Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Miscibility Phase Diagrams of the Mixtures of Side-on Side Chain Liquid Crystalline Polymers and Low Molar Mass Liquid Crystals

M.-C. Chang [a] , H.-W. Chiu [a] , T. Kyu [a] , N. Leroux [b] & L.-C. Chien [b]
[a] Institute of Polymer Engineering, The University of Akron, Akron, OH, 44325
[b] Liquid Crystal Institute, Kent State University, Kent, OH, 44242

Version of record first published: 04 Oct 2006

To cite this article: M.-C. Chang, H.-W. Chiu, T. Kyu, N. Leroux & L.-C. Chien (1997): Miscibility Phase Diagrams of the Mixtures of Side-on Side Chain Liquid Crystalline Polymers and Low Molar Mass Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 299:1, 253-258

To link to this article: http://dx.doi.org/10.1080/10587259708042002

Mol. Cryst. Liq. Cryst., 1997, Vol. 299, pp. 253–258
Reprints available directly from the publisher
Photocopying permitted by license only

MISCIBILITY PHASE DIAGRAMS OF THE MIXTURES OF SIDE-ON SIDE CHAIN LIQUID CRYSTALLINE POLYMERS AND LOW MOLAR MASS LIQUID CRYSTALS

M.-C. Chang,[1] H.-W. Chiu,[1] T. Kyu,[1] N. Leroux[2] and L.-C. Chien[2]
[1]Institute of Polymer Engineering , The University of Akron, Akron, OH 44325
and [2]Liquid Crystal Institute, Kent State University, Kent, OH 44242

Abstract: Miscibility phase diagrams of mixtures of a side-on side-chain liquid crystalline polymer (s-SCLCP) and low molar mass liquid crystals have been investigated experimentally and theoretically. The theoretical calculation on equilibrium phase diagrams of binary nematic mixtures involves a combination of the Flory-Huggins (FH) free energy for isotropic mixing in conjunction with the Maier-Saupe (MS) free energy for nematic ordering of the mesogenic units. This combined FH-MS theory predicts a variety of phase diagrams depending on relative strength of cross-interaction between two dissimilar mesogens to that in the same species. The s-SCLCP synthesized is polyacrylate with a mesogenic side group connected by a butyl spacer. The temperature-composition phase diagrams of the mixtures of s-SCLCP and eutectic low molar mass liquid crystal (E44 and E48) have been established by a cloud point method. The calculated phase diagrams are found to accord well with the experimental phase diagrams.

INTRODUCTION

One of the inherent problems in the applications of polymer dispersed liquid crystal (PDLC) may be identified as the poor wide-angle viewability when subjected to the applied electric field[1,2]. To circumvent such a problem, an epoxy based end-on side chain liquid crystalline polymer (e-SCLCP) grafted with mesogenic amine was synthesized to use as a matrix polymer[3]. The stability limit of the dispersing low molar mass liquid crystals (LC) in the SCLCP matrix was determined by establishing the miscibility phase diagrams and examining the dynamics of phase separation behavior of these SCLCP/LC mixtures. As a continuing effort, we have synthesized side-on side chain liquid crystalline polymers (s-SCLCP) based on polyacrylate in which a side group mesogen was grafted to the backbone chain through a flexible linkage. The phase equilibria of these s-SCLCP/LC systems have been analyzed in the context of the combined the Flory-Huggins (FH) theory representing isotropic mixing[4] and the Maier-Saupe (MS) theory of nematic ordering[5-7].

EXPERIMENTAL SECTION

The side-on side-chain liquid crystalline polymer (s-SCLCP) that is synthesized in our laboratory is polyacrylate grafted with 2,5 bis-(4-butoxybenzoyloxy) benzoate mesogen connected by a butyl spacer. The s-SCLCP exhibits a glass transition temperature around 42°C and nematic-isotropic transition temperature of 114°C. The dispersing liquid crystals, commercially known as E44 and E48, were purchased from EM Industries. The composition of E44 or E48 may be complex; however, these LCs exhibit a single NI transition at 105 and 80°C, respectively. Various ratios of s-SCLCP/E44 and s-SCLCP/E48 were dissolved in tetrahydrofuran by stirring at ambient temperature. The solutions were then solvent cast onto glass slides. The thin films (about 10 μm thick) thus formed were heated on a heating stage at 120°C for 2 min then a cover glass was placed on the sample. The evolution of phase separated structure was followed by time-resolved light scattering technique and optical microscopy. A polarizing optical microscope (a Nikon Optiphot 2-pol) equipped with polarizers was utilized to determine the coexistence regions such as liquid-liquid, nematic-liquid, etc. by monitoring the structure change during heating and cooling cycles.

