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Nematic to Isotropic Transition in Chemically Disordered or Multicomponent Liquid-Crystalline Polymers

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ABSTRACT: A Landau theory is presented for the nematic to isotropic (N–I) transition of main-chain liquid-crystalline polymers that are chemically disordered, i.e., statistical copolymers. The two constituent monomers are assumed to differ in flexibility but could be otherwise identical. For such a system, the chemical disorder contributes a random component to the local bending elastic constant of each chain. We find a coupling between the conventional nematic (orientational) order parameter and a compositional order parameter that expresses nonuniformity in the density of flexible monomers. This coupling leads to a biphasic region at the N–I transition in accordance with the recent experiments of Stupp et al. (*Macromolecules* **1988**, *21*, 1217–1234). In the limit of high molecular weight, the width of the biphasic window is proportional to the difference between the elastic constants of the two monomers and is inversely proportional to the square root of the molecular weight. Segregation by flexibility at the N–I transition is also analyzed for binary blends of thermotropic homopolymers.

I. Introduction

Thermotropic liquid-crystalline polymers are materials with remarkable mechanical, optical, and electrical properties. Recent advances in synthetic methods, purification, and processing techniques are stimulating new commercial applications of these materials, as well as careful scientific studies.[1,2]

While the myriad of phase transitions exhibited by low molecular weight liquid crystals have been exhaustively studied for decades, the corresponding transitions in liquid-crystalline polymers have received much less attention. Experimental and theoretical investigations of phase transitions in flexible macromolecular systems have revealed interesting physics that are not realized in low molecular weight systems. Hence, it is natural to expect new phenomena in liquid-crystalline polymers. Indeed, such phenomena have been evidenced in a number of recent studies.[3–8]

Of particular relevance to the present paper are a set of experiments by S. I. Stupp and colleagues.[6–8] These authors synthesized two thermotropic copolymers, both containing (on average) equal amounts of three types of monomers (A–C). Two of the monomers (A and B) were rigid (mesogenic), while the third (C) was flexible. The first polymer was an *ordered* copolymer with repeat unit (CABCBA) and was found to exhibit a sharp nematic to isotropic (N–I) transition at 275 °C. The second polymer was a *disordered* statistical copolymer of the same average composition but, in contrast to its ordered isomer, exhibited a broad biphasic region over the temperature range 250–400 °C. In this temperature range, an isotropic fluid phase was observed to coexist in varying proportions with a nematic, birefringent phase. Pure nematic and isotropic phases, respectively, were observed at temperatures below and above the biphasic region.

Stupp et al.[8] provided a very plausible explanation for the curious behavior of the disordered copolymer. Because of statistical fluctuations in the composition of each chain, the various polymers in the sample differ in their effective flexibility. Here, "effective flexibility" refers to an average persistence length or bending elastic constant that characterizes each copolymer molecule in the sample (see, e.g., eq 3.8). Stupp et al. coined the term "polyflexibility" to describe the distribution of effective flexibilities present in a random copolymer sample. This multicomponent character of a statistical copolymer melt opens the possibility that it could segregate into two or more phases (each differing in effective flexibility) at the N–I transition. In order to test this hypothesis, the authors of ref 8 numerically sampled a large number of copolymer sequences that were representative of their sample. For each generated chain, an effective flexibility was computed and a theory for the N–I transition of a homopolymer[9] (with that flexibility) was used to estimate the corresponding N–I transition temperature. The spread in calculated transition temperatures was consistent with the width of the experimentally observed biphasic region.[10] The authors also provided convincing evidence

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that the distribution of molecular weights was not sufficiently broad to produce an equivalent effect, namely, that the biphasic region is a consequence of polyflexibility and not of polydispersity.

While the arguments of Stupp et al. are appealing, a quantitative theory for the observed phenomena is needed. In the present paper we construct a Landau theory to describe the N–I transition of random copolymers that contain two types of monomers with different flexibilities. The theory is one of the simplest that can be constructed, although we believe it incorporates the essential physics of the problem. To facilitate presentation of the theory, it is convenient to first discuss the simpler problem of the N–I transition in a binary blend of two semiflexible homopolymers. This problem is interesting in its own right and of practical importance, but it also clarifies the nature of the random copolymer transition.

In the present paper we shall be exclusively concerned with the possibility of segregation near the N–I transition, associated with differences in flexibility. As will be demonstrated explicitly below, the driving force for such a segregation is proportional to the difference between the bending elastic constants of the stiff and flexible monomers. For simplicity, we ignore all other mechanisms that could lead to a biphasic region. In particular, polydispersity and composition-dependent anisotropic interactions[11] are *not considered.* We briefly discuss such alternative mechanisms in section IV.

The organization of the paper is as follows. In section II we derive a Landau expansion for the free energy of a binary blend in powers of orientational and compositional order parameters. Section II also contains an analysis of the N–I transition and biphasic region based on this free energy expression. In section III we extend the analysis to the case of a melt of statistical copolymers that contains monomers of different flexibilities. A pseudobinary approximation, which takes advantage of the results of section II, proves to be instructive. Finally, section IV provides a discussion of our results in view of the experiments of Stupp et al. and suggests additional experiments.

II. Binary Blend of Semiflexible Homopolymers

A. Derivation of the Landau Free Energy. In the present section we consider a blend of n_1 molecules of a semiflexible homopolymer 1 with n_2 molecules of a second homopolymer 2 in a volume V. For simplicity, both polymers are assumed to be monodisperse and to contain N monomers. The monomers of the two species are also assumed to occupy the same volume. Moreover, the bonds that connect successive monomers are taken to be of fixed length b. Finally, we assume no volume change on mixing and incompressibility. The total monomer number density is thus given locally and globally by $\rho_0 = (n_1 + n_2)N/V$. To describe the thermodynamic properties of such a blend, we propose the following microscopic Hamiltonian ($\beta = 1/k_{\mathrm{B}}T$)

$$\beta H\{\mathbf{r}\} = \beta H_0\{\mathbf{r}\} - \rho_0\chi\int \mathrm{d}\mathbf{x}\,\hat{\psi}^2(\mathbf{x}) - \rho_0 \upsilon\int \mathrm{d}\mathbf{x}\,\hat{S}^2(\mathbf{x}) \qquad (2.1)$$

where

$$\beta H_0\{\mathbf{r}\} = -\kappa_1 \sum_{\alpha=1}^{n_1}\sum_{i=1}^{N}\mathbf{u}_\alpha(i)\cdot\mathbf{u}_\alpha(i+1) - \kappa_2 \sum_{\alpha=n_1+1}^{n_1+n_2}\sum_{i=1}^{N}\mathbf{u}_\alpha(i)\cdot\mathbf{u}_\alpha(i+1) \qquad (2.2)$$

The first contribution, $\beta H_0\{\mathbf{r}\}$, is a discretized version of the wormlike-chain Hamiltonian[12] for $n_1 + n_2 = n$ independent chains. Here, $\mathbf{r}_\alpha(i)$ denotes the position of the ith monomer on chain α and $\mathbf{u}_\alpha(i) = [\mathbf{r}_\alpha(i+1) - \mathbf{r}_\alpha(i)]/b$ is a unit vector in the direction of the bond connecting the ith and $(i + 1)$th monomers. The quantities κ_1 and κ_2 are dimensionless bending elastic constants that characterize the flexibility of pure homopolymers 1 and 2, respectively. Persistence lengths for the two polymers can be defined by $\lambda_i = b\kappa_i$ (i = 1 or 2), and the contour length of each chain is denoted $L = Nb$. We assume throughout the present paper that the two species have similar, although not identical, persistence lengths and that species 1 has the more rigid units.

