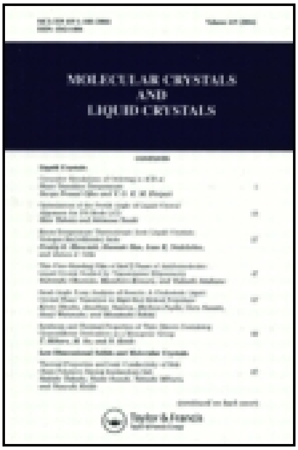

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Effect of Molecular Weight on Miscibility Phase Diagrams in Mixtures of Polymer and Liquid Crystals

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Effect of Molecular Weight on Miscibility Phase Diagrams in Mixtures of Polymer and Liquid Crystals

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Phase diagrams in mixtures of side chain liquid crystalline polymers (SCLCP) and liquid crystals (LC) have been computed by combining Flory-Huggins (FH) theory for isotropic mixing and Maier-Saupe (MS) theory for nematic ordering. In the calculation, two orientational order parameters with two different clearing transitions are taken into consideration for nematic mixtures. In the case of flexible homopolymer and liquid crystal mixtures, only one orientational order parameter with one nematic-isotropic transition is necessary. he effects of molecular weight of matrix polymer on phase diagrams of polymer/liquid crystal mixtures have been investigated using polymethyl methacrylate having varying molecular weights as matrix resins.

Keywords: Polymer dispersed liquid crystals, nematic interaction, orientational order parameter, molecular weight effect, phase diagrams.

INTRODUCTION

In a previous paper,[1] we have calculated a phase diagram of a mixture of polymer and nematic liquid crystals, known as polymer dispersed liquid crystal (PDLC), based on a mean-field approach by combining the Flory-Huggins (FH) theory for isotropic mixing and Maier-Saupe (MS) theory for nematic ordering. In the calculation, the nematic stability was assumed to arise from the repulsive interaction of the mesogenic dipoles. The combined FH/MS theory predicted a complex phase diagram that consists of isotropic, liquid-liquid, liquid-nematic, and pure nematic regions. The theoretical calculation accorded well with the experimental cloud points phase diagram of the mixture of polybenzyl methacrylate and eutectic liquid crystals (E7).[1]

In a subsequent paper,[2] we have generalized the combined FH/MS theory for the elucidation of phase behavior in nematic mixtures containing side-chain liquid crystalline polymers and low molar mass liquid crystals by taking into consideration the two nematic order parameters having two different clearing temperatures of the constituent mesogens. In the combined FH/MS theory, a "*c*" parameter that characterizes the relative strength of cross-interaction between the two mesogens as compared to that in

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the same species, has been introduced. Subsequently, we have demonstrated that a rich variety of nematic phase diagrams can be generated by simply varying the c value from weak ($c < 1$) to strong ($c > 1$) cross-nematic interactions. Further, we have shown that this c value can be determined experimentally, if an azeotrope exists in the phase diagram. The phase diagram for such azeotropic systems can be calculated without any adjustable parameter. The theory was found to conform remarkably well with the experimental phase diagrams of various mixtures containing side-chain liquid crystalline polymers and monomeric liquid crystals.[3-6]

In polymer blends, it has been generally known that molecular weight difference (or ratio) of constituent polymers exerts profound effect on polymer-polymer phase diagrams.[7] A similar effect is expected to occur in the polymer/nematic mixtures which is the purpose of the present study. The present paper is concerned with (1) predictions on influence of molecular weight on the liquid-nematic phase diagrams of conventional PDLC and related systems containing side-chain liquid crystalline polymers and (2) tests of the theory with experimental phase diagrams of PDLC systems. Various narrow molecular weight polymethyl methacrylate (PMMA) fractions were mixed with E7 eutectic liquid crystals to produce PDLC films. The cloud point phase diagrams of the PMMA/E7 mixtures were established and compared with the theoretical predictions.