THEORETICAL SCHEME

The combined FH/MS theory under consideration is basically a mean-field model in which the stability of the nematic phase is assumed to arise from the nematic interaction of the mesogenic groups[6-8]. The flexibility of polymer backbone chains is not considered here as it may be insignificant for side-chain liquid crystalline polymers. Other transitions associated with crystal and smectic phases as well as glass transitions, even if they exist, are ignored in the present calculation. In the combined FH/MS theory, the total free energy for binary nematic mixtures is customarily described in terms of a simple addition of the free energy of mixing of isotropic liquids, g^i, and the free energy of nematic ordering of liquid crystals, g^n, i.e., the dimensionless total free energy density of the system may be expressed as $g = g^i + g^n$.

The free energy of isotropic mixing of a binary polymer blend may be expressed in terms of the Flory-Huggins theory;[4,] 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, whereas r_2 represents the number of sites or segments occupied by a single liquid crystalline polymer chain. ϕ_1 and ϕ_2 represent the volume fractions of component 1 and 2, respectively $n = n_1r_1 + n_2r_2$, where, n_1 and n_2 are the numbers of liquid crystal 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., $\chi = A + B / T$, where A and B are constants.[5]

The contribution of nematic ordering to the total free energy of binary nematic mixtures is generally given by the Maier-Saupe mean-field theory[5-7]. 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[8],

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

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} represent the cross-nematic interaction between the dissimilar mesogens. The self-consistent orientational order parameters s_1 and s_2 are further defined as[6]

$$s_j = \frac{1}{2}(3\langle\cos^2\theta_j\rangle - 1), \qquad (3)$$

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

$$\langle\cos^2\theta_j\rangle = \int \cos^2\theta_j \cdot f(\theta_j)\, d\cos\theta_j. \qquad (4)$$

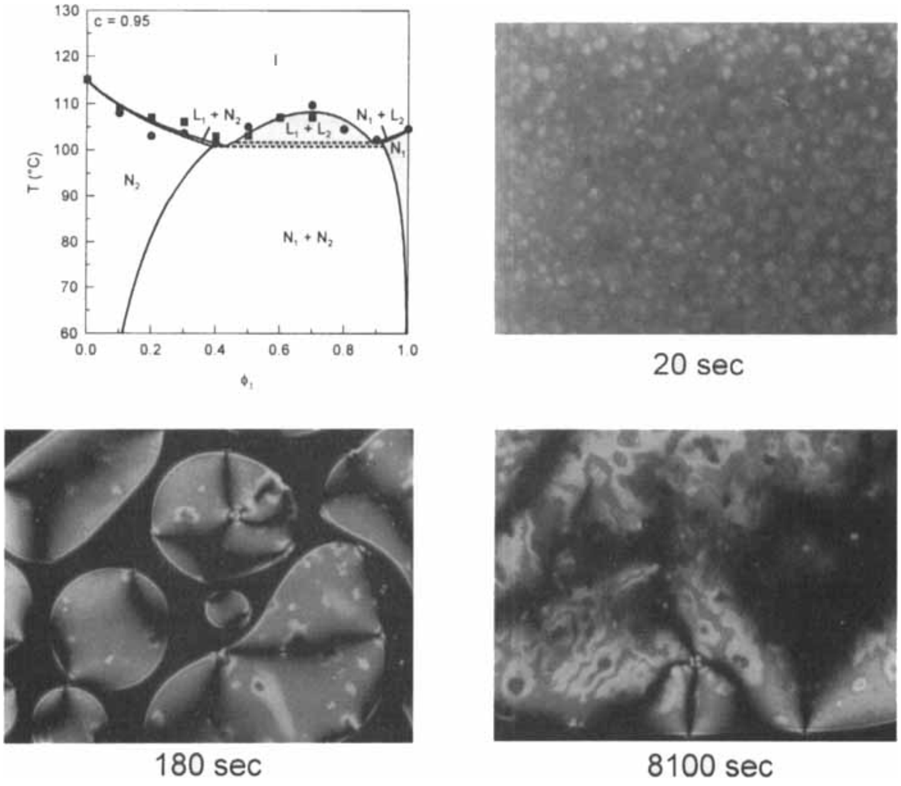
Here, $f(\theta_j)$ represents the normalized orientation distribution function and is considered to be symmetric around the reference axis. The nematic interaction parameters, ν_{11} and ν_{22}, of the individual mesogenic component may be defined as before[9,10]

$$\nu_{jj} = 4.541\frac{T_{NI,j}}{T} \qquad (5)$$

assuming that $\nu_{12} = \nu_{21}$. ν_{12} is generally expressed according to the geometric mean, but it may be allow to depart from this geometric mean, i.e., $\nu_{12} = c\sqrt{\nu_{11}\nu_{22}}$, where c is the proportionality constant characterizing the relative strength of the cross-interaction between the two dissimilar mesogens as compared to that in the same mesogens. The stability limit of the system can be established by equating the chemical potentials of each component.

