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Phase behaviour of rod with flexible side chains/coil/solvent systems: poly(α,l-glutamate) with tri(ethylene glycol) side chains, poly(ethylene glycol), and dimethylformamide

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Phase behaviour is investigated for ternary solutions composed of rodlike α-helical poly(α,L-glutamate) having triethylene glycol monomethyl ether at the end of the side chains (P3EGLG), randomly-coiled poly(ethylene glycol), and N,N-dimethylformamide (DMF) as solvent. The solution containing lower molecular weight poly(ethylene glycol) (PEG10) separates into an isotropic phase, which is rich in PEG10, and an anisotropic (cholesteric) phase, which is rich in P3EGLG, when the total polymer volume fraction is higher than ca 0.13. The homogeneous anisotropic region, in which a detectable amount of PEG10 exists, is recognized along the P3EGLG-DMF axis in the triangle phase diagram. When the molecular weight of poly(ethylene glycol) is larger, additional phase-separation regions are observed: That is, isotropic–isotropic biphasic region and anisotropic–isotropic–isotropic triphasic region. Theoretical treatments based on the lattice model for nematic solutions are conducted for these rod/coil/solvent ternary systems. Calculated phase diagrams with considering flexible side chains of rodlike solute and isotropic interaction parameters are found to qualitatively reproduce the variation of the experimental phase behaviour with the change of the molecular weight of the coiled component. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In 1978, Flory[1] predicted on the basis of a lattice model for ordered nematic solution of rigid rods[2,3] that a ternary solution containing a rodlike polymer and a randomly-coiled polymer would give a wide isotropic–anisotropic coexisting region on its phase diagram. According to this theory, the ternary solution would phase-separate into an isotropic phase mainly containing the coiled solute, and an ordered anisotropic phase which mainly consists of the rodlike component and rejects the coiled molecules with high selectivity. The binodal curve for the latter nematic phase would practically coincide with the axis connecting the vertex of the rodlike solute to that of the solvent. This phase separation is due to the unfavourable entropy of mixing when random coils are immersed in an ordered phase.

Flory's theoretical prediction has been verified by experimental investigations for ternary solutions consisting of a rodlike polymer, a coiled polymer, and a solvent, reported by several researchers[4-12]. Some of these studies also intended to prepare a molecular composite, in which the rodlike polymers were dispersed on molecular level to reinforce the matrix polymer. Cifferi and coworkers investigated phase behaviours of ternary solutions of poly(p-benzamide) (PBA), polyterephthalamide of p-aminobenzhydrazide and N,N-dimethylacetamide (DMAc) containing 3% LiCl[5], and of PBA, polyacrylonitrile and DMAc containing 3% LiCl[6]. The phase diagrams of these

systems suggested strong demixing of the anisotropic and isotropic phases. There have been some reports on the formation of a liquid crystalline phase for rod/coil/solvent ternary solutions[7-10]. Sasaki and Uzawa[11] investigated phase behaviour of a ternary solution comprising poly(γ-benzyl L-glutamate) (PBLG), polystyrene (PS) and benzyl alcohol. The observed phase diagram indicated the presence of a region in which one cholesteric and two isotropic phases coexisted at equilibrium. Similar phase behaviour was also reported recently by DavÉ et al.[12]. They studied compatibility of the system involving flexible and semirigid polysaccharides, and discussed the phase diagrams on the basis of Flory's theory, with the introduction of soft intermolecular force by using familiar interaction parameters.

The theory of Flory was extended to the system comprising a rodlike polymer bearing flexible side chains[13-15]. Ballauff[14,15] introduced the modified orientational distribution function reported by Flory and Ronca[16] in his theory. The results showed that the flexible side chains attached to rigid-rod main chains play a role of solvent. That is, the obtained ternary phase diagrams[15] demonstrated that the flexible side chains markedly enhanced the compatibility of rodlike and coiled polymers in the isotropic phase, and that the region where the coiled polymers form a homogeneous anisotropic mixture with rodlike polymers had a considerable width. There have been no systematic experimental studies that can be compared with the theoretical predictions for roles of the side chains attached to the rodlike component.

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In this work, we study phase behaviours of ternary systems involving a rodlike polymer bearing flexible side chains, a randomly-coiled polymer, and solvent. α-Helical poly(L-glutamate) having triethylene glycol monomethyl ether at the end of the side chains ($[-NH-C^{\alpha}HR-CO-]_n$ with $R = -CH_2CH_2COO(CH_2CH_2O)_3CH_3$; P3EGLG), which was prepared by the ester exchange reaction of PBLG[17], is used as a rodlike component with flexible side chains. For coiled polymers, we use two kinds of poly(ethylene glycol) (PEG) having molecular weights of 10 000 (PEG10) and 110 000 (PEG110), respectively. *N,N*-dimethylformamide (DMF) is adopted as solvent. The similarity of the chemical structure between the side chains of P3EGLG and PEG is expected to decrease the repulsive interaction between rodlike and flexible polymers, and to enhance the compatibility of these components. The obtained phase diagrams for these two systems, P3EGLG/PEG10/DMF and P3EGLG/PEG110/DMF, are compared with those theoretically calculated by the lattice model.

