Original Research

Phase Equilibria of Flexible Polymer and Monomer Liquid Crystal Blends

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Academic Editor: Hossein Hosseinkhani

Abstract

In this study, we explored the phase equilibria in blends of a nematic liquid crystal monomer and a nematic liquid crystal flexible polymer within the whole composition of the phase diagram. The crystal-nematic and nematic-isotropic transition temperatures, as well as the transition enthalpies and entropies, indicated the total miscibility in this mesogenic blend system. We also extracted an empirical axial ratio of 4.52 for the polymer from the nematic-isotropic transitions of the blends. Further, from the biphasic nematic-isotropic transitions of the blends in low concentration regions, we estimated the entropies of pure monomer and polymer from a theoretical lattice model. The calculated and experimental results showed good agreement. This work will be continued with a more detailed study of phase equilibria and comparison with other theoretical models in nematic flexible polymer and non-mesogenic rigid-rod monomer blends will be made.

Keywords

Phase equilibria; nematic; blends; flexible polymer; monomer; liquid crystal; phase transition

1. Introduction

The structure and phase equilibria in the liquid crystalline states of chain macromolecules have been the subject of growing interest in recent years. Similar to the monomeric liquid crystalline systems, the appearance of the mesomorphic phases in polymers give rise to the macroscopic order, which originates from the anisotropy of the molecular interactions.

The discovery of high modulus/high strength fibers from lyotropic mesophase has stimulated the applied research on the synthesis, characterization, and manufacturing of specialty polymers from lyotropic and thermotropic states. The existence of these two classes of mesophases is the reflection of entropic and energetic contributions of liquid crystalline phase stabilities. These contributions have been considered in the early theoretical treatments of the ordered states [1–3]. In the later development of molecular theories, the inclusion of both energetic and entropic contributions [4], mixtures of hard rods [5–6], chain flexibility [7], generalized pair potential [8], generalized Van der Walls approach [9], and the extension of Landau's theory [10–12] have been considered. Besides this, thermodynamic theories based on the extension of the Flory-Huggins model [13] and regular solution theory [14] have also been proposed.

The lack of sufficient experimental data in polymer/polymer and polymer/diluent liquid crystalline systems motivated us to explore this area further. In the present study, we report the phase equilibria in a nematic monomer and a nematic flexible polymer within the total phase diagram. This work is part of a more detailed investigation on the phase equilibria in non-mesogenic rigid-rods and mesogenic polymer liquid crystal blends and a comparative analysis with few theoretical models, which will be the subject of our future report.

We employed polarized optical microscopy and DSC methods to determine the temperatures, enthalpies, and entropies of phase transitions in this polymer/monomer liquid crystal blend system. We verified the effect of the molecular geometry of the nematic monomer on the phase equilibria of its blends with nematic polymer and estimated the empirical axial ratio of the polymer mesophase. We also determined the enthalpies and entropies of blends within the whole phase diagram, as well as made a preliminary comparison between the experimental and calculated nematic-isotropic transition entropies.

2. Experimental

2.1 Materials

The polymer used in this investigation was a flexible homo-polyester based on 4'−hydroxyphenyl 1-4-hydroxyenzoate rigid backbone and a flexible [- $(CH_2)_n$ -] moiety with n = 7. The chemical structure of the polymer repeat units designated as S7 could be given as follows:
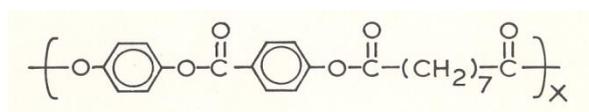
The synthetic procedure of polymer S7 by trans-esterification has already been reported elsewhere [15]. However, the S7 used in this study was prepared by distinct characteristic phase transitions and stable nematic mesophase other than that obtained from the trans-esterification approach [16]. The polymer S7 exhibits an enantiotropic nematic phase within 468–519 K

temperature range and a nematic-isotropic phase transition enthalpy within the order of magnitude of a thermotropic monomer liquid crystal.

The monomer liquid crystal material was an N-N'-Bis (p-ethoxy-benzylidene)-alpha-alpha'-bi-p-toluidine dimer designated as MT that has the following chemical structure:

$$\left(CH_3-O-\bigcirc-CH=N-\bigcirc-CH_2\right)_2$$
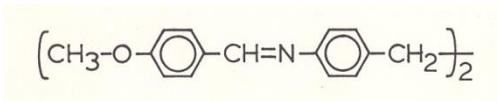
The MT compound was procured from Eastman Kodak Co. and was purified by crystallization from benzene and dried overnight in the vacuum oven at 353 K. The nematic phase of MT was within 454–570 K temperature range.