The second and third terms in eq 2.1 describe the interactions among monomers and involve two microscopic order parameter fields $\hat{\psi}(\mathbf{x})$ and $\hat{S}(\mathbf{x})$. The first field, $\hat{\psi}(\mathbf{x})$, is a measure of the deviation of the local composition (volume fraction of 1) from the uniform composition, $\phi = n_1/n$. More precisely

$$\hat{\psi}(\mathbf{x}) = (1 - \phi)\hat{\phi}_1(\mathbf{x}) - \phi\hat{\phi}_2(\mathbf{x}) \qquad (2.3)$$

where the microscopic volume fractions of 1 and 2 are given by

$$\hat{\phi}_1(\mathbf{x}) = \rho_0^{-1}\sum_{\alpha=1}^{n_1}\sum_{i=1}^{N}\delta[\mathbf{x} - \mathbf{r}_\alpha(i)] \qquad (2.4)$$

$$\hat{\phi}_2(\mathbf{x}) = \rho_0^{-1}\sum_{\alpha=n_1+1}^{n}\sum_{i=1}^{N}\delta[\mathbf{x} - \mathbf{r}_\alpha(i)] \qquad (2.5)$$

With this definition, the term $-\rho_0\chi\hat{\psi}^2(\mathbf{x})$ in eq 2.1 is evidently the contribution to the free energy density arising from isotropic interactions (e.g., van der Waals) and, provided that the dimensionless Flory parameter χ is positive, favors demixing of the two components. Note that the equilibrium ensemble average of $\hat{\psi}(\mathbf{x})$ (subsequently denoted $\psi(\mathbf{x})$) vanishes if the system is homogeneous and single phase. Furthermore, the volume integral of the fluctuating field $\hat{\psi}(\mathbf{x})$ over the entire system is zero.

The third term in eq 2.1 is a Maier–Saupe expression that describes quadrupolar interactions favoring mutual alignment of the various monomers. While the source of these interactions is not addressed by the present theory, we comment that they may derive from the anisotropic part of the van der Waals force or from steric (packing) effects.[13,14] The dimensionless parameter υ describes the strength of the interactions, and $\hat{S}(\mathbf{x})$ is the microscopic counterpart of the conventional nematic order parameter:

$$\hat{S}(\mathbf{x}) = \rho_0^{-1}\sum_{\alpha=1}^{n}\sum_{i=1}^{N}\delta[\mathbf{x} - \mathbf{r}_\alpha(i)]P_2[\mathbf{u}_\alpha(i)\cdot\hat{\mathbf{p}}] \qquad (2.6)$$

In this expression, $P_2(x) = (3x^2 - 1)/2$ is the second-order Legendre polynomial and $\hat{\mathbf{p}}$ is a unit vector in the direction of the nematic alignment (the director) that we select by imposing an infinitesimal magnetic field. The average of $\hat{S}(\mathbf{x})$, which is subsequently denoted by $S(\mathbf{x})$, vanishes in an orientationally disordered (isotropic) phase but is nonzero in a nematic phase.

It is worth commenting that certain enthalpic coupling terms arising from the more general expression $\sum_{ij}\upsilon_{ij}\hat{\phi}_i\hat{\phi}_j\hat{S}_i\hat{S}_j$ (i,j = 1 or 2) have been omitted from eq 2.1. In this expression, $\hat{S}_i$ is the analogue of eq 2.6 (an orientational order parameter) for a melt of pure species i. By writing the Maier–Saupe interaction in the simplified form of eq 2.1, we implicitly assume that $\upsilon_{ij} = \upsilon$. Hence, our idealized monomers are identical as regards their anisotropic interactions. We make this simplification in order to isolate the effects of differences in flexibility, but it should be noted that couplings introduced by other choices of the v_{ij} can produce much richer (and more complicated) phase behavior of the type found in ref 11.

Having explained the various terms in eq 2.1, we now consider the free energy that is obtained from this Hamiltonian. To describe the N–I transition in a multicomponent system, at least two order parameters are required. For the present case of a binary blend, the natural order parameters are clearly S and ψ. As we shall be primarily concerned with the onset of weak nematic order in the vicinity of the N–I transition and with phases characterized by slight differences in composition, a Landau expansion of the free energy in powers of S and ψ should be sufficient. We emphasize, however, that the low-temperature nematic phase is not adequately described by such an expansion. As has been discussed in detail elsewhere,[14–18] this region is inaccessible by perturbation theory in S and is characterized by additional length scales other than the persistence and contour lengths.

The partition function of interest is

$$Z = \int D\mathbf{r} \exp[-\beta H\{\mathbf{r}\}] \tag{2.7}$$

where the Hamiltonian is given in eq 2.1 and $\int D\mathbf{r}$ denotes a functional integral over the positions of all monomers.[19] Equation 2.7 can be rewritten as

$$Z = \int DS \int D\psi \int D\mathbf{r}\ \delta(S - \hat{S})\ \delta(\psi - \hat{\psi}) \exp[-\beta H\{\mathbf{r}\}] \tag{2.8}$$

where the functional Dirac δ's constrain the hatted and unhatted fields at all points in space. By introducing conjugate fields $J_S(\mathbf{x})$ and $J_\psi(\mathbf{x})$ to remove the δ functionals, eq 2.8 can be further rewritten as[20]

$$Z = Z_0 \int DS \int D\psi \exp[-\beta F(S, \psi)] \tag{2.9}$$

where the "effective Hamiltonian" $F(S, \psi)$ is given by

$$\beta F(S, \psi) = -\rho_0 \int \mathrm{d}\mathbf{x}\ [\chi\psi^2(\mathbf{x}) + \upsilon S^2(\mathbf{x})] - \ln \int DJ_S \int DJ_\psi \times \exp[i \int \mathrm{d}\mathbf{x}\ (J_S S + J_\psi \psi) + \ln G(J_S, J_\psi)] \tag{2.10}$$

In eq 2.9, the partition function for a noninteracting system is

$$Z_0 = \int D\mathbf{r} \exp[-\beta H_0\{\mathbf{r}\}] \tag{2.11}$$

and the function $G(J_S, J_\psi)$ in eq 2.10 is defined by

$$G(J_S,J_\psi) = \langle \exp[-i \int \mathrm{d}\mathbf{x}\ (J_S \hat{S} + J_\psi \hat{\psi})] \rangle_0 \tag{2.12}$$

Here, $\langle \cdots \rangle_0$ denotes a Boltzmann-weighted average with the noninteracting Hamiltonian (eq 2.2).