RESULTS AND DISCUSSION

The temperature versus composition phase diagrams of s-SCLCP/E48 and s-SCLCP/E44 mixtures were established by the cloud point method with a heating and cooling rate of 1 °C/min. Theoretical phase diagrams were calculated based on the combined FH/MS theory described previously[3]. The calculated coexistence curves were compared with the experimental phase diagram of the s-SCLCP/E44 system by assuming the densities of the side-chain liquid crystalline polymers and LC to be the same, respectively. Figure 1 depicts the cloud point temperatures of the side-on SCLCP/E44 system along with the calculated phase diagram (solid lines). The c parameter, which accounts for the relative strength of the cross-nematic interaction to that in the same species, was set to 0.95, and the segmental ratio $r_2/r_1 = 9/1$. The temperature dependence of χ may be estimated by choosing an appropriate A value (-1.0) to account for the broadness of the temperature versus composition curve. The B value in turn may be estimated from the critical temperature of the liquid-liquid equilibrium, i.e., $B = (\chi_c - A)T_c$. Although, the choice of A value may be arbitrary in determining the liquid-liquid coexistence region, the effect of χ is less significant for the nematic-nematic coexistence region. The value of T_c may be estimated from the experimental cloud point (i.e., 107 °C). The calculated phase diagram reveals the existence of two pure nematic regions; one being at the high E44 content (N_1) and the other being at the high concentration of s-SCLCP (N_2). The two dotted lines are the peritectic lines which represent coexistence of three different phases consisting of two liquids plus one nematic or one liquid plus two nematics. There are two narrow nematic-liquid coexistence regions labeled $N_1 + L_2$ and $L_1 + N_2$. When the temperature reaches below the second peritectic line, a two-phase nematic region ($N_1 + N_2$) appears. These coexistence regions may be identified by mimicking the evolution of the phase separated mesomorphic structures during several isothermal quenches at various temperatures and various compositions. An example is shown together with the phase diagram in Figure 1 in which the transition occurs from liquid-liquid to two-phase nematic coexistence regions via the liquid-nematic phase.



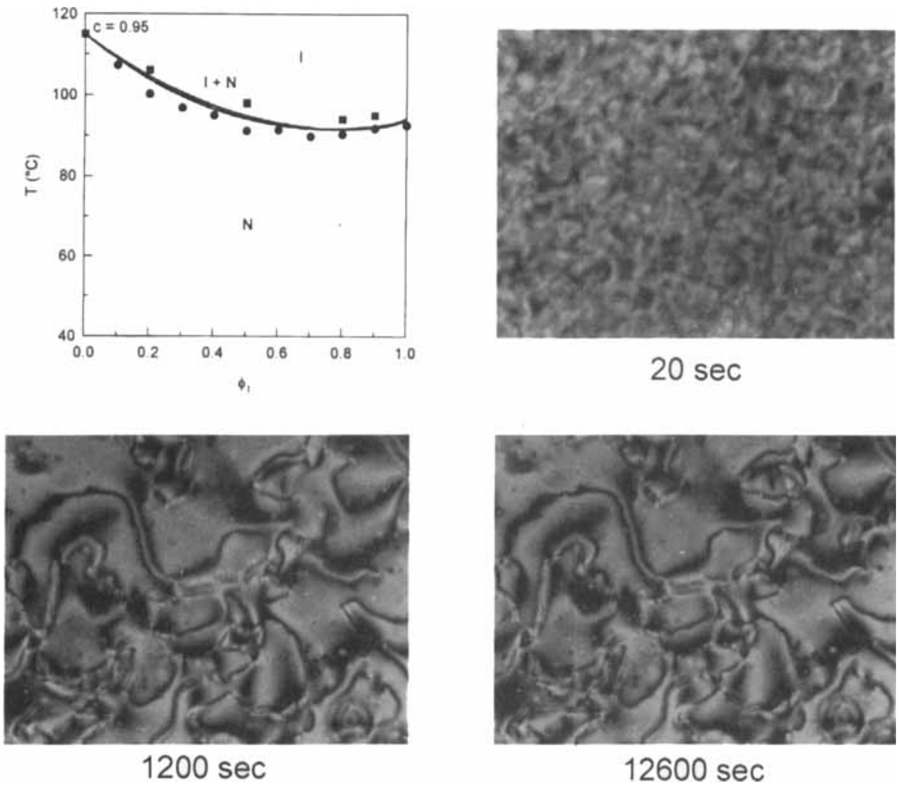
20 sec

180 sec

8100 sec

Figure 1. Cloud point phase diagram of the s-SCLCP/E44 system (filled symbols) in comparison of with the calculated ones (solid curves) along with the temporal evolution of structure at the 30/70 s-SCLCP/E44 following a thermal quench to 100 °C displaying the transition from liquid-liquid, liquid nematic and two-phase nematic phases.
(See Colour Plate II).

