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Properties

Phase Behavior of Poly(γ-Benzyl L-Glutamate) Solutions in Benzyl Alcohol

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SUMMARY

Poly(γ-benzyl L-glutamate) (PBLG) exists in the rodlike α-helical conformation and forms a thermoreversible gel in benzyl alcohol (BA). Phase diagram of the system PBLG/BA was investigated. The gel network comprises crystalline aggregates. There are two types of aggregated structures depending on the gelation temperatures; one (A) is the so-called complex phase (volume fraction of polymer is 0.76), and the other (B) is the crystal containing few solvent molecules. Melting temperatures of B type gels (in the range of 62–70°C) are slightly higher than those of A type gels. Above the gel–sol transition temperature, the solution forms a cholesteric liquid crystal, provided the polymer concentration exceeds about 15 vol%. Mechanism of the formation of A and B was discussed in the phase diagram.

The solution with concentration between 10 and 20 vol% (depending on molecular weight) contains the isotropic and anisotropic phases at equilibrium. The composition and fractionation effect within conjugate phases were investigated at 80°C for solutions containing two PBLG samples differing in molecular weights. The biphasic region was widened by mixing the two PBLG samples, and the isotropic phase showed a tendency to exclude the high-molecular-weight fraction.

INTRODUCTION

Phase equilibrium of relatively dilute solutions of rigid rodlike molecules was first treated by Onsager (1949) and Ishihara (1951). They revealed that separation into the isotropic and anisotropic phases might occur in solutions of long rods. The lattice model treatment of Flory (1956) predicted the phase diagram over the whole concentration range, which is characterized by a narrow biphasic region connected to a wide biphasic region (see Fig. 1). Miller et al. (1978) reported that the phase diagram of PBLG in N,N-dimethylformamide (DMF) was in agreement with the Flory's diagram. The system PBLG/DMF, however, has been shown to form a thermoreversible gel comprising crystalline aggregates (so-called complex phase) (PARRY and ELLIOTT 1967; SASAKI et al. 1982). Therefore, the equilibrium with the formation of complex phase should overlap the Flory's diagram. Papkov (1977) suggested that some types of equilibria, for instance, isotropic solution $\rightleftharpoons$ crystal, anisotropic solution $\rightleftharpoons$ crystal, and isotropic solution $\rightleftharpoons$ anisotropic solution, might be superposed in real systems because of the difference in the nucleation rates of the new phases. Balbi et al. (1980) described the phase diagram of poly(*p*-benzamide) in N,N-dimethylacetamide/LiCl solutions by taking into account these various equilibria. Ciferri and Krigbaum (1981) suggested that the composite phase diagram might offer an explanation for the mechanism of the formation of biological supermolecular organizations. As a simple system of rodlike polymers, the authors have dealt with the system PBLG/BA (SASAKI et al. 1982). Our objective is to offer the phase diagram of this system.

In a biphasic region, an isotropic phase (concentration v_2^*) is in equilibrium with a denser anisotropic phase (v_2^{**}). Molecular-weight dependences of v_2^* and v_2^{**} have been compared with theoretical predictions (ROBINSON 1966; SAMULSKY 1978). The agreement was not so complete. One reason is that the real systems comprise polydisperse polymers. The earlier theories by Onsager (1949) and Flory (1956) were developed for the system of monodisperse particles. Recently, Flory et al. (1978) presented a theory for polydisperse system. Abe and Flory (1978) described ternary diagram involving two monodisperse rodlike solutes differing in axial ratio. They predicted that boundaries of the biphasic region would be widened in comparison with the ones derived for monodisperse systems, and that the higher-molecular-weight fraction would be preferentially partition into the anisotropic phase, while the lower-molecular-weight portion would concentrate into the isotropic phase. This tendency has been observed for some systems of liquid crystalline polymers (AHARONI and WALSH 1979; CONIO et al. 1981). In this work, we have prepared PBLG/BA solutions in the biphasic region at 80°C, and isolated the coexisting phases to determine their composition and molecular-weight partition.

EXPERIMENTAL

Samples of PBLG were synthesized by the N-carboxyanhydride method using triethylamine as the initiator in dioxane. Low-molecular-weight fraction was cut off by precipitating the polymer from the dichloroethane solution with a relatively small amount of methanol. Samples with $\bar{M}_w/\bar{M}_n$ = 1.1–1.2 could be thus obtained (YAHAGI and UEMATSU). Molecular weights were determined from intrinsic viscosities in dichloroacetic acid at 25°C using the relation given by Doty et al. (1956),

$$[\eta] = 2.78 \times 10^{-5}\ M^{0.87},\ [\mathrm{dL/g}]$$

Solutions of PBLG/BA were prepared in the manner described before (SASAKI et al. 1982). Melting points of PBLG/BA gels were measured by differential scanning calorimetry at a heating rate of 10°/min. Temperatures at main endothermic peaks in the thermograms were regarded as the melting points.

