

Anisotropic Features in the Dynamics of Nematic-Nematic Phase Separation

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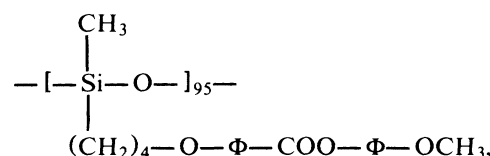
We have studied the dynamics of a nematic-nematic phase separation in mixtures of a mesomorphic polymer with a low-molecular-weight liquid crystal by performing temperature quenches at a number of compositions. The appearance of a new phase and its subsequent growth were observed with an optical microscope. A striking result is the formation of a regular striated pattern whose period increases with time according to a $\frac{1}{3}$ -power law.

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While the dynamics of phase separation has been studied in isotropic liquids,^{1,2} there have been no experiments reported on the equivalent problem in anisotropic fluid systems, e.g., in nematic mesomorphic solutions. The recent discovery^{3,4} of systems in which phase separation occurs into two nematic phases affords an opportunity for such studies. A family of such systems that has been carefully investigated consists of mixtures of conventional low-molecular-weight liquid crystals and grafted nematic polymers with polysiloxane backbones.⁵ Phase equilibria have been studied for several binary mix-

tures^{3,5} and it has been demonstrated that the phase diagrams depend strongly on the length of the terminal hydrocarbon chain of the low-molecular-weight component. Of particular interest is a critical solution temperature associated with phase separation into polymer-rich and polymer-poor fluid phases. This critical temperature, T_c , increases with increasing chain length of the hydrocarbon, so that by variation of the chain length it is possible to position this critical point in the nematic or isotropic regions of the phase diagram. The large variety of possible phase diagrams is well accounted for by mean-field phenomenological models^{6,7} in which the essential feature is the balance between the enthalpy of mixing and the nematic interactions.

We are concerned here with a phase diagram in which T_c is located in the middle of the nematic domain so that the coexisting phases are both nematic. Preliminary studies² have shown that there were interesting dynamic phenomena when such a system was quenched from a one-phase region to a two-phase region in the nematic field of the phase diagram. The binary mixtures which we have studied are composed of the polymer (P) with the formula



with the low-molecular-weight liquid crystal (M) with the formula



The nematic-isotropic transition for pure P occurs at 103°C while that for pure M occurs at 86.5°C.

These mixtures have a very simple phase diagram (shown schematically in Fig. 1) in which the critical

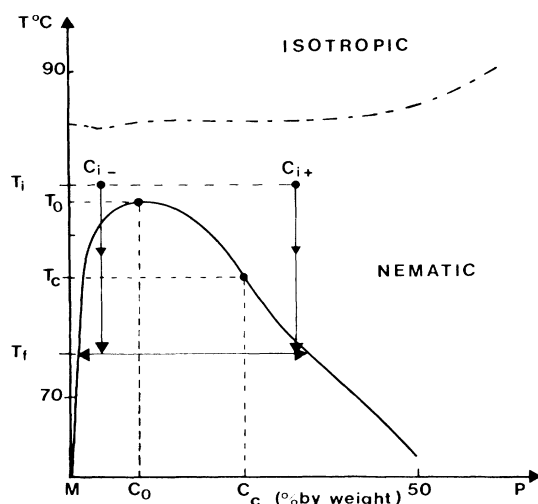


FIG. 1. Schematic monomer-polymer phase diagram. Long-short-dashed line is the isotropic-nematic phase transition. T_0, C_0 are the coordinates of the top of the two-phase curve and T_c, C_c are those of the critical point. Two schematic quenches are shown: one starting at C_{i-} leading to the formation of a polymer-rich phase and the other, starting at C_{i+} , leading to the formation of polymer-poor phase.

temperature and a substantial region of two-phase coexistence lie in the nematic field. The details of this diagram are described elsewhere,⁸ but two features of the phase-separation curve, which are of significance in the present experiments, should be emphasized: (1) The curve has a precise experimental meaning. Beneath the curve, mixtures separate into two macroscopic phases within a time of the order of one day. Above the curve, mixtures have been observed to remain homogeneous for times as long as one month. (2) The critical point does not coincide with the top of the two-phase curve ($T_0=82^\circ\text{C}$, $C_0=10\%$) because of the polydispersity of the polymer.⁹ It is shifted to higher concentration and can be estimated⁸ to lie at $T_c=77^\circ\text{C}$, $C_c=25\%$.

We have studied phase separation in $P+M$ mixtures by a temperature quench method. Starting in a homogeneous state in the nematic phase at concentration C_i and temperature T_i (Fig. 1), we rapidly decrease the temperature to T_f , which lies below the two-phase curve. We then observe the evolution of the system with time t under an optical microscope, either in polarized light or with a phase-contrast attachment. The experiments have been performed either on planar samples, oriented between two glass slides with a separation of $40\text{ }\mu\text{m}$, or on free-surface droplets. The two kinds of samples give quite similar results, but the measurements on the droplets are easier because the contrast is better.

