

## Nematic ordering and microphase segregation in a diblock polymer–liquid-crystal-polymer

R. A. Sones and R. G. Petschek

*Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7079*

(Received 15 March 1994)

A theory of nematic ordering and microphase segregation in an incompressible melt of  $AB$  diblock copolymers is developed for the case when the  $A$  block is a polymer composed of  $N_A$  monomers and the  $B$  block is a main-chain liquid crystal polymer composed of  $N_B$  freely jointed nematogens. Isotropic monomer-nematogen interactions are characterized by a Flory parameter  $\chi$ , and anisotropic nematogen-nematogen interactions are characterized by a Maier-Saupe parameter  $J$ . Long chains ( $N_A, N_B \gg 1$ ) in the strong segregation limit ( $\chi^N \gg 1$ , with  $N = N_A + N_B$ ) are considered. An approximate free energy of the melt is given for the following segregation morphologies: homogeneous, lamellar, cylindrical micelles, and spherical micelles. The free energy is minimized to determine the equilibrium morphology, lattice constant, and degree of nematic order as a function of  $\chi^N$ ,  $J$ , and  $N_A/N$ . Both morphological and isotropic-nematic transitions occur, and the ordinary diblock copolymer phase diagram is significantly altered.

PACS number(s): 61.25.Hq, 61.30.Cz, 64.70.Md, 64.75.+g

### I. INTRODUCTION

A polymer is called a diblock copolymer if it consists of two subchains (or blocks), one containing type- $A$  monomers and the other type- $B$ . Typically, if the temperature is sufficiently low, a melt of  $AB$  diblock copolymers spontaneously segregates into  $A$ -rich and  $B$ -rich domains. The linkage between  $A$  and  $B$  blocks precludes macroscopic phase segregation and leads to interesting microscopic ordering—called microphase segregation—on a scale of the radius of gyration of the polymer.

Over the past twenty years, the theory of microphase segregation in  $AB$  diblock copolymers has been extensively developed [1–3]. If a polymer molecule is modeled as a chain of freely jointed segments, with  $N_A$  type- $A$  segments and  $N_B$  type- $B$  segments, and if both types of segments have the same length, then mean field theory predicts a phase diagram like Fig. 1, where  $N$  is the total number of segments per molecule ( $N = N_A + N_B$ ),  $f_A$  is the fraction of each molecule which is type- $A$  ( $f_A = N_A/N$ ), and  $\chi$  describes the degree of incompatibility of  $A$  and  $B$  segments ( $\chi \sim 1/T$  where  $T$  is temperature). When temperature is sufficiently high ( $\chi N < 10$ ) the melt is homogeneous (no segregation) for all values of  $f_A$ ; when temperature is sufficiently low ( $\chi N \gg 1$ , the strong segregation regime) one of three segregation morphologies—lamellar (parallel planes), cylindrical micelles, or spherical micelles—appears, depending on the value of  $f_A$ . Experiments confirm the general features of this phase diagram for many diblock copolymer materials [4].

In this paper, we calculate a phase diagram analogous to Fig. 1 for the case when the  $A$  block is an ordinary polymer, and the  $B$  block is a main chain liquid crystal polymer (LCP) composed of a freely jointed chain of rigid-rod segments which are capable of nematic ordering. We will refer to this material as a polymer-LCP di-

block copolymer, or P-LCP for short. In such a material one expects to observe both morphological and isotropic-nematic transitions. The Semenov theory of microphase segregation [3] successfully describes morphological phase boundaries in the strong segregation regime, and gives a reasonable estimate of the order-disorder phase boundary (see Fig. 1). The Maier-Saupe theory of liquid crystals [5] successfully describes the isotropic-nematic transition. We will combine the Semenov and Maier-Saupe theories in order to describe P-LCP's. We will consider

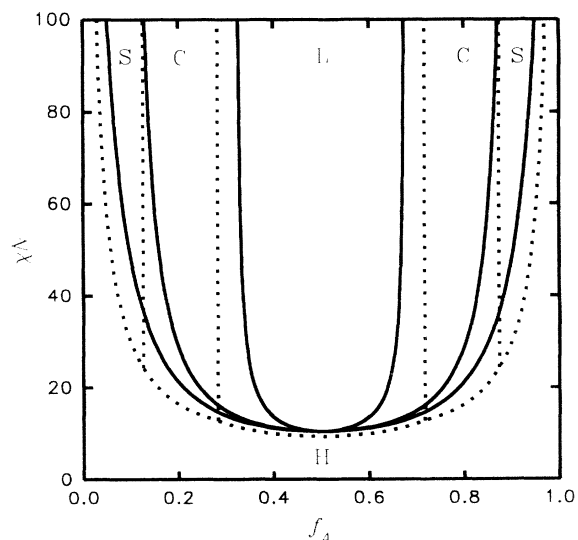


FIG. 1. Diblock copolymer phase diagram showing equilibrium morphology (homogeneous  $H$ , lamellar  $L$ , cylindrical micelles  $C$ , spherical micelles  $S$ ) versus type- $A$  fraction  $f_A$  and incompatibility parameter  $\chi N$ . Solid curves are an exact solution of mean field theory [7]; dotted curves are Semenov's results [3].

long molecules ( $N_A, N_B \gg 1$ ) in the strong segregation limit ( $\chi N \gg 1$ ), and will also assume  $\chi \ll 1$ , which is typical of most pairs of polymers. Thus we will take  $N \gg \chi N \gg 1$ .

