Phase Behavior of Ternary Systems Involving a Conformationally Variable Chain and a Randomly Coiled Polymer: Effect of External Orientational Field

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ABSTRACT: The lattice theory regarding ternary systems involving a conformationally variable polypeptide and a randomly coiled polymer presented recently is extended to the case where an external orientational field of quadrupole type is present. The mixing partition function is elaborated by inclusion of the energy term arising from the external field to the lattice scheme previously developed. The calculations carried out show that the external field exerts a marked effect on the phase behavior of the ternary systems. The isotropic−anisotropic biphasic gap is predicted to shift to lower polymer concentrations and becomes narrower when the external field exists. The entrance of the randomly coiled polymers into the anisotropic phase is promoted. Influences of the external field intensity, molecular structure parameters, and compositions have also been studied.

Introduction

Phase behavior of ternary systems comprising a rigid-rod polymer, a randomly coiled polymer, and a solvent was first studied by Flory on the basis of the lattice model.[1] According to the theory, above a critical polymer concentration the ternary solution would phase separate into an isotropic phase exhibiting somewhat miscibility between the rigid and coiled polymers and an ordered anisotropic phase mainly consisting of rodlike component and rejecting the coiled polymer with high selectivity. Such a phase separation is due to the unfavorable low entropy of the mixing of rods and coils. The general feature of the theoretical predictions has been verified by the experimental observations.[2−7] The theoretical treatment carried out by Flory was restricted to somewhat idealized conditions. For instance, the two solute species considered only represent extremes, the one being rigid and rodlike and the other sufficiently flexible to adopt a randomly coiled chain conformation.

Since the original success of the Flory lattice theory, many efforts have been directed toward improving the original model to cover much more complex situations. For example, Ciferri et al.[3,8] and Sasaki et al.[5] have analyzed the effect of the interaction parameter χ_{23} for the pairs of the mesogenic and coiled polymers. It was found that if $\chi_{23} > \chi_{23}^c$ (the critical value for mixing), the two polymers should demix at some percentage composition in the undiluted state. As in the case of $\chi_{23} \ll \chi_{23}^c$, the phase separation would be triggered by entropy effects related to the formation of the mesophase. The contribution from the anisotropic interactions to the phase equilibria of the ternary systems has been examined by Blonski et al.[9] and Bianchi et al.[10] The calculation results show that the anisotropic phase becomes acceptable for a certain amount of the flexible component after the orientation-dependent interactions are incorporated into the lattice scheme. Theoretical extension for the ternary solutions which contain a rigid-rod solute with flexible side chains, a randomly

coiled polymer, and a solvent was reported by Ballauff[11,12] and Inomata et al.[13,14] It has been found that the presence of the flexible side chains could enhance the miscibility between the rodlike and coiled polymers in both isotropic and anisotropic phases. Polymer chain conformation changes in the isotropic−anisotropic transition present an important issue associated with the phase behavior, and they may pertain to semirigid macromolecules in general.[15−23] Recently, Lin et al. have analyzed the effect of the chain conformation variation of the mesogenic polymer on the phase diagrams of the ternary systems.[23] The conformationally variable chain is exemplified by polypeptide in which each unit is able to assume either a helix or a random coil form. The mobile equilibria between the two states determine the overall chain rigidity. The theoretical treatment was carried out by introducing of a term related to the free energy contributed from the chain conformation changes into the original lattice model proposed by Flory. A pronounced increase of the miscible isotropic zone was predicted when the chain rigidity of the polypeptide in the isotropic phase is reduced. The polypeptide chain tends to adopt a fully rigid helix form as long as it enters the anisotropic phase where the randomly coiled polymer is essentially excluded.

On the other hand, the effect of an external orientational field on the isotropic−anisotropic equilibria presents an interesting problem in relation to both fundamental studies and fabrication process.[24−27] Within the framework of the lattice model, Marrucci and Ciferri have first studied the influence of the external orientational field on the binary solution of the rigid-rod molecules.[28] They concluded that the application of an external orientational field results in narrowing the region of the biphasic phase separation and shifting the isotropic−anisotropic transition concentration to a lower value. On the basis of the lattice model, Shibaev et al. have studied the influence of the external orientational field on the phase behavior of a thermotropic liquid crystal polymer containing stiff and flexible fragments.[29] Phase diagrams for various strengths of the external

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field and various polymer chain structures were constructed. It was found that the external field could stiffen the flexible fragments in the polymer chain, resulting in stabilization of the liquid crystal phase. Recently, a detailed study of the effect of the external orientational field on the phase behavior of a binary system involving a conformationally variable polypeptide has been performed by Lin et al.[30] It turns out, from the calculations, that the isotropic−anisotropic phase transition induced by an external orientational field is possible for the polypeptide even with very high chain flexibility as long as the coil−helix chain conformational changes are allowed. The external orientational field promotes the combined action of the coil−helix transition and liquid crystal formation. Since the phase behavior of the ternary systems involving a conformationally variable chain and the influence of the external field on the binary systems are rather well understood, it is of crucial interesting to know the effect of the external field on the phase behavior of the ternary systems.

