Liquid-crystalline phases of semiflexible diblock copolymer melts

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Self-consistent field theory is used to study the phase behavior of melts of semiflexible diblock copolymers. Repulsion between the incompatible blocks leads to micro-phase separation, while anisotropic external fields and interactions between polymers induce liquid-crystalline phases. Considering symmetric diblocks with quadrupolar interactions, we obtain a nematic-isotropic transition which extends into the lamellar phase and terminates at an internal critical point. For dipolar interactions, ferroelectric nematic and lamellar phases and a novel Lifshitz point are obtained.

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Diblock copolymers melts have been studied intensely due to their tendency to micro-phase separate into various ordered structures [1]. The driving force for this behavior is a repulsion between the two different blocks comprising the polymer, and in the simplest case of blocks of similar length, it leads to the formation of a lamellar (L) phase in which the A and B monomers separate into A-rich and B-rich lamellae. Liquid-crystalline polymers, which form orientationally ordered phases due to anisotropic steric and dispersive interactions between rigid polymers [2] have constituted a rather distinct area of intense research.

In this Letter we consider the phase behavior of melts of semiflexible diblock copolymers under the action of anisotropic external fields and interactions. Using self-consistent field theory, we concentrate on the interplay between the two separate tendencies to form spatially modulated and orientationally ordered structures, which leads to interesting new phase behavior. The interactions include a repulsion of strength χ between chemically distinct A and B monomers. External anisotropic fields are of the dipolar and quadrupolar type. The former corresponds to the situation in which a magnetic or electric field couples to dipoles along the polymer chain or, in the case of the electric field, to opposite charges at the two ends of the polymer; the latter corresponds to a magnetic or electric field coupling to an anisotropic polarizability of the monomers or a compressing/dilating flow field [3]. Both fields enhance the formation of a lamellar phase, in contrast to the null effect predicted for completely flexible, Gaussian diblock copolymers [4]. In addition, we consider dipolar and quadrupolar anisotropic interactions between polymers. The former arise in the presence of permanent dipoles along the chain. Dipolar interactions in model spherical fluids induce formation of ordered chains, i.e., living dipolar polymers, which exhibit ferromagnetic order for large enough densities [5]. For the simple dipolar contact potential considered here, we find a line of continuous transitions from the isotropic, disordered phase to a ferroelectric, nematic phase N^*. This line meets the lamellar phase at a Lifshitz point. For strong repulsion, χ, a ferroelectric lamellar phase L^* appears. Quadrupolar interactions are due to anisotropic van der Waals forces between neighboring chains and were first considered by Maier and Saupe in order to account for the isotropic-nematic phase transition in hard-rod systems [6]. Such interactions represent the first term in a multipole expansion of the steric interaction between rigid elongated molecules which was first introduced by Onsager [7]. We find a strongly discontinuous nematic-isotropic transition for small diblock repulsion. This transition extends into the lamellar phase region separating two lamellar phases, one with weak, the other strong nematic order. We associate them with the L_α and L_β phases observed in amphiphilic systems. The line of first-order transitions terminates at an inter-nal critical point. We believe these phase topologies to be generally applicable to a variety of systems; genuine liquid-crystalline polymers, low-molecular-weight liquid crystals, and self-assembling colloidal systems.

The partition function for a system of n copolymers consisting of N segments with volume $1/\rho_0$ each is

$$Z = \int \prod_{\alpha=1}^{n} \tilde{\mathcal{D}} \mathbf{r}_\alpha \exp \left\{ -\rho_0 \int d\mathbf{r} \, \mathcal{L}(\hat{\Phi}_A, \hat{\Phi}_B, \hat{\mathbf{U}}, \hat{\mathbf{M}}) \right\}, \quad (1)$$

where the functional integral over all copolymer configurations $\tilde{\mathcal{D}} \mathbf{r}_\alpha \equiv \mathcal{D} \mathbf{r}_\alpha(\cdot) P[\mathbf{r}_\alpha(\cdot); 0, 1] \, \delta[1 - \hat{\Phi}_A - \hat{\Phi}_B]$ contains the incompressibility condition and is weighted with the measure appropriate for semiflexible chains [8]

$$P[\mathbf{r}_\alpha(\cdot); s_1, s_2] = \exp \left\{ -\frac{\kappa}{2N} \int_{s_1}^{s_2} ds (d\mathbf{n}_\alpha(s)/ds)^2 \right\}.$$