2.2 Preparation Method

The S7/MT blends were prepared by direct weighing and mechanical mixing of the components in DSC pans above nematic-isotropic temperatures. In order to achieve the optimum blending, the DSC thermograms were carried on for repeated heating/cooling cycles until they were reproducible. The optical microscopic studies were then performed on these samples accordingly. The transition temperatures and the corresponding enthalpies and entropies of the mixtures were obtained by optical microscopy and DSC measurements. The optical measurements were carried out on an Olympus model BH–2 polarizing microscope equipped with a Mettler FP52 microscopic hot stage and an FP5 temperature control unit. The DSC thermograms of pure compounds and the blends were carried out by a Dupont model 910 DSC equipped with a model 1090 thermal analyzer and model 1091 single-disk memory unit.

In order to minimize the thermal degradation of the polymer and monomers, both DSC and optical studies were carried out at the maximum heating/cooling rates of 10 K/min. The transition temperatures and enthalpies were calibrated against the pure indium as standard. Since neither DSC nor optical microscopy can give true transition temperatures at the thermodynamic equilibrium, we eliminated the effect of heating and cooling rates by measuring the transitions optically at three different rates and calculated them at the zero rate by extrapolation. The optical microscopic data reported in this study were obtained accordingly.

The densities of pure components were determined by the floating technique at the ambient temperature. The estimated overall errors in these measurements were within 0.02 g/ml range. The average asymmetry of the molecular structures of the monomer and polymer repeat unit was determined using a molecular model in the extended trans-configurations. Accordingly, we evaluated the average values of the "axial ratio" (x=L/D), where L and D values are the average molecular length and width at trans-configuration, respectively. In order to calculate the axial ratio, we utilized the average width of the aromatic rings of D = 4.7 Angstrom from an earlier report [3]. The physical and thermal properties of S7 and MT compounds are summarized in Tables 1 and 2, respectively.

Table 1 Physical properties of nematic S7 polymer and MT monomer.

Compound	Mesogen Molecular Weight	Mesogen Molecular Volume	Molecular Axial Ratio	Density (g/ml)
S7	385	310.5	3.7	1.24
MT	448.5	370.7	5.0	1.21

Table 2 Thermal properties of nematic S7 polymer and MT monomer.

Compound	TCN ((°K)	TNI ((°K)	Enthalpy (KJ/mol)	Entropy (J/°K.mol)
S7	466	520	C (10.6) N (4.2) I	C (22.7) N (8.1) I
MT	460	608	C (48.7) N (6.5) I	C (106) N (10.7) I

3. Results and Discussions

In Figure 1, the phase transitions in S7/MT blends determined by both DSC and optical microscopy are detailed. The transition temperatures were obtained as a function of volume fraction of S7, where relatively wide biphasic regions at both crystal-nematic (Tcn) and nematic-isotropic (Tni) transition temperatures were exhibited. The biphasic spread in polymer/monomer liquid crystal blends has been reported in the literature [17]. The Tcn and Tni transition temperatures (Figure 1) also showed an overall agreement between the DSC and optical microscopic measurements.

Regarding the S7/MT data shown in Figure 1, we observed the lowering of Tcn transitions in the phase diagram and exhibition of a eutectic point at S7 composition of around $v_{S7} = 0.7$. In the case of biphasic spread, the overall linear trend of Tni within the most part of the phase diagram also indicated the miscibility of S7 and MT in the nematic phase. We have already reported the miscibility of rigid and flexible liquid crystal polymer blends [18, 19]. A direct correlation with aniso-symmetry of MT monomer could be observed from the general behavior of S7/MT phase diagram, which is reflected in the stability of the nematic phase and appearance of the eutectic point.
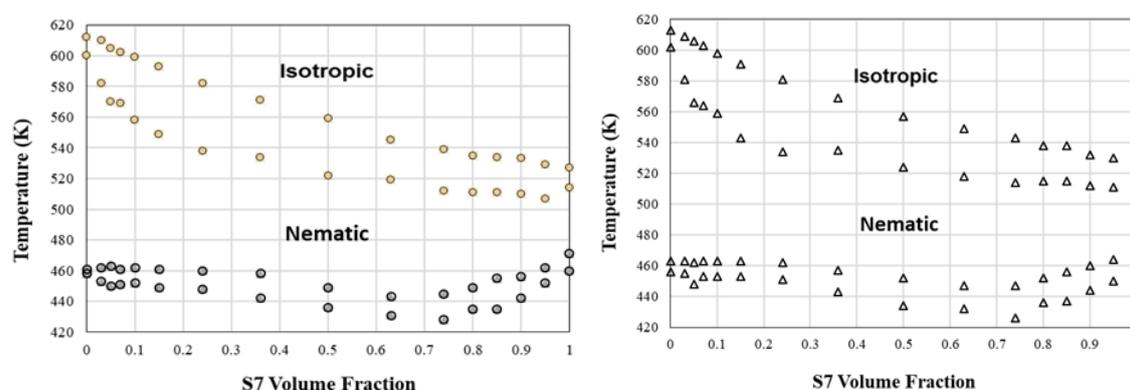
Figure 1 Transition temperatures of S7/MT blends by optical (left) and DSC (right) methods.