In the present work, the lattice model regarding ternary systems involving a polypeptide and a polymer with inherently flexible chain conformation, which was proposed in our previous work, was further generalized by introducing an energy term contributed from an external orientational field of quadrupole symmetry. The calculations carried out show that the isotropic−anisotropic phase boundary shifts to lower polymer concentrations and becomes narrower when an external orientational field is applied to the ternary systems. The randomly coiled polymers are facilitated to enter the anisotropic phase by the external field. The effects of the external field intensity, molecular structure parameters, and compositions were also examined.

Theory

The external orientational field considered in the present studies is a quadrupole symmetry field, i.e., a field in which the potential energy of a rectilinear chain fragment is proportional to $-\cos^2 \phi$, where ϕ is the angle between the direction of the fragment and the orientation axis. Such a field appears when nonpolar polymeric chains with uniaxial anisotropic susceptibility are subjected to an electrical or magnetic field.[29−32] Therefore, the dipole term of polymer chain is not considered in the current model. When the external orientational field is applied to the ternary systems involving a polypeptide and a randomly coiled polymer, an extra energy term should be included in the lattice scheme. According to our previous work[30] and Shibaev et al.,[29] the energy term is written as

$$E_{ex}/kT = -\epsilon_0 n_2[\theta x_2 \langle \cos^2 \Psi_i \rangle + (1 - \theta)x_2 \langle \cos^2 \Psi_j \rangle] \quad (1)$$

where n_2 is the number of the polypeptide consisting of x_2 segments, θ is the fraction of units in the helical conformation, and the dimensionless parameter ϵ_0 defines the intensity of the external orientational field. As shown in Figure 1 where the mesogenic polymer with conformationally variable chain is schematically illustrated, the averaging in eq 1 is performed over all angles Ψ_i between the rigid helix segment and the orientation axis and over all Ψ_j between the links of the flexible coil component and the orientation axis. Since the electrical or magnetic anisotropy of the polypeptide is much larger than that of the coiled polymer, the
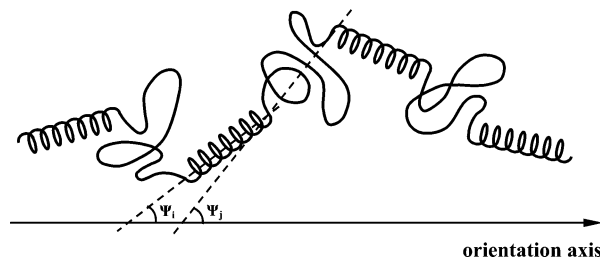

Figure 1. Schematic representation of the conformationally variable chain considered in the present theory.

interaction between the external orientational field and coiled polymer is neglected for simplicity in the present work.

The mixing free energy expression for a ternary system involving a conformationally variable chain and a randomly coiled polymer has been written out in our previous work.[23] If the ternary system is subjected to an external field, an extra term as expressed by eq 1 should be included in the lattice scheme. After incorporating eq 1, the mixing free energy expression for an athermal ternary system in the presence of the external field becomes

$$-\ln Z_M = n_1 \ln v_1 + n_2 \ln v_2 + n_3 \ln v_3 + \bar{x}n_p(1 - 1/\bar{x}) - n_0[(1 - Q) \ln(1 - Q) + Q] - mx_2n_2[\theta(\beta + \ln s) + \rho \ln(\sigma S_0) - (1 - \theta - \rho) \ln(1 - \theta - \rho) - \rho \ln \rho + (1 - \theta) \ln(1 - \theta)] - \epsilon_0 n_2[\theta x_2 \langle \cos^2 \Psi_i \rangle + (1 - \theta)x_2 \langle \cos^2 \Psi_j \rangle] \quad (2)$$

where n_1, n_2, and n_3 are the numbers of the solvent, polypeptide, and coiled polymer with lengths of 1, x_2, and x_3, respectively, $\bar{x}$ is the number-average of x_2 and x_3, v_1, v_2, and v_3 represent the volume fractions of the corresponding components, n_0 and n_p equal $(n_1 + x_2n_2 + x_3n_3)$ and $(n_2 + n_3)$, respectively, s and σ denote respectively the statistical weight for a unit in the helical state relative to the coil and the weighting factor for initiation of a helical sequence, m represents the number of repeat units (i.e., peptide residues) in the lattice segment, ρ is the fraction of units that mark the beginning of a helical sequence, β is a Lagrangian multiplier, and Q and S_0 are orientation-related quantities that have been defined in ref 23.

