

# Phase Behavior of Ternary Systems Involving a Conformationally Variable Chain and a Randomly Coiled Polymer<sup>1</sup>

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**ABSTRACT:** Ternary systems consisting of a conformationally variable chain capable of assuming either a rodlike helix or a random coil conformation, a randomly coiled polymer, and a solvent were treated according to the lattice model proposed by Flory. The partition function has been derived in consideration of the Flory–Matheson expression related to the free energy contribution from the chain conformation changes. A marked increase of the miscible isotropic zone was predicted when the chain rigidity of the conformationally variable polymer in the isotropic phase is reduced. The conformationally variable chain tends to adopt a rodlike form as long as it enters the anisotropic phase in which the randomly coiled polymer is essentially excluded. The influence of various molecular structure parameters, solvent–polymer interaction, and temperature was also studied.

## Introduction

Phase behavior for ternary systems consisting of a solvent, a rigid rod solute, and a randomly coiled polymer chain was first studied by Flory using the lattice model.<sup>2</sup> The theoretical calculations show that the isotropic phase tolerates an appreciable portion of the rodlike species if the concentration of the random coil is low. Most notable is the fact that the coiled polymer chains are virtually excluded from the anisotropic phase. These predictions have been qualitatively confirmed by the experimental observations.<sup>3–8</sup> For instance, Bianchi et al. have reported experiments on the system involving a rigid polymer, poly(*p*-benzamide) (PBA), a randomly coiled polymer, polyacrylonitrile (PAN), and a diluent that verify the predictions.<sup>4</sup> The anisotropic phase separates at compositions in the range predicted. PAN does not occur in detectable quantities in the anisotropic phase. Similar results have been obtained by Hwang et al.<sup>5</sup> They have determined the phase diagram for the ternary system: methanesulfonic acid/poly(phenylene benzothiazole) (PBT)/poly(2,5(6)-benzimidazole). Molecules of the second component, PBT, approach the ultimate in rodlike rigidity, while the third component is a nonmesogenic random coil. In confirmation of Bianchi et al.'s results and of the theory as well, the random coil component is not detectable in the anisotropic phase. The phase diagram determined bears a close resemblance to that of the theoretical calculations.

However, throughout the early theoretical treatments as carried out by Flory,<sup>2</sup> it has been assumed that the conformation of the mesogenic chains is the same in both the isotropic and anisotropic phase. It is readily apparent that such an assumption of the invariable chain conformation fails if the mesogenic molecules are

able to adopt a variety of chain conformations, some more extended and rodlike than others. The chain conformation changes usually play an important role in the real case, and for sufficiently large macromolecules this effect may be dominant.

With respect to the influence of the chain conformation variation, lattice theory concerning the binary systems has already been developed.<sup>9–11</sup> The binary systems are composed of a solvent and a polymer chain being able to assume either a rigid helix or a random coil conformation. A marked enhancement of the propensity to adopt the rodlike conformation was shown to accompany the formation of the anisotropic phase. The chain conformation changes have an appreciable effect on the isotropic–anisotropic equilibrium in the binary systems. Recently, this theory was adopted to account for the phase behavior and ordering characteristics of polypeptide solution where the polypeptide chain conformation is variable.<sup>12–16</sup> After taking some assumptions, the modified theory provides a reasonable picture for the polypeptide phase behavior, including a low-temperature reentrant zone where the anisotropic phase contains chains that are substantially more rigid than those inhabiting the isotropic phase. The phase diagrams calculated are in satisfactory agreement with the experimental observations. The theory also allows us to predict many phase and conformation characteristics of the polypeptide binary systems that have not yet been observed by the experiments. The early theoretical generalization regarding the ternary systems only associates the behavior of two extremes: perfectly rigid, impenetrable rods and random coils. Therefore, it is of interest to study the role of the chain conformation variation of the mesogenic polymer in determining the phase behavior.