In addition, the entropy and enthalpy values within of S7/MT phase diagram at all compositions were determined by DSC for both crystal-nematic (T_{cn}) and nematic-isotropic (T_{ni}) transitions and the results are plotted in Figures 2 and 3, respectively.

The trends of both, ΔH_{ni} and ΔS_{ni} with the S7 mole fraction, showed a monotonous decrease in the maximum part of the phase diagram; this clearly demonstrates the effect of MT axial ratio in the nematic phase of blends. This suggests that the anisotropic molecular interactions between the MT monomer and rigid portion of the S7 repeat unit are enhanced due to the similarity of their mesogenic moieties.
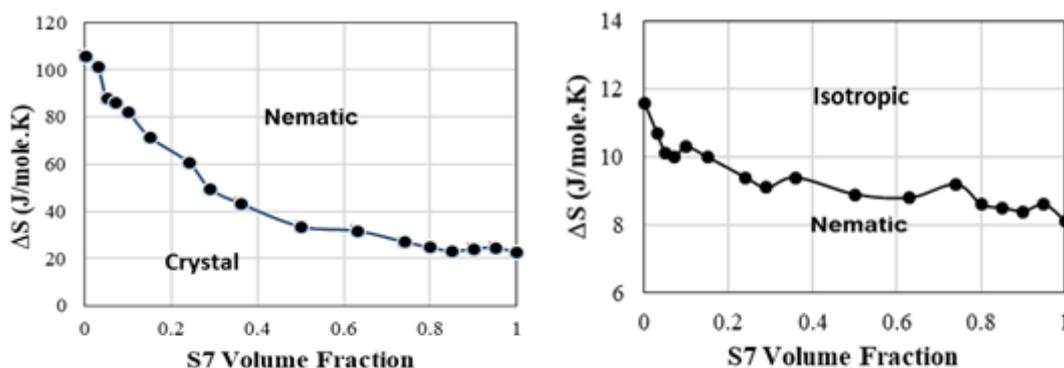
Figure 2 Entropies of crystal-nematic (left) and nematic-isotropic (right) transitions of S7/MT blends.
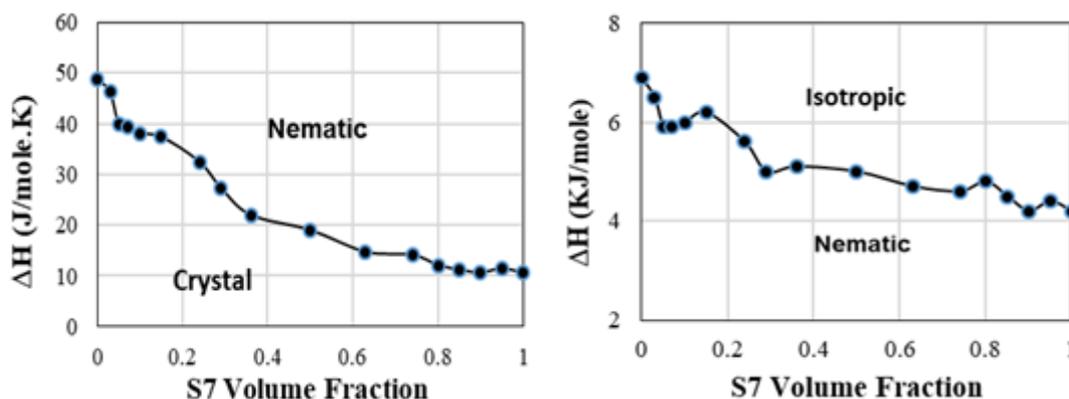
Figure 3 Enthalpies of crystal-nematic (left) and nematic-isotropic (right) transitions of S7/MT blends.