Extensive computations of $-\ln Z_M$ of eq 2 demonstrate that the free energy of mixing invariably decreases with increasing θ. The minimum value of $-\ln Z_M$ is located at $\theta = 1$ for all the parameters examined. Including the energy term of the external orientational field does not change the general feature of the dependence of $-\ln Z_M$ on θ as reported in our previous work.[23] In the anisotropic phase, the maximum stability occurs at $\theta = 1$. Under such a circumstance, the last term of eq 2, which is contributed from the external orientational field, reduces to $-\epsilon_0 n_2 x_2 \langle \cos^2 \Psi_i \rangle$. With further substituting the conditions for the anisotropy as specified in ref 23, eq 2 becomes

$$-\ln Z_M = n_1 \ln v_1 + n_2 \ln v_2 + n_3 \ln v_3 + \bar{x}n_p(1 - 1/\bar{x}) - n_0[(1 - Q) \ln(1 - Q) + Q] - n_2[\ln(y/x_2)^2 + mx_2 \ln s + \ln \sigma] - \epsilon_0 n_2 x_2 \langle \cos^2 \Psi_i \rangle \quad (3)$$

Since the polypeptide chain takes a fully helix form in the anisotropic phase, the exact lattice treatment according to Flory and Ronca[33] is utilized for the

deduction of the disorientation parameter y. The external field also affects the orientational distribution which, hence, makes a further contribution to the reduced free energy. Therefore, f_p adopted by Flory and Ronca is redefined as[29,30]

$$f_p = \int_0^{\pi/2} \sin^p \Psi \, \exp(-\alpha \sin \Psi - \epsilon_0 x_2 \sin^2 \Psi) \, d\Psi \quad (4)$$

$$\alpha = -(4/\pi) x_2 \ln[1 - v_2'(1 - y/x_2)] \quad (5)$$

$$y = (4/\pi) x_2 (f_2/f_1) \quad (6)$$

and the quantity Q is given by

$$Q = v_2'(1 - y/x_2) \quad (7)$$

where the prime symbol (′) is appended to denote the anisotropic phase.

Chemical potentials of the components in the anisotropic phase can be readily obtained by partially differentiating eq 3 with auxiliary eqs 4−7. The results are shown as

$$(\mu_1' - \mu_1^{\circ\prime})/RT = \ln v_1' + v_p'(1 - 1/\bar{x}) - \ln(1 - Q) - Q \quad (8)$$

$$(\mu_2' - \mu_2^{\circ\prime})/RT = \ln v_2' + x_2 v_p'(1 - 1/\bar{x}) - x_2 Q - \ln f_1 - m x_2 \ln s - \ln \sigma - \epsilon_0 x_2 \quad (9)$$

$$(\mu_3' - \mu_3^{\circ\prime})/RT = \ln v_3' + x_3 v_p'(1 - 1/\bar{x}) - x_3 \ln(1 - Q) - x_3 Q \quad (10)$$

where v_p is equal to $v_2 + v_3$.

In the state of the isotropy, the orientational order parameter $S = (3\langle\cos^2 \Psi_j\rangle - 1)/2 = 0$; thus, $\langle\cos^2 \Psi_j\rangle = 1/3$. The $\langle\cos^2 \Psi_j\rangle$ term is also equal to $1/3$ due to the random orientations.[29,30] Therefore, the last term of eq 2 appears to be $-\epsilon_0 n_2 x_2/3$. Incorporating this result, together with the conditions obtained for the isotropy according to ref 23, into eq 2 gives

$$-\ln Z_M = n_1 \ln v_1 + n_2 \ln v_2 + n_3 \ln v_3 + \bar{x} n_p(1 - 1/\bar{x}) + m x_2 n_2 \ln[1 - \rho/(1 - \theta)] - \epsilon_0 n_2 x_2/3 \quad (11)$$

Partial differentatiation of the above equation yields the reduced chemical potentials of the components in the isotropic phase.