In the present work, ternary systems consisting of a solvent, a conformationally variable chain capable of assuming either a rodlike helix or a random coil conformation, and a randomly coiled polymer were treated according to the Flory lattice scheme and our

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theoretical model proposed in the previous work.<sup>12–16</sup> The conformationally variable chain is exemplified by polypeptide in which each unit is eligible to assume either a helix or a random coil form and in which mobile equilibria between the two states determine the overall chain rigidity. The calculated phase diagrams show that the area of the miscible isotropic phase is enlarged if the chain rigidity of the polypeptide in the isotropic phase is relaxed. The polypeptide molecule transforms into rigid-rod form as long as it enters the anisotropic phase where the randomly coiled polymer is invariably excluded. The influence of various molecular structure parameters was also examined.

### Theory

Free energy expression for mixing of a solvent, a rigid rod solute, and a randomly coiled polymer has been prescribed by Flory.<sup>2</sup> If the mesogenic polymers are able to assume either a rodlike or a random coil conformation such as polypeptides, an extra term related to the free energy change of introducing helical sequence into the polymer molecules should be included in the lattice scheme. According to Flory and Matheson,<sup>9</sup> such a term is given by

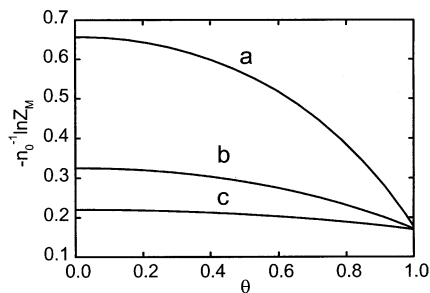
$$-\sum_i mx_i(\theta \ln s + \rho \ln \sigma) \quad (1)$$

where  $x_i$  is the number of segments comprising polymer component differing in chain length,  $s$  and  $\sigma$  denote respectively the statistical weight for a unit in the helical state relative to the coil and the weighting factor for initiation a helical sequence,  $m$  represents the number of repeat units (i.e., peptide residues) in the lattice segment,  $\theta$  is the fraction of units in the helical conformation, and  $\rho$  is the fraction of units that marks the beginning of a helical sequence. For the polypeptide with identical chain length considered in the present work, eq 1 becomes  $-mx_2n_2(\theta \ln s + \rho \ln \sigma)$ , where  $n_2$  is the number of polypeptide consisting of  $x_2$  segments. The parameter  $s$  can be further interpreted as an equilibrium constant for the growing of a helical sequence. Thus,  $s$  is related to the change in free energy for transformation of a residue from the coil state to an existing helical sequence. The free energy change associated with the parameter  $\sigma$  is the free energy required to initiate a helix sequence after a run of random coil sequence. In such interpretations, the term of  $-mx_2n_2(\theta \ln s + \rho \ln \sigma)$  is directly related to the free energy change due to introduction of the helical sequences in the polymer molecules.

After incorporating the above term into the lattice scheme proposed by Flory,<sup>2</sup> the mixing free energy expression for a ternary system involving a conformationally variable chain becomes

$$\begin{aligned} -\ln Z_M = & n_1 \ln v_1 + n_2 \ln v_2 + n_3 \ln v_3 + \\ & \bar{x}n_p(1 - 1/\bar{x}) - n_0[(1 - Q) \ln(1 - Q) + Q] + \\ & \chi\bar{x}(n_p n_1/n_0) - mx_2n_2[\theta(\beta + \ln s) + \rho \ln(\sigma S_0) - \\ & (1 - \theta - \rho) \ln(1 - \theta - \rho) - \rho \ln \rho + \\ & (1 - \theta) \ln(1 - \theta)] \quad (2) \end{aligned}$$

where  $n_1$ ,  $n_2$ , and  $n_3$  are the numbers of solvent, mesogenic solute, and coiled polymer with lengths of 1,  $x_2$ , and  $x_3$ , respectively,  $\bar{x}$  is the number-average value of  $x_2$  and  $x_3$ ,  $v_1$ ,  $v_2$ , and  $v_3$  represent the volume fraction of the corresponding components,  $n_0$  and  $n_p$  equal ( $n_1 +$



**Figure 1.** Reduced free energy per lattice site as a function of the helix fraction  $\theta$  for the systems with  $v_2 = 0.8$ ,  $v_3 = 0.1$  (a);  $v_2 = 0.5$ ,  $v_3 = 0.2$  (b);  $v_2 = 0.3$ ,  $v_3 = 0.3$  (c). Invariant parameters used in the calculations are  $x_2 = 100$ ,  $x_3 = 100$ ,  $\sigma = 10^{-4}$ ,  $\rho = 0$ ,  $s = 1$ ,  $m = 10$ ,  $\beta = 0$ , and  $\chi = 0$ .