In the present context of a mean-field theory, the effective Hamiltonian given in eq 2.10 is the Landau thermodynamic potential.[21] As a result, we subsequently refer to $F(S, \psi)$ as the free energy. Unfortunately, the functional integrals in eq 2.10 and the average in eq 2.12 cannot be exactly evaluated. However, a Landau expansion to any order in S and ψ can be obtained by developing $G(J_S, J_\psi)$ in a cumulant expansion to the desired order and then performing the J_S and J_ψ integrations by a saddle function method. The technical details of this procedure are strictly analogous to the calculations presented in Appendix A of ref 20. Here we comment that because our interest is in phenomena at wavelengths larger than the size of individual molecules, i.e., macroscopic phase behavior, all nonlocal terms in the free energy (e.g., square-gradient terms) are dropped. Furthermore, we retain only the lowest order coupling term between the two-order parameter fields S and ψ and truncate the expansion at fourth order.

By introducing a dimensionless free energy per monomer

$$f(S, \psi) = \frac{\beta F(S, \psi)}{\rho_0 V} \tag{2.13}$$

the Landau expansion can be written

$$f(S, \psi) = [A_2 - \upsilon]S^2 - A_3 S^3 + A_4 S^4 + [B_2 - \chi]\psi^2 - B_3\psi^3 + B_4\psi^4 - C_2 S^2 \psi \tag{2.14}$$

The Landau coefficients A_i in general depend on N and on the two elastic constants κ_1 and κ_2. Equivalently, they can be expressed as functions of an *average elastic constant*

$$K = \phi\kappa_1 + (1 - \phi)\kappa_2 \tag{2.15}$$

and a reduced difference in elastic constants

$$D = (\kappa_1 - \kappa_2)/K \tag{2.16}$$

We shall be exclusively concerned in the present paper with situations of large molecular weight in which the contour length $L = Nb$ greatly exceeds the average persistence length Kb, $K/N \ll 1$, and with small differences in elastic constants, $D \ll 1$. To leading order in K/N and D, the A_i are given by

$$A_2 = 15/4K \qquad A_3 = 75/28K \qquad A_4 = 1185/196K \tag{2.17}$$

It should be noted that these limiting expressions are independent of both molecular weight and D. Similarly, for the coefficients B_i we find

$$B_2 = \frac{1}{2N\phi(1 - \phi)} \qquad B_3 = \frac{1}{6N}[\phi^{-2} - (1 - \phi)^{-2}]$$

$$B_4 = \frac{1}{12N}[\phi^{-3} + (1 - \phi)^{-3}] \tag{2.18}$$

Finally, to leading order in K/N, the coupling coefficient is given by

$$C_2 = 15D/4K \tag{2.19}$$

The free energy given by eq 2.14 with the above coefficients has a form that is quite simple and intuitive. The first three terms in eq 2.14, involving only S, are simply a Landau–de Gennes expansion of the nematic free energy for a *homopolymer with elastic constant K*. Such an expansion for a semiflexible homopolymer melt was first worked out by ten Bosch, Maissa, and Sixou[9] and was later corrected by Rusakov and Shliomis.[23] (Our coefficients agree with those of ref 23.) The next three terms in eq 2.14, which involve only ψ, also have a simple interpretation. They are obtained by expanding the Flory–Huggins free energy of mixing expression

$$f_{FH}(\psi) = \frac{\phi_1}{N} \ln \phi_1 + \frac{\phi_2}{N} \ln \phi_2 + \chi\phi_1\phi_2 \tag{2.20}$$

in powers of ψ, where $\phi_1 = \phi + \psi$ and $\phi_2 = 1 - \phi - \psi$. Finally, the coupling term in eq 2.14 (last term) describes the extent to which the orientational entropy can be modified by a nonuniform placement of the two types of chains. From the sign of the term, it is clear that the free energy can be reduced by concentrating molecules of species 1 (stiff) in regions of high nematic order and molecules of species 2 (flexible) in regions of low nematic order.

B. Analysis of the N–I Transition. The N–I transition in a binary blend is easily analyzed with the Landau free energy 2.14. For an isotropic phase we can set $S = 0$ to obtain

$$f_I(\psi) = (B_2 - \chi)\psi^2 - B_3\psi^3 + B_4\psi^4 \qquad (2.21)$$

Minimizing eq 2.14 with respect to S for a nematic phase, we find

$$S = \{3A_3 + [9A_3^2 - 32A_4(A_2 - C_2\psi - v)]^{1/2}\}/8A_4 \qquad (2.22)$$

and the nematic free energy can be written

$$f_N(\psi) = f_I(\psi) + f_S(\psi) \qquad (2.23)$$

where

$$f_S(\psi) = (A_2 - v)S^2 - A_3S^3 + A_4S^4 - C_2S^2\psi \qquad (2.24)$$

and $S = S(\psi)$ is given by eq 2.22. Provided that $(B_2 - \chi) > 0$ (i.e., the two components will not phase separate on the basis of isotropic interactions alone), it proves sufficient to expand $f_S(\psi)$ to second order in ψ. The nematic free energy to that order is given by

$$f_N(\psi) = f_S(0) - C_2S_0^2\psi + \left[B_2 - \chi + \frac{2C_2^2S_0}{3A_3 - 8A_4S_0}\right]\psi^2 \qquad (2.25)$$

where $S_0 = S(\psi{=}0)$.

As will be shown explicitly below, *weak segregation* at the N–I transition (i.e., separation into phases with $|\psi| \ll 1$) is obtained in the present problem only if C_2 is $O(N^{-1})$ or smaller. According to eq 2.19, this can be achieved if the two species have very similar flexibilities, $D \sim N^{-1}$. Because our Landau expansion is restricted to such cases of weak segregation, the third term in the brackets of eq 2.25 is $O(N^{-2})$ and can be neglected relative to B_2 and χ, which are $O(N^{-1})$. Thus, we rewrite eq 2.25 as

$$f_N(\psi) = f_S(0) - C_2S_0^2\psi + (B_2 - \chi)\psi^2 \qquad (2.26)$$

The quantity $f_S(0)$ is the free energy per monomer in the nematic phase of a hypothetical homopolymer described by elastic constant K and Maier–Saupe parameter v and is given by eq 2.22 and 2.24 with $\psi = 0$. This free energy changes sign at a temperature T_{NI} that is defined by

$$A_2 - v = A_3^2/4A_4 \qquad (2.27)$$

(Note that $v \propto 1/T$ if the anisotropic interactions are purely enthalpic and that $K \propto 1/T$.) The temperature T_{NI} is the N–I transition temperature of this hypothetical melt. At T_{NI}, S_0 jumps from zero in the isotropic phase to

$$S_0 = A_3/2A_4 = 0.222 + O(K/N) \qquad (2.28)$$

in the nematic phase. Thus, to leading order for $K/N \to 0$, S_0 is finite and the (homopolymer) transition is *first order*.[22]