$$(\mu_1 - \mu_1^{\circ})/RT = \ln v_1 + v_p(1 - 1/\bar{x}) \quad (12)$$

$$(\mu_2 - \mu_2^{\circ})/RT = \ln v_2 + x_2 v_p(1 - 1/\bar{x}) + m x_2 \ln[1 - \rho/(1 - \theta)] - \epsilon_0 x_2/3 \quad (13)$$

$$(\mu_3 - \mu_3^{\circ})/RT = \ln v_3 + x_3 v_p(1 - 1/\bar{x}) \quad (14)$$

Numerical Calculations

The relations governing the phase equilibria of the ternary systems in the presence of the external orientational field can be obtained by equating eq 8 to eq 12, eq 9 to eq 13, and eq 10 to eq 14 with auxiliary relations of eqs 4−7.

Figure 2 illustrates the influence of the external field intensity on the phase diagrams of the ternary systems. Typical results are shown for $\epsilon_0 = 0.225$ (a) and 0.265 (b). Other parameters used in the calculations are
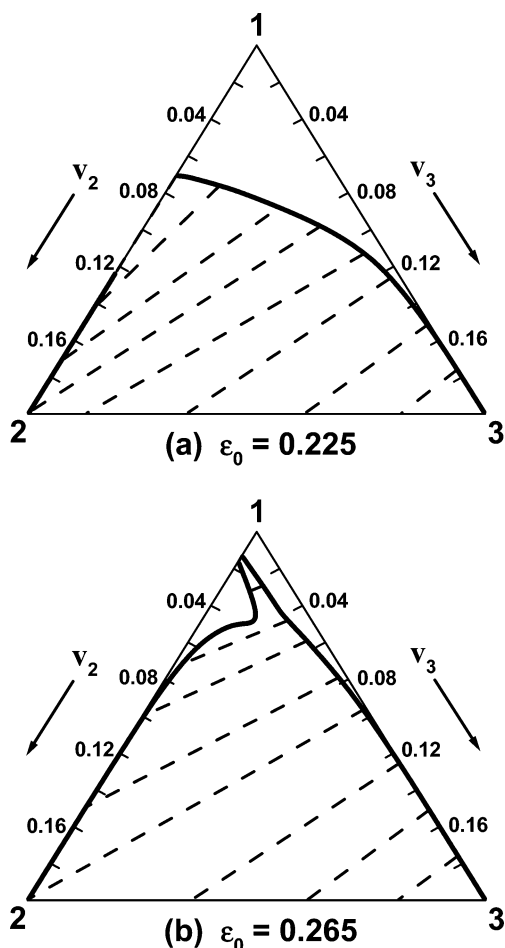

Figure 2. Ternary phase diagrams calculated for $\epsilon_0 = 0.225$ (a) and $\epsilon_0 = 0.265$ (b). Components are solvents (1), polypeptide solute (2), and randomly coiled polymer (3). Invariant parameters used in the calculations are $x_2 = 100$, $x_3 = 100$, $\theta = 0.8$, $\sigma = 10^{-4}$, and $m = 10$.

indicated in the caption. Binodals for the isotropic and anisotropic phases are heavy lined. Tie lines joining conjugate phases in equilibrium are light dashed. The length of the tie line indicates the broadening of the biphasic gap. The longer the tie line, the wider the isotropic−anisotropic phase boundary. For clarity, only the upper portion of the phase diagram, where $v_p < 0.20$, is shown. From Figure 2, it can be seen that the phase separation tends to begin at lower overall polymer concentrations (v_p) with increasing the ϵ_0 value. Concomitantly with the shift of the biphasic gap, the isotropic−anisotropic phase boundary becomes narrower as indicated by the variation of the tie line length. When the intensity of the external field is lower, as shown in Figure 2a, the binodal for the anisotropic phase coincides with the binary polypeptide−diluent axis, suggesting a nearly complete exclusion of the randomly coiled polymer from the anisotropic phase. However, when the external field intensity becomes stronger (Figure 2b), the binodal tends to depart from the polypeptide−diluent axis, which indicates that the anisotropic phase becomes acceptable for a certain amount of the flexible component. It should be noted that the equilibrium anisotropic phase contains polypeptide chains that are substantially more rigid than those inhabiting the isotropic phase. A coil−helix transition takes place in the polypeptide chain upon the anisotropic phase formation. The coupled transitions are pro-
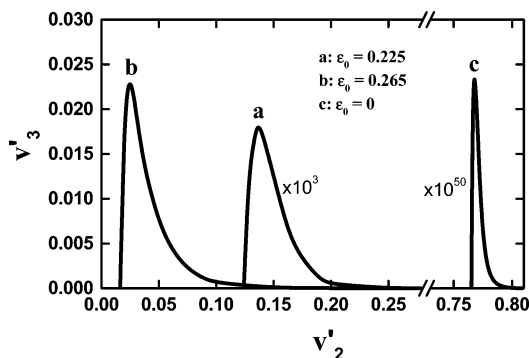
Figure 3. Plots of volume fractions v_3' of the randomly coiled polymer in the anisotropic phase against v_2' for the polypeptide solute in that phase for $\epsilon_0 = 0.225$ (a), $\epsilon_0 = 0.265$ (b), and $\epsilon_0 = 0$ (c). Invariant parameters used in the calculations are similar to those in Figure 2.

