Hjelm, and M. Nutter, *Mol. Cryst. Liq. Cryst.* 180A:101 (1990).
8. R. P. Hjelm, *J. Appl. Cryst.* 21:618 (1988).
9. P. A. Seeger and R. P. Hjelm, *J. Appl. Cryst.* 24:467 (1991).