$x_2n_2 + x_3n_3$ ) and  $(n_2 + n_3)$ , respectively,  $\chi$  is the solvent–polymer interaction parameter,  $\gamma_\xi$  is the total number of helical sequences with length of  $\xi$ ,  $\gamma_{\xi y}$  is the number of such helical sequence characterized by disorientation parameter  $y$ , and the quantity  $Q$  is given by

$$Q = \theta v_2(1 - y/\xi) \quad (3)$$

and  $S_0$  has been shown to be given by<sup>9</sup>

$$S_0 = \sum \omega_\xi \exp(-\beta\xi) \quad (4)$$

$$\omega_\xi = \prod (\omega_{\xi y} \gamma_\xi / \gamma_{\xi y})^{\gamma_{\xi y} / \gamma_\xi} \quad (5)$$

where  $\beta$  is a Lagrangian multiplier and  $\omega_{\xi y}$  is the a priori probability of disorientation  $y$  for a helical sequence with length of  $\xi$ . For the explicit evaluation of  $Q$  and  $S_0$ , eqs 3 and 4 can be further written as<sup>9</sup>

$$Q = v_2(\theta - \bar{y}m\rho) \quad (6)$$

where  $\bar{y} = y[1 + (1 - ym)/(2S_0)]$  and

$$S_0 = (ym)^2 [\pi^2/6 - \sum_1^{\zeta \leq ym} \zeta^{-2} - 1/(ym)_1] + 2ym \quad (7)$$

respectively. The  $(ym)_1$  is the integer part of  $ym$ .

Analysis of eq 2 shows that the free energy of mixing in the anisotropic state reaches its minimum value at complete helicity for all the conditions examined, suggesting the polypeptide chain takes helical form as long as it exists in the anisotropic phase. Figure 1 shows a typical calculation result where  $-n_0^{-1} \ln Z_M$  is plotted against helix fraction  $\theta$  for various polymer concentrations. In the calculations, the values of  $Q$  and  $S_0$  are determined by eqs 6 and 7. Other parameters used are listed in the caption. As it can be seen, the free energy invariably decreases with  $\theta$ , its minimum value being located at  $\theta = 1$ . It exhibits similar results as that of binary systems containing a conformationally variable chain.<sup>9</sup> The introduction of the randomly coiled chain into the anisotropic system does not change the feature of the dependence of mixing free energy on  $\theta$ ; i.e., the state  $\theta = 1$  is preferred.

In the limit of complete helicity,  $\theta$  may be replaced by 1,  $\rho$  is set equal to  $1/mx_2$ , and also<sup>9</sup>

$$S_0 = (y/x_2)^2 \exp(-\beta mx_2) \quad (8)$$

With these substitutions, eq 2 becomes

$$-\ln Z_M = n_1 \ln v_1 + n_2 \ln v_2 + n_3 \ln v_3 + \bar{x}n_p(1 - 1/\bar{x}) - n_0[(1 - Q) \ln(1 - Q) + Q] + \chi\bar{x}(n_p n_1/n_0) - n_2[\ln(y/x_2)^2 + mx_2 \ln s + \ln \sigma] \quad (9)$$

The mixing free energy in the isotropic phase can be readily written down by setting  $Q = 0$  and also, according to ref 9,

$$S_0 = e^{-\beta}/(1 - e^{-\beta}) \quad (10)$$

$$\beta = -\ln(1 - \rho/\theta) \quad (11)$$

$$s = (1 - \rho/\theta)/[1 - \rho/(1 - \theta)] \quad (12)$$

$$\sigma = \rho^2/(\theta - \rho)(1 - \theta - \rho) \quad (13)$$

Substitution of these conditions in eq 2 yields

$$-\ln Z_M = n_1 \ln v_1 + n_2 \ln v_2 + n_3 \ln v_3 + \bar{x}n_p(1 - 1/\bar{x}) + \chi\bar{x}(n_p n_1/n_0) + mx_2 n_2 \ln[1 - \rho/(1 - \theta)] \quad (14)$$