Over the entire concentration range, changes are seen with the microscope only if T_f is on or below the two-phase curve. In such quenches, the phenomena observed depend markedly on C_i . For values of C_i that lie below a concentration $C_s \approx 14\%$, small spherical objects with a radius of the order of $1\text{ }\mu\text{m}$ appear randomly throughout the sample [Fig. 2(a)], grow to several microns in size, and settle to the bottom of the cell so that they rarely coalesce. On the other hand, for concentrations greater than C_s , the phase separation always begins with the appearance of a periodic pattern of striations [Fig. 2(b)]; an initial formation of droplets is never seen. The width of the striations increases with time. Eventually transverse instabilities appear in the striations and they break

up into anisotropic droplets.

We focus here on the initial stage of development of the polymer-poor phase ($C_i > C_s$), corresponding to the striated regime. The intermediate stage is too complex to be analyzed and the last one, the evolution of the non-spherical droplets, is discussed in another communication.¹⁰ The characteristic features of the striations are the following: (1) The striations are parallel to the director orientation. (2) They are visible with unpolarized illumination. If the striations are observed between crossed polarizers, they do not vanish whatever the relative orientations of the director and the polarization of the light. This observation and the fact that the period of the striations varies with time at constant temperature make it clear that the striations do not result simply from a modulation of the nematic orientation. (3) The time dependence of l , the width of the striations, can be represented by a power law $l \propto t^\phi$ with $\phi = 0.33 \pm 0.03$ independent of the initial concentration or final temperature, as shown in Fig. 3.

It is tempting to picture the phase separation as occurring by the mechanism of spinodal decomposition,^{2,11} in which the growth of a new phase begins by the amplification of long-wavelength concentration fluctuations. The striations that we observe would then correspond to alternate polymer-rich and polymer-poor regions, the optical contrast being due to the difference in concentration of the siloxane backbones of the polymer. Such periodic precipitation patterns are often observed in the phase separation of alloys.

Although the quantitative features of growth are not consistent with either the simple linear theory of spinodal decomposition or more complex models, the behavior is in several respects similar to that observed¹ in the phase separation of simple fluid mixtures when the volume fraction of new phase is well in excess of the percolation limit (or, in a classical picture of the two-phase region, when the quench is into the spinodal region). In such systems, when the volume fraction of the precipitating phase is high, the initial stages of growth follow a $t^{1/3}$ power law. The tubular regions of the two phases that

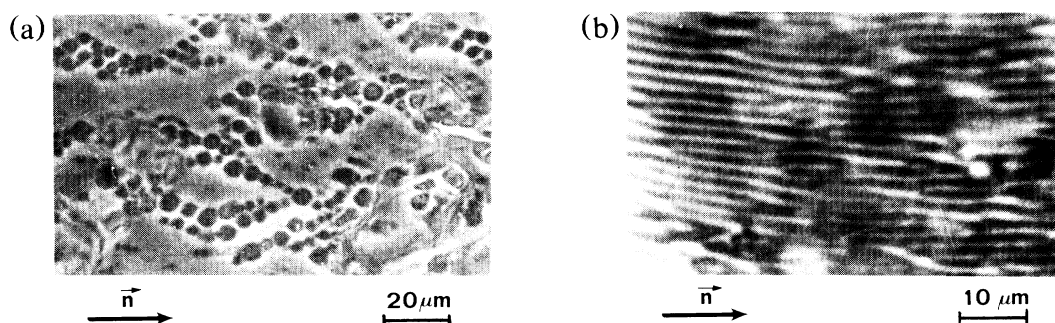


FIG. 2. Optical micrographs of nematic solutions after quenches into the two-phase region. (a) Low-concentration range ($C_i=5\%$); (b) high-concentration range ($C_i=43\%$). \mathbf{n} is the nematic director.

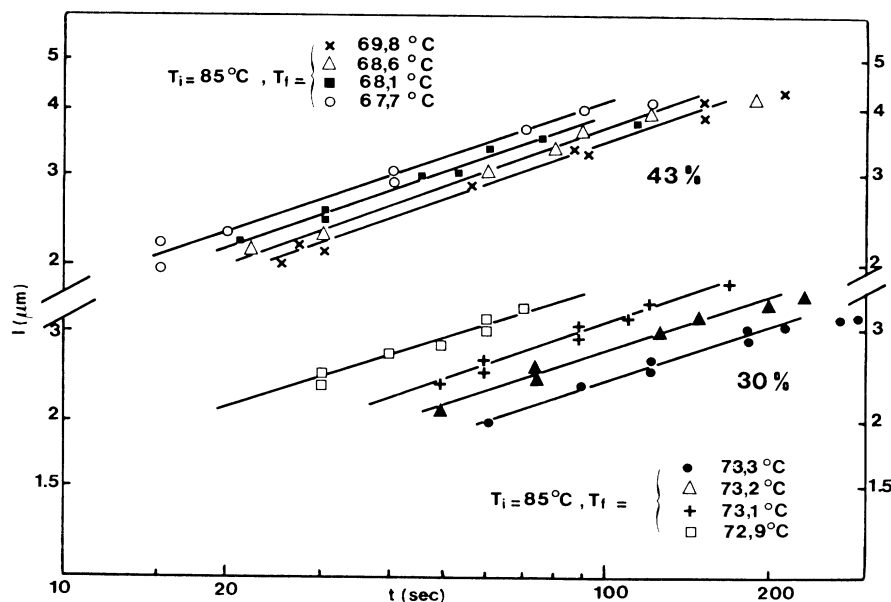


FIG. 3. Time variation of the period of the striation pattern. Upper portion, $C_i = 43\%$; lower portion, $C_i = 30\%$.