Figure 2 exhibits the cloud point temperature versus composition phase diagram of the s-SCLCP/E48 mixture in which the solid curves represent the calculated phase diagram using $c = 0.95$, $r_2/r_1 = 9/1$, and $T_c < T_g$. The theoretical phase diagram appears straight forward relative to that of the s-SCLCP/E44 system. At elevated temperatures, the system is isotropic and homogeneous. In the descending order of temperature, the system passes through an isotropic liquid-nematic coexistence region (I + N) into a single phase nematic region (N). This transition is evident in the case of isothermal quenching to 80 °C as the system has the memory of its path. Upon further lowering the temperature, the coexistence of two separated nematic phases ($N_1 + N_2$) is predicted, but the critical point could be located below the glass transition temperature of the s-SCLCP and thus it may not be observable for the present system. A similar phase diagram had been reported by Finkelmann and co-workers[11] for a mixture of a low molar mass liquid crystal (4-propyloxy phenyl 4'-hexyloxybenzoate) with a SCLCP (polydimethyl siloxane grafted with methoxyphenyl benzoate side group connected by a flexible spacer (4 methylene units) to the backbone. It is striking to notice the great similarity between the phase diagrams of the s-SCLCP/E44 and the end-on SCLCP/E7 having even number methylene linkages as well as that of the s-SCLCP/E48 and the e-SCLCP/E7 having odd number flexible spacers. This observation may be attributed to the differences in the T_c of the systems.



20 sec

1200 sec

12600 sec

Figure 2. Cloud point phase diagram of the s-SCLCP/E48 system (filled symbols) in comparison of with the calculated ones (solid curves) along with the temporal evolution of structure at the 50/50 s-SCLCP/E48 following a thermal quench to 80 °C displaying the transition from isotropic to liquid-nematic then to a single nematic phase. (See Colour Plate III).

CONCLUSIONS

We have demonstrated that the combined FH/MS theory having two orientational order parameters and two clearing transition temperatures is capable of predicting various phase diagrams for nematic mixtures containing a side-chain liquid crystalline polymer as one component. The s-SCLCP/E44 exhibits the liquid + liquid and nematic + nematic coexistence regions. However, the s-SCLCP/E48 shows a single nematic region below the isotropic + nematic coexistence region. It is striking to notice the great similarity between the phase diagrams of the s-SCLCP/E44 and e-SCLCP/E7 having even number spacers as well as that of the s-SCLCP/E48 and e-SCLCP/E7 having odd number methylene spacers.

Acknowledgment: Support of this work by the NSF Science and Technology Center-ALCOM, Grant No. DMR 89-20147 is gratefully acknowledged.

REFERENCES

1. J. West, in Liquid-Crystalline Polymers, R. A Weiss.; C.K Ober, Eds., (Am. Chem. Soc. Symp. Series # 435, 1990), Chap. 32, 475.
2. J. W. Doane in "Liquid Crystals: Their Applications and Uses", B Bahadur, Ed., (World Scientific, New Jersey, 1990), p. 361.
3. H.-W. Chiu, Z.L. Zhou, T. Kyu, L.G. Cada and L.C. Chien, Macromolecules, 29, 1051 (1998).
4. O. Olabisi, L. M. Robeson and M. T. Shaw, "Polymer-Polymer Miscibility", (Academic Press, New York, 1979).
5. W. Maier and A. Saupe, Z. Naturforsch, Teil A 14, 1959, 882; ibid., 15, 287, 1960.
6. S. Chandrasekhar, "Liquid Crystals", 2nd Ed., (Cambridge Univ. Press, 1992).
7. P. G. de Gennes, J. Prost, "The Physics of Liquid Crystals", 2nd Ed., (Oxford. Sci. Publ., London, 1993).
8. F. Brochard, J. Jouffroy and P. Levinson, J. Physique, 45, 1125, (1984)
9. C. Shen and T. Kyu, J. Chem. Phys., 102, 556, (1995)
10. H.-W. Chiu and T. Kyu, J. Chem. Phys., 103, 7471, (1995).
11. H. Finkelmann, H.-J. Kock and G. Rehage, Mol. Cryst. Liq. Cryst., 89, 23 (1982).