Taking partial derivatives of  $-\ln Z_M$  for the anisotropic and isotropic phase with respect to  $n_1$ ,  $n_2$ , and  $n_3$ , the chemical potentials of the components in both anisotropic and isotropic phase can be obtained. Using the equilibrium conditions

$$(\mu_i - \mu_i^0)_{\text{aniso}} = (\mu_i - \mu_i^0)_{\text{iso}} \quad (15)$$

where  $\mu$  designates the chemical potentials for each component in the mixture, the equations for equilibrium between an isotropic and anisotropic phase are

$$\ln(v_1'/v_1) + (v_p' - v_p)(1 - 1/\bar{x}) + \chi(v_p'^2 - v_p^2) = \ln(1 - Q) + Q \quad (16)$$

$$(1/x_2) \ln(v_2'/v_2) + (v_p' - v_p)(1 - 1/\bar{x}) + \chi(v_1'^2 - v_1^2) - m \ln s - \ln \sigma/x_2 - m \ln[1 - \rho/(1 - \theta)] = (4/\pi)(f_2/f_1) \ln(1 - Q) + Q + (1/x_2)[\ln f_1 + \alpha(f_2/f_1)] \quad (17)$$

$$(1/x_3) \ln(v_3'/v_3) + (v_p' - v_p)(1 - 1/\bar{x}) + \chi(v_1'^2 - v_1^2) = \ln(1 - Q) + Q \quad (18)$$

where the prime symbol ' is appended to denote the anisotropic phase. Auxiliary relations required for the equilibrium conditions in the individual phase are

$$f_p = \int_0^{\pi/2} \sin^p \Psi \exp(-\alpha \sin \Psi) d\Psi \quad (19)$$

$$\alpha = -(4/\pi)x_2 \ln[1 - v_2'(1 - y/x_2)] \quad (20)$$

$$y = (4/\pi)x_2(f_2/f_1) \quad (21)$$

and  $Q$  of eq 3 becomes

$$Q = v_2'(1 - y/x_2) \quad (22)$$

in the limit of complete helicity.

If a small amount of denaturing component is present in the ternary system, the chain conformation of the polypeptide may change with temperature, e.g., trans-

form from the helix to random coil with decreasing temperature. As stated in our previous work,<sup>13,14</sup> such a conformation variation can be described by a modified Zimm and Bragg model for the helix-coil transition.<sup>18,19</sup> The statistical weight  $s$  of eq 12 can be related to a change in Gibbs free energy  $\Delta G_0$  for the helix formation<sup>18</sup>

$$s = \exp(-\Delta G_0/RT) = \exp(-\Delta H_0/RT + \Delta S_0/R) \quad (23)$$

where  $\Delta G_0$  is broken up into an intrinsic enthalpy and entropy change,  $\Delta H_0$  and  $\Delta S_0$ , respectively. For polypeptides with high molecular weight, the helix fraction  $\theta$  is given by<sup>19</sup>

$$\theta = 1/2 + (s - 1)/2[(1 - s)^2 + 4\sigma s]^{1/2} \quad (24)$$

To properly account for the helix-coil transition in acid-mediated solutions of polypeptides, the factor of  $s$  should be replaced by<sup>19</sup>

$$s_c = s(1 + aK) \quad (25)$$

where  $a$  is the acid activity and  $K$  is the equilibrium constant due to the binding which occurs through hydrogen bonding to exposed amide linkages in the coiled state.  $K$  is written in an expression form<sup>19</sup>