moted by the external orientational field as indicated by the shift of the biphasic gap to lower polymer concentrations.

Shown in Figure 3 is a plot where the volume fractions v_3' along the binodal for the anisotropic phases are plotted against v_2' for the ternary systems corresponding to those in Figure 3, i.e., systems with $\epsilon_0 = 0.225$ (a) and 0.265 (b). The result for $\epsilon_0 = 0$ (c) is also included for comparison. With increasing v_2', the value of v_3' increases sharply from the point at v_2' for the binary system of solvent and polypeptide to a maximum, then followed by a decrease toward zero. For the system with $\epsilon_0 = 0$, the v_3' values are negligible small. When ϵ_0 is increased, the curve shifts to the lower value of v_2' and turns broader. Concomitantly, the maximum value of v_3' increases. For example, v_3'(max) is 2.417×10^{-52} for $\epsilon_0 = 0$ and becomes 1.806×10^{-5} for $\epsilon_0 = 0.225$ and 2.331×10^{-2} for $\epsilon_0 = 0.265$.

Figure 4 gives typical results showing the influence of the variation of θ parameter in the isotropic phase at a given value of $\epsilon_0 = 0.265$. With increasing θ value from 0.7 to 0.8, the biphasic region shifts upward to lower polymer concentrations. Meanwhile, the isotropic–anisotropic phase boundary turns narrower, and the binodal for the anisotropic phase departs from the polypeptide–diluent axis. The energy provided by the external orientational field both facilitates the coil–helix transformation in the isotropic–anisotropic phase transition and accelerates the entrance of the random coils into the anisotropic phase. When the helix fraction in the isotropic phase is increased, the conformational energy penalty associated with the transition to the helix form in the anisotropic phase becomes smaller. Therefore, much more random coils are forced into the anisotropic phase, as shown by Figure 4a.

Another important structure parameter of polypeptide chain is σ which is associated with the length of the helical sequence; i.e., the smaller σ, the longer the rigid sequence. According to the calculations not included, decrease of σ shows a similar effect on the phase diagrams to that of the increase in the θ parameter. No features are revealed.

Figure 5 shows the effect of the chain length on the phase equilibria of the ternary systems. Typical phase diagrams are shown for the systems with (a) $x_2 = 100$, $x_3 = 100$ and (b) $x_2 = 100$, $x_3 = 50$. At given values of x_2 and ϵ_0, the binodal for the anisotropic phase becomes markedly departing from the polypeptide–dilute axis when the chain length of the randomly coiled polymer
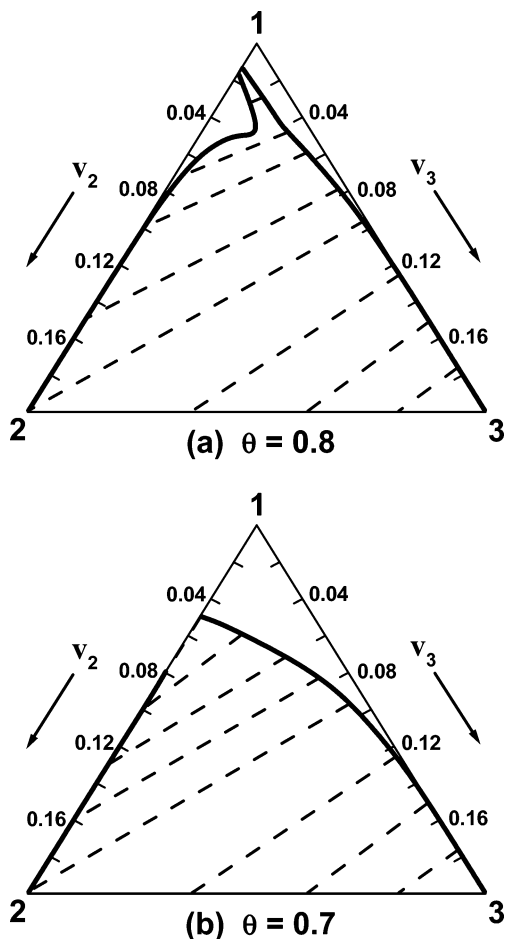