EXPERIMENTAL

PBLG sample was synthesized by the *N*-carboxyanhydride method in 1,4-dioxane with triethylamine as initiator, and fractionally precipitated from dichloromethane/methanol solution. The molecular weight was estimated to be about 128 000 from the intrinsic viscosity measurement in dichloroacetic acid at 25°C and the Mark–Howink–Sakurada relation reported by Doty *et al.*[18]. P3EGLG was prepared by transesterification of PBLG with triethylene glycol monomethyl ether in 1,2-dichloroethane with *p*-toluenesulfonic acid as catalyst at 60°C for 1 week, and precipitated into diethyl ether[19,20]. This process was repeated twice, and the final conversion of ester exchange reaction was 83 mol% determined by ^{1}H nuclear magnetic resonance (n.m.r.) spectrum, and the molecular weight of P3EGLG was determined to be 155 000. Both-end methoxylated PEG10 was prepared by methoxylation of the hydroxy-end groups of the commercially available poly(ethylene glycol) (Aldrich, $M_w = 10000$) with potassium hydroxide and methyl iodide in tetrahydrofuran[21]. The reaction product was fractionally precipitated from octane/methanol solution in order to remove the low-molecular-weight fraction[22]. Commercially available PEG110 (American Polymer Standards Corp., $M_w = 110000$, $M_w/M_n = 1.07$) was used without further purification. Reagent grade DMF was dried over molecular sieves and distilled under vacuum before use.

Weighted amounts of polymers and solvent were mixed

in a calibrated glass tube (3.4 mm inner diameter). The tube was sealed tightly by a Teflon cap, and the mixture was homogenized with stirring at 50°C, and cooled down to be maintained at 25°C for at least 1 day. The initially turbid viscous solution was separated into two or three layers, and the lowermost anisotropic phase was dark under crossed polars. It was centrifuged at about 3000 gravities at 25°C for 4 h in order to separate the isotropic and anisotropic phases completely. The volume of each phase was determined from its column height. A small portion of each layer was carefully picked by a syringe, transferred into a n.m.r. tube, and dissolved in a $CDCl_3/CF_3COOD$ (70/30 v/v) mixture. The compositions of polymers and solvent in each phase were determined by the peak area of n.m.r. spectra for methoxy protons at the end of the side chain of P3EGLG, methylene protons of oxyethylene groups for PEG and side chains of P3EGLG, and aldehyde proton of DMF. The volume fraction of each component was calculated assuming additivity from the corresponding weight fraction by using the specific volumes of 0.755 ml g^{-1} for P3EGLG, 0.814 ml g^{-1} for PEG10 and PEG110, and 1.059 ml g^{-1} for DMF. The probable error in volume fraction of the n.m.r. technique was about 0.004, which was estimated by the measurement of a homogeneously-isotropic ternary solution.

EXPERIMENTAL RESULTS

In *Table 1*, the experimental results of phase separation for the P3EGLG/PEG10/DMF ternary system are summarized. The volume of each phase relative to the total solution volume is denoted by ϕ, and the compositions of P3EGLG and PEG10 expressed in volume fraction are denoted by v_{rod} and v_{coil}, respectively. The values of v_{rod} and v_{coil} are determined by their weights for the original solution, and by the n.m.r. spectra for each separated phase. The concentration of PEG10 was limited below 15% because of crystallization of PEG10 in the upper layer upon standing. All the ternary solutions and binary solution listed in *Table 1* separated into the upper isotropic solution (I) and the lower anisotropic (cholesteric) solution (A). Further phase separations in each layer were not observed. *Figure 1* shows the upper portion (where the volume fraction of solvent, $v_{solvent}$, is higher than 0.5) of the ternary phase diagram constructed from the data in *Table 1*. The compositions of the original solutions are represented by crosses, and those for the I and A phases are represented by open triangles and circles, respectively. Solid curves are binodials for I and A phases estimated from the composition of each separated phase.

Table 1 Phase separation Data for the P3EGLG (rod)/PEG10 (coil)/DMF system at 25°C

Solution number	Original		Isotropic phase			Anisotropic phase		
	v_{rod}	v_{coil}	ϕ	v_{rod}	v_{coil}	ϕ	v_{rod}	v_{coil}
1	0.158		0.15	0.139		0.85	0.160	
2	0.141	0.013	0.63	0.118	0.020	0.37	0.151	0.009
3	0.103	0.049	0.74	0.072	0.057	0.26	0.187	0.009
4	0.121	0.050	0.60	0.050	0.083	0.40	0.193	0.012
5	0.107	0.058	0.64	0.044	0.088	0.36	0.196	0.012
6	0.129	0.060	0.51	0.029	0.110	0.49	0.221	0.010
7	0.202	0.005	0.00			1.00		

ϕ, volume of each separated phases relative to the total solution volume
v_{rod}, volume fraction of P3EGLG
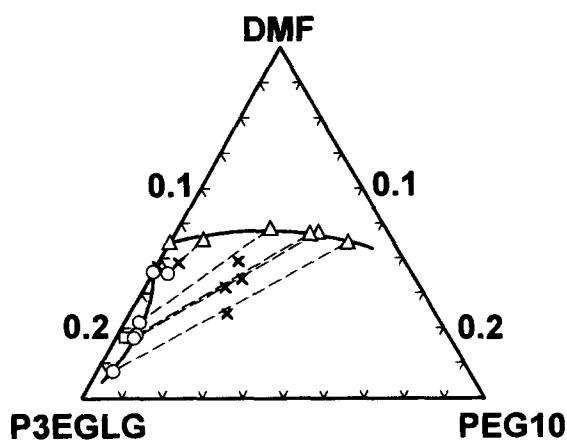v_{coil}, volume fraction of PEG10

DMF

Figure 1 Experimental ternary phase diagram of P3EGLG/PEG10/DMF system. Crosses, circles, triangles, and squares represent compositions of overall mixtures, separated anisotropic phases, separated isotropic phases, and homogeneous anisotropic phase, respectively. Thick solid lines are coexistence curves of anisotropic and isotropic phases, and thin dashed lines are tie lines

anisotropic phase (A), the middle isotropic 2 phase (I2), and the uppermost isotropic 1 phase (I1). The coiled chain is strongly excluded from A and I2 phases but mainly exists in I1 phase, and the value of v_{coil} in I2 phase is evidently larger than that in A phase. The compositions of these three phases are nearly independent of the solution for the three solutions (number 4, 5, and 6). More dilute solutions (number 7 and 8) separated into two isotropic phases. The lower isotropic 2 phase (I2) contains more rodlike component than the upper 1 phase (I1). In the case of the most dilute solution (number 9), we cannot find any phase boundaries after the centrifugation. However, the compositions of the small portions of the solution at the top and bottom of the sample tube are not the same as seen in the last row of *Table 2*.