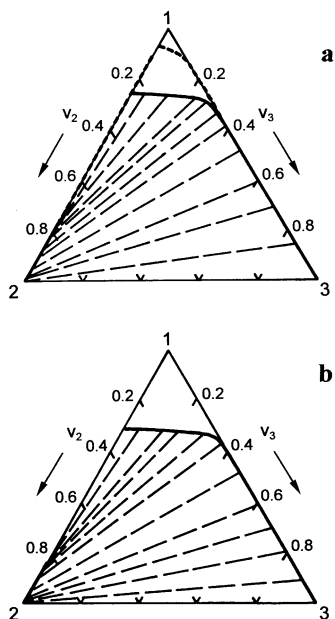
$$K = \exp(-\Delta G_c/RT) = \exp(-\Delta H_c/RT + \Delta S_c/R) \quad (26)$$

where  $\Delta H_c < 0$  and  $\Delta S_c < 0$ . Thus, the polypeptide chains are predicted to take random coil form at both high and low temperatures. For a ternary system containing a small amount of denaturing acid, the parameter  $s$  of eq 12 is replaced by  $s_c$  of eq 25 in the present work.

## Numerical Calculations

The relationships that determine the conditions for stable coexistence of an anisotropic phase involving fully helical rods with an isotropic phase can be obtained by eqs 16–18 with auxiliary relations 19–22. If the presence of a denaturing component is considered, the molecular conformation of the polypeptides in the isotropic phase as manifested by the degree of the helicity  $\theta$  is followed by eqs 23–26. The  $\chi$  parameter in the acid-mediated condition, according to our previous work,<sup>12–14</sup> is considered to be negative and corresponds to a good solvent. It is further assumed to take the form  $A + B/T$  with  $A$  and  $B$  specified as  $-1.667$  and  $352$ .<sup>13</sup>

The phase diagrams calculated for the ternary systems with helix fraction  $\theta = 0.8$  and  $0.5$  are shown in parts a and b of Figure 2, respectively. Other parameters applied in the numerical calculations are indicated in the caption. Binodals for the isotropic and anisotropic phase are heavily lined. The lines joining conjugated phase are lightly dashed. Shown in Figure 2a by the heavily dashed lines are also the binodals for the system with  $\theta = 1$ . It corresponds to the fully rigid rods in a ternary system containing a solvent and a randomly coiled polymer which was originally treated by Flory.<sup>2</sup> As it can be seen, when the chain rigidity of polypeptide in the isotropic phase is relaxed ( $\theta$  changing from 1 to 0.5), the miscible isotropic region is enlarged. Concomitantly with the enlargement of the isotropic phase, the downward slopes of the isotropic binodals become small, suggesting that the incorporation of the random coil component in the isotropic phase tends to have less



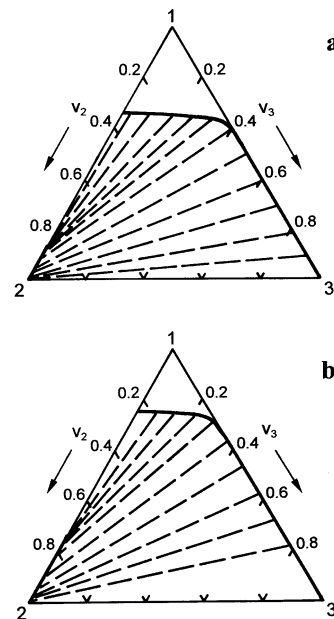
**Figure 2.** Phase diagrams calculated for the ternary systems with  $\theta = 0.8$  (a) and  $\theta = 0.5$  (b). Components are solvent (1), conformationally variable chain (2), and randomly coiled polymer (3). Invariant parameters used in the calculations are  $x_2 = 100$ ,  $x_3 = 100$ ,  $\sigma = 10^{-4}$ ,  $m = 10$ , and  $\chi = 0$ . Shown by heavily dashed lines are the binodals for the system with  $\theta = 1$  according to Flory.<sup>2</sup>

effect on increase in the combined concentration of solutes ( $v_p = v_2 + v_3$ ) in the isotropic phase. The binodal for the anisotropic phase coincides with the binary conformationally variable chain–diluent axis, illustrating the complete exclusion of the randomly coiled polymer from the anisotropic phase. The calculation results show that, with increasing  $\theta$ , the anisotropic phase becomes more severe, excluding the randomly coiled polymers. For instance, at  $v_3 = 0.05$ , the corresponding concentration at conjugated anisotropic phase  $v_3' = 8.8 \times 10^{-6}$  for  $\theta = 1$  and  $1.9 \times 10^{-52}$  for  $\theta = 0.8$ .