To investigate the possibility of a biphasic region in our semiflexible blend, we must equate the chemical potentials of each species in isotropic and nematic phases. However, it is instructive to first consider the two free energy expressions in eq 2.21 and 2.26. In Figure 1 the qualitative behaviors of $f_I(\psi)$ and $f_N(\psi)$ are schematically illustrated. At high temperatures, $T > T_1$, the nematic free energy is positive for all $\psi \geq 0$ and the lowest free energy state of the system is a single homogeneous and isotropic phase with $\psi = 0$. As the temperature is lowered to T_1, the coexistence of isotropic and nematic phases first becomes energetically favorable. At this temperature, the absolute minimum of $f_N(\psi)$ passes through zero. The minimum occurs at $\psi = \psi^*$, where

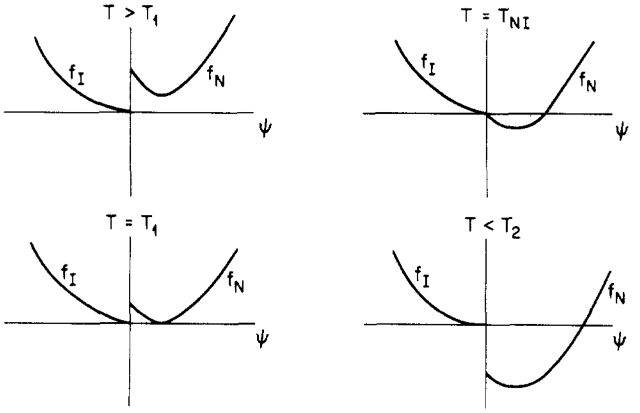

Figure 1. Schematic behavior of the free energies of isotropic and nematic phases for a binary blend of semiflexible homopolymers. At temperatures greater than T_1, the system minimizes the free energy by exhibiting a single homogeneous, isotropic phase with $\psi = 0$. At T_1, the upper boundary of the biphasic region, the minimum value of $f_N(\psi)$ first changes sign. For $T_1 > T > T_2$, isotropic and nematic phases coexist in varying proportions. T_{NI}, which lies between T_1 and T_2, is the first order N–I transition temperature of a hypothetical homopolymer melt with the average elastic constant K. Below T_2, a single nematic phase minimizes the free energy, at least until the stability limit of this phase is reached (see Figure 2).

$$\psi^* = C_2S_0^2/2(B_2 - \chi) \qquad (2.29)$$

The condition $f_N(\psi^*) = 0$ provides an equation that can be used to determine T_1:

$$f_S(0) = (B_2 - \chi)(\psi^*)^2 \qquad (2.30)$$

As the temperature is reduced below T_1, the total free energy of the system is minimized by segregation of the polymers into a nematic phase with positive ψ (rich in the more rigid species 1) and an isotropic phase with negative ψ (rich in the more flexible species 2). Note that because of the definition in eq 2.3, the relative amounts of the two phases must be such that the global ψ vanishes (lever rule). The compositions of the coexisting phases can be determined by equating the exchange chemical potentials ($\mu \equiv \partial f/\partial\psi$) and the osmotic pressure ($\Pi \equiv \mu\psi - f$) of the two phases, where f refers to $f_I(\psi)$ or $f_N(\psi)$ as appropriate. These conditions lead to

$$\psi_+ = f_S(0)/2\psi^*(B_2 - \chi) + \psi^*/2 \qquad (2.31)$$

$$\psi_- = f_S(0)/2\psi^*(B_2 - \chi) - \psi^*/2 \qquad (2.32)$$

where ψ_+ and ψ_- denote the compositions of the nematic and isotropic phases, respectively. For $T_1 > T > T_{NI}$, the inequality $|\psi_+| > |\psi_-|$ is satisfied, while $|\psi_+| = |\psi_-|$ at the temperature T_{NI} where $f_S(0) = 0$. The difference in compositions between the two phases, $\psi_+ - \psi_-$, is simply ψ^* given in eq 2.29. For the present Landau theory to provide an accurate description of the biphasic region, it is necessary that this difference be small compared with unity. Because of denominator of eq 2.29 is of the order N^{-1}, we conclude that the numerator must also be $O(N^{-1})$ or smaller. Thus, as mentioned above, the theory can be controlled by requiring that the ratio D/K be $O(N^{-1})$.

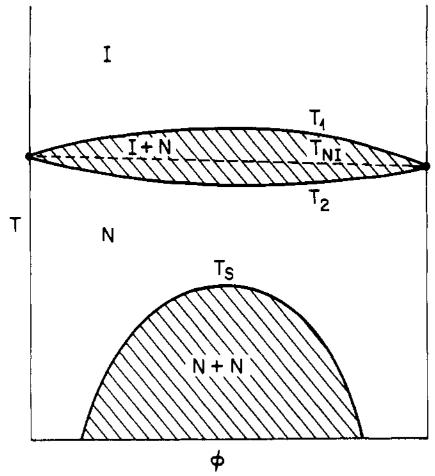

Figure 2. Schematic phase diagram of the model binary mixture considered in section II. The volume fraction of semiflexible polymer component 1 is denoted ϕ, and the temperatures T_1, T_2, T_{NI}, and T_S are, respectively, the upper and lower boundaries of the N–I biphasic region, the N–I transition temperature for a single component with the average elastic constant, and the spinodal temperature for segregation into two nematic phases. The regions denoted I, N, I + N, and N + N contain, respectively, the following phases: isotropic, nematic, biphasic–isotropic coexisting with nematic, and biphasic–nematic 1 coexisting with nematic 2.

Experimentally, this is achieved by choosing the two types of monomers to have similar, but large, persistence lengths. It is apparent that there will be a very strong tendency for demixing of semiflexible chains at the N–I transition when substantial differences in flexibility exist.

The relative fraction of the isotropic phase, q, follows from the lever rule mentioned above:

$$q = \psi_+/(\psi_+ - \psi_-) = \psi_+/\psi^* \tag{2.33}$$

From eq 2.30 and 2.31, it is evident that $q = 1$ at T_1, confirming that T_1 is the upper boundary of the biphasic region. As the temperature is lowered below T_{NI}, the biphasic region persists down to a temperature T_2, at which $q = 0$. This condition corresponds to

$$f_S(0) = -(B_2 - \chi)(\psi^*)^2 \tag{2.34}$$

and provides a means of calculating T_2.