These data for the P3EGLG/PEG110/DMF ternary system in *Table 2* are plotted in *Figure 2*. In this phase diagram, the compositions of the original solutions, and the separated I1, I2, and A phases are represented by crosses, triangles, squares, and circles, respectively. Smaller symbols in *Figure 2* denote the compositions for the

Table 2 Phase separation data for the P3EGLG (rod)/PEG110 (coil)/DMF system at 25°C

Solution number	Original		Isotropic 1 phase			Isotropic 2 phase			Anisotropic phase		
	V_{rod}	V_{coil}	ϕ	V_{rod}	V_{coil}	ϕ	V_{rod}	V_{coil}	ϕ	V_{rod}	V_{coil}
1	0.125	0.030	0.33	0.015	0.088	–	–	–	0.67	0.172	0.001
2	0.125	0.050	0.44	0.010	0.113	–	–	–	0.56	0.207	0.002
3	0.149	0.049	0.42	0.012	0.121	–	–	–	0.58	0.252	0.001
4	0.128	0.018	0.22	0.018	0.087	0.21	0.132	0.007	0.57	0.150	0.003
5	0.130	0.010	0.10	0.019	0.069	0.62	0.128	0.004	0.28	0.154	0.001
6	0.089	0.030	0.38	0.017	0.068	0.55	0.125	0.006	0.07	0.152	0.004
7	0.075	0.030	0.42	0.019	0.061	0.58	0.103	0.010	–	–	–
8	0.056	0.030	0.54	0.021	0.046	0.46	0.085	0.013	–	–	–
9	0.044	0.024	–	0.022	0.032	–	0.055	0.018	–	–	–

ϕ, volume of each separated phases relative to the total solution volume
v_{rod}, volume fraction of P3EGLG
v_{coil}, volume fraction of PEG110

The broken lines are tie lines which connect the corresponding pairs of triangle and circle.

As shown in *Figure 1*, the binodial for the anisotropic solution is located away from the P3EGLG-DMF axis. This means that there is a homogeneous anisotropic region observable in the rod/coil/solvent ternary phase diagram. The solution of number 7 in *Table 1*, which contains a considerable amount of the coiled PEG10, is confirmed to form a homogeneous anisotropic mixture and represented by the square in *Figure 1*. Such a region has not been clearly reported experimentally for other rodlike polymer/coiled polymer/solvent ternary systems.

Table 2 shows the results of the phase separation experiment for the system of P3EGLG/PEG110/DMF, which contains higher molecular weight poly(ethylene glycol) than PEG10 as a coiled component. As seen in the first, second, and third rows in *Table 2*, the concentrated solutions separate into lower anisotropic phase (A) and upper isotropic 1 phase (I1). However, the miscibility of the rodlike and coiled component is markedly depressed by the increase of the chain length of coil, as suggested by the values of v_{rod} in the isotropic phase and v_{coil} in the anisotropic phase lower than those of the P3EGLG/PEG10/DMF system in *Table 1*. The solutions of number 4, 5, and 6 separate into three phases, i.e. the lowest

triphasic-separated solutions, and estimated triphase-coexisting region is indicated by a hatched triangle. Pairs of symbols for biphasic solutions are connected by thin broken tie lines, and thick solid lines are binodials.

From the phase diagrams in *Figures 1 and 2*, we can summarize the variation of the phase behaviour of P3EGLG / PEG / DMF systems caused by the change of the molecular weight of the coiled PEG as follows.

(1) For the biphasic region in which the solution separates into isotropic and anisotropic phases, the difference in composition of rod and coil components between two phases is larger in the system containing higher molecular weight PEG, i.e. the binodials for A and I1 phases in *Figure 2* are closer to the DMF-P3EGLG and DMF-PEG110 axis, respectively, than those in *Figure 1*.

(2) The homogeneous anisotropic region located along the DMF-P3EGLG axis is detectable in the phase diagram of P3EGLG/PEG10/DMF, but is too narrow to confirm in the phase diagram of P3EGLG/PEG110/DMF.

(3) I1-I2 biphasic separation occurs in P3EGLG/PEG110/DMF. In this region, PEG110 enters mainly into I1, and tends to be excluded from the I2 phase. Tie lines in this region have a similar inclination to those in the A-I1 region.
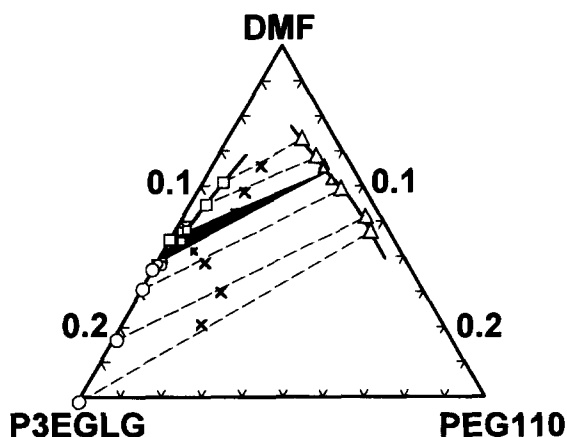
Figure 2 Experimental ternary phase diagram of P3EGLG/PEG110/DMF system. Crosses, circles, triangles, and squares represent compositions of overall mixtures, separated anisotropic phases, separated isotropic 1 phases, and isotropic 2 phases, respectively. The thick solid lines are coexistence curves of anisotropic and isotropic phases, and the thin dashed lines are tie lines. The smaller symbols indicate the composition for triphasic solution. The hatched triangle represents the triphasic region