Williams and Halperin [6] recently published a theoretical study of a P-LCP for the case of a LCP with finite rigidity—a so-called semiflexible chain. In their model the splay elastic energy of the LCP is a dominant term in the free energy, particularly at low temperatures when the LCP becomes rodlike. In our model the P-LCP has zero rigidity—a freely jointed chain—and splay elastic energy can be neglected (see the Results and Discussion section). Our model includes three effects which Williams and Halperin exclude: (i) corrections to the micelle surface free energy due to the presence of nematic order; (ii) the possibility that the interior of a micelle can be composed of either polymer or LCP; (iii) and the possibility that the isotropic-nematic transition can occur at a higher temperature than the segregation transition. These differences between the models lead to very different phase diagrams. Also, the analysis for a freely jointed chain is simpler and more surveyable than that for a semiflexible chain.

## II. THEORY

We assume the melt has one of the following morphologies: homogeneous ( $d = 0$ ), lamellar ( $d = 1$ ), cylindrical micelles ( $d = 2$ ), or spherical micelles ( $d = 3$ ), where  $d$  is the morphological order parameter. Let  $R$  be the radius of a cylindrical or spherical micelle, and let  $L/2$  be the radius of the concentric unit cell. (The assumption of a cylindrical or spherical unit cell is an approximation, since such cells are not space filling. At the level of this approximation we do not distinguish between various ways of packing micelles [3,7]). For convenience we define a lamellar “micelle” as an infinite slab parallel to the lamellae containing one . . .  $BAAB$  . . . section of thickness  $L$ , and define the lamellar “radius”  $R$  as the distance from the center of the  $AA$  region (the center of the micelle) to the  $AB$  interface. For  $d = 1, 2, 3$  we consider only the strong segregation regime, where segregation is nearly complete and the interfacial thickness (the region of  $AB$  junctions) is small compared to the micellar lattice constant  $L$ .

Regard each molecule as a freely jointed chain of  $N$  segments, where the first  $N_A$  segments are *monomers* and the remaining  $N_B$  segments are *nematogens*. We assume the monomer and nematogen segments both have the same statistical segment length  $\ell$ , defined such that

$$\mathcal{R}^2 = N\ell^2/6, \quad (1)$$

where  $\mathcal{R}$  is the (hypothetical) radius of gyration of a chain in the absence of segment-segment interactions. We also assume the chains are very long ( $N_A, N_B \gg 1$ ); in this limit our results will be independent of  $N$ .

### A. Order Parameters

Let  $R + r$  be the distance from the center of a micelle, where  $r$  is a radial coordinate defined so that  $r = 0$  corresponds to the micelle’s surface and  $r = -R$  corresponds to the micelle’s center; for the homogeneous morphology the coordinate  $r$  is irrelevant; for a lamellar micelle “radial” means “perpendicular to the lamellae.” Let  $\phi_A(r)$  and  $\phi_B(r)$  be the volume fractions of monomers and nematogens at  $r$  and impose the incompressibility constraint

$$\phi_A(r) + \phi_B(r) = 1. \quad (2)$$

Introduce the segregation order parameter

$$h = \frac{\langle \phi_A^2 \rangle - f_A^2}{f_A f_B}, \quad (3)$$

where

$$\begin{aligned} f_A &= \frac{N_A}{N} = \langle \phi_A \rangle, \\ f_B &= \frac{N_B}{N} = \langle \phi_B \rangle = 1 - f_A \end{aligned} \quad (4)$$

are the overall fractions of type- $A$  and type- $B$  material in the melt, and the angle brackets denote spatial averaging. The definition of  $h$  and the incompressibility constraint imply

$$\begin{aligned} \langle \phi_A^2 \rangle &= f_A - \langle \phi_A \phi_B \rangle, \\ \langle \phi_B^2 \rangle &= f_B - \langle \phi_A \phi_B \rangle, \\ \langle \phi_A \phi_B \rangle &= (1 - h)f_A f_B. \end{aligned} \quad (5)$$

The segregation order parameter  $h$  ranges from zero for a homogeneous melt to unity for complete segregation. In the strong segregation regime  $h \simeq 1$ , so we let

$$h_d = \begin{cases} 0 & \text{if } d = 0 \\ 1 & \text{if } d = 1, 2, 3, \end{cases} \quad (6)$$

be the (approximate) segregation order parameter associated with morphology  $d$ . We also introduce the micelle order parameter

$$g = \begin{cases} 0 & \text{if micelles are type } A \\ 1 & \text{if micelles are type } B, \end{cases} \quad (7)$$

which indicates whether the micelles are formed of monomers or nematogens. For homogeneous and lamellar morphologies we define  $g = 0$ . The subscripts *in* and *ex* will be used to denote the material type ( $A$  or  $B$ ) in the interior ( $r < 0$ ) or exterior ( $r > 0$ ) of a micelle: if  $g = 0$  then *in*  $\rightarrow A$  and *ex*  $\rightarrow B$ ; if  $g = 1$  then *in*  $\rightarrow B$  and *ex*  $\rightarrow A$ .