The tangent vector $\mathbf{n}_\alpha(s) \equiv (d\mathbf{r}_\alpha(s)/ds)/bN$ satisfies $(\mathbf{n}_\alpha(s))^2 = 1$, i.e., the contour length of each segment, b, is constant. The "Lagrangian" $\mathcal{L}$ in (1) depends only on local densities. The dimensionless A-monomer density is defined by

$$\hat{\Phi}_A = \frac{N}{\rho_0} \sum_{\alpha=1}^{n} \int_0^f ds \, \delta[\mathbf{r} - \mathbf{r}_\alpha(s)]$$

with a similar expression for $\hat{\Phi}_B$ where the integral over s goes from f to 1. The vectorial orientational density is

$$\hat{\mathbf{U}} = \frac{N}{\rho_0} \sum_{\alpha=1}^{n} \int_0^1 ds \, \delta[\mathbf{r} - \mathbf{r}_\alpha(s)] \mathbf{n}_\alpha(s)$$

and the tensorial orientational density is

$$\hat{M}_{ij} = \frac{N}{\rho_0} \sum_{\alpha=1}^{n} \int_0^1 ds \, \delta[\mathbf{r} - \mathbf{r}_\alpha(s)] \left(n_\alpha^{(i)}(s) n_\alpha^{(j)}(s) - \frac{1}{3} \delta_{ij} \right).$$

Note that all these densities depend explicitly on the configurations of all polymers. Employing a Hubbard-Stratonovich transformation, one introduces collective density variables Φ, U_i, and M_{ij} (which are independent of the individual polymer configurations) and conjugate fluctuating field variables W, H_i, and B_{ij}, respectively. The partition function transforms exactly to

$$Z \propto \int \mathcal{D}\Phi_A \mathcal{D}W_A \mathcal{D}W_B \mathcal{D}\mathbf{U} \mathcal{D}\mathbf{H} \mathcal{D}\mathbf{M} \mathcal{D}\mathbf{B} \exp \left(\frac{-F}{k_B T} \right) \quad (2)$$

where a new functional is defined by

$$F/n k_B T \equiv -\ln \mathcal{Q} + V^{-1} \int d\mathbf{r} \, \{ N\mathcal{L}(\Phi_A, 1 - \Phi_A, \mathbf{U}, \mathbf{M})$$
$$-W_A \Phi_A - W_B (1 - \Phi_A) - H_i U_i - B_{ij} M_{ij} \}. \quad (3)$$

The single-chain partition function is given by $\mathcal{Q} = \int d\mathbf{r} \, d\mathbf{n} \, q(\mathbf{r}, \mathbf{n}, 1)$, where

$$q(\mathbf{r},\mathbf{n},s) \equiv \int \mathcal{D}\mathbf{r}(\cdot)\, P[\mathbf{r}(\cdot);0,s]\, \delta[\mathbf{r}-\mathbf{r}(s)]\, \delta[\mathbf{n}-\mathbf{n}(s)]$$

$$\exp\left\{-\int_0^s dt\ \left[\gamma(t)W_A[\mathbf{r}(t)] + [1-\gamma(t)]W_B[\mathbf{r}(t)]\right.\right.$$

$$\left.\left. + H_i[\mathbf{r}(t)]n_i(t) + B_{ij}[\mathbf{r}(t)]\left(n_i(t)n_j(t)-\frac{\delta_{ij}}{3}\right)\right]\right\} \quad (4)$$

is the end-segment distribution function of a single copolymer subject to external potentials $W_A(\mathbf{r})$ and $W_B(\mathbf{r})$ and vectorial and tensorial fields $\mathbf{H}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$. The step function, $\gamma(t)$, is equal to 1 for $t < f$ and 0 otherwise. Equation (2) expresses the partition function of the many-polymer system in terms of the partition functions of single polymers coupled by external, fluctuating, fields. The self-consistent field theory approximates (2) by the integrand evaluated at those values of the fields, w_A, w_B, $\mathbf{h}$, $\mathbf{b}$ and densities, ϕ_A, $\mathbf{u}$, $\mathbf{m}$, which minimize the functional F. From the definition of F, which approximates the free energy, it follows that these functions satisfy the self-consistent equations

$$w_A(\mathbf{r}) - w_B(\mathbf{r}) = N\frac{\partial\mathcal{L}}{\partial\phi_A(\mathbf{r})},$$

$$\phi_A(\mathbf{r}) = -\frac{V}{Q}\frac{\delta Q}{\delta w_A(\mathbf{r})} = \frac{V}{Q}\frac{\delta Q}{\delta w_B(\mathbf{r})} + 1,$$

$$h_i(\mathbf{r}) = N\frac{\partial\mathcal{L}}{\partial u_i(\mathbf{r})} \quad,\quad u_i(\mathbf{r}) = -\frac{V}{Q}\frac{\delta Q}{\delta h_i(\mathbf{r})}.$$

$$b_{ij}(\mathbf{r}) = N\frac{\partial\mathcal{L}}{\partial m_{ij}(\mathbf{r})} \quad,\quad m_{ij}(\mathbf{r}) = -\frac{V}{Q}\frac{\delta Q}{\delta b_{ij}(\mathbf{r})}.$$