(4) A-I1-I2 triphase-coexisting region is recognized for P3EGLG/PEG110/DMF below the I1-I2 and above the A-I1 regions, as seen in *Figure 2*. The small open squares in *Figure 2*, which represent the composition of I2 phase for three-phases-equilibrium solution, are located away from the DMF-P3EGLG axis.

THEORETICAL CONSIDERATIONS BASED ON THE LATTICE MODEL

Theoretical phase diagrams of ternary rod/coil/solvent systems are calculated according to Flory's lattice model[1], with considering the modified orientational distribution function reported by Flory and Ronca[16]. In this model, the system contains rigid-rod particles with axial ratio x_r, random coil polymers consisting of x_c segments, and solvent. The diameter of the rodlike chain is taken to be unity. The size of the segment of the coiled component as well as the diameter of the solvent molecule is taken to be equal to the size of a segment of the rodlike backbone part. First, we tried to calculate the phase diagrams without considering the presence of the flexible side chains for the rodlike particle, although the rodlike P3EGLG molecules have flexible oligo(ethyleneglycol) side chains. The free energy of mixing can be expressed as follows.

$$- \ln Z_M = - (n_0 - n_x x_r)\ln[1 - v_x(1 - \bar{y}/x_r)] + n_1 \ln v_1$$

$$+ n_x \ln(v_x/x_r) + n_c \ln(v_c/x_c) + n_x(\bar{y} - 1)$$

$$+ n_c(x_c - 1) - n_x \ln(\sigma f_1) \qquad (1)$$

where n_0 is the total number of the lattice sites, and n_x, n_c, and n_1 are the number of rigid rods, random coils, and solvent molecules, respectively. The quantities $v_x = n_x x_r/n_0$, $v_c = n_c x_c/n_0$, and $v_1 = n_1/n_0$ denote the volume fractions of the rod, coil, and solvent, respectively. Parameter $\bar{y}$ is the averaged value of disorder index, $y = (4/\pi)x_r \sin\psi$, of the rodlike main chain, and ψ is the angle of inclination towards the domain axis; σ is a constant, and f_1 is expressed by

$$f_1 = \int_0^{\pi/2} \sin\psi \exp\{-(4/\pi)a x_r \sin\psi\} d\psi$$

where $a = -\ln[1 - v_x(1 - \bar{y}/x_r)]$. From the chemical

potentials derived from equation (1), the volume fraction of the polymer in the coexisting isotropic and anisotropic phases can be obtained. When the system has an anisotropic–isotropic triphasic region, the points for the compositions of coexisting three phases for this region are determined as the intersection of respective binodals for two-phase regions.

The X-ray diffraction pattern of bulk P3EGLG at room temperature gives sharp peaks which correspond to Bragg spacings of 13.9, 9.80, and 6.92 Å. From these values, interchain distance between the neighbouring rods in the hexagonal unit cell is obtained as 16.0 Å. Since the segment number of side chain is assumed to be zero, a dimension of one segment is obtained as $d = (\sqrt{3}/2 \times 16.0^2)^{1/2} = 14.9$ Å. In this case, the volume of one segment becomes 3310 Å^3. The contour length of P3EGLG was calculated from the unit height (1.5 Å) of α-helical polypeptide along its helix axis. Then, the axial ratio, x_r, of P3EGLG, and the segment numbers, x_c, of PEG10 and PEG110 can be deduced from their molecular volume: $x_r = 59$, $x_c = 4$ for PEG10 and $x_c = 41$ for PEG110.

The experimentally-observed three-phases-coexisting region in *Figure 2* cannot be reproduced by the theory with assuming athermal solution, i.e. the net exchange energy of the mixing process is zero. The phase behaviour in P3EGLG/PEG110/DMF is considered to arise from the immiscibility of rodlike and coiled components, as pointed out by Sasaki *et al.*[11] The interaction parameter, χ_{rc}, is introduced for the interaction between the segments of rodlike and coiled components. The heat of mixing is taken to be proportional to the number of segments of one type and the volume fraction of the other species even in the anisotropic phase. Upper portion ($v_{solvent} > 0.5$) of calculated phase diagrams with $\chi_{rc} = 0.5$ are shown in *Figure 3*. When the segment number of coiled component is small (*Figure 3a*), the anisotropic–isotropic (A–I) phase separation occurs at relatively high polymer concentration, and then only the A–I region can be confirmed. Because of its small segment number, some coiled components can exist in the anisotropic phase, and we can recognize the area of homogeneous anisotropic phase near the solvent-rod axis, as shown in *Figure 3a*. In *Figure 3b*, isotropic–isotropic (I–I) and anisotropic–isotropic–isotropic (A–I–I) regions can be recognized in the system containing the longer coiled component. These changes of phase behaviour with a change of length of the coiled component are consistent with the experimental results.