Figure 4. Ternary phase diagrams calculated for $\theta = 0.8$ (a) and $\theta = 0.7$ (b). Invariant parameters used in the calculations are $x_2 = 100$, $x_3 = 100$, $\sigma = 10^{-4}$, $m = 10$, and $\epsilon_0 = 0.265$.

is decreased, suggesting the entrance of the randomly coiled polymer into the anisotropic phase is promoted. The calculations also show that the isotropic–anisotropic phase boundary tends to be narrower with decreasing the x_3 value. As revealed by calculations not included, at given values of x_3 and ϵ_0, an increase in x_2 also renders more random coils enter the anisotropic phase. Simultaneously, the transition region shifts to lower concentrations and becomes narrower.

Figure 6 gives the calculated maximum value fractions of randomly coiled polymers accepted in the anisotropic phase as a function of chain length. Shown in Figure 6a is a plot where v_3'(max) is plotted against x_3 at a given value of x_2 for various ϵ_0. As can be seen, the maximum amount of random coils in the anisotropic phase increases with decreasing x_3. When the external orientational field is present, the curve shifts upward to higher positions, suggesting more random coils enter the anisotropic phase. The effect of the external field tends to be more pronounced as the value of x_3 is decreased. The influence of the variation of x_2 at a given value of x_3 is demonstrated in Figure 6b for various ϵ_0. The v_3'(max) increases gradually with increasing x_2, then followed by a sharp rise. The existence of the external field is shown to accelerate the entrance of the random coils into the anisotropic phase.

The above considerations are readily turned to the binary systems consisting of a polypeptide chain and a randomly coiled polymer by setting $v_1 = 0$ and $v_1' = 0$. The calculation results show that above a critical value
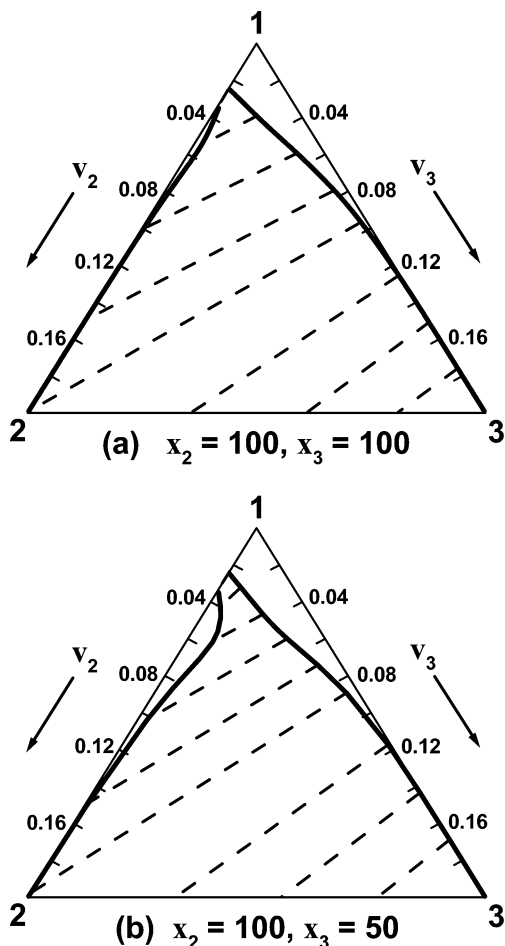
Figure 5. Ternary phase diagrams calculated for $x_2 = 100$, $x_3 = 100$ (a) and $x_2 = 100$, $x_3 = 50$ (b). Invariant parameters used in the calculations are $\epsilon_0 = 0.258$, $\theta = 0.8$, $\sigma = 10^{-4}$, and $m = 10$.

Figure 6. Plots of volume fractions v_3' of randomly coiled polymer accepted in the anisotropic phase as a function of chain length of randomly coiled polymer x_3 (a) and polypeptide x_2 (b) for various ϵ_0 at given values of $x_2 = 100$ and $x_3 = 100$, respectively. Invariant parameters used in the calculations are $\theta = 0.8$, $\sigma = 10^{-4}$, and $m = 10$.

