Critical point in a random side-chain nematic copolymer: Mean-field theory

Deng-Ke Yang[a]; Chester A. Vause[a]

[a] Department of Physics and Astronomy, University of Hawaii at Manoa, Honolulu, Hawaii, U.S.A.

PLEASE SCROLL DOWN FOR ARTICLE

Critical point in a random side-chain nematic copolymer: mean-field theory

by DENG-KE YANG and CHESTER A. VAUSE

Department of Physics and Astronomy, University of Hawaii at Manoa, Honolulu, Hawaii 96822, U.S.A.

A model for anisotropic phases in a random side-chain nematic copolymer is proposed and solved in the mean-field approximation. The main results of the calculation are the appearance of paranematic and nematic phases and a critical point, without the application of external electric or magnetic fields.

The occurrence of nematic phases in polymeric liquid crystals (PLCs) has been firmly established [1]. These phases have features which are common to their low molecular weight thermotropic counterparts (monomolecular liquid crystals, MLCs), namely weakly first-order isotropic-nematic transitions which can be qualitatively described in terms of a classical mean-field (Maier–Saupe) theory [2]. The question that naturally arises is are there any theoretically new phase transition phenomena in PLCs not found in MLCs? In this paper, we propose such a case.

The system to be studied consists of a PLC made of a long polymeric backbone, with MLC side-chains of two varieties, say A and B, connected to the backbone by flexible non-liquid crystalline spacers. If the MLC side-chains are connected to the backbone at random, the resulting PLC is known as a random side-chain nematic copolymer (RNC) [1, 3]. Such RNCs have a property that is unlike the MLC binary mixture counterpart; the backbone provides a constraint to disallow phase separation of the A–B components as there is no overriding energetic or entropic reason to do so. Also, one should bear in mind that the RNC is an effectively infinite component mixture and therefore is entropically more prone to a single miscible phase. Such a system, therefore, does not introduce the complications that arise in systems which phase separate, such as in the binary mixture MLC system.

Under the above assumptions, a simple mean-field (MF) model of the Maier–Saupe type [2] can be constructed as follows. At zeroth order, we assume that the main effect of the backbone is to prevent A B immiscibility, and is rather passive otherwise. Hence, the RNC is an effective miscible single-phase 'mixture' of A and B MLCs which are acted upon by the usual dispersive forces. The MF hamiltonian for a single A and B MLC is

$$\left.\begin{aligned}
H_A &= -[xV_{AA}S_A + (1-x)V_{AB}S_B]P_2(\cos\theta_A), \\
H_B &= -[xV_{AB}S_A + (1-x)V_{BB}S_B]P_2(\cos\theta_B),
\end{aligned}\right\} \tag{1}$$

where x is the molar concentration of A molecules ($0 \leqslant x \leqslant 1$), the couplings $V_{ij} > 0$ are the effective (long-range) attractive orientational interaction strengths between like molecules (V_{AA}, V_{BB}), and unlike molecules ($V_{AB} = V_{BA}$), $P_2(\cos\theta)$ is the second-order
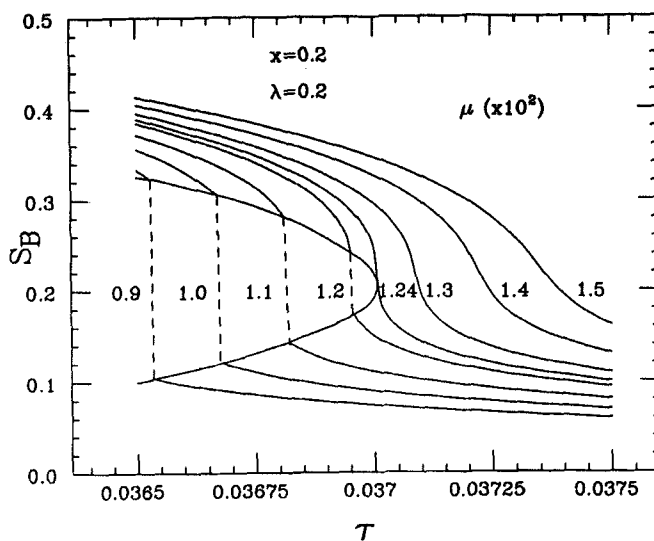
(a)
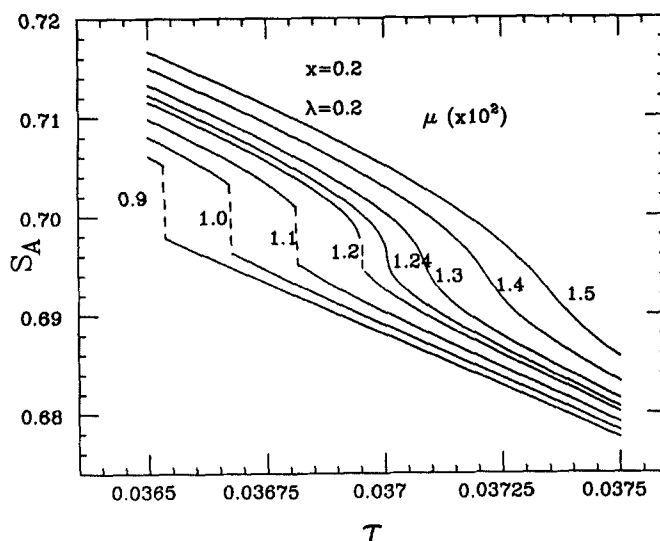
(b)