Although the molecular weights of P3EGLG and PEG110 are similar to each other, the solvent concentration of P3EGLG-rich isotropic phase is lower than that of PEG110-rich isotropic phase as indicated by inclination of the tie lines in I–I region against the rod–coil axis in the phase diagram of P3EGLG/PEG110/DMF (*Figure 2*). Calculations of the phase diagram with considering the difference in miscibility with solvent between the rodlike and coiled component are also performed by including interaction parameter, χ_{rs}, between the rodlike solute and solvent, and the interaction between the coil and solvent is assumed to be zero. There is only small change in the phase diagram when χ_{rs} is small. However, when the value of $\chi_{rs} = 0.2$, the system strongly separates into isotropic and anisotropic phases which mainly contain coil and rod, respectively, as shown in *Figure 4*. As reported by Flory[2], the increase of χ parameter induces the distinct broadening of A–I biphasic region in the rod–solvent binary phase diagram. Such phase behaviour in the binary solution also dominates the phase diagram of ternary systems.
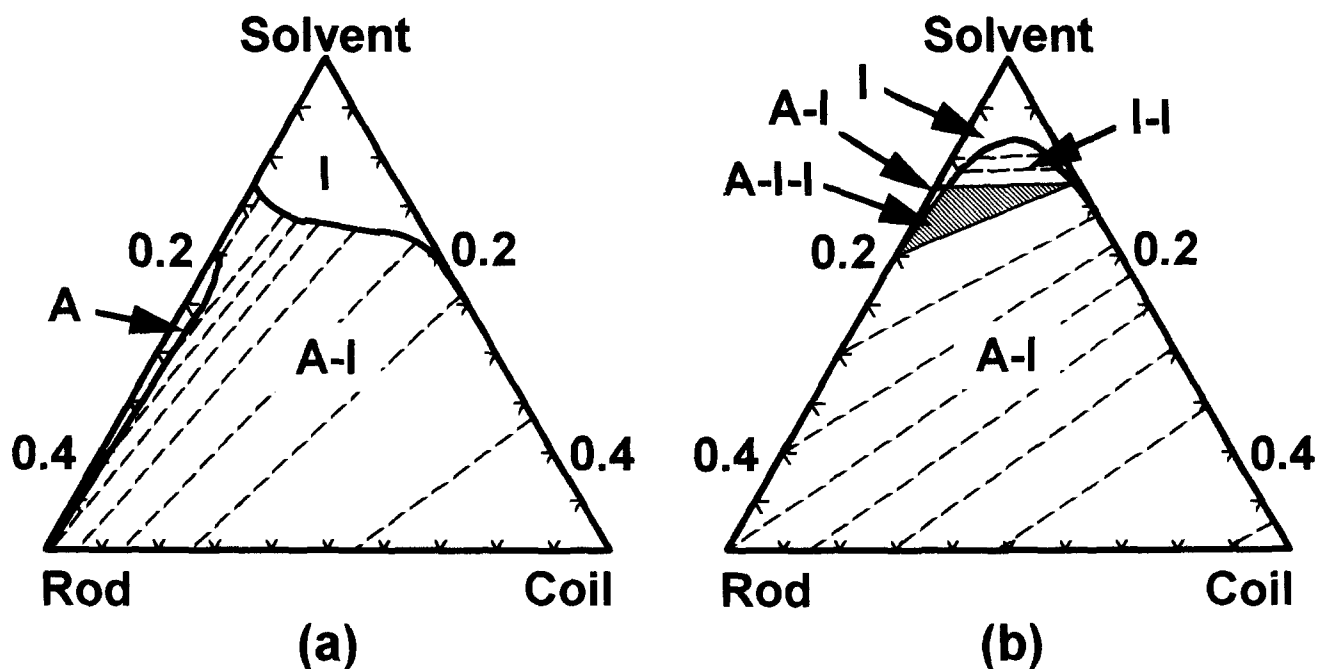
Figure 3 Theoretical phase diagrams of rod/coil/solvent systems according to the lattice model: $x_r = 59$; $\chi_{rc} = 0.5$; and (a) $x_c = 4$; and (b) $x_c = 41$. A and I represent the anisotropic and isotropic phase, respectively. The thick solid lines and thin dashed lines are coexistence curves and tie lines, respectively. The hatched triangle represents the triphasic region
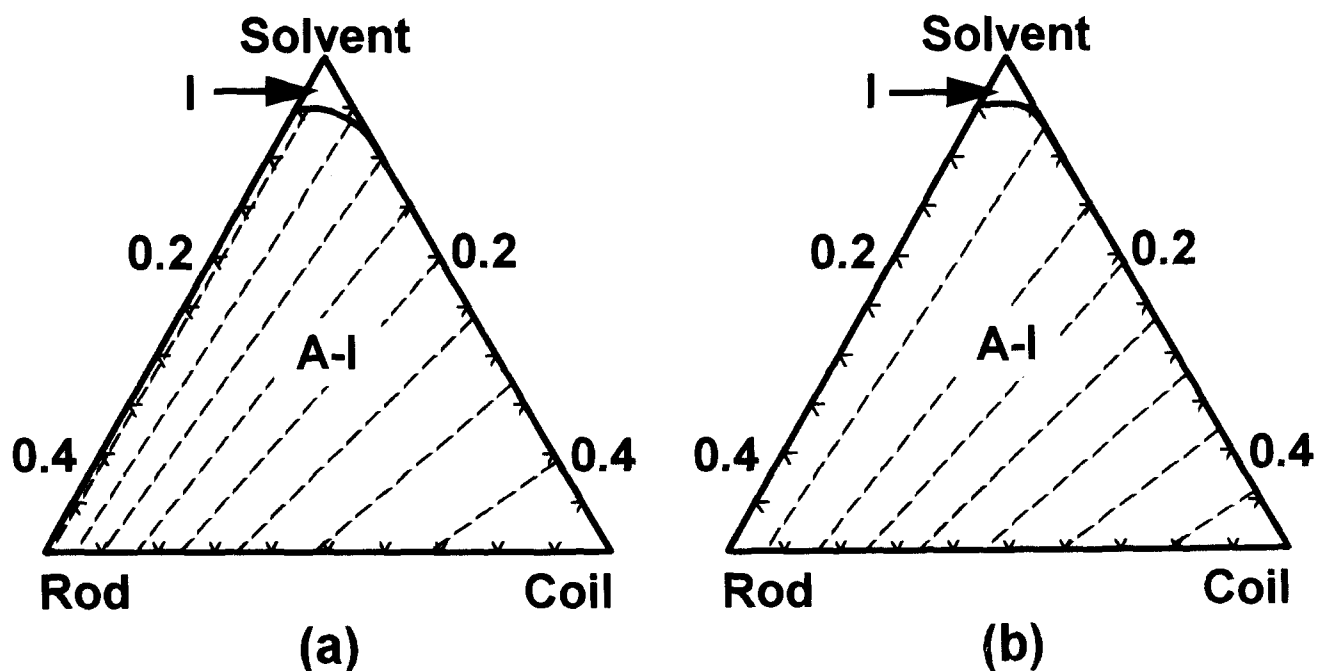