X-ray diffraction measurements were carried out with Ni-filtered Cu Kα radiation using a flat-plate camera. Specimens were prepared by sealing the solutions in thin glass-capillary tubes. Reflection spacings were calibrated against silicon.

By using two PBLG samples (sample I: $\bar{M}_V$ = 347,000, II: $\bar{M}_V$ = 99,000) and their blends, solutions with concentrations in the biphasic region were prepared in test tubes and hold at 80°C. During a week, the solution was gravimetrically separated into two phases; the upper layer is isotropic and the lower is anisotropic. Difference of 1 % in the volume fraction of polymer corresponds to the difference in solution density of 0.0023 g/cm^3. Separation was much accelerated by centrifugation even of the rotation of 20 *g*. After the position of the meniscus between conjugate phases was settled, the solution was quenched from 80°C to room temperature to form a gel. The parts corresponding to the isotropic and anisotropic phases were easily separated at the meniscus, and subsequently weighed and dried at 100°C in vacuo. The weights of the dried materials were measured to determine the polymer concentrations, which were finally figured in volume fractions by using values of specific volume of 0.815 cm^3/g for PBLG and 1.001 cm^3/g for BA. Molecular weights in the respective phases were determined from their viscosities.

RESULTS AND DISCUSSION

In a previous paper, we reported that two kinds of aggregates are formed in PBLG/BA gel network (SASAKI et al. 1982). One (A) is prepared when the gelation is allowed to take place between 48 and 60°C. The melting points fall onto the line *a* in Fig. 1. The volume fraction of polymer in A type aggregate (0.76) is independent of the total concentration. Another type of aggregate (B) is prepared by repetition of quenching of the solution (with concentration exceeding v_2^{**}) from 61–62°C (near the melting point of A type gel) to a temperature below 48°C. Melting points of B type gels are higher than those of A, and fall onto the line *b* in Fig. 1. X-ray diffraction photographs of both types of lyogels are shown in Figs. 2a and 2b. Reflection spacings observed for B are also independent of the total concentration. In the previous study, we could neither determine the volume fraction of polymer in

B type aggregate nor explain why B type gel exhibits the higher melting point than A.

In this study, we have prepared solid films by drying B type gel at room temperature in vacuo. The X-ray pattern of B type xerogel (Fig. 2c) is essentially the same as that of B type lyogel. Spacings are compared in Table I. The first five reflections of B type lyogel were observed at spacings in a simple ratio of 1:1/2:1/3:1/4:1/6. Therefore, the structure has the one-dimensional periodicity with a repeat distance of 4.4 nm, which becomes 5 % smaller for the xerogel (about 4.2 nm). This suggests that the polymer volume fraction in B type aggregate is about 95 %. However, B type aggregate may be regarded as a crystal containing few solvent molecules, and it may exist in a swollen state in the actual condition. Accordingly, the line *a* in Fig. 1 corresponds to the equilibrium with the formation of complex phase, while the line *b* corresponds to the equilibrium with the formation of a crystal.

PBLG gel network has been considered to be maintained by the interaction between side-chain benzene

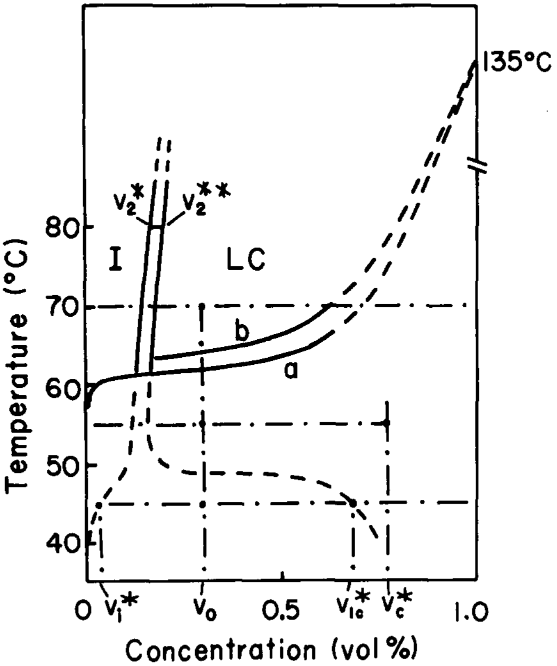

Fig. 1. Phase equilibria proposed for PBLG/BA system. I: isotropic region. LC: liquid crystalline (anisotropic) region.

rings. Melting of the gel accompanies the collapse of the stacking structure of benzene rings. The xerogel obtained from A type lyogel has the structure which has been termed Form A (MCKINNON and TOBOLSKY 1968), and exhibits an irreversible transition at 135°C associated with the collapse of the stacking structure (FUKUZAWA et al. 1974). The B type xerogel also showed an irreversible transition at 135°C. The structure of the annealed form was rather close to Form C (BAMFORD et al. 1956). The lines *a* and *b* in Fig. 1 may converge the position of 135°C at solid state.