The theoretical models predicting the nature and phase behavior of nematic-isotropic transition are not satisfactory for the nematic monomer and polymeric systems. The experimental studies on nematic-isotropic phase transitions are even more scarce and the verification of theoretical models is incomplete.

According to the theoretical treatment of semi-flexible nematic polymers with mesomorphic monomers, the phase diagram of binary polymer/monomer system is predicted on the basis of the orientation dependency of the Van der Waals interactions [10]. The experimental verification of this theory, which does not include the biphasic separation, requires the knowledge of the persistence length and degree of polymerization. Since these two parameters were not evaluated in the present study, we could not test the above theory. On the other hand, the theory based on

the lattice treatment of polymer hard-rods requires the knowledge of the anisotropy of molecular shape as a dominant factor determining the nematic-isotropic phase transition [4]. Regarding the speculation of this lattice model, the upper limit of the molecular asymmetry for the stability of nematic phase is x = 6.4. In addition, it has been reported that according to the molecular field approach of the lattice model, the lower nematic phase stability limit of rigid rod asymmetry would be x > 3.65 [20]. This lower limit value is supported by some experimental evidence for small thermotropic molecules.

As a first-order approximation, assuming that the axial ratio of the mesogenic moiety is the predominant factor influencing the nematic-isotropic phase transition, then the average asymmetry of single or multi-component nematic phase should lie within 6.4 > x > 3.65 range. Furthermore, since the T_{ni} transition of S7 is promoted by the addition of MT, an empirical value which could be the "apparent axial ratio" of the polymer chain, can be designated by <x> and it should be referred to as a steric factor obtained from the rationale of nematic behavior as a function of purely geometrical parameter. As an empirical factor, <x> represents the degree of anisotropy of molecular interaction of polymer's mesogenic units in the nematic phase. In order to estimate the <x> value of S7 from the phase diagram, in Figure 4, we plot the ($T–T_0$) as a function of <x> = v. x, where v is the S7 volume fraction and x is the axial ratio of MT. Within the limit of experimental uncertainty, the plot shows a linear trend and its intercept at $T–T_0$ = 0 provides the estimated value of $<x>_{S7}$ = 4.52 for pure (v=1.0) S7 polymer.
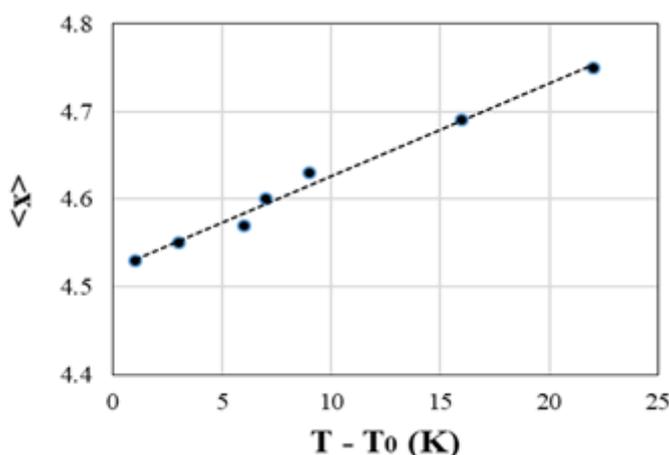

Figure 4 The plot of <x> as a function of reduced nematic-isotropic transitions in S7-MT blends.

We further attempted to evaluate <x> and calculated the S7 and MT entropies from the S7/MT phase diagram. It is known that solutes depress the Tni transition in a nematic medium accompanied by the formation of a biphasic region. This is consistent with thermodynamic laws and with the first-order nature of Tni phase transition. Within the limited solute concentration range (Rault-Duhem relation), the phase equilibrium (Gibbs-Duhem relation) could be deduced for nematic-isotropic phase equilibrium by the following biphasic expressions [6]:

$$[v_i – v_n] = [(1/B_n) – (1 / B_i)].(1-T^*) = [\Delta S_{ni} / R] . (1-T^*) \qquad (1)$$

$$[T_i^* – T_n^*] = v. [B_i – B_n] \qquad (2)$$

where v_n and v_i are the volume fractions of solute at the appearance of isotropic phase and disappearance of the nematic phases, respectively, at a fixed temperature, B_n and B_i are the corresponding biphasic slopes in the phase diagram. ΔS_{ni} is the entropy of nematic-isotropic phase transition, T_n^* and T_i^* are the corresponding reduced temperatures at a fixed volume fraction and R is the gas constant. As the solute MT is nematic mesogen, the values of B_n, B_i, and $[T_i^* - T_n^*]$ are expected to be small.