Figure 1. (a) The temperature dependence of the order parameter S_B for fixed x (concentration of A side-chains) and λ (reduced B-B interacting strength), ($x = 0.2$, $\lambda = 0.2$), but various values of μ (reduced A-B interacting strength). (b) The temperature dependence of the order parameter S_A in the vicinity of the ordering of S_B under the same conditions as in (figure 1 (a).)

Legendre polynomial, and $S_i = \langle P_2(\cos\theta_i)\rangle$ is the usual nematic order parameter for species $i = A, B, 0 \leqslant S_i \leqslant 1$, which must be determined self-consistently. It should be emphasized that such a MF hamiltonian could not be written for the MLC binary mixture since the concentration variable must be a statistically fluctuating degree of freedom with interactions present which promote phase separation [4]. The

appropriate equations that represent a self-consistent MF solution are

$$S_i = \int_{-1}^{1} d(\cos\theta_i)\exp(-H_i/k_B T)P_2(\cos\theta_i) \Big/ \int_{-1}^{1} d(\cos\theta_i)\exp(-H_i/k_B T) \quad (2)$$

and the total Helmholtz MF free energy

$$F = \sum_{i=A,B} x_i \left[-\tfrac{1}{2}\langle H_i \rangle - k_B T \ln \int_{-1}^{1} d(\cos\theta_i)\exp(-H_i/k_B T) \right], \quad (3)$$

with $x_A = x$, $x_B = 1 - x$.

The set (2) and (3) were solved numerically as follows. Without loss of generality, we choose $V_{AA} > V_{BB}$, and define dimensionless coupling strengths $\mu = V_{AB}/V_{AA}$, and $\lambda = V_{BB}/V_{AA}$. For a given x, μ and λ, a reduced temperature τ ($\tau = k_B T/V_{AA}$) is chosen, values of S_A and S_B are obtained by solving (2), and the equilibrium values are determined by using (3).

The results of the MF calculation are summarized in the following figures. Figure 1 shows the τ-dependence of the parameters S_A and S_B for the fixed values $x = 0.2$, $\lambda = 0.2$, with μ variable. This displays the typical behaviour of the model. For μ less than a critical value μ_c (which in this case is $\mu_c \cong 0.0124$), S_A orders first (since $\lambda < x/(1-x) = 0.25$) at around $\tau = 0.042$ (not shown) via the usual first-order transition. However, after the ordering takes place, S_B finds itself in an effective 'external field' and orders paranematically [5] until it reaches its own first-order phase transition (figure 1 (a); S_A undergoes similar behaviour as a result of its coupling with S_B (figure 1 (b)). (If $\mu = 0$, then one obtains two independent isotropic-nematic transitions.) As $\mu \to \mu_c$ from below, a critical point develops in both order parameters, signifying the point at which the distinction between the nematic and paranematic phase disappears. For $\mu > \mu_c$, only there is the paranematic phase present in S_B and therefore no phase transition as shown in figure 1 (a). Figure 2 illustrates the paranematic–nematic behaviour in S_B via a critical point by varying the
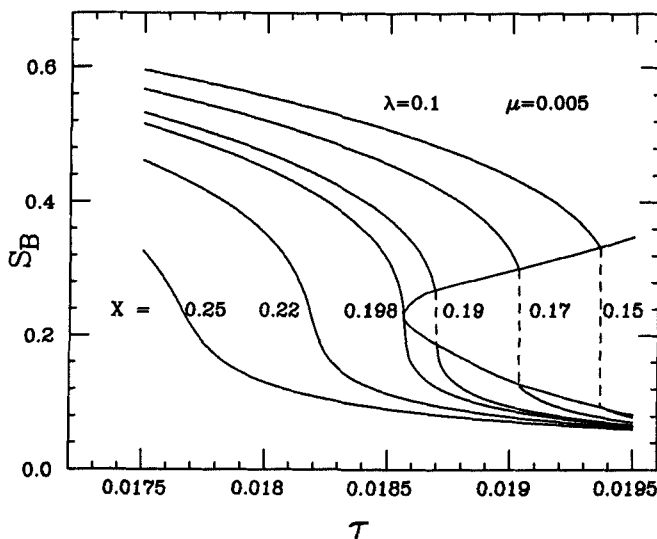
Figure 2.   The temperature dependence of the order parameter S_B for fixed λ and μ ($\lambda = 0.1$, $\mu = 0.005$), but various values of x.
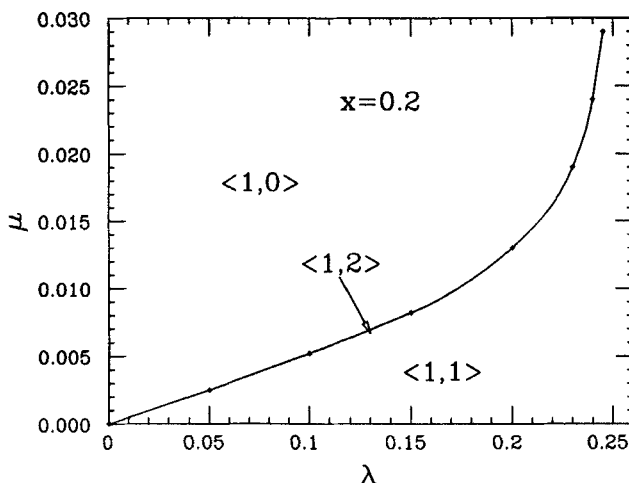
Figure 3.   The phase diagram in the (λ, μ) plane $0 < \lambda < x/(1 - x)$ with $x = 0{\cdot}2$. The notation $\langle 1,0 \rangle$, etc, is explained in the text.