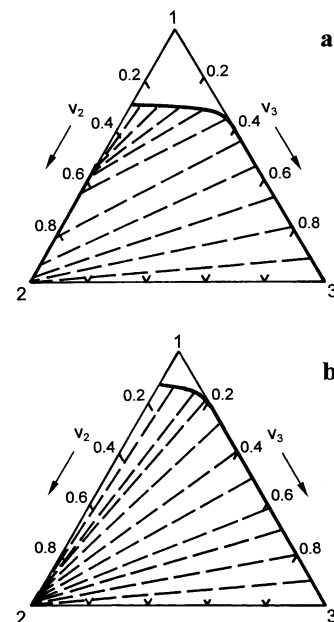
The effect of the parameter  $\sigma$  of polypeptide chain on the phase equilibria is illustrated in Figure 3a,b. The  $\sigma$ , which is variously referred to as a nucleation or cooperativity parameter, is related to the length of the helical sequence, i.e., the smaller  $\sigma$ , the longer the rigid sequence in the polypeptide chain. Two cases are shown for the molecules with  $\sigma$  values of  $10^{-3}$  (Figure 3a) and  $10^{-5}$  (Figure 3b). The phase equilibria calculated for  $\sigma = 10^{-4}$  can be found in Figure 2a. It is seen that, upon increasing the value  $\sigma$ , the phase separation tends to begin at higher overall concentration (larger  $v_p$ ). Simultaneously, the tie lines become longer, suggesting the isotropic–anisotropic phase boundaries are widened.

The role of  $\chi$ , the polymer–solvent interaction parameter, is illustrated in Figure 4a,b. Typical results are shown for  $\chi = -0.2$  (a) and  $0.2$  (b). The value of  $\chi$  has little effect on the phase equilibria if  $\chi < 0$ . On the other hand, as is the case for  $\chi > 0$ , a variation of the  $\chi$  value has a pronounced influence on the phase equilibria for the ternary system. Concomitantly with the decrease in the area of the miscible isotropic region upon increasing  $\chi$ , a significant broadening of the isotropic–anisotropic phase boundary is noted.

The effect of the chain length of both polypeptide chain and randomly coiled polymer on the phase equilibria was also examined. Figure 5a presents the calculations for the ternary system with  $x_2 = 200$ ,  $x_3 =$



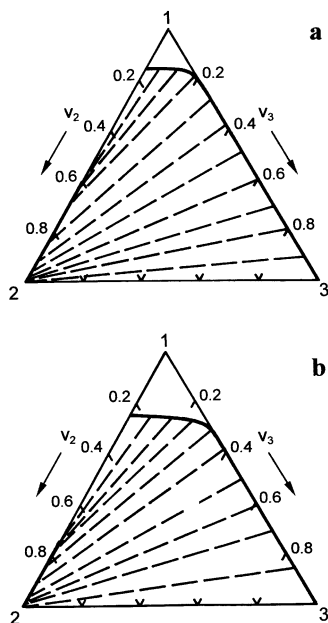
**Figure 3.** Phase diagrams calculated for the ternary systems with  $\sigma = 10^{-3}$  (a) and  $\sigma = 10^{-5}$  (b). Invariant parameters used in the calculations are  $x_2 = 100$ ,  $x_3 = 100$ ,  $\theta = 0.8$ ,  $m = 10$ , and  $\chi = 0$ .



**Figure 4.** Phase diagrams calculated for the ternary systems with  $\chi = -0.2$  (a) and  $\chi = 0.2$  (b). Invariant parameters used in the calculations are  $x_2 = 100$ ,  $x_3 = 100$ ,  $\theta = 0.8$ ,  $\sigma = 10^{-4}$ , and  $m = 10$ .