Figure 4 Theoretical phase diagrams of rod/coil/solvent systems according to the lattice model: $x_r = 59$; $\chi_{rc} = 0.5$; $\chi_{rs} = 0.2$; and (a) $x_c = 4$; and (b) $x_c = 41$. See legend to *Figure 3*

Theoretical extension for nematic solution of rodlike particles bearing flexible side chains was reported by Ballauff[14]. The results showed that the flexible side chains act like solvent. This model was applied to the ternary system which contains a rigid rod with flexible side chains, random coils, and solvent[15]. The obtained ternary phase diagrams indicated that the presence of the flexible side chains markedly enhanced the miscibility of rodlike and coiled polymers in the isotropic phase, and the region where the coiled polymers form a homogeneous anisotropic mixture with rodlike polymers is of considerable width. His theory assumes that the flexible side chain takes

randomly-coiled conformation although there exists the orientational order of rodlike part. As pointed out from the ^{2}H n.m.r. analysis by Poliks et al.[19], orientation of the terminal O–CH$_3$ bond in oligo(oxyethylene) side chains of P3EGLG is weakly correlated to the orientation of the main chain in the liquid crystalline state. We evaluated phase diagrams of the ternary solution, considering the flexible side chains in rodlike component in order to compare with the experimental results in *Figures 1 and 2*. In this model, the system contains rigid-rod particles of axial ratio x_r bearing z side chains with each of them having m segments, random coil polymers consisting of x_c segments, and

solvent. The size of segments of the side chains, as well as those of the coils and solvent molecules, is taken to be equal to the size of a segment of the rodlike backbone part. As derived in ref. [15], the free energy of mixing for this system can be evaluated as follows.

$$- \ln Z_M = - (n_0 - n_x x_r) \ln[1 - v_x(1 - \bar{y}/x_r)] + n_1 \ln v_1$$

$$+ n_x \ln(v_x/x_r) + n_c \ln(v_c/x_c) + n_x(\bar{y} - 1 + zm)$$

$$+ n_c(x_c - 1) - n_x \ln(\sigma f_1)$$

$$+ \chi_{rc}(n_c x_c + n_x zm)v_x + \chi_{rs} n_1 v_x \qquad (2)$$

In order to consider the interaction between solute molecules as mentioned previously, the last two terms containing χ_{rc} and χ_{rs} are incorporated. The total number of lattice sites, n_0, is expressed as $n_x(x_r + zm) + n_c x_c + n_1$. The rodlike solute, P3EGLG, has to be separated into two parts, i.e. rodlike backbone and flexible side chains, in order to compare the theoretical phase diagrams with the real systems. If the rodlike part is assumed to have an identical diameter (12 Å) with α-helical poly(γ-methyl L-glutamate) (PMLG)[23], the volume of one segment becomes 1390 Å^3, and the remaining triethylene glycol chains are treated as flexible side chains. Therefore, the axial ratio x_r and the total segment numbers of side chain zm of P3EGLG are obtained as 78 and 61, respectively. The segment number of a coiled chain is calculated as $x_c = 10$ for PEG10 and $x_c = 97$ for PEG110.

The existence of flexible side chains strongly enhanced the miscibility between rods and coils, especially in the system that contains the shorter coiled component. The experimentally-observed A–I–I triphasic region was not found in the theoretical prediction for the athermal solution, but was recognized in that calculated by introducing the interaction parameter, χ_{rc}, between rod and coil, which is similar to the case of the systems of rod without side chain. Calculated phase diagrams with using $\chi_{rc} = 0.5$ are presented in *Figure 5*. As shown in *Figure 5a*, the

isotropic–anisotropic biphasic region near the rod–solvent axis is very narrow because the segment number of the coiled polymer is fairly small compared with that of the flexible side chains of the rodlike polymer. In the system containing longer coils with $x_c = 97$ (*Figure 5b*), there are regions of I–I, A–I, and A–I–I, and the tie lines in I–I and A–I regions are nearly parallel to the rod–coil axis.

