Effect of external field on phase behavior of ternary systems involving polypeptide

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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 is present. Chemical potentials of the components in the isotropic and anisotropic phases were obtained. 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 become narrower when the external field exists. The entrance of the randomly coiled polymers into the anisotropic phase is promoted. Influences of chain conformation of polypeptide, chain length and temperature have been studied in the presence of the external field. The comparison between theory and experimental results was also carried out.

Keywords: lattice theory, polypeptide, external field, phase behavior, chain conformation.

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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\cite{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. These predictions have been qualitatively confirmed by the experimental observations\cite{2–5}. 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, composed of N, N-dimethylacetamide + 3% LiCl that verify the predictions\cite{3}. 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.\cite{4}.

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\cite{6–10}. For example, Ciferri et al.\cite{6,7} and Sasaki et al.\cite{8} have analyzed the effect of the interaction parameter $\chi_{23}$ 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
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Equilibria of the ternary systems has been examined by Blonski et al.\(^9\). 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. Recently, the authors analyzed the effect of the chain conformation variation of the mesogenic polymer on the phase diagrams of the ternary systems involving polypeptide, a random coil polymer and a solvent\(^{10}\). The conformationally variable chain is exemplified by polypeptide in which each unit is able to assume either a helix or a random coil form. Polypeptides have the ability to exist in \(\alpha\)-helix, a well-defined chain conformation of long chain order and retain such a structure in numerous organic solvents that support intramolecular hydrogen bonding. Polypeptide solution can undergo a conformational change from the \(\alpha\)-helix to random coil form due to the changes in solvent composition, temperature or both\(^{11}\). The theoretical treatment on the phase behavior of ternary systems 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\(^{10}\).

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\(^{12-15}\). 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\(^{12}\). 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, Aikawa et al. carried out the influence of the external field on the phase behavior of a binary system involving a mesogenic polymer and a solvent\(^{14}\). Toyoshima et al. studied the phase-transition behavior of lyotropic polypeptide solution when an external field is present\(^{16}\). Yang et al. have first described the phase behaviors of mixtures of flexible polymers and small molecular liquid crystals in an external magnetic field\(^{17}\). It is found that, due to the field-induced ordering, the phase boundaries shift upwards and the anisotropic phase becomes acceptable for a certain amount of the flexible polymers. Recently, on the basis of Flory-Matheson lattice model\(^{18}\), a detailed study on the phase behavior of a binary system involving a conformationally variable polypeptide has been performed by the authors\(^{11, 19-21}\). The effect of the external orientational field on the phase behavior was also carried out. 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\(^{22}\).

Since the phase behavior of the ternary systems involving a conformationally variable polypeptide and the influence of the external field on the binary systems are rather well understood, it is of crucial interest to know the effect of the external field on the phase behavior of the ternary systems. To the best of authors’ knowledge, there are no studies of the phase behavior of ternary systems involving polypeptide, a randomly coiled polymer and a solvent in the presence of an external field reported so far.

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. 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...