Finally, introduce the nematic order parameter

$$s = \left\langle \frac{3(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}})^2 - 1}{2} \right\rangle, \quad (8)$$

where  $\hat{\mathbf{u}}$  is the unit vector along a nematogen and the angle brackets denote a thermal average over all nematogens. In writing this expression for  $s$  we make two simpli-

fying assumptions: the local nematic director  $\hat{\mathbf{n}}$  always points along the coordinate  $r$ , so that  $\hat{\mathbf{n}} = \hat{\mathbf{r}}$ ; and  $s$  is independent of  $r$ . We discuss these assumptions in the Results and Discussion section. Note that  $s$  ranges from zero for an isotropic distribution to unity for complete nematic ordering.

### B. Free Energy

First consider the free energy of the segregated morphologies ( $d = 1, 2, 3$ ) in the strong segregation regime. It is convenient to decompose the free energy into four components:

$$F = F_{AB} + F_{BB} + F_{\text{grad}} + F_{\text{conf}}, \quad (9)$$

where  $F$  is the free energy per chain,  $F_{AB}$  and  $F_{BB}$  are internal energies due to monomer-nematogen and nematogen-nematogen interactions,  $F_{\text{grad}}$  is a surface tension term which depends on  $(\nabla\phi_A)^2$  and  $(\nabla\phi_B)^2$ , and  $F_{\text{conf}}$  is a configurational entropy term due to stretching and nematic ordering of the chains.

From the Flory-Huggins theory of phase segregation the internal energy per chain due to isotropic monomer-nematogen interactions is [8]

$$F_{AB} = T\chi N \langle \phi_A \phi_B \rangle, \quad (10)$$

and from the Maier-Saupe theory of nematic ordering the internal energy per chain due to anisotropic nematogen-nematogen interactions is [5]

$$F_{BB} = -\frac{1}{2}TJNs^2 \langle \phi_B^2 \rangle = -\frac{1}{2}TJNs^2 (f_B - \langle \phi_A \phi_B \rangle). \quad (11)$$

Here  $T$  is temperature (in energy units), and the interaction parameters  $\chi$  and  $J$  are both positive and vary (approximately) as  $1/T$ . Adding the internal energies together we find

$$F_{AB} + F_{BB} = T\tilde{\chi}N \langle \phi_A \phi_B \rangle - \frac{1}{2}TJNf_Bs^2, \quad (12)$$

where

$$\tilde{\chi} = \chi + \frac{1}{2}Js^2 \quad (13)$$

is the effective  $\chi$  for the P-LCP system, incorporating both Flory-Huggins and Maier-Saupe interactions [9]. The product  $\phi_A \phi_B$  is nonzero only in a thin region  $|r| \ll R$  about the micelle surface, so we neglect the curvature of the micelle surface and write

$$\langle \phi_A \phi_B \rangle = \Lambda_d \int_{-\infty}^{+\infty} dr \phi_A(r) \phi_B(r), \quad (14)$$

where

$$\Lambda_d = dR^{d-1} \left( \frac{2}{L} \right)^d \quad (15)$$

is the ratio of micelle surface area to unit cell volume.

The density gradient contribution to the free energy per chain is [3,10]

$$\begin{aligned} F_{\text{grad}} &= \frac{\Lambda_d TN \ell^2}{24} \left\langle \frac{(\nabla\phi_A)^2}{\phi_A} + \frac{(\nabla\phi_B)^2}{\phi_B} \right\rangle \\ &= \frac{\Lambda_d TN \ell^2}{24} \int_{-\infty}^{+\infty} dr \frac{(d\phi_A/dr)^2}{\phi_A(1-\phi_A)}, \end{aligned} \quad (16)$$

where we again neglect curvature of the micelle surface. Equations (12)–(16) imply

$$\begin{aligned} F_{AB} + F_{BB} + F_{\text{grad}} &= \Lambda_d TN \int_{-\infty}^{+\infty} dr \left( \frac{\ell^2 (d\phi_A/dr)^2}{24\phi_A(1-\phi_A)} + \tilde{\chi}\phi_A\phi_B \right) \\ &\quad - \frac{1}{2}TJNf_Bs^2. \end{aligned} \quad (17)$$

The minimal value of the integral is  $\ell\sqrt{\tilde{\chi}/6}$ , corresponding to the distribution [3]

$$\phi_A(r) = \frac{1}{2} + \frac{1}{2} \tanh\left(\sqrt{6\tilde{\chi}} \frac{r}{\ell}\right), \quad (18)$$

so, in equilibrium,

$$F_{AB} + F_{BB} + F_{\text{grad}} = 2TC_{dg}\sqrt{\tilde{\chi}N} \frac{R}{L} - \frac{1}{2}TJNf_Bs^2, \quad (19)$$

where  $C_{dg}$  is defined in Eqs. (30) below, and we have used the fact that  $R = f_{\text{in}}^{1/d}L/2$  in an incompressible melt.