Inclination of the tie lines against the bottom axis for the system of $x_c = 97$, and expansion of the A–I biphasic region for that of $x_c = 10$ can be achieved by introducing a somewhat large interaction parameter between rod and solvent, i.e. $\chi_{rs} = 1.0$. Upper portions ($v_{solvent} > 0.5$) of resulting phase diagrams are presented in *Figure 6*. In *Figure 6c* and *6d*, the experimental data of phase separation are plotted in the same concentration region of *Figure 6a* and *b*. Comparisons of *Figure 6a* with *Figure 6c*, and *Figure 6b* with *Figure 6d* indicate that the theoretical phase diagram, with considering the flexible side chains and interaction parameter χ_{rc} and χ_{rs}, can qualitatively reproduce the experimental results (1)–(4) summarized at the end of Section 3.

DISCUSSION

In the calculation of phase diagrams in *Figure 6*, we used relatively large values of interaction parameter between rod and coil as $\chi_{rc} = 0.5$, and between rod and solvent as $\chi_{rs} = 1.0$. In the lattice model for nematic solution, the diameter of the rodlike component is defined as unity, so that the size of one segment becomes larger than that of the usual randomly-coiled polymer. Then, these χ values correspond to those per the volume of 1390 Å^3 as mentioned in the preceding section. Taking the reference volume of one segment as 100 cm^3/mol ($= 166$ Å^3 per segment), the above χ values correspond to $\chi_{rc} = 0.06$ and $\chi_{sr} = 0.12$. These values of χ may be consistent with those calculated from solubility parameters δ of PMLG and PEG ($\delta = 11.2$ and 10.6 (cal cm^{-3})$^{1/2}$, respectively, obtained by
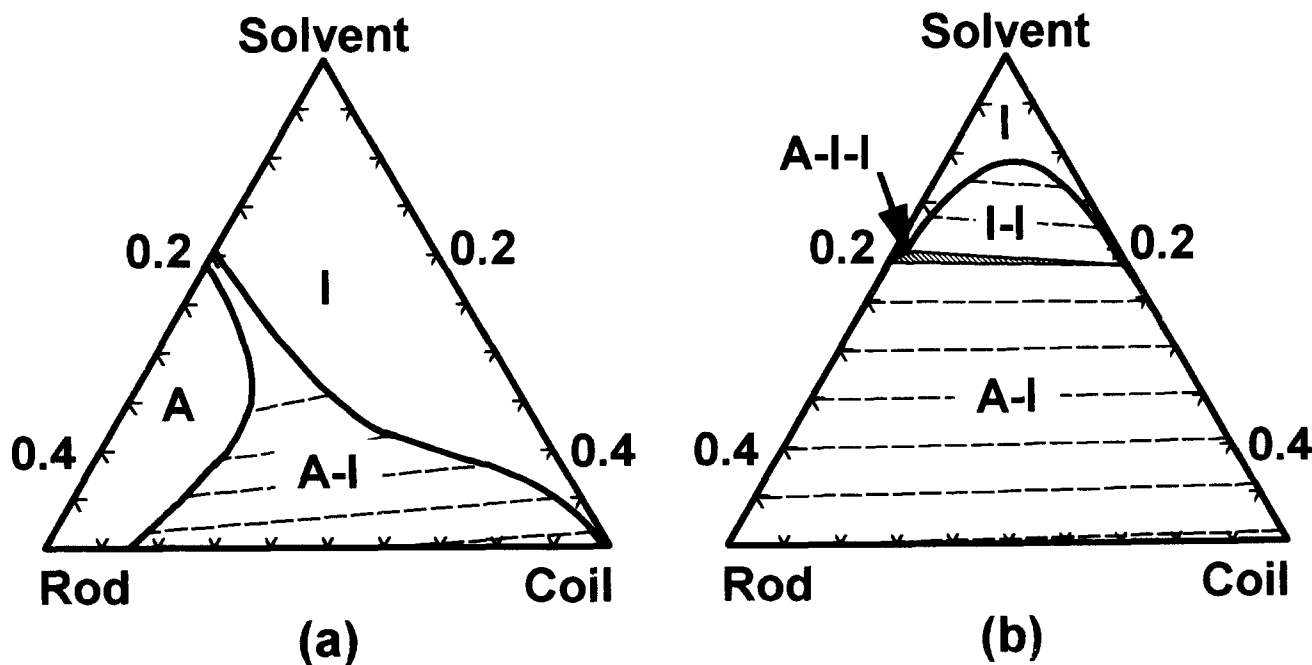