For a range of temperatures below T_2, a single homogeneous nematic phase minimizes the total free energy of the system (see Figure 2). As the temperature is further lowered, however, a phase separation into two coexisting nematic phases can be effected. The stability envelope (to local fluctuations, i.e., the spinodal) for this separation is obtained from the condition that the ψ^2 coefficient in eq 2.25 vanishes $[\partial^2 f_N/\partial\phi^2 = 0]$:

$$B_2 = \chi + \frac{2C_2^{\,2}S_0}{8A_4S_0 - 3A_3} \tag{2.35}$$

Because the second term on the right-hand side of eq 2.35 is positive in the present temperature regime, $T < T_2$, it is apparent that the spinodal for separation into two nematic phase occurs at a higher temperature than the corresponding spinodal in the absence of nematic order, $B_2 = \chi$. The shift, however, is slight because the second term in eq 2.35 is $O(N^{-1})$ smaller than $B_2 > \chi$. Clearly, our description of this phase transition is suggestive at best, as the present Landau theory is not capable of accurately describing situations with such strong nematic order. A schematic phase diagram of the model binary blend is shown in Figure 2.

III. Semiflexible Random Copolymers

A. Model Hamiltonian. In the present section we consider a melt of semiflexible random copolymers that contain two types of monomers, denoted A and B. For simplicity, each chain has a total of N monomers, and the occupancies of adjacent or nonadjacent pairs of sites by A and B monomers are assumed to be uncorrelated. Hence, the polymers are ideal (Bernoullian) statistical copolymers. The two monomers are further assumed to have different bending elastic constants denoted by κ_A and κ_B, which could in principle be determined by measurements on the corresponding homopolymers. Finally, we restrict consideration to the case of *quenched* disorder, unless explicitly stated otherwise. This corresponds to a situation in which the sequences of A and B monomers that are produced at synthesis remain unchanged (are frozen) on the experimental time scale. While there is evidence that some rearrangements of the sequences can occur in the materials studied by Stupp et al.[6-8] (via transesterification reactions), we defer consideration of such effects to a future study.

It is convenient to associate with each monomer a discrete (Ising-like) random variable σ that takes the value +1 or −1, depending on whether the monomer is of type A or B, respectively. The normalized distribution function for σ is

$$P(\sigma) = c\delta_{\sigma,1} + (1 - c)\delta_{\sigma,-1} \tag{3.1}$$

where c is the overall volume fraction of A monomers in the system, i.e., the average composition of the copolymer. To the ith monomer on chain α is then assigned an elastic constant $\kappa_{\alpha i}$ defined by

$$\kappa_{\alpha i} = \frac{1}{2}[\kappa_A(1 + \sigma_{\alpha i}) + \kappa_B(1 - \sigma_{\alpha i})] \tag{3.2}$$

with $\sigma_{\alpha i}$ distributed according to eq 3.1 (and independent of the $\sigma_{\beta j}$ for the other monomers). Equation 3.2 clearly associates κ_A with each A monomer and κ_B with each B monomer.

For a given realization of the $\{\sigma_{\alpha i}\}$, the noninteracting Hamiltonian can be written

$$\beta H_0\{\mathbf{r},\sigma\} = -\sum_{\alpha=1}^{n}\sum_{i=1}^{N}\kappa_{\alpha i}\mathbf{u}_\alpha(i)\cdot\mathbf{u}_\alpha(i+1) \tag{3.3}$$

where n is the total number of polymers in the volume V. Microscopic volume fractions of A and B can be defined by analogy with eq 2.4 and 2.5

$$\hat{\phi}_A(\mathbf{x}) = \frac{1}{2\rho_0}\sum_\alpha\sum_i\delta[\mathbf{x} - \mathbf{r}_\alpha(i)](1 + \sigma_{\alpha i}) \tag{3.4}$$

$$\hat{\phi}_B(\mathbf{x}) = \frac{1}{2\rho_0}\sum_\alpha\sum_i\delta[\mathbf{x} - \mathbf{r}_\alpha(i)](1 - \sigma_{\alpha i}) \tag{3.5}$$

with $\rho_0 = nN/V$. Furthermore, it is useful to introduce a compositional order parameter field $\hat{Q}(\mathbf{x})$ that reflects inhomogeneities in these volume fractions (cf. eq 2.3):

$$\hat{Q}(\mathbf{x}) = (1 - c)\hat{\phi}_A(\mathbf{x}) - c\hat{\phi}_B(\mathbf{x}) \tag{3.6}$$

The full Hamiltonian for a random copolymer melt can thus be written as

$$\beta H\{\mathbf{r},\sigma\} = \beta H_0\{\mathbf{r},\sigma\} - \rho_0\int d\mathbf{x}[\chi\hat{Q}^2(\mathbf{x}) + v\hat{S}^2(\mathbf{x})] \tag{3.7}$$

where the parameters have the same meaning as before, except that χ is now the Flory parameter characterizing A–B interactions. This Hamiltonian can be treated by the methods of the previous section to compute a free energy. However, in the present case there remains the task of averaging the resulting expression over the quenched distribution of $\{\sigma_{\alpha i}\}$. Before embarking on this program, we first consider a simpler, more intuitive, approach that makes use of the blend results of section II.

B. Pseudobinary Approximation. As discussed in the Introduction, the biphasic region exhibited by the random copolymer of Stupp et al.[6-8] apparently reflects a segregation of chains by flexibility. To elucidate the physics behind this segregation, however, we first idealize our random copolymer melt as a binary blend in the manner described below.

For each chain in the copolymer sample, an effective (average) elastic constant can be defined by

$$\kappa_\alpha = \frac{1}{N}\sum_i \kappa_{\alpha i} \tag{3.8}$$

In the limit of large N, it follows from the Central Limit Theorem[24] that κ_α is gaussianly distributed. The distribution function is uniquely specified by its mean and variance, which follow from eq 3.1 and 3.2

$$\langle \kappa_\alpha \rangle_\sigma \equiv \bar{\kappa} = c\kappa_A + (1-c)\kappa_B \tag{3.9}$$

$$\langle (\kappa_\alpha - \bar{\kappa})^2 \rangle_\sigma = \bar{\kappa}^2\Delta^2 c(1-c)/N \tag{3.10}$$

In the above equations, $\langle ... \rangle_\sigma$ denotes an average over the $\{\sigma_{\alpha i}\}$ with eq 3.1 and we have introduced a reduced difference in elastic constants, Δ, defined by

$$\Delta = (\kappa_A - \kappa_B)/\bar{\kappa} \tag{3.11}$$

For a random copolymer chain with N monomers that can be either A or B, there are 2^N possible sequences of monomers (provided the two ends are distinguishable). Each of these sequences represents a distinct chemical species; however, in a macroscopic sample many of the species are present in very low concentration. Here we idealize the system as if it contains an equal amount of only two components. Component 1 is a homopolymer with an elastic constant that is larger than the average by 1 standard deviation, while component 2 has an elastic constant that is smaller than $\bar{\kappa}$ by the same amount. More precisely

$$\kappa_1 = \bar{\kappa} + \bar{\kappa}\Delta[c(1-c)/N]^{1/2} \tag{3.12}$$

$$\kappa_2 = \bar{\kappa} - \bar{\kappa}\Delta[c(1-c)/N]^{1/2} \tag{3.13}$$

In the notation of section II, the global volume fractions of 1 and 2 are equal, $\phi = 1 - \phi = 1/2$, and $\hat{\psi}(\mathbf{x})$ defined in eq 2.3 is a microscopic measure of the deviation of the composition from the average.