Figure 7. Volume fractions v_3 of randomly coiled polymer in the isotropic phase of biphasic systems plotted against x_2 for various values of ϵ_0 and θ. Invariant parameters used in the calculations are $x_2 = x_3$, $\sigma = 10^{-4}$, and $m = 10$.

of x_2 the binary systems phase separate into an anisotropic phase containing fully helical polypeptides and an isotropic phase. Curves a–d in Figure 7 show v_3 in the isotropic phase of the biphasic systems in equilibrium as a function of x_2 for various values of ϵ_0 and θ. Curves a and b have calculated for $\epsilon_0 = 0.15$ and 0 at a given θ value of 0.8, while the curves c and d are for $\epsilon_0 = 0.15$ and 0 at $\theta = 0.2$. As shown by curves a–d, increase in chain flexibility in the isotropic phase, i.e., decrease in θ value, renders the phase separation take place at larger values of x_2. In the isotropic phase the polypeptide and coiled polymer exhibit some miscibility when x_2 is small. With increasing x_2, the volume fractions of polypeptide ($1 - v_3$) become vanishingly small, indicating the polypeptide component is almost completely excluded from the isotropic phase. When an external orientational field is present, the critical x_2 value for the isotropic–anisotropic phase separation tends to shift toward lower values. Comparison of curves a, b with curves c, d also demonstrates that the external field effect is more pronounced when the θ value becomes smaller.

Figure 8 shows the ratio of v_3' to v_2 in the conjugate isotropic phase for the binary systems corresponding to those shown in Figure 7. As can be seen, the rejection of the random coils from the anisotropic phase is quite severe. When an external orientational field is applied, the ratio of v_3'/v_2 becomes larger, indicating that the random coils are forced into the anisotropic phase. A
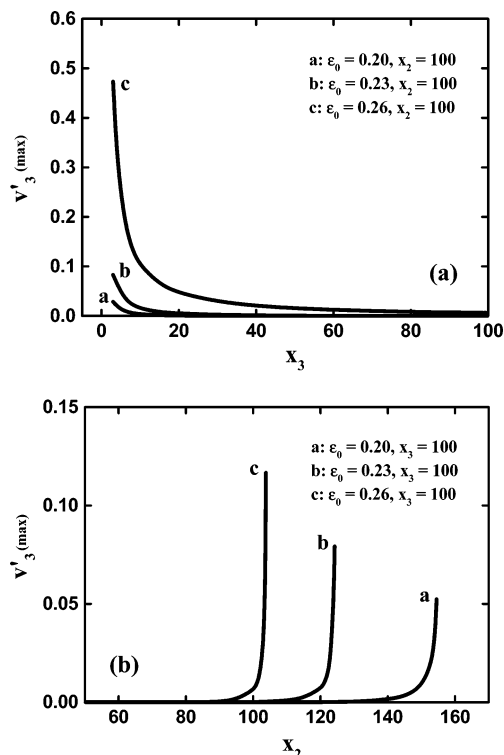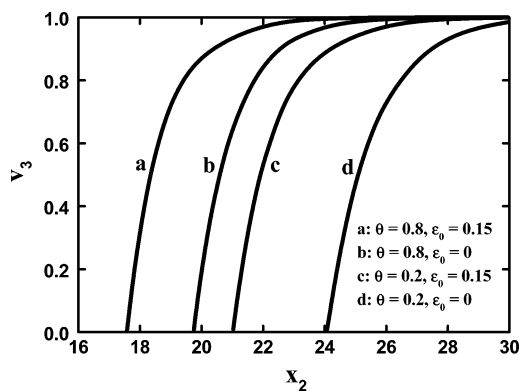
larger external field intensity gives rise to more random coils to enter the anisotropic phase, according to the calculations. It is also found that the external field has a stronger influence on the systems with smaller θ values as comparing curves a, b with curves c, d. However, such an effect is less marked.

Discussion

It appears from the calculations of the present work that the external orientational field exerts a pronounced influence on the properties of the phase equilibria of the ternary systems. It shifts the isotropic–anisotropic phase boundary to lower polymer concentrations and narrows the biphasic gap. The anisotropic phase becomes stable when the external field exists. For both the ternary and binary systems examined, the randomly
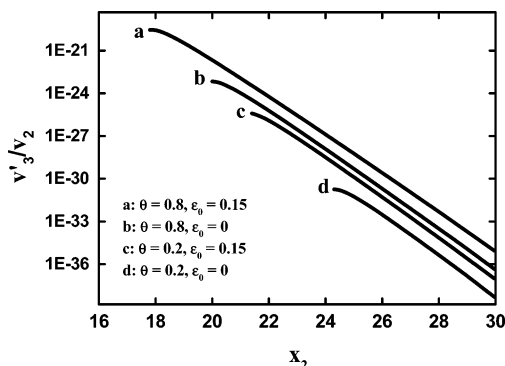
Figure 8. Ratio of volume fractions v_3' to v_2 in the conjugate isotropic phase plotted against x_2 for various values of ϵ_0 and θ. Invariant parameters used in the calculations are similar to those in Figure 7.