MODEL SIMULATION

In the combined FH/MS theory, the total free energy (g) for binary nematic mixtures is customarily described in terms of a simple addition of free energy of mixing of isotropic liquids (g^i) and free energy of nematic ordering of liquid crystals (g^n), i.e., $g = g^i + g^n$. The free energy of isotropic mixing of a binary polymer blend is expressed customarily in terms of the Flory-Huggins theory;[7] viz.,

$$g^i = \frac{G^i}{nkT} = \frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \chi\phi_1\phi_2, \tag{1}$$

where k is Boltzmann constant and T absolute temperature. r_1 is the number of sites occupied by one liquid crystal molecule and is equal to unity for a low molar mass liquid crystal assuming that each liquid crystal molecule occupies one lattice site. On the other hand, r_2 represents the number of sites (or segments) occupied by a single liquid crystalline polymer chain, i.e., each statistical segment is assumed to occupy one lattice site.[7] ϕ_1 and ϕ_2 represent the volume fractions of component 1 and 2, respectively. n is the total number of sites, i.e., $n = n_1 r_1 + n_2 r_2$, where, n_1 and n_2 are the numbers of liquid crystals and liquid crystalline polymer molecules, respectively. χ is known as the Flory-Huggins interaction parameter which is generally assumed to be a function of reciprocal absolute temperature, i.e.,

$$\chi = A + B/T, \tag{2}$$

where A and B are constants.[7]

The contribution of nematic ordering to the total free energy of binary nematic mixtures is generally given by the Maier-Saupe mean-field theory.[8,9] Following the theoretical scheme of Brochard *et al.*[10], the free energy density of binary nematic mixtures containing side-chain liquid crystalline polymers and/or low molar mass liquid crystals may be described as

$$g^n = \frac{G^n}{nkT} = -\Sigma_1\phi_1 - \Sigma_2\phi_2 - \frac{1}{2}\nu_{11}s_1^2\phi_1^2 - \frac{1}{2}\nu_{22}s_2^2\phi_2^2 - \nu_{12}s_1s_2\phi_1\phi_2, \tag{3}$$

where Σ_1 and Σ_2 represent the decrease of entropy due to the alignment of individual LC molecule of component 1 and the mesogenic group of component 2, respectively. ν_{11} and ν_{22} are the nematic interaction parameters of the pure components, whereas ν_{12} represents the cross-interaction between the dissimilar mesogens. The self-consistent orientational order parameters s_1 and s_2 are further defined as[8,9]

$$s_j = \tfrac{1}{2}(3\langle\cos^2\theta_j\rangle - 1), \tag{4}$$

in which θ_j is the angle between a reference axis and the director of a liquid crystal molecule belonging to component j ($j = 1$ or 2). The angle-bracket denotes the ensemble average which is defined as

$$\langle\cos^2\theta_j\rangle = \int \cos^2\theta_j \cdot f(\theta_j)\, d\cos\theta_j. \tag{5}$$

Here, $f(\theta_j)$ represents the normalized orientation distribution function and is considered to be symmetric around the reference axis, which can be expressed by

$$f(\theta_j) = \frac{1}{4\pi Z_j}\exp\left[-\frac{u(\theta_j)}{kT}\right], \tag{6}$$

where Z_j is the partition function defined as

$$Z_j = \int \exp\left[-\frac{u(\theta_j)}{kT}\right] d\cos\theta_j, \tag{7}$$

and, $u(\theta_j)$ is the potential of a director orientation which may be expressed in terms of the second order Legendre polynominals, i.e.,

$$\frac{u(\theta_j)}{kT} = -\frac{1}{2}m_j(3\cos^2\theta_j - 1), \tag{8}$$

in which m_j is a dimensionless mean field parameter characterizing the strength of the potential field.[9]

The order parameter, s_j, can then be related to Z_j through

$$s_j = \int f(\theta_j) \cdot \frac{1}{2}(3\cos^2\theta_j - 1)\, d\cos\theta_j = \frac{1}{Z_j}\frac{dZ_j}{dm_j}, \tag{9}$$

and the entropy Σ_j can be deduced as

$$\Sigma_j = -\int f(\theta_j)\cdot\ln[4\pi f(\theta_j)]d\Omega_j = \ln Z_j - m_j s_j, \tag{10}$$

where Ω_j denotes the solid angle. In a previous paper,[2] the nematic interaction parameters, ν_{11} and ν_{22}, of the individual mesogenic component have been shown to have an inverse temperature dependence as follows:

$$\nu_{jj} = 4.541\frac{T_{NI,j}}{T} \tag{11}$$

In general, the exact relation of ν_{12} to ν_{11} and ν_{22} is not known. We assume that $\nu_{12} = \nu_{21}$ and is proportional to the square-root of the product of ν_{11} and ν_{22}, i.e.,