The configurational entropy of a chain with its  $AB$  junction at  $r = 0$ , type- $A$  free end at  $r = r_A$ , and type- $B$  free end at  $r = r_B$  is (see Appendix)

$$S = S_{\text{MS}} + S_{\text{str}}, \quad (20)$$

where

$$S_{\text{MS}} = N_B \mathcal{D} \left[ \frac{3}{2}Js \right] - \frac{1}{2}N_B Js(2s+1) \quad (21)$$

is the Maier-Saupe orientational entropy of the nematic portion of the chain [5],

$$S_{\text{str}} = -\frac{3r_A^2}{2N_A \ell_A^2} - \frac{3r_B^2}{2N_B \ell_B^2} \quad (22)$$

is the entropy reduction due to chain stretching [11],

$$\mathcal{D}[x] = \ln \int_0^1 d\gamma e^{x\gamma^2}, \quad (23)$$

$$\Omega[x] = \frac{3 \int_0^1 d\gamma \gamma^2 e^{x\gamma^2}}{\int_0^1 d\gamma e^{x\gamma^2}},$$

and

$$\begin{aligned}\ell_A^2 &= \ell^2, \\ \ell_B^2 &= \Omega \left[ \frac{3}{2} J s \right] \ell^2,\end{aligned}\quad (24)$$

where  $\ell_B$  is the effective segment length for the random walk of the nematic portion of the chain in the  $\hat{\mathbf{r}}$  direction. The free energy associated with  $S_{MS}$  is  $-TS_{MS}$ , and the free energy associated with  $S_{str}$  is obtained by minimizing  $-TS_{str}$  over all distributions of chains consistent with the incompressibility constraint, which gives [3]

$$\langle -TS_{str} \rangle = \frac{TNf_{in}}{V_d} (U_0 + U_1), \quad (25)$$

where

$$\begin{aligned}U_0 &= \frac{\pi^2 \lambda_d R^{d+2}}{32 a_{in}^2 N_{in}^2}, \\ U_1 &= \frac{\pi \kappa_d R^{d+2}}{4 a_{ex}^2 N_{in}^2},\end{aligned}\quad (26)$$

$$\begin{aligned}a_A^2 &= \frac{\ell_A^2}{6}, \\ a_B^2 &= \frac{\ell_B^2}{6},\end{aligned}\quad (27)$$

and

$$\begin{aligned}\lambda_1 &= \frac{4}{3}, & \kappa_1 &= \frac{\pi}{6} \left( \frac{1}{f_{in}} - 1 \right), & V_1 &= 2R, \\ \lambda_2 &= \frac{\pi}{3}, & \kappa_2 &= \frac{1}{4} \ln \left( \frac{1}{f_{in}} \right), & V_2 &= \pi R^2, \\ \lambda_3 &= \frac{4\pi}{15}, & \kappa_3 &= \frac{4}{9} \left( 1 - f_{in}^{1/3} \right), & V_3 &= \frac{4\pi}{3} R^3.\end{aligned}\quad (28)$$

Equations (20)–(28) imply

$$\begin{aligned}\frac{F_{conf}}{T} &= \left( \frac{\mathcal{A}_{dg}}{\Omega \left[ \frac{3}{2} J s g \right]} + \frac{\mathcal{B}_{dg}}{\Omega \left[ \frac{3}{2} J s (1-g) \right]} \right) \left( \frac{L}{\mathcal{R}} \right)^2 \\ &+ \frac{1}{2} J N f_B s (2s+1) - N f_B \mathcal{D} \left[ \frac{3}{2} J s \right],\end{aligned}\quad (29)$$

where

$$\begin{aligned}\mathcal{A}_{00} &= 1, & \mathcal{B}_{00} &= 1, & \mathcal{C}_{00} &= 0, \\ \mathcal{A}_{10} &= \frac{\pi^2}{192} f_A, & \mathcal{B}_{10} &= \frac{\pi^2}{192} f_B, & \mathcal{C}_{10} &= 1, \\ \mathcal{A}_{20} &= \frac{\pi}{384}, & \mathcal{B}_{20} &= \frac{1}{64} \ln(1/f_A), & \mathcal{C}_{20} &= 2f_A^{1/2}, \\ \mathcal{A}_{21} &= \frac{\pi}{384}, & \mathcal{B}_{21} &= \frac{1}{64} \ln(1/f_B), & \mathcal{C}_{21} &= 2f_B^{1/2}, \\ \mathcal{A}_{30} &= \frac{\pi}{640} f_A^{-1/3}, & \mathcal{B}_{30} &= \frac{1}{48} (f_A^{-1/3} - 1), & \mathcal{C}_{30} &= 3f_A^{2/3}, \\ \mathcal{A}_{31} &= \frac{\pi}{640} f_B^{-1/3}, & \mathcal{B}_{31} &= \frac{1}{48} (f_B^{-1/3} - 1), & \mathcal{C}_{31} &= 3f_B^{2/3}.\end{aligned}\quad (30)$$