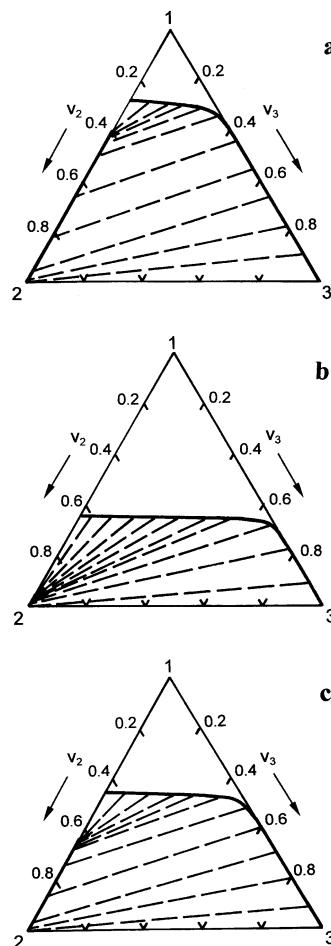
100, while Figure 5b shows the results for the system with  $x_2 = 100$ ,  $x_3 = 50$ . Comparison of the results of Figure 5a with the phase equilibria for  $x_2 = 100$ ,  $x_3 = 100$ , as presented by Figure 2a, shows the effect of the chain length change of the polypeptide. With increasing  $x_2$  value, the biphasic region tends to be narrowed, and the phase separation begins at lower overall concentration ( $v_p$ ). The influence of the chain length of the coiled polymer, however, is less marked as it can be seen from the comparison of Figure 5b and Figure 2a. The binodal for the isotropic phase shifts slightly toward lower position, when the value of  $x_3$  is decreased.

The chain conformation of the polypeptide is maintained in the  $\alpha$ -helix in the solvents that support the



**Figure 5.** Phase diagrams calculated for the ternary systems with  $x_2 = 200$ ,  $x_3 = 100$  (a) and  $x_2 = 100$ ,  $x_3 = 50$  (b). Invariant parameters used in the calculations are:  $\theta = 0.8$ ,  $\sigma = 10^{-4}$ ,  $m = 10$ , and  $\chi = 0$ .

intramolecular hydrogen bond. However, a change in environment, notably the temperature or addition of denaturing acid, may destabilize the  $\alpha$ -helix by disrupting the hydrogen bonding, and the molecules then adopt a flexible random coil conformation. Under such circumstances, the degree of the helicity  $\theta$  was calculated according to eqs 23–26. The calculated value of  $\theta$  is close to 1 at intermediate temperature and becomes small at both low and high temperatures, indicating a helix–coil transition takes place with decreasing and increasing temperature. Shown in Figure 6a is the calculation result for a ternary system where the presence of the denaturing acid is considered. The temperature is at 300 K, the acid activity ( $a$ ) is set to be 0.075 and the  $\theta$  is calculated to be 0.986. The parameters related to the polypeptide structure are taken to be the same values of those adopted in ref 13, which are indicated in the caption. As the temperature is decreased, the acid molecules disrupt the hydrogen bond involved in the polypeptides and a helix–coil transition takes place. Accordingly, the isotropic binodal shifts toward the higher  $v_p$  as shown by a typical result at 245 K in Figure 6b where  $\theta = 0.265$ . Further decreasing temperature results in an entire elimination of the anisotropic phase due to the random coil polypeptide structure being unable to support the anisotropic ordering. On the other hand, upon increasing temperature, the diminishing of the anisotropic–isotropic biphasic area is also calculated, and it is shown in Figure 6c for a result at 350 K ( $\theta = 0.534$ ). The high temperature diminishing is related to the enhanced chain flexibility of polypeptide (the helix structure is maintained) caused by the thermal energy at elevated temperatures. In the present calculations, such a relaxation of the chain rigidity is artificially described by a helix-to-coil transition at higher temperatures according to our previous work.<sup>12,13</sup> Thus, our theoretical model predicts that, in the presence of the denaturing acid, the formed biphasic phase for the ternary system involving a polypeptide and a coiled polymer may transform into pure isotropic state with either an increase or a decrease in temperature, with



**Figure 6.** Phase diagrams calculated for the ternary systems at 300 K (a), 245 K (b), and 350 K (c). Invariant parameters used in the calculations are  $x_2 = 100$ ,  $x_3 = 100$ ,  $\Delta H_0 = -1000$  cal/mol,  $\Delta S_0 = -2.5$  cal/(mol K),  $\Delta H_c = -3000$  cal/mol,  $\Delta S_c = -6.67$  cal/(mol K),  $a = 0.075$ ,  $\sigma = 10^{-4}$ , and  $m = 10$ .

latter the result of the intramolecular helix–coil transition.