$$\nu_{12} = c\sqrt{\nu_{11}\nu_{22}} \tag{12}$$

where c is the proportionality constant that characterizes the relative strength of the cross-interaction between the two dissimilar mesogens as compared to that in the same species. The stability limit of the system can be established by calculating the chemical potentials of each component, i.e., taking the first derivative of the free energy of the system with respect to the number of molecules of each component. Similar to the free energy of mixing, the total chemical potential of mesogenic mixtures is contributed by the isotropic mixing and the nematic ordering, i.e., $\mu_j = \mu_j^i + \mu_j^n$. By equating the chemical potentials of each component in the individual phase and solving the simultaneous equations for various temperatures, the binodal curves may be constructed.

Further, the equilibrium coexistence points at a given temperature can be determined by a double tangent method where the equilibrium volume fractions of the individual phase (ϕ^α and ϕ^β) fall on the same tangent line of the free energy curve. The first derivatives of the total free energy with respect to volume fraction are equivalent at these two compositions and also equal to the slope connecting these two points. In this manner, the coexistence points may be determined as a function of temperature. By connecting the loci of the coexistence points, the temperature versus composition phase diagram may be established. Regarding the detailed calculations, the interested readers are referred to our previous paper.[2]

For the mixture of polymer and liquid crystals such as a PDLC, Equation (3) is simply reduced to

$$g^n = \frac{G^n}{nkT} = -\Sigma_1\phi_1 - \frac{1}{2}\nu_{11}s_1^2\phi_1^2. \tag{13}$$

The coexistence curves can be established by determining the chemical potential using the double tangent method.[1]

EXPERIMENTAL SECTION

The matrix polymer used in the PDLC system was polymethyl methacrylate (PMMA) having three different molecular weights. The narrow molecular weight PMMA samples were synthesized by group transfer polymerization in THF between 25 and 70 °C.[12] The molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC) using ultra-styrogel columns and PMMA standards. The observed weight average molecular weight of the three PMMA samples were 23,000, 55,000, and 120,000 g/mol with a molecular weight distribution of $M_W/M_n \sim 1.06$ for the three PMMA. The dispersing liquid crystal, E7, was puchased from EM Industries. E7 is basically a eutectic mixture of 4-cyano 4'-methyl biphenyl's (CB), that exhibits a single nematic-isotropic transition at 60 °C. Therefore, the E7 based PDLC system may be viewed as a quasi-binary system.

In the preparation of the PDLC films, the polymers and liquid crystals were dissolved in a common solvent such as tetrahydrofuran (THF) at room temperature. An aliquot of the solution was spread on a glass slide to form a thin film. This sample was dried at room temperature under vacuum for three days. Subsequently, the thin PDLC film was sandwiched between two glasses by first heating the film to 100 °C on a hot stage for 3 min to remove trapped solvent, and then covering it with a cover glass. Small-angle light scattering (SALS)[13] was employed to determine the cloud point temperatures as a function of composition for PMMA/E7 mixtures. All specimens were subjected to a heating and cooling cycle at a rate of 0.5 °C/min. In the homogeneous state, the scattered intensity was low, but it increased immensely when the system phase-separated into a heterogeneous two-phase state during the course of cooling. The temperature at which the scattered intensity changed abruptly was designated as the cloud point.

RESULTS AND DISCUSSION

In a previous paper,[2] we have shown that the effects of χ parameter as well as of molecular weight of liquid crystalline polymer on nematic phase diagrams are less significant if the strength of the cross-nematic interaction is stronger than that in the pure mesogens. In order to appreciate the effect of molecular weight on equilibrium phase diagrams, the calculation was carried out for a weakly interacting nematic mixture consisting of a side-chain liquid crystalline polymer and a monomeric liquid crystal. Figure 1 depicts the molecular weight dependence of phase diagrams for a hypothetical SCLCP/LC mixture having $c = 0.8$, $T_c = 75$ °C and T_{NI} of 70 and 60 °C for the SCLCP and LC, respectively. The ratio of r_2/r_1, which corresponds to the ratio of number of sites (segments) occupied by a single SCLCP chain to that by a single LC molecule, has been varied from 1/1, 9/1 and 16/1. The phase diagram consists of liquid-liquid ($L_1 + L_2$), liquid-nematic ($L_1 + N_2$), nematic-liquid ($N_1 + L_2$), pure nematics (N_1 or N_2) and nematic-nematic ($N_1 + N_2$) coexistence regions. The critical point of liquid-liquid equilibrium moves to a higher LC composition with increasing molecular weight of the SCLCP. The liquid-liquid region gets narrower, while the nematic-isotropic region (bound by the two peritectic lines) expands with increase of