Equations (19) and (29) give for the total free energy

$$\begin{aligned}\left( \frac{F}{T} \right)_{d=1,2,3} &= \left( \frac{\mathcal{A}_{dg}}{\Omega \left[ \frac{3}{2} J s g \right]} + \frac{\mathcal{B}_{dg}}{\Omega \left[ \frac{3}{2} J s (1-g) \right]} \right) \left( \frac{L}{\mathcal{R}} \right)^2 \\ &+ 2\mathcal{C}_{dg} \sqrt{\tilde{\chi} N} \left( \frac{\mathcal{R}}{L} \right) \\ &+ \frac{1}{2} J N f_B s (s+1) - N f_B \mathcal{D} \left[ \frac{3}{2} J s \right].\end{aligned}\quad (31)$$

Minimizing with respect to  $L$  gives, in equilibrium,

$$\begin{aligned}\left( \frac{F}{T} \right)_{d=1,2,3} &= 3\mathcal{C}_{dg}^{2/3} \left( \frac{\mathcal{A}_{dg}}{\Omega \left[ \frac{3}{2} J s g \right]} \right. \\ &+ \left. \frac{\mathcal{B}_{dg}}{\Omega \left[ \frac{3}{2} J s (1-g) \right]} \right)^{1/3} (\tilde{\chi} N)^{1/3} \\ &+ \frac{1}{2} J N f_B s (s+1) - N f_B \mathcal{D} \left[ \frac{3}{2} J s \right],\end{aligned}\quad (32)$$

and

$$\frac{L}{\mathcal{R}} = \mathcal{C}_{dg}^{1/3} \left( \frac{\mathcal{A}_{dg}}{\Omega \left[ \frac{3}{2} J s g \right]} + \frac{\mathcal{B}_{dg}}{\Omega \left[ \frac{3}{2} J s (1-g) \right]} \right)^{-1/3} (\tilde{\chi} N)^{1/6}.\quad (33)$$

Now consider the free energy of the unsegregated morphology ( $d=0$ ). The gradient and stretching terms are no longer applicable, and the dilution of the nematogens requires that  $J$  be replaced by  $Jf_B$ . Then Eqs. (12) and (21) give

$$\begin{aligned}\left( \frac{F}{T} \right)_{d=0} &= \chi N f_A f_B + \frac{1}{2} J N f_B^2 s (s+1), \\ &- N f_B \mathcal{D} \left[ \frac{3}{2} J f_B s \right].\end{aligned}\quad (34)$$

Finally, combine Eqs. (32) and (34) to get a single expression valid for all  $d$ :

$$\begin{aligned}\frac{F}{T} &= 3h_d \mathcal{C}_{dg}^{2/3} \left( \frac{\mathcal{A}_{dg}}{\Omega \left[ \frac{3}{2} J s g \right]} + \frac{\mathcal{B}_{dg}}{\Omega \left[ \frac{3}{2} J s (1-g) \right]} \right)^{1/3} (\tilde{\chi} N)^{1/3} \\ &+ (1-h_d) \chi N f_A f_B \\ &+ \frac{1}{2} J N f_B (h_d f_A + f_B) s (s+1) \\ &- N f_B \mathcal{D} \left[ \frac{3}{2} J (h_d f_A + f_B) s \right].\end{aligned}\quad (35)$$

This is our central result. One can minimize  $F/T$  with respect to  $d$ ,  $g$ , and  $s$  to determine the equilibrium morphology and degree of nematic order, and then calculate  $L/\mathcal{R}$  from Eq. (33).

We are interested in the case  $N \gg \chi N \gg 1$ . Then the values of  $d$ ,  $g$ , and  $s$  which minimize  $F/T$  depend only on  $f_A$ ,  $\chi N$ , and  $J$ , and the task of minimizing Eq. (35) is quite simple. The key thing to notice is that the last two terms dominate for large  $N$ , and that they represent the Maier-Saupe free energy with an effective interaction parameter  $J(h_d f_A + f_B)$ . The critical value of the interaction parameter in Maier-Saupe theory is 4.541 [5], so for  $J > 4.541$  and  $h_d = 1$  the Maier-Saupe free energy is negative (with  $s$  nonzero), and for  $J \leq 4.541$  it is zero (with  $s$  zero) independent of  $h_d$ . Thus, for  $J > 4.541$  the melt segregates ( $h_d = 1$ ) and becomes nematic ( $s$  assumes its ordinary Maier-Saupe value, corresponding to  $J$ ), the second term of Eq. (35) is zero, and the first term dictates which of the segregated morphologies gives

the overall lowest free energy; for  $J < 4.541$  the melt is isotropic ( $s = 0$ ), the last two terms of Eq. (35) are zero, and the first two terms reduce to Semenov's free energy.

### III. RESULTS AND DISCUSSION

Phase diagrams derived from Eq. (35) for the case  $N \gg \chi N \gg 1$  are shown in Fig. 2 where we plot equilibrium morphology versus  $f_A$  and  $\chi N$  for several values of  $\eta$ , where

$$\eta = \frac{J}{\chi N}. \quad (36)$$

Both  $\chi N$  and  $J$  vary as  $1/T$ , so  $\eta$  is independent of tem-

perature. In the phase diagrams, moving upward along a line of constant  $f_A$  corresponds to reducing temperature. When  $\eta = 0$  the Semenov results of Fig. 1 are reproduced, with phase boundaries at  $f_A = 0.13, 0.28, 0.72,$  and  $0.87$ . For  $\eta > 0$  an isotropic-nematic transition occurs at  $J = \eta\chi N = 4.541$ . Once the nematic transition occurs, the melt is necessarily segregated for all  $f_A$ : in this sense the nematic transition drives segregation. As  $\chi N$  increases beyond the isotropic-nematic transition the phase boundaries approach  $f_A = 0.02, 0.16, 0.58,$  and  $0.68$ . For  $\chi N \gg 1$  radially nematic spherical micelles can constitute up to 32% of the volume of the melt.