From eq 2.15 and 2.16, we find that $K = \bar{\kappa}$ and $D = 2\Delta[c(1-c)/N]^{1/2}$ characterize our pseudobinary system. Furthermore, the Landau free energy is given by eq 2.14 with the coefficients of eq 2.17–2.19. For the present case of a random copolymer, however, it is more meaningful to change variables from ψ to Q in the expression for $f(S,\psi)$. The quantity Q is an average order parameter that corresponds to the microscopic $\hat{Q}(\mathbf{x})$ defined in eq 3.6. $Q \neq 0$ reflects nonuniformities in the volume fractions of A and B monomers. The relationship between Q and ψ is simply

$$Q = 2\psi[c(1-c)/N]^{1/2} \tag{3.14}$$

Hence, $O(1)$ changes in the volume fraction of hypothetical species 1 imply $O(N^{-1/2})$ changes in the volume fraction of monomer A. Making the substitution of Q for ψ and inserting the above expressions for K and D into eq 2.14 lead to

$$f(S,Q) = [A_2 - v]S^2 - A_3S^3 + A_4S^4 + [B_2 - \chi]Q^2 - B_3Q^3 + B_4Q^4 - C_2S^2Q \tag{3.15}$$

where

$$A_2 = 15/4\bar{\kappa} \qquad A_3 = 75/28\bar{\kappa} \qquad A_4 = 1185/196\bar{\kappa} \tag{3.16}$$

$$B_2 = 1/2c(1-c) \qquad B_3 = 0 \tag{3.17}$$

$$B_4 = N/12c^2(1-c)^2$$

$$C_2 = 15\Delta/4\bar{\kappa} \tag{3.18}$$

Equation 3.15 has a physical interpretation similar to eq 2.14 for the blend case. The first three terms are a Landau–de Gennes expansion of the nematic free energy for a homopolymer with elastic constant $\bar{\kappa}$. Similarly, the coupling term (last term) has the same form as in eq 2.14 and C_2 is proportional to the difference between κ_A and κ_B. The three terms in eq 3.15 that involve only Q describe the change in free energy of mixing associated with segregating chains according to the amount of monomer A they contain. Provided $|Q| < N^{-1/2}$, which will prove to be required for weak segregation in the biphasic region, the dominant term among these involving only Q is the quadratic term, $(B_2 - \chi)Q^2$. It should be noted that the expression for B_2 in eq 3.17 is $O(1)$, while the blend expression in eq 2.18 is $O(N^{-1})$. In the present case of a copolymer, B_2Q^2 describes the translational entropy loss incurred by segregating the system into regions that differ slightly in volume fraction of A. It is interesting that the coefficient B_2 for the random copolymer is precisely the same as for a regular solution of A and B monomers (i.e., unpolymerized). (Note, however, that B_4 is different in the two situations.) This will have important consequences on the properties of the biphasic region that will be explored in the next section.

The N–I transition for a random copolymer can be studied in the pseudobinary approximation by applying the analysis of section II to eq 3.15. We postpone such analysis to the next section, where it is demonstrated that eq 3.15 is also obtained from a direct projection of eq 3.7 onto the variables S and Q.

C. A More Detailed Approach. While the pseudobinary approximation is physically appealing, it is more satisfying to derive the Landau free energy directly by starting with eq 3.7. To carry out such a procedure, we assume that two order parameters, S and Q [the thermodynamic averages of $\hat{S}(\mathbf{x})$ and $\hat{Q}(\mathbf{x})$], are sufficient to describe the N–I transition of random copolymers.[25] We then follow the steps of eq 2.7–2.12 in order to obtain a formal expression for $\beta F(S,Q)$. The intermediate formulas are identical to eq 2.7–2.12, except that $\psi(\mathbf{x})$ is replaced by $Q(\mathbf{x})$ and $\hat{\psi}(\mathbf{x})$ by $\hat{Q}(\mathbf{x})$.

Of particular interest is the equation that corresponds to 2.12

$$G(J_S,J_Q) = \langle \exp[-i\int d\mathbf{x}(J_S\hat{S} + J_Q\hat{Q})] \rangle_0 \tag{3.19}$$

in which $\langle \cdots \rangle_0$ denotes an ensemble average with the noninteracting Hamiltonian in eq 3.3. As written, $G(J_S,J_Q)$ is a function of the $\{\sigma_{\alpha i}\}$, both through the explicit σ dependence of $\hat{Q}$ and through the average with $\beta H_0\{\mathbf{r},\sigma\}$. It is convenient to isolate the contributions to $\hat{S}$ and $\hat{Q}$ from each chain by writing

$$\hat{S}(\mathbf{x}) = \sum_\alpha \hat{S}_\alpha(\mathbf{x}) \tag{3.20}$$

$$\hat{Q}(\mathbf{x}) = \sum_{\alpha} \hat{Q}_{\alpha}(\mathbf{x}) \qquad (3.21)$$

Equations 2.6, 3.6, 3.20, and 3.21 serve as definitions of the fields $\hat{S}_{\alpha}(\mathbf{x})$ and $\hat{Q}_{\alpha}(\mathbf{x})$. Because the average in eq 3.19 can be factorized by chain, we can write

$$\ln G(J_S,J_Q) = \sum_{\alpha} \ln \langle \exp[-i \int d\mathbf{x}(J_S\hat{S}_{\alpha} + J_Q\hat{Q}_{\alpha})] \rangle_0 \qquad (3.22)$$

In the thermodynamic limit (n, $V \rightarrow \infty$, $nN/V \rightarrow \rho_0$), however, the sum over chains effects an average over all realizations of the $\{\sigma_{\alpha i}\}$. Hence

$$\ln G(J_S,J_Q) = n\langle \ln \langle \exp[-i \int d\mathbf{x}(J_S\hat{S}_{\alpha} + J_Q\hat{Q}_{\alpha})] \rangle_0 \rangle_{\sigma} \qquad (3.23)$$

and the free energy expression

$$\beta F(S,Q) = -\rho_0 \int d\mathbf{x}[\chi Q^2(\mathbf{x}) + vS^2(\mathbf{x})] - \ln \int DJ_S \int DJ_Q \exp[i \int d\mathbf{x}(J_S S + J_Q Q) + \ln G(J_S,J_Q)] \qquad (3.24)$$

are independent of the $\{\sigma_{\alpha i}\}$ in the thermodynamic limit. As a result, there is no need to further average $\beta F(S,Q)$ over the quenched disorder.