concentration x with fixed interaction strengths ($\mu = 0{\cdot}005$, $\lambda = 0{\cdot}1$), a situation which may be more accessible experimentally. Finally, figure 3 illustrates a cross-section at $x = 0{\cdot}2$ of the global phase diagram in the variables (x, λ, μ). The various regions are labelled by the symbol $\langle o_A, o_B \rangle$, which denote the type of transition occurring at the point where S_B orders, o_i ($i = A, B$) is the order of the phase transition: $o_i = 0$ (paranematic, no phase transition), 1 (first-order), 2 (second-order)/critical points). The main feature of the phase diagram is that there is a line of critical points, suggesting that there may be some flexibility in obtaining the critical point by molecular design. In the global phase diagram, one expects a surface of critical points, the determination of which needs future study.

In summary, if the assumptions of the model for RNCs is qualitatively correct, the results of a MF analysis suggests the possibility of designing a RNC which has paranematic and nematic phases and a critical point. The possibility of experimentally realizing such behavior may be promising since one avoids the complications that arise in thermotropic MLCs from applying external electric or magnetic fields [6]. As a result, one not only has an interesting system to study critical phenomena, but also a material with potentially novel optical characteristics.

Finally, we would like to thank the referee for several helpful suggestions and for pointing out that a similar idea has been used in the discussion of nematic phases in comb polymers [7].

References

[1] For reviews, see; CIFERRI, A., KRIGBAUM, W. R., and MEYER, R. B. (editors), 1982. *Polymer Liquid Crystals* (Academic Press). New York, 1982; Chapoy, L. L. (editor), 1985, *Recent Advances in Liquid Crystalline Polymers* (Elsevier Science).
[2] MAIER, W., and SAUPE, A., 1958, *Z. Naturf. (a)*, **13**, 564; 1959, *Ibid.*, **14**, 882; 1960, *Ibid.*, **15**, 287. See also: CHANDRASEKHAR, S., 1977, *Liquid Crystals* (Cambridge University Press).
[3] SAMULSKI, E., 1982, *Physics Today* (May), p. 40.

[4] For an elementary review on phase separation in binary mixtures, see: WALKER, J.S., and VAUSE, C. A., 1987, *Sci. Am.*, **255**, 98; 1983, *J. chem. Phys.*, **79**, 2660.

[5] WOJTOWICZ, P. J., and SHENG., 1974, *Physics Lett.* A, **48**, 235. HORNREICH, R. M., 1985, *Physics Lett.* A, **109**, 232. VAUSE, C. A., 1986, *Physics Lett*, A, **114**, 485.

[6] NICASTRO, A. J., and KEYES, P. H., 1984, *Phys. Rev.* A, **30**, 3156.

[7] WARNER, M., 1988, *Molec. Crystals liq. Crystals*, **155**, 433.