Figure 3 shows the relationship between  $s$  and  $J$ , which is the same as in Maier-Saupe theory [5]. There is a first order isotropic-nematic transition ( $s$  jumps from zero to 0.429) at  $J = 4.541$ .

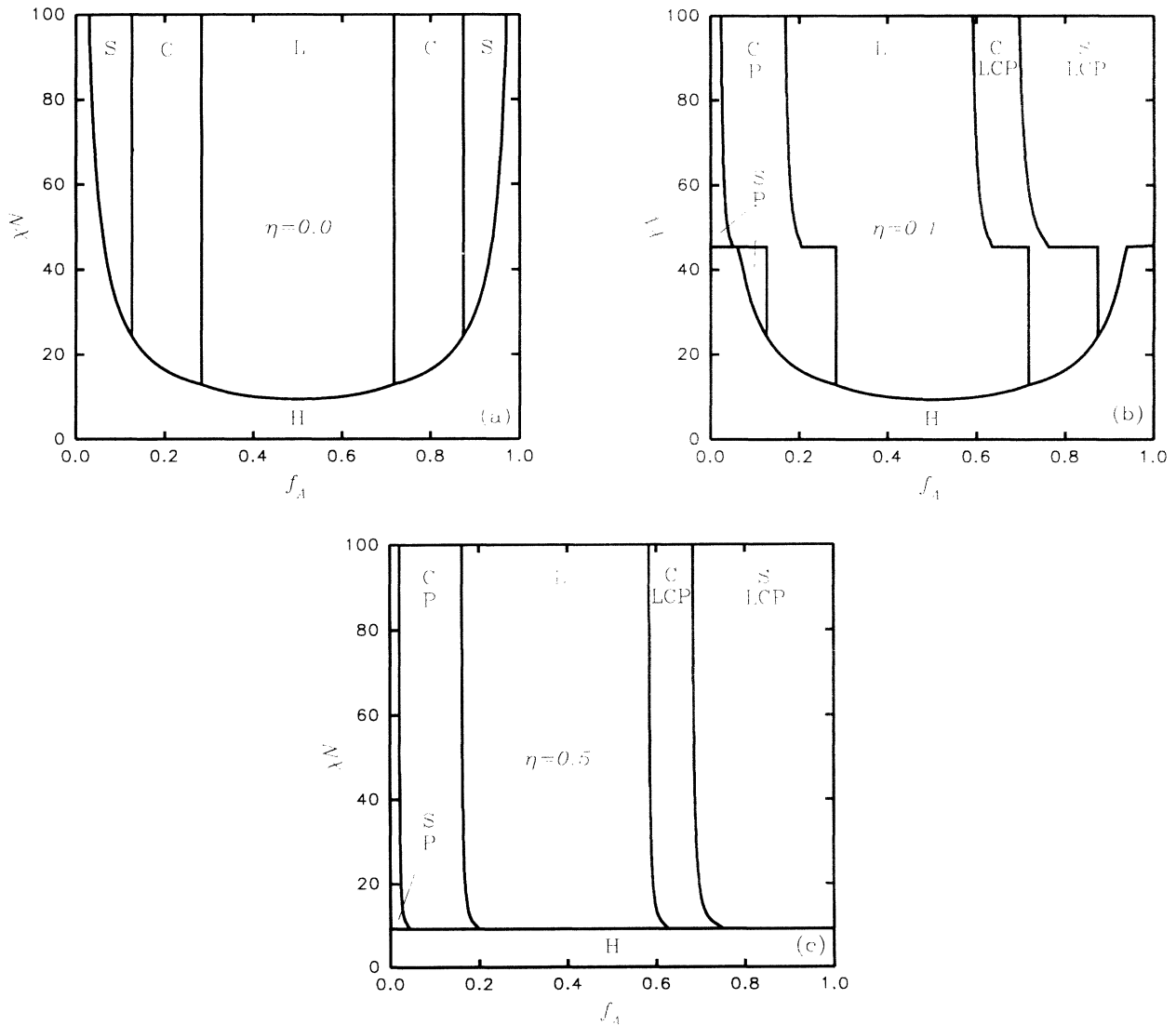


FIG. 2. Diblock polymer-liquid-crystal-polymer phase diagrams showing equilibrium morphology (homogeneous  $H$ , lamellar  $L$ , cylindrical micelles  $C$ , spherical micelles  $S$ ) and micelle composition (polymer  $P$ , liquid crystal polymer  $LCP$ ) versus polymer fraction  $f_A$  and incompatibility parameter  $\chi N$  for several nematic interaction strengths  $\eta = J/(\chi N)$ . In (a)  $\eta = 0$  and there is no nematic ordering; in (b)  $\eta = 0.1$  and there is an isotropic-nematic transition at  $\chi N \simeq 45$ ; in (c)  $\eta = 0.5$  and there is an isotropic-nematic transition at  $\chi N \simeq 9$ .