As in section II, we develop $\ln G(J_S,J_Q)$ in a cumulant expansion to fourth order in the J's (retaining only the lowest order coupling term and taking the long-wavelength limit as before). The functional integrals in eq 3.24 are then performed by saddle points. To leading order for small $\Delta = (\kappa_A - \kappa_B)/\bar{\kappa}$ and small $\bar{\kappa}/N$, we find that the Landau free energy can again be written in the form of eq 3.15. With the exception of B_3 and B_4, we find *exactly* the same coefficients as were obtained from the pseudobinary approximation (eq 3.16–3.18). For B_3 and B_4, eq 3.17 is modified to

$$B_3 = \frac{1}{6}[c^{-2} - (1-c)^{-2}] \qquad B_4 = N/4c^2(1-c)^2 \qquad (3.17b)$$

Note that, at the symmetric composition $c = 1/2$, $B_3 = 0$ is the same in both approaches. Furthermore, the more detailed calculation merely changes the coefficient 1/12 in the pseudobinary expression for B_4 to 1/4.

We now proceed to study the N–I transition on the basis of eq 3.15–3.18 with the modified coefficients of eq 3.17b. As will soon become apparent, the tendency for phase separation near the N–I transition is again very great, and *weak segregation* is attained only if $C_2 < O(N^{-1/2})$. Initially, we restrict consideration to this case and treat strong segregation later in the section. The method for the weak segregation case is strictly analogous to that of section II. In particular, the free energy per monomer of an isotropic phase is obtained by setting $S = 0$ in eq 3.15, and, to second order in Q, the free energy of a nematic phase is given by

$$f_N(Q) = f_S(0) - C_2S_0^2Q + [B_2 - \chi + 2C_2^2S_0/(3A_3 - 8A_4S_0)]Q^2 \qquad (3.25)$$

Here, $f_S(0)$ and S_0 have the same meaning as in section II, except that they are evaluated with the coefficients of eq 3.16–3.18 and 3.17b. Because C_2 is restricted to be less than $O(N^{-1/2})$, the last term in the brackets of eq 3.25 can be neglected and the nematic free energy simplifies to

$$f_N(Q) = f_S(0) - C_2S_0^2Q + (B_2 - \chi)Q^2 \qquad (3.26)$$

The analysis of the phase transition now proceeds exactly as in section II. The temperature T_{NI} is defined by eq 2.27, and eq 2.30 with ψ^* replaced by

$$Q^* = C_2S_0^2/2(B_2 - \chi) \qquad (3.27)$$

defines the temperature T_1 that delimits the isotropic and biphasic regions. The lower temperature T_2 that locates the biphasic–nematic boundary is obtained from eq 2.34 (again with $\psi^* \rightarrow Q^*$). Furthermore, the compositions of the two phases in the biphasic region, Q_+ and Q_-, are given by eq 2.31 and 2.32, respectively. Because C_2 is assumed to be smaller than $O(N^{-1/2})$ in the present analysis, it follows from eq 3.27 that the difference between the compositions of the coexisting phases, Q^*, is also $<O(N^{-1/2})$. This is consistent with our restriction to the case of weak segregation, as *saturation* (complete segregation into pure components 1 and 2) in the pseudobinary approximation corresponds to $Q^* = 2[c(1-c)/N]^{1/2}$. Finally, we note that the fraction of the isotropic phase, q, in the biphasic region is given by $q = Q_+/Q^*$.

The width of the biphasic region is easily established from eq 2.30 and 2.34. Because T_1 and T_2 are very near T_{NI} for $Q^* < O(N^{-1/2})$, $f_S(0)$ can be expanded about T_{NI} as follows:

$$f_S(0) \approx C_0(T - T_{NI}) \qquad (3.28)$$

Here, $C_0 > 0$ is an $O(1)$ constant that is determined by the temperature dependence of v and $\bar{\kappa}$. From eq 2.30 and 2.34 it immediately follows that the width of the biphasic region is

$$T_1 - T_2 = (2/C_0)(B_2 - \chi)(Q^*)^2 \qquad (3.29)$$

Hence, in the *weak segregation limit* the temperature range over which nematic and isotropic phases coexist is *at most* $O(N^{-1})$.

As the molecular weight of the random copolymer is increased, all other conditions being held fixed, the criterion $C_2 < O(N^{-1/2})$ for weak segregation will eventually be violated. This follows because C_2 given by eq 3.18 is independent of N (for $N/\bar{\kappa} \rightarrow \infty$). As $N^{-1/2}$ becomes of order the of C_2 or smaller, a *strong segregation* is effected that cannot be described by a Landau expansion in powers of Q. We can investigate this regime, however, by returning to the pseudobinary approximation and by recalling that $f_I(\psi)$ is a Landau expression of the Flory–Huggins free energy given in eq 2.20. In particular, it is readily apparent that, to fourth order in Q, eq 3.15 for a random copolymer melt is equivalent to

$$f(S,Q) = f_S(S,Q) + f_I(Q) \qquad (3.30)$$

with

$$f_S(S,Q) = (A_2 - v)S^2 - A_3S^3 + A_4S^4 - C_2S^2Q \qquad (3.31)$$

$$f_I(Q) = [(1 + EN^{1/2}Q)/2N] \ln (1 + EN^{1/2}Q) + [(1 - EN^{1/2}Q)/2N] \ln (1 - EN^{1/2}Q) - \chi Q^2 \qquad (3.32)$$

and

$$E \equiv [1/c(1-c)]^{1/2} \qquad (3.33)$$

The full unexpanded form of eq 3.32, however, is necessary to describe the strong segregation regime.

When eq 3.31 is minimized with respect to S and exchange chemical potentials and osmotic pressure are equated as before, the N–I transition in the strong segregation limit can be investigated on the basis of eq 3.30–3.32. To leading order for $N \rightarrow \infty$ we find a biphasic region bounded above by a temperature T_1, defined by

$$f_S(0) = C_2S_0^2/EN^{1/2} \qquad (3.34)$$

and below by T_2, defined by

$$f_S(0) = -C_2S_0^2/EN^{1/2} \qquad (3.35)$$

When these results are combined with eq 3.28, it follows that the width of the biphasic region in the strong segregation limit is given by

$$T_1 - T_2 = 2C_2S_0^2/C_0EN^{1/2} \qquad (3.36)$$

Hence, the temperature range over which nematic and isotropic phases can coexist asymptotically decreases as $N^{-1/2}$. The finding that there is no biphasic region for $N \to \infty$ is intuitive because every chain is chemically identical in that limit. It is also interesting to note that eq 3.36 crosses over smoothly to the weak segregation prediction of $T_1 - T_2 \sim N^{-1}$ (eq 3.29) as C_2 is reduced to be $O(N^{-1/2})$.