## Discussion

The early theoretical model regarding the ternary system as proposed by Flory rests solely on the entropy consideration based on the interference of the random coil with the mutual orientation of the rodlike molecules in the mesophase. 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. The treatment was restricted to the athermal condition.

As further developments of the theory, some extension of the early model to cover more complex situations has been reported. For instance, Ciferri et al.<sup>4,8,20</sup> and Sasaki et al.<sup>6</sup> have analyzed the effect of the interaction parameter  $\chi_{23}$  for the pairs of the mesogenic and coiled polymers. They concluded that if  $\chi_{23} > \chi_{23}^c$  (the critical  $\chi$  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 value of  $\chi_{23}$  could also influence the slope of the tie lines that link the conjugated isotropic and anisotropic phase. A larger positive value of  $\chi_{23}$  gives rise to a reduced inclination of the tie lines. The contribution from the anisotropic interactions to the

phase equilibrium of the ternary systems has been examined by Blonski et al.<sup>17</sup> and Bianchi et al.<sup>21</sup> It has been found that the anisotropic phase becomes acceptable for a certain amount of the flexible component after the orientation-dependent interactions are incorporated into the lattice model.

In the present work, the chain conformation variation, as exemplified by the helix-coil equilibrium in the polypeptide, in the ternary systems is studied. The chain conformation change in the isotropic-anisotropic transitions is an important issue associated with the phase behavior, and it may pertain to semirigid macromolecules in general. The remarkable result of the present studies is that a relaxation of the mesogenic chain rigidity in the isotropic phase renders the binodal of isotropic phase shift toward higher overall polymer concentration.

Some experimental evidence that supports this theoretical prediction is available in the literature. Bianchi et al. investigated the mixtures of poly(*p*-benzamide)/polyacrylonitrile in a common solvent.<sup>4</sup> It was found that the experimental binodal for the isotropic phase is below the theoretical one, indicating that the phase separation begins at higher overall concentration than theoretical expected. The experimental results for the ternary system involving a rigid and a randomly coiled polymer reported by Hwang et al. also show that the phase separation begins at larger overall concentration than calculated.<sup>5</sup> The theoretical calculations carried out in these studies were based on the Flory early generalization for the perfectly rigid specification where the chain conformation change has not been considered. However, in the experimental cases, the formation of the anisotropic phase might involve some chain stiffening of mesogenic polymers. The discrepancy between the experiments and calculations could be attributed to the impact of the free energy penalty associated with the transition of the chain conformation to more rigid form in the anisotropic phase. After considering such an impact in the present work, the shift of the isotropic binodal toward the higher overall concentration is predicted, and a reasonable explanation for the discrepancy has been provided.

The present studies are relevant not only to the thermodynamics of the anisotropic solutions but also to the processing of two polymer systems. From a technological standpoint, there is a great deal of interest in mixed systems including a rigid and a flexible polymer as a way to produce composite materials based on ultrahigh modulus polymers.<sup>22,23</sup> However, it is difficult to get a heterogeneous composite with a fine dispersion of the components due to the limited miscibility of the rigid rods and coiled polymers. The use of block copolymers instead of rigid rods has been shown to be a promising approach toward overcoming this difficulty.<sup>23-25</sup> The equilibria of the helix-coil type are not unlike the case of alternating rigid-flexible block copolymers. Qualitatively, it is not surprising as the

helix-coil sequence can be described in terms of a rigid-flexible sequence. According to the present theoretical analyses, the miscible isotropic areas may be increased if the rigid-rod polymers are replaced by a rigid-flexible block copolymer. The flexible blocks could enter the anisotropic phase and contribute to the overall anisotropy as long as the allowance is made for the chain conformational changes. However, the randomly coiled polymers are severely excluded from the anisotropic phase. These results and considerations should offer useful guidelines for the identification of conditions under which one could prepare technological relevant composites based on a rigid-flexible block copolymer and a coiled polymer.

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