The distribution function $q(\mathbf{r},\mathbf{n},s)$ satisfies the diffusion equation [9]

$$\frac{\partial q}{\partial s} + bN\mathbf{n}\cdot\nabla_r q = \frac{N}{2\kappa}\triangle_n q - [1-\gamma(s)]w_B(\mathbf{r})$$

$$-\gamma(s)w_A(\mathbf{r}) - h_i(\mathbf{r})n_i - b_{ij}(\mathbf{r})\left(n_i n_j - \frac{\delta_{ij}}{3}\right) \quad (5)$$

and the initial conditions $q(\mathbf{r},\mathbf{n},0) = 1$ [10]. The above equation can be simplified by expanding all functions depending on $\mathbf{r}$ and $\mathbf{n}$ in a complete, orthonormal set of eigenfunctions of the Laplacian operators $\triangle_n$ and $\triangle_r$ which possesses the symmetry of the ordered phase considered [11,12]. Eq. (5) is thereby reduced to a system of linear equations, the solution of which can be obtained numerically by standard methods [11].

The Lagrangian we employ to describe interacting copolymers in external fields is

$$\mathcal{L} = \chi\phi_A\phi_B - \mu_D E_i U_i - \frac{3}{2}\mu_Q E_i M_{ij} E_j$$

$$-\tau_D U_i U_i - \frac{3}{2}\tau_Q M_{ij} M_{ij}. \quad (6)$$

The parameter χ is proportional to the repulsion between A and B monomers and drives micro-phase separation. The external field $\mathbf{E}$ couples to the vectorial and tensorial orientational densities via the dipolar and quadrupolar constants μ_D and μ_Q. The last two terms are anisotropic dipolar and quadrupolar interactions with coupling constants τ_D and τ_Q.

For a uniaxial phase, such as the lamellar phase, the tensorial order parameter m_{ij} can be written as $m_{ij} = \delta_{ij}S(\delta_{i1} - 1/3)$. The nematic order parameter S is defined by $S \equiv \frac{1}{2}\langle 3n_1^2 - 1\rangle$. The simultaneous eigenfunctions of $\triangle_r$ and $\triangle_n$ are products of sines and cosines, $\sin(2\pi kr_1/D)$ and $\cos(2\pi kr_1/D)$, and Legendre polynomials $P_l(n_1)$ with $k,l = 0,1,2,\ldots$. The lamellar repeat distance is given by D. All densities and fields are translationally invariant in a plane perpendicular to the lamellar wave vector pointing along the 1-direction. For the external field $\mathbf{E}$ parallel to the lamellar wavevector the Lagrangian (6) simplifies to $\mathcal{L} = \chi\phi_A\phi_B - \mu_D EU - \mu_Q E^2 S - \tau_D U^2 - \tau_Q S^2$.

Fig. 1 shows the phase behavior of symmetric copolymers with rigidity $\kappa/N = 1/10$ in the presence of external dipolar and quadrupolar fields. A dipolar field of rescaled strength $\mu_D EN$ enhances the formation of the lamellar phase, and for large fields the transition saturates at $(\chi N)_C \simeq 5.1$ (see Fig.1a). In this limiting case one has stretched copolymers pointing predominantly along the direction of the field, as demonstrated by the behavior of the orientational order parameter U (short dashes in Fig.1b). A positive quadrupolar field of strength $\mu_Q E^2 N$ also enhances lamellar ordering (Fig.1c), in contrast to the null effect on Gaussian copolymers [4]. For large fields, the polymers are parallel to the external field but point randomly up and down, as can be seen from the behavior of S given by long dashes in Fig.1d and noting that $U = 0$. The transition saturates at the even lower value of $(\chi N)_C \simeq 3.9$ for large positive fields. The difference in the asymptotic values of the critical repulsion χN is due to the bilayer structure in quadrupolar fields, indicated by a reduced lamellar spacing D/bN at the transition which is larger than unity (solid line in Fig.1d) and almost twice the spacing in dipolar fields, Fig.1b, therefore reducing the number of enthalpic disfavored $A-B$ interfaces. The asymptotic critical repulsions are independent of the value of κ/N and are to be compared with the critical value for rigid rods in an isotropic space, $(\chi N)_C \simeq 6.1$ [12].