form eventually become unstable and breakup into droplets, which continue to grow.^{2,12}

In some respects, however, the analogy between the behavior of simple fluids and the liquid-crystalline system does not hold. The striations appear even in shallow quenches in which the volume fraction of new phase is small (when the system is quenched into the metastable region) and a nucleation and growth mechanism should be expected. Moreover, the change in the character of the precipitated phase at C_s has no parallel in simple fluid systems, where there is a symmetry in behavior around the critical composition.¹

Krishnamurthy and Bansil,¹³ in their study of nucleation and growth in polystyrene+cyclohexane, found a marked asymmetry in the kinetics of phase separation, which they attributed to strong composition dependences of the viscosity, diffusion coefficient, and correlation length in polymer solutions. They studied only two mixtures, one above and one below the critical composition. The rates at which polymer-poor droplets appeared and grew in the polymer-rich phase were much slower than those for the polymer-rich droplets that appear in the solvent-rich phase. Such a dissymmetry should also be expected in systems we have studied, but we see no reason why it should produce a sharp change in mechanism or why the change should occur at C_s .

The orientation of the striations is also puzzling. If, as is usual in phase separation mechanisms, the growth is controlled by diffusion, the orientation of the striations parallel to the director would suggest that the diffusion constant is smaller in that direction than in the perpendicular one. Just the opposite is observed¹⁴ in conven-

tional nematic media. Experiments are now underway to determine the anisotropy of the diffusion in the systems we have studied.

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¹J. S. Huang, W. I. Goldberg, and A. W. Bjerkaas, *Phys. Rev. Lett.* **32**, 921 (1974); N.-C. Wong and C. M. Knobler, *J. Chem. Phys.* **66**, 4707 (1977); D. Beysens, *J. Chem. Phys.* **71**, 2557 (1979).

²For a general review, see J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 8, p. 269.

³C. Casagrande, M. Veyssie, and H. Finkelmann, *J. Phys. Lett.* **43**, 671 (1982).

⁴R. Pratibha and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst. Lett.* **1**, 111 (1985).

⁵H. Finkelmann and H. Benthack, *Makromol. Chem.* **186**, 1895 (1985).

⁶F. Brochard, J. Jouffroy, and P. Levinson, *J. Phys. (Paris), Lett.* **45**, 1125 (1984).

⁷P. Palfy-Muhory, J. R. deBruyn, and D. A. Dunmur, *Mol.*

Cryst. Liq. Cryst. **127**, 301 (1985).

⁸C. Casagrande and M. Veyssie, to be published.

⁹R. Koningsveld and A. J. Staverman, in Adv. Colloid Interface Sci. **2**, 150 (1969).

¹⁰C. Casagrande, P. Fabre, M. A. Gudeau, and M. Veyssie, Europhys. Lett. **3**, 73 (1987).

¹¹J. W. Cahn, J. Chem. Phys. **42**, 93 (1965).

¹²E. D. Siggia, Phys. Rev. A **20**, 595 (1979).

¹³S. Krishnamurthy and R. Bansil, Phys. Rev. Lett. **50**, 2010 (1983).

¹⁴P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974), p. 206.

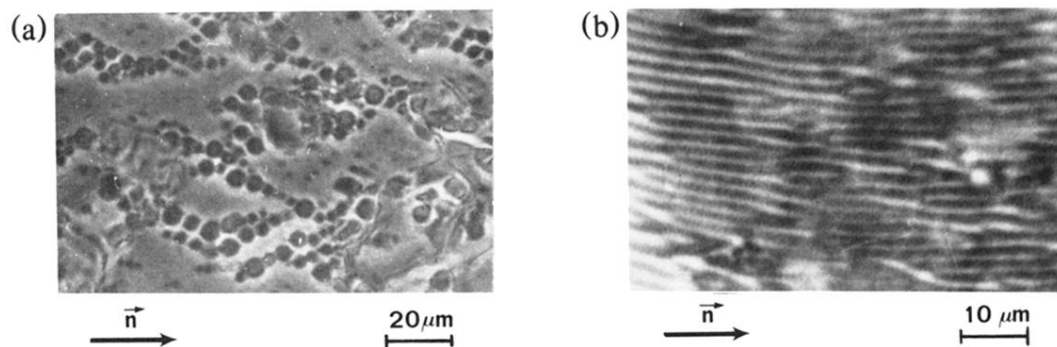


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