At high molecular weight, the two coexisting phases are exponentially close to being saturated. Saturation here refers to the situation (in our pseudobinary approximation) in which the two phases are pure in components 1 and 2. As described by eq 3.12–3.14, these fictitious components have elastic constants and compositions that differ by $O(N^{-1/2})$. Near saturation, the compositions of the coexisting phases are given by

$$Q_\pm = \pm(1/N^{1/2}E)[1 - \exp(-G_\pm N^{1/2})] \qquad (3.37)$$

where

$$G_+ = C_2S_0^2/E + N^{1/2}f_S(0) \qquad (3.38)$$

$$G_- = C_2S_0^2/E - N^{1/2}f_S(0) \qquad (3.39)$$

It should be noted that the $G_\pm$ values are >0 and $O(1)$ in the biphasic region, $T_2 < T < T_1$. The fraction of the isotropic phase in this region is given by the lever rule expression, $q = Q_+/(Q_+ - Q_-)$.

IV. Summary and Discussion

In the present paper we have developed a Landau theory to study the nematic to isotropic transition in binary blends of main-chain liquid-crystalline polymers and in thermotropic statistical copolymers. The essence of the theory for the binary blend is that a coupling term of the form $C_2S^2\psi$ emerges in the Landau free energy. This coupling between the orientational (S) and compositional (ψ) order parameters produces a biphasic region at the N–I transition in which a nematic phase (rich in the species with higher rigidity) coexists with an isotropic phase (lean in the species with higher rigidity). The tendency for this phase separation was found to be very great in all cases investigated. For the blend, a weak segregation (one with $|\psi| \ll 1$ in both phases) is effected only if C_2 in eq 2.19 is $O(N^{-1})$ or smaller. Experimentally, this condition can be satisfied by choosing the two components to have very similar persistence lengths. For this weak segregation regime we found that the width (in temperature) of the biphasic region is on the order of NC_2^2, which is at most $O(N^{-1})$. We emphasize that our theory is incapable of describing strong nematic order and is thus restricted to the vicinity of the phase transition. Different methods[14–18] are required to treat the nematic phase at low temperatures.

For the statistical copolymer, it was assumed that the chemical disorder is quenched and, hence, that the monomer sequences produced at synthesis are permanent. As a result, the various polymers in the sample have fixed compositions that can differ from the global composition. Because these fluctuations are $O(N^{-1/2})$, the maximum composition difference that can be achieved if the chains fully segregate (i.e., according to the amount of monomer species A that they contain) is of the same order. We employed a pseudobinary approximation for the copolymer melt in section III in order to take advantage of the blend results, but we also found that the same Landau free energy could be obtained by a direct projection of the order parameter fields S and Q out of a microscopic Hamiltonian. The cubic coupling term found for the blend case reemerged, but with $C_2 = 15\Delta/4\bar{\kappa}$. For the statistical copolymer, weak segregation is obtained only if C_2 is $O(N^{-1/2})$ or smaller. The Landau analysis for this situation led to the prediction that the width of the biphasic region is on the order of C_2^2, i.e., at most $O(N^{-1})$.

From an experimental standpoint, the most relevant regime is that of *strong segregation*, achieved when $C_2 > O(N^{-1/2})$. For random copolymers of moderate molecular weight and with substantial differences in flexibility among the consistent monomers, such as the materials of Stupp et al.,[6–8] C_2 will easily exceed this value. In the biphasic regime under these conditions, the copolymers that contain an excess of A monomers are almost completely segregated from the chains that contain an excess of B. The difference between the compositions of the isotropic and nematic phases in the strong segregation limit is $O(N^{-1/2})$ [with small corrections on the order of $N^{-1/2}\exp(-N^{1/2})$]. Furthermore, we found that the width of the biphasic region is asymptotically on the order of $C_2N^{-1/2}$ for large N.

The cubic coupling term in the Landau free energy proportional to $S^2\psi$ (or S^2Q) was found to be responsible for the interesting biphasic behavior described above. This *entropic* coupling term emerged naturally in our formalism due to differences in flexibility of the monomers. However, as per the discussion that followed eq 2.6, *enthalpic* couplings are also possible if the Maier–Saupe parameter has a dependence on composition. Such couplings have been investigated by Brochard et al.[11] and can lead to phase behavior much more complicated than that depicted in Figure 2. In the simplest case, the $C_2S^2\psi$ coupling term might be preserved but with an additional enthalpic contribution to C_2. The obvious question then arises as to which contribution is dominant in real physical systems.

Experiments to address the above predictions and questions would be very helpful. An obvious experiment would be to repeat the measurements of Stupp et al. on a set of random copolymers with different molecular weights but that are otherwise identical. One would hope to see the width of the biphasic region vary as $N^{-1/2}$. Other experiments might be aimed at trying to determine which component of C_2 is dominant. In particular, is the driving force for segregation the difference in flexibility between the two types of monomers, Δ, or is it some composition dependence of the Maier–Saupe parameter? If it is the former, one would expect to find that the width of the biphasic region scales linearly with Δ. A possible means of answering the above question would be to perform a measurement that is sensitive to the temperature dependence of C_2. The first contribution, $15\Delta/4\bar{\kappa}$, should be proportional to T, while any Maier–Saupe contribution to C_2 should scale inversely with T. Independent experiments on homopolymers synthesized from the various constituent monomers might prove valuable in the interpretation of such measurements.

Other questions arise with regard to the experiments of Stupp et al.[6–8] There is evidence that transesterification reactions may produce some rearrangements of the copolymer sequences. If the chemical disorder were truely *annealed*, i.e., able to equilibrate on the experimental time scale, then quite different behavior would be expected at the N–I transition. For annealed disorder, the degree of polymerization is irrelevant because the monomers can exchange among all positions on the various chains. An analysis for the annealed case, similar to the one used to obtain eq 3.15, indicates that B_2 is unchanged from the situation of quenched disorder, but B_4 is $O(1)$ for annealed disorder. This implies that the Landau expansion is quite useful in the annealed case, even if C_2 is as large as $O(1)$. It also follows that the difference in compositions between the two phases in the biphasic window (eq 3.27) can be $O(1)$ for the annealed case, while it is asymptotically $O(N^{-1/2})$ for the quenched case. This result is easily understood. For annealed disorder, the monomers can respond to the forces acting to segregate them by rearranging such that the typical fluctuations in composition among different chains are $O(1)$. (Hence, chains are produced that are predominantly A or B.) A system with quenched disorder does not have this luxury, as the characteristic fluctuations are frozen at synthesis to be $O(N^{-1/2})$. It follows in the annealed case that the width of the biphasic region (eq 3.29) is on the order of C_2^2 can be controlled by making Δ sufficiently small.

The present theory can be extended in a number of obvious ways. It is straightforward to treat statistical copolymers that contain more than two different monomers, such as the terpolymers considered in ref 6–8. We anticipate that all of our qualitative conclusions would remain intact. Similarly, three (or more) component homopolymer blends can be addressed by the methods of section II. It is also possible to avoid the Landau expansion in S by extending the techniques of ref 14–17 to the present case of random copolymers. This would be particularly straightforward in the pseudobinary approximation.

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