Figure 5 Theoretical phase diagrams of rod with side chains/coil/solvent systems according to the lattice model: $x_r = 78$; $zm = 61$; $\chi_{rc} = 0.5$; and (a) $x_c = 10$; and (b) $x_c = 97$. See legend to *Figure 3*
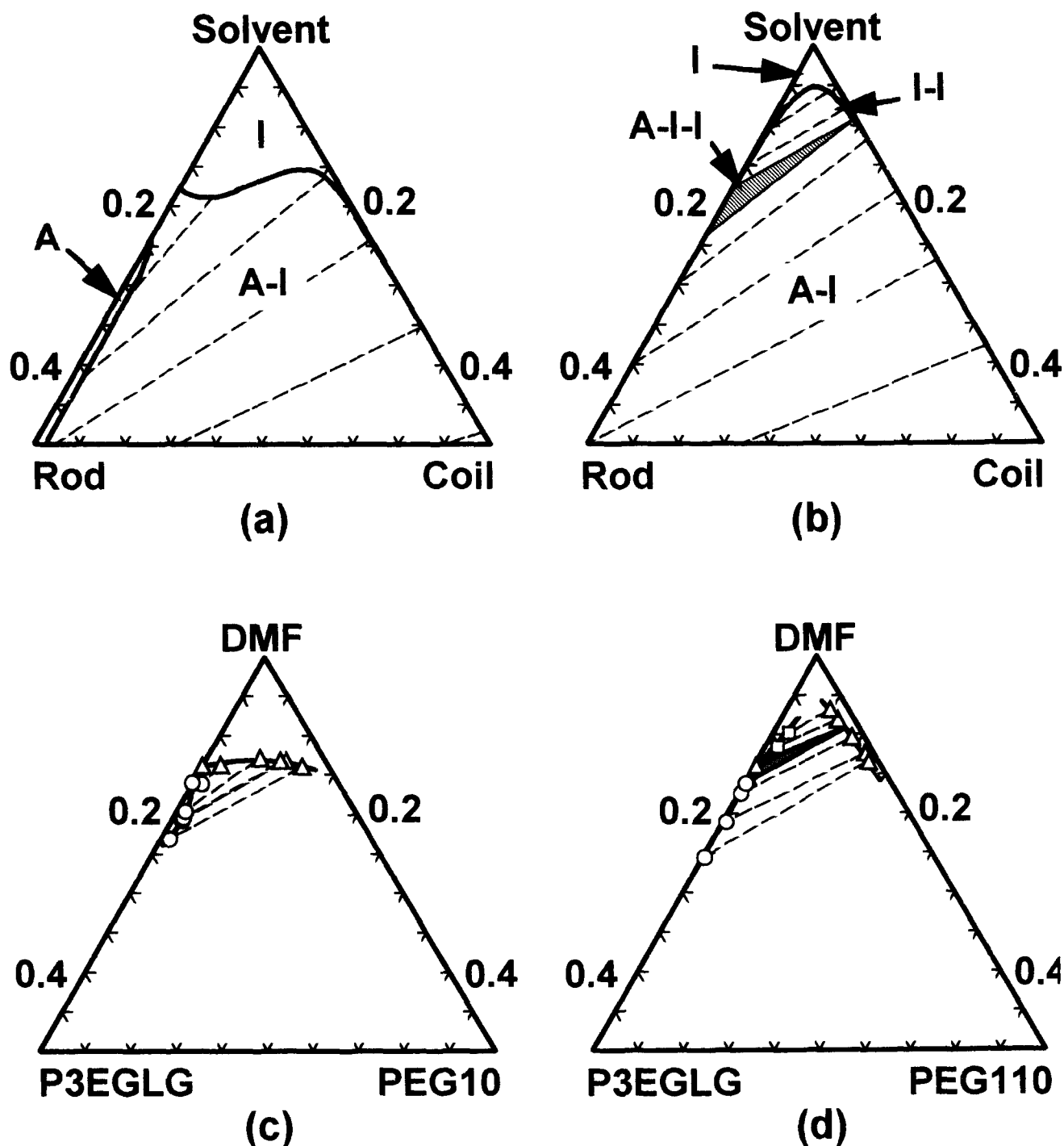
Figure 6 Comparison of experimental and theoretical ternary phase diagrams: (a) and (b) are calculated according to the lattice model by using: $x_r = 78$; $zm = 61$; $\chi_{rc} = 0.5$; $\chi_{rs} = 1.0$; and (a) $x_c = 10$; and (b) $x_c = 97$. (c) and (d) are experimental results of (c) P3EGLG/PEG10/DMF and (d) P3EGLG/PEG110/DMF (see *Figures 1 and 2*). Circles, triangles, and squares represent the composition of separated anisotropic, isotropic 1, and isotropic 2 phases, respectively. See legend to *Figure 3*

group-contribution method of constituent atomic group), and DMF ($\delta = 12.1$ (cal cm^{-3})$^{1/2}$)^{24}.

The A–I–I triphasic region is recognized in the phase diagram of P3EGLG/PEG110/DMF. Although the volume fraction of PEG110 in the isotropic P3EGLG-rich phase (I2) is small ($v_{coil} = 0.004-0.007$ as shown in *Table 2*), its value is certainly larger than that of anisotropic phase ($v_{coil} = 0.001-0.004$). As the result, the composition of I2 phase is located away from the rod–solvent axis, as shown in *Figure 2*. The theoretical phase diagram also predicts such phase behaviour, which is clearly shown in *Figure 3b*. This indicates that there should exist another A–I biphasic region

near the rod–solvent axis. In this region, the solution will separate into isotropic and anisotropic phase, and both phases are rich in P3EGLG. However, we cannot confirm the presence of such a biphasic region because this region is too narrow to prepare the ternary solution of an expected composition.

In the theoretical calculations of phase diagrams based on the lattice model, we considered the existence of side chains attached to the rodlike backbone, i.e. one rodlike polymer having m side chains, and each of them has z segments. *Figures 3–6* suggest that the experimentally-obtained phase diagrams are reproduced more reasonably by inclusion of

side chains' contribution in the calculation of free energy. However, in the theory, the contribution of the flexible side chain is introduced as the total number of segments in a rodlike polymer, zm. Phase-separation experiments for the rodlike poly(α,L-glutamate)s, which have longer oligo- or poly(ethylene glycol) side chains with various contents, are in progress.

CONCLUSION

Phase behaviour has been investigated for ternary solutions of rodlike poly(α,L-glutamate) having flexible oligo(ethylene glycol) side chains, randomly-coiled PEG in DMF. When the molecular weight of PEG coiled chains is low, a homogeneous anisotropic phase in the phase-separated solution is demonstrated to contain an appreciable amount of PEG coiled chains. On the other hand, the solution containing higher molecular weight PEG has an isotropic–isotropic biphasic region and an anisotropic–isotropic–isotropic triphasic region as well as the anisotropic–isotropic region. Theoretical calculations based on the lattice model for nematic solution, with considering flexible side chains of rod-like solute and isotropic interaction parameters, are found to qualitatively reproduce these variations of the experimental phase behaviour with the change of the molecular weight of coiled component.

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