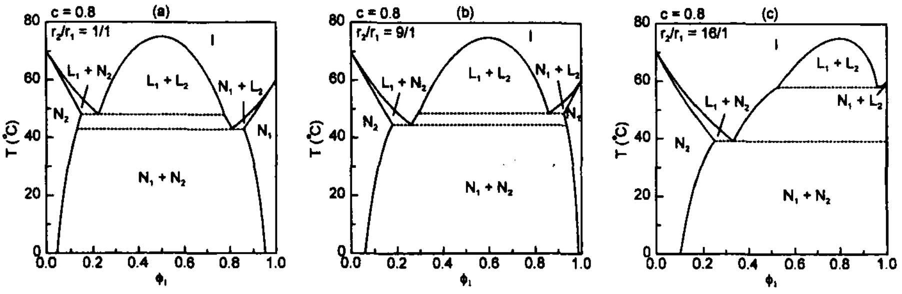

FIGURE 1 Temperature versus composition phase diagrams of a nematic mixture as a function of r_2/r_1 ratio analogous to the ratio of the degree of polymerization of side-chain liquid crystalline polymers to monomeric LC.

molecular weight. Concomitantly, the pure nematic region of SCLCP gets larger while the N_1 region shrinks. A similar trend can be observed for the case $c = 1$, where nematic interaction occurs with equal magnitude. The theoretical prediction of the effect of molecular weight on nematic phase diagrams is extremely instructive, but at the present time we do not have experimental results on a SCLCP/LC system with varying molecular weights to compare with the theory. We therefore focus on the mixtures of polymer and monomeric liquid crystals since the narrow molecular weight polymers such as PMMA are easier to synthesize through established synthetic routes.[12]

Figure 2 shows the cloud point phase diagrams of PMMA/E7 having various PMMA molecular weight (a) 23,000,[14] (b) 55,000,[15] and (c) 120,000 g/mol. The parameter that has a direct impact on the molecular weight of polymers is the ratio of r_2/r_1. We assume that each liquid crystal molecule occupies a single lattice site, therefore r_1 is equal to unity. In polymer blends, it is customary to assume that one statistical segment occupies one lattice site.[7] Hence, r_2 represents the number of sites (or segments) occupied by a single polymer chain. Based on the observed critical composition, $\phi_{1c} = \sqrt{r_2}/(\sqrt{r_1} + \sqrt{r_2})$, the r_2 value may be estimated to be around 4 for PMMA having a weight average molecular weight of PMMA of 23,000. Therefore, the molecular weight of one statistical segment (that occupied one latice site) is approximately 5,500 g/mol. Since the molecular weight of one MMA repeat unit is 100 g/mol, the Kuhn's statistical segment value is about 55 for a PMMA chain in anisotropic solvent (E7). This value is large as compared to the literature value for the Kuhn's statistical segment length of PMMA in benzene which is 7 repeat units.[16] It should be pointed out that (i) the Kuhn's statistical segment in a theta solvent measured in dilute solution is not the same in a condensed phase and (ii) polymer chains do expand in good solvent, but collapse in poor solvent such as anisotropic solvent (E7). The observed phase diagram points to the fact that PMMA and E7 are immiscible below the critical point in which PMMA chains are expected to collapse. It should be borne in mind that we are dealing with the statistical segment length in three dimension, thus the estimated Kuhn's segment length of 55 repeat units for PMMA chains in the nematic LC solvent appears reasonable.