We further examined Equation 1 and evaluated ΔS_{ni} of pure S7 and MT from the plot of $[v_i - v_n]$ vs. $(1 - T^*)$ obtained from the biphasic nematic-isotropic transitions of S7/MT phase diagram (Figure 1) at low volume fraction (v < 0.1) regions of S7 and MT. An example at a low concentration range of S7 is shown in Figure 5 and as predicted from Equation 1, the plot exhibits a linear trend.
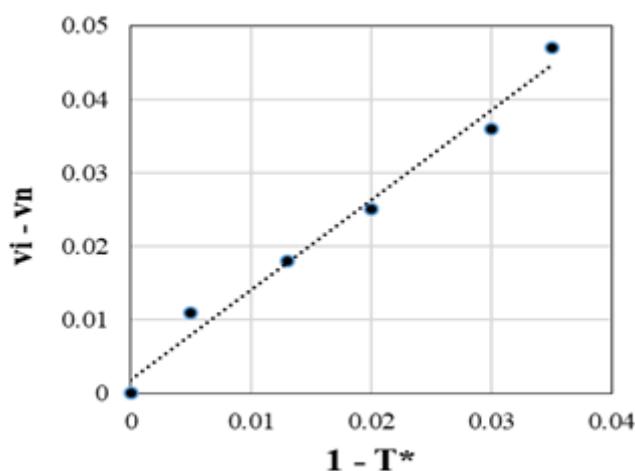

Figure 5 The plot of Equation 1 from biphasic nematic-isotropic transitions of S7/MT blends.

A comparison between calculated and experimental ΔS_{ni} values of pure S7 and MT components lead to the estimation of the following values:

Calculated (Equation 1): ΔS_{ni} (S7) = 7.5; ΔS_{ni} (MT) = 10.2 J/mole.K.

Experimental (DSC): ΔS_{ni} (S7) = 8.1; ΔS_{ni} (MT) = 10.7 J/mole.K.

Considering the errors in the calculation and experiment, the entropy values are in good agreement with each other. Further verification of this and other theoretical models will be the subject of our future work on the phase equilibria of S7 and rigid-rod blends.

4. Conclusions

We studied the phase equilibria in the total compositions of nematic monomer MT and nematic polymer S7 blends. Within the limits of experimental errors, we found good agreements between the crystal-nematic and nematic-isotropic phase transitions measured by optical and DSC methods.

The phase diagram of S7/MT indicates complete miscibility of S7 polymer and MT monomers in the nematic phase and its stability is directly proportional to the molecular anisotropy of MT monomers. From the comparison of nematic-isotropic transition data with the average axial ratio

of MT diluent, we extracted an empirical axial ratio value of <x > = 4.52 for S7 polymer, which is within the theoretical range of 3.65< <x> <6.7 for the thermotropic nematic phase.

The values of enthalpy and entropy at the nematic-isotropic transition of the S7/MT phase diagram correlate with the axial ratio of the diluent. The experimental data of ΔS_{ni} agree well with the corresponding theoretical values obtained from the thermodynamic theory of the dilute solutions. As a general conclusion, the molecular models of rigid-rod polymers based on the lattice model are in semi-quantitative agreement with S7/Mt experimental data. The phase equilibria of liquid crystal polymer and non-mesogenic rigid-rod monomers and comparison with other theoretical models will be reported in the future.

Author Contributions

These authors contributed equally to this work.

Competing Interests

The authors have declared that no competing interests exist.

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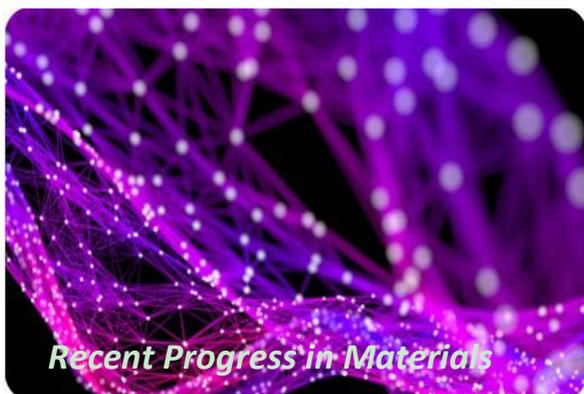
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