Anisotropic interactions induce liquid-crystalline phases [13,14]. We first study the regime of weak repulsion χN. Fig.2a shows the value of $\tau_D\kappa$ (solid line) and $\tau_D N$ (broken line) at the continuous transition between the isotropic phase and the ferroelectric nematic phase for different values of the rigidity κ/N. In the limit of rigid rods one obtains a transition at the asymptotic value $\tau_D N = 3/2$ and in the Gaussian limit at $\tau_D\kappa = 3/4$ with a rather narrow crossover region in between. The

analogous phase diagram for the quadrupolar interaction, first obtained by Ten Bosch and Maïssa [15], is shown in Fig.2b with the rescaled interaction strengths $\tau_Q \kappa$ (solid line) and $\tau_Q N$ (broken line). The transition occurs at $\tau_Q N \simeq 2.27$ in the limit of rigid rods and at $\tau_Q \kappa \simeq 3.33$ in the Gaussian limit and is strongly discontinuous. The inset shows the discontinuity of the nematic order parameter ΔS at the transition which exhibits a characteristic dip at intermediate bending rigidities.

Now we can turn to the central question of the interplay between the nematic and lamellar ordering. Fig.3 shows the phase diagram as a function of the dipolar interaction $\tau_D N$ for fixed rigidity $\kappa/N = 1/10$. The continuous isotropic-nematic transition occurs at $\tau_D N = 8.333$; it terminates at a Lifshitz point involving the lamellar phase (Fig.3a). The continuous transition between the ferroelectric nematic N^* and lamellar L^* phases terminates at a critical end point (CEP) and saturates at large interactions at the same value as in a strong external field (Fig.1a). The discontinuous transition between the two lamellar phases extends into the strong-segregation regime ($\chi N \gg 1$). This intricate phase structure occurs for positive values of τ_D, corresponding to polymers which prefer parallel orientations. There is ample evidence that simple dipolar systems form ferroelectric phases, and this novel phase structure might be observable in suitable polymeric systems. For negative τ_D, i.e. for polymers which favor antiparallel orientation, the transition moves to higher values of χN and finally saturates at $\chi N \simeq 11.05$, leading to a highly interdigitated lamellar structure (Fig.3b).

At the same rigidity $\kappa/N = 1/10$, the discontinuous N-I transition due to a quadrupolar interaction extends into the lamellar phase and terminates at a critical point embedded in the lamellar phase (Fig.4). The continuous transition between the lamellar phase and the homogeneous phases I and N both terminate at critical end points. The two lamellar phases are distinguished by their degree of nematic order, so this transition is analogous to the $L_\alpha - L_\beta$ transition, which is ubiquitous in lyotropic, membrane [16,17] and monolayer [18] systems.

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FIG. 1. Copolymers with bending rigidity $\kappa/N = 0.1$, subject to external anisotropic fields. a) Phase diagram as a function of a dipolar field of strength $\mu_D E N$, showing a continuous transition from a ferroelectric nematic phase N^* to a ferroelectric lamellar phase L^*. b) The lamellar spacing D/bN (solid line), the dipolar ordering U (short dashes), and the nematic order parameter S (long dashes) at the N^*-L^* transition. c) Phase behavior as a function of a uniaxial quadrupolar field of strength $\mu_Q E^2 N$. d) The lamellar spacing D/bN (solid line) and the nematic order parameter S (long dashes) at the nematic–lamellar (N–L) phase transition.

FIG. 2. a) Dipolar interaction strength $\tau_D \kappa$ (solid line) and $\tau_D N$ (broken line) at the continous isotropic–ferroelectric nematic phase transition for varying bending rigidities κ/N. b) Quadrupolar interaction strength $\tau_Q \kappa$ (solid line) and $\tau_Q N$ (broken line) at the isotropic–nematic phase transition. The inset shows the discontinuity ΔS at the transition.

FIG. 3. Copolymers of bending rigidiy $\kappa/N = 0.1$ with dipolar interactions of strength $\tau_D N$. a) Interaction favoring polymers to be parallel, showing a Lifshitz point (LSP) at the meeting of the isotropic (I), lamellar (L), and ferroelectric nematic (N^*) phases. For large values of the interaction a ferroelectric lamellar phase (L*) appears. The two lamellar phase are separated by a discontinuous transition (denoted by a double line). b) Interaction favoring antiparallel alignment, leading to a strongly interdigitated lamellar phase.

FIG. 4. Copolymers of bending rigidiy $\kappa/N = 0.1$ with quadrupolar interactions of strength $\tau_Q N$. The discontinuous nematic-isotropic transition extends into the lamellar phase, separates two distinct lamellar phases L_α and L_β, and terminates at an internal critical point (CP).