The phase diagrams are then calculated in accordance with the temperature dependence of χ as described empirically by Equation 2. Choosing an appropriate value

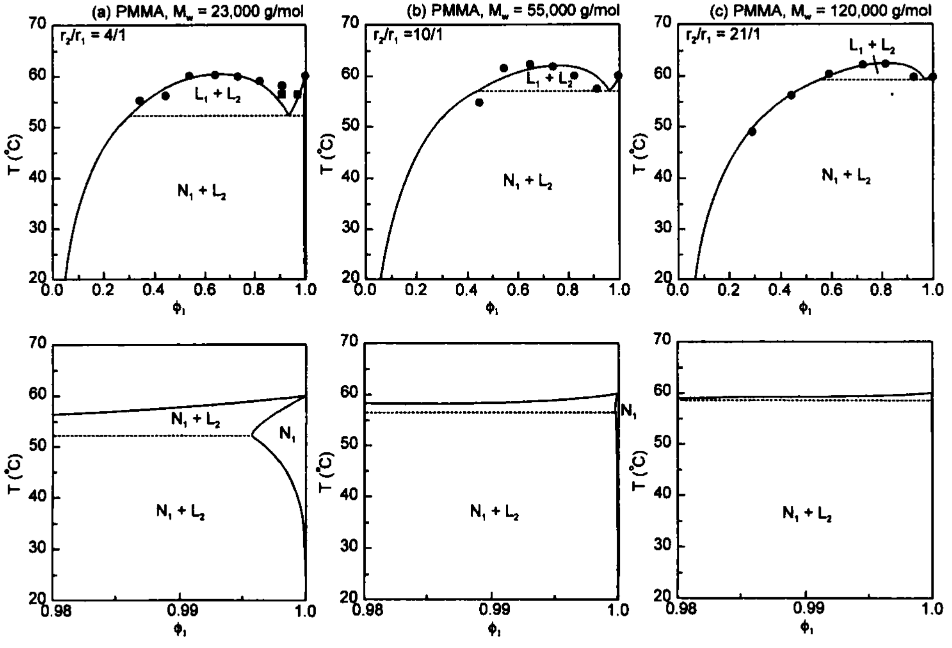

FIGURE 2 Comparison of theoretical predictions (solid curves) and experimental cloud point (filled circles) phase diagrams of PMMA/E7 systems with varying molecular weight: (a) 23,000 g/mole, (b) 55,000 g/mole, and (c) 120,000 g/mole. The bottom row is the expanded version of the pure nematic region.

of A, the value of B can be evaluated through the critical condition, i.e., $\chi = A + (\chi_c - A)T_c/T$. Here, the parameter A was taken as -8.0 to account for the width of the UCST curves. Since the broadness of the three experimental UCST data appears almost comparable, we employ the same A value for the three PMMA molecular weights. Hence, the choice of A value should be inconsequential in comparing the phase diagrams of PDLC systems of varying PMMA molecular weights.

As can be seen in Figure 2, the calculated phase diagrams (solid lines) generally capture the trend of the measured cloud points of the PDLC system. Comparing the three phase diagrams, it is seen that the critical point moves progressively toward the pure liquid crystal limit as the molecular weight of the polymer (or r_2/r_1 ratio) increases. However, the critical temperature shows only a slight increase with increasing molecular weight. The critical temperature of the PMMA ($M_W = 23{,}000$)/E7 mixture is about 60 °C, but it increases in a limited manner to about 62 ~ 63 °C as M_W increases to 55,000 g/mol, and then to 120,000 g/mol.

The peritectic line that separates the liquid-liquid coexistence region from the liquid-nematic region moves up to a higher temperature with increasing temperature. Consequently, the $L_1 + L_2$ coexistence region gets smaller. The pure nematic region (solid lines) as well as the liquid-nematic spinodal region (shown by the dashed line) at the extreme LC-rich compositions become narrower. Similarly, the pure nematic region (polymer being totally rejected) becomes narrower in the phase diagrams with increase of polymer molecular weight (the bottom row of Figure 2). The critical point changes in a subtle manner although the molecular weight of the matrix polymer has changed significantly.

CONCLUSIONS

The PMMA/E7 PDLC systems with the higher molecular weight polymer caused the critical point to shift toward the nematic phase limits; but the critical temperature increased slightly. The liquid-liquid coexistence region reduced with increasing molecular weight as the peritectic line moved to a higher temperature. This tendency was more pronounced in the mixtures of SCLCP/LC. The critical point of the PMMA/E7 changes in a subtle manner even though the molecular weight of PMMA has changed significantly. The pure nematic region gets narrower with increasing molecular weight of PMMA.

Acknowledgements

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