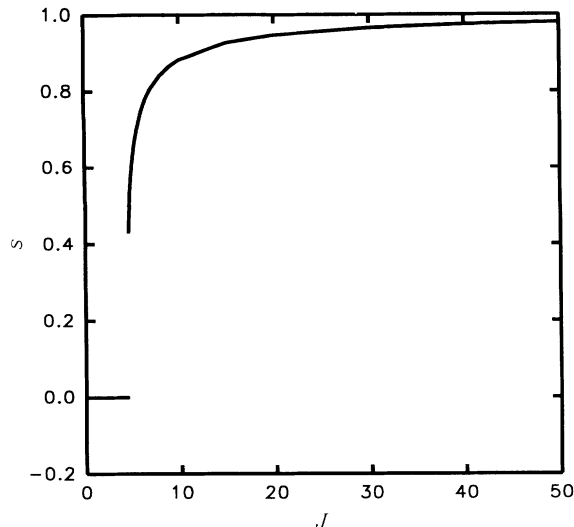


FIG. 3. Nematic order parameter  $s$  versus nematic interaction parameter  $J$ . Note the first order isotropic-nematic transition at  $J = 4.541$ .

Figure 4 is a plot of the lamellar period versus  $J$ , calculated from Eq. (33) with  $N = 1000$ ,  $\chi N = 50$ ,  $f_A = 1/2$ , and  $s[J]$  as in Fig. 3. (The equilibrium morphology is always lamellar for  $f_A = 1/2$ .) Note the abrupt increase in the period when the melt becomes nematic. The ratio of the nematic period to the non-nematic period is 2 when  $J \simeq 6$  ( $s \simeq 0.75$ ); the ratio is 3 when  $J \simeq 40$  ( $s \simeq 0.97$ ).

Chains in the interior or exterior of a micelle are stretched radially [3]. Nematic ordering reduces the free energy cost of stretching the  $B$  subchain along the nematic director. This justifies our assumption that  $\hat{\mathbf{n}} = \hat{\mathbf{r}}$ , since it is the configuration of minimum free energy.

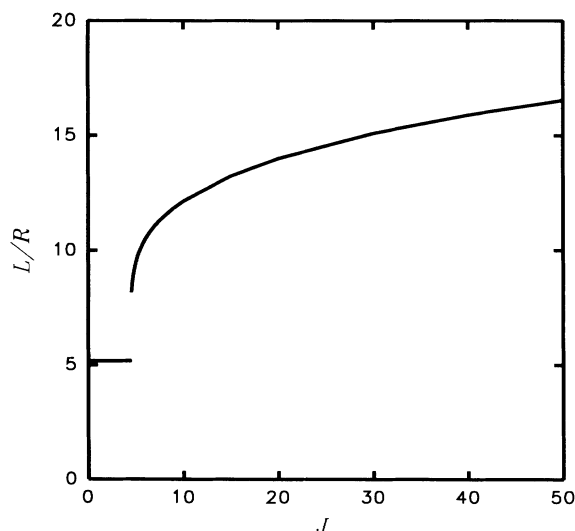


FIG. 4. Lamellar period  $L/R$  versus nematic interaction parameter  $J$  for  $N = 1000$ ,  $f_A = 1/2$ , and  $\chi N = 50$ . The period increases abruptly with the onset of nematic order, and continues to increase gradually as the extent of nematic ordering increases.

In the expression for the internal energy due to nematogen-nematogen interactions [see Eq. (11)] we neglect the free energy cost due to splay. The splay free energy density goes as  $(\nabla \cdot \hat{\mathbf{n}})^2$ , so, given that  $\hat{\mathbf{n}} = \hat{\mathbf{r}}$ , the splay free energy per chain goes as  $\ln(R)/R^2$  and  $1/R^2$  for cylindrical and spherical micelles, respectively [12]. But  $R \sim \mathcal{R} \sim \sqrt{N}$ , so in the limit of large  $N$  the splay free energy per chain goes to zero. Since the splay free energy is negligible there is no significant coupling of  $s$  to  $r$ , which justifies our assumption that  $s$  is independent of  $r$ . (Note, however, that for the case of a semiflexible LCP Williams and Halperin [6] have shown that the splay free energy becomes important as temperature is lowered, since the entire LCP block tends to become rigid.)

The expression for  $F_{\text{grad}}$  [see Eq. (16)] assumes the random walk behaviors of the  $A$  and  $B$  subchains are identical, which is not correct when the  $B$  subchain is nematically ordered. When  $s = 1$  the effective segment length for the  $B$  subchain's random walk in the  $\hat{\mathbf{r}}$  direction is  $\sqrt{3}\ell$ , not  $\ell$ . Helfand [13] has shown how to calculate interfacial free energy when  $\ell_A \neq \ell_B$ : he replaces them with the effective value

$$\tilde{\ell} = \frac{2}{3} \left( \frac{\ell_B^3 - \ell_A^3}{\ell_B^2 - \ell_A^2} \right). \quad (37)$$

It is possible to incorporate this correction into our model by multiplying  $C_{dg}$  by the factor

$$\zeta[J s] = \frac{2}{3} \left( \frac{(\Omega[\frac{3}{2} J s])^{3/2} - 1}{\Omega[\frac{3}{2} J s] - 1} \right). \quad (38)$$

Since the value of  $\zeta[x]$  ranges from 1 to 1.4 as  $x$  goes from 0 to  $\infty$ , the corrections are small, and we have chosen to neglect them. Furthermore,  $\zeta[x]$  does not depend on morphology, and in the limit of large  $N$  it has no influence on phase boundaries.