coiled chains are forced into the anisotropic phase. The existence of the external field facilitates the coupled transitions of the liquid crystal formation and the coil–helix transformation. The coiled parts of the polypeptide chains are promoted to convert into the helix rigid form and contribute to the overall anisotropy of the liquid crystal. In other words, the conformational ordering effect,[18,19] i.e., intermolecular orientational order promoting intramolecular conformational changes, becomes more pronounced when an external field is present. With respect to the polymer chains having fixed randomly coiled conformation, when they are forced into the anisotropic phase by the external field, the order of the liquid crystal could be perturbed due to the dilution effect, as it can be easily traced through eqs 4–7.

Some experimental evidences are available in the literature, supporting the theoretical results. Toyoshima et al. have examined the effect of external electrical field on the phase behavior of poly(γ-benzyl L-glutamate) dissolved in an organic solvent.[34] It was found that the anisotropic to isotropic transition temperatures increase with increasing the intensity of the applied field, indicating the external field could stabilize the anisotropic phase. Similar results have also been reported in a recent study on the phase behaviors of poly(γ-benzyl L-glutamate)/organic solvent solutions.[35] The presence of the external electrical field was found to shift the isotropic–anisotropic phase boundary to lower polymer concentrations, giving a stabilized anisotropic phase. These experimental systems can be regarded as the case where $v_3 = 0$ and $v_3' = 0$ in the present work. As can be seen from the binary polypeptide–diluent axis in Figure 2, the critical volume fraction for the anisotropic formation shifts to lower value when the intensity of the external field increases. It suggests that the anisotropic phase tends to be stabilized as the external field intensity becomes higher. Such a result is qualitatively in line with the experimental observations as reported. So far, the experimental data available are limited. More observations are being expected for the comparison with the theoretical results.

Since the equilibria of the helix–coil type can serve as a model for the alternating rigid–flexible block copolymers,[21] the conclusions reached through the present analyses should be quite general. Mixed systems comprising rigid and flexible polymers show important applications in fabrication of high-performance composites.[36,37] These kinds of systems are also commonly found in nature, such as connective tissue, vitrous body of the eye, etc.[37,38] Therefore, the elucidation of the phase behavior of the ternary systems involving a rigid-rod polymer and a randomly coiled polymer is of great significance from both a fundamental and an applied point of view. Because of the unfavorable low entropy of mixing of the rigid and flexible polymers, it is usually difficult to process a composite with a fine dispersion of the components in an anisotropic state. Several ways have been suggested to improve the poor miscibility. One is to modify the rodlike polymer by attaching substituents of similar structure to that of the matrix polymer.[11–14] The other is to increase the compatibility through specific intermolecular interactions between the rigid and coiled polymers,[39] such as hydrogen bonding,[40] charge-transfer complex formation,[41] and ion–ion interactions.[42,43] The random coils are also predicted to enter the anisotropic phase, when the orientation-dependent interactions between the molecules are considered. Such an effect could become more pronounced for the systems with larger polarizabilities along their bond axes than perpendicular thereto.[18] The present theoretical calculations show that the anisotropic phase becomes capable of admitting flexible components when an external orientational field is present. The obtained results might provide a useful guidance for processing mixed systems where two polymers could be well dispersed in an anisotropic condition.

As put forth by Flory,[44] the lattice model, despite its artificiality, has proved successful in the treatments of the liquid crystallinity in the polymeric systems.[18,19] The versatility of this theory has permitted its extensions to polydisperse systems,[45,46] mixtures of rodlike polymers with random coils,[1] and some of the many kinds of semirigid chains.[47,48] In our series work, the lattice model is further extended to the treatments of the biopolypeptide systems, such as reentrant transitions in the polypeptides,[20–22] ternary mixtures involving a polypeptide and a random coil,[23] and binary mixtures of a polypeptide and a solvent in the presence of an external orientational field.[30] The subject studied in this work presents another example of the versatility of the lattice theory. After including the free energy arising from the external orientational field into the lattice scheme, the lattice theory provides a reasonable insight for the phase behaviors of the ternary systems containing a polypeptide and a random coil in the presence of the external field.

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