In conclusion, the phase diagram for a melt of P-LCP reveals an interesting interplay of morphological and isotropic-nematic transitions. The onset of nematic order increases the micelle lattice constant by roughly a factor of two. Radially nematic spherical micelles can constitute up to 32% of the volume of the melt. These results may be of interest in the field of polymer dispersed liquid crystals.

#### ACKNOWLEDGMENTS

We would like to thank David Williams for helpful suggestions. This work was supported by the NSF Material Research Group program under Grant No. DMR-91-22227.

#### APPENDIX: CONFIGURATIONAL ENTROPY

Consider a single chain with its  $AB$  junction at  $r = 0$ , type- $A$  free end at  $r = r_A$ , and type- $B$  free end at  $r = r_B$ . The partition function for the  $B$  subchain is

$$Z = \int d\hat{\mathbf{u}}_1 \int d\hat{\mathbf{u}}_2 \cdots \int d\hat{\mathbf{u}}_{N_B} e^{-\beta(E[\hat{\mathbf{u}}_1] + E[\hat{\mathbf{u}}_2] + \cdots + E[\hat{\mathbf{u}}_{N_B}])} \\ \times \delta[r_B - \ell \hat{\mathbf{r}} \cdot (\hat{\mathbf{u}}_1 + \hat{\mathbf{u}}_2 + \cdots + \hat{\mathbf{u}}_{N_B})], \quad (\text{A1})$$

where  $\beta = 1/T$  and

$$E[\hat{\mathbf{u}}] = -TJs \left( \frac{3(\hat{\mathbf{u}} \cdot \hat{\mathbf{r}})^2 - 1}{2} \right) \quad (\text{A2})$$

is the Maier-Saupe energy of a nematogen in the mean nematic field characterized by the order parameter  $s$  and director  $\hat{\mathbf{r}}$ . If we use the form

$$\delta[x] = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dk e^{ikx} \quad (\text{A3})$$

for the  $\delta$  function, and assume  $r \ll N_B \ell$  and  $N_B \gg 1$ , the expression for  $Z$  can be integrated [14]:

$$Z \simeq \left( \frac{3}{2\pi N_B \ell_B} \right)^{1/2} \left( \int_0^1 d\gamma e^{\frac{3}{2} J s \gamma^2} \right)^{N_B} \\ \times \exp \left( -\frac{1}{2} J N_B s - \frac{3r_B^2}{2N_B \ell_B^2} \right), \quad (\text{A4})$$

where  $\ell_B$  is defined in Eq. (24). The internal energy of the  $B$  subchain in the mean nematic field is

$$N_B \langle E[\hat{\mathbf{u}}] \rangle = -T J N_B s^2, \quad (\text{A5})$$

so, neglecting terms of order  $\ln N_B$ , the configurational entropy of the  $B$  subchain is

$$S_B \simeq N_B \mathcal{D} \left[ \frac{3}{2} J s \right] - \frac{1}{2} J N_B s (2s + 1) - \frac{3r_B^2}{2N_B \ell_B^2}, \quad (\text{A6})$$

where  $\mathcal{D}$  is defined in Eq. (23). The corresponding configurational entropy of the  $A$  subchain may be obtained by replacing  $B$  with  $A$  and letting  $J = 0$ :

$$S_A \simeq -\frac{3r_A^2}{2N_A \ell_A^2}. \quad (\text{A7})$$

Then the configurational entropy of the entire chain is  $S = S_A + S_B$ .

- 
- [1] E. Helfand, *Macromolecules* **8**, 552 (1975).  
 [2] L. Leibler, *Macromolecules* **13**, 1602 (1980).  
 [3] A. N. Semenov, *Zh. Eksp. Teor. Fiz.* **88**, 1242 (1985) [*Sov. Phys. JETP* **61**, 733 (1985)].  
 [4] F. S. Bates, *Science* **251**, 898 (1991).  
 [5] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1977), p 46.  
 [6] D. R. M. Williams and A. Halperin, *Phys. Rev. Lett.* **71**, 1557 (1993).  
 [7] J. D. Vavasour and M. D. Whitmore, *Macromolecules* **25**, 5477 (1992).  
 [8] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1977), p 72.  
 [9] F. Brochard, *C. R. Acad. Sci. Paris Ser. B* **289**, 229 (1979).  
 [10] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1977), p 254.  
 [11] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1977), p 31.  
 [12] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1977), p 110.  
 [13] E. Helfand and A. M. Sapse, *J. Chem. Phys.* **62**, 1327 (1975).  
 [14] P. J. Flory, *Statistical Mechanics of Chain Molecules* (Wiley, New York, 1969), p 314.