In order to obtain B type gel, it is necessary to repeat quenching of the solution from 60—62°C to a temperature below 48°C. A single process of quenching gives a gel containing both A and B aggregates. This may suggest that the Flory's narrow biphasic region connects to the wide biphasic region at about 48°C, as shown in Fig. 1. By holding the solution at a temperature between 48 and 60°C, a slow crystallization may occur to form the complex phase of $v_c^* = 0.76$. By quenching the v_o solution, for instance, from 70°C to 45°C, the system may pass into the region where separation into isotropic (v_i^*) and liquid crystalline (v_{lc}^*) phases can occur. On formation of the phase v_{lc}^*, the supersaturation becomes great to cause the nucleation of the crystalline B phase. The system may pass finally into the equilibrium state with crystallization.

TABLE I
X-ray Diffraction Spacings Observed for PBLG/BA gel (B) and its xerogel

B-lyogel	B-xerogel
4.4 nm	4.1 nm
2.2	2.1
1.47	1.41
1.1	-
0.74	0.71
0.59	0.59
0.50	0.50
0.45	0.45

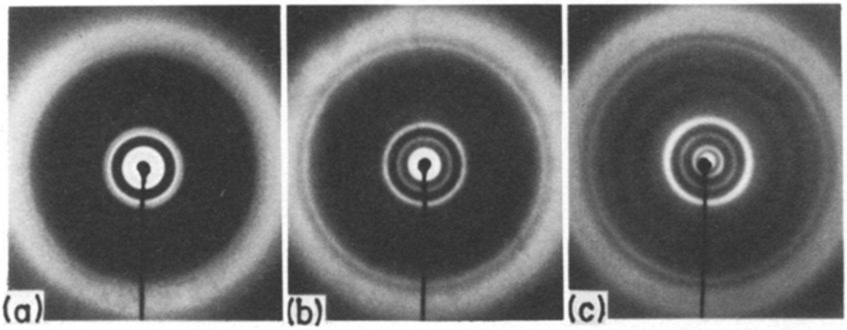

Fig. 2. X-ray diffraction photographs of (a) A type lyogel, (b) B type lyogel, and (c) B type xerogel.

Phase separation from a solution of polydisperse polymer in a single solvent accompanies fractionation; the polymer-rich phase has a tendency to exclude low-molecular-weight components which would concentrate in the polymer-lean phase. It was theoretically shown that the fractionation effect might be remarkable in rodlike polymer systems (FLORY et al. 1978). Abe and Flory (1978) showed that in athermal, three-component systems involving two monodisperse rodlike solutes, even a small amount of low-molecular-weight solute might cause a considerable increase of v_2^{**}, and that the high-molecular-weight fraction would be almost rejected from the isotropic phase. These effects were examined for PBLG/BA system, and compared with the theoretical prediction.

PBLG/BA solutions in the biphasic region at 80°C were prepared, and separated into the isotropic and anisotropic phases at equilibrium. In order to confirm that the separation was successfully achieved, both of the isotropic and anisotropic phases were separated into two pieces, respectively (Fig. 3). As will be mentioned below, fractionation within conjugate phases was actually observed. Therefore, if the sedimentation is incomplete, molecular weights of polymers contained in the phases I_1 and I_2, and in A_1 and A_2 should be different, respectively. Polymers recovered from I_1 and I_2 (A_1 and A_2) showed the same viscosities. Therefore, both of the isotropic and anisotropic phases were regarded as homogeneous.

Ternary solutions with the total volume fraction of polymer v_2 (between v_2^* and v_2^{**}) were prepared by using two PBLG samples, and hold at 80°C until the equilibrium was reached. Composition and fractionation data within conjugate isotropic and anisotropic phases were listed in Table II.

The volume fraction of the isotropic phase in bulk solution, ϕ, is given in the third column. Concentrations were adjusted so that the solutions might have roughly equal amounts of conjugate phases.

Viscosity-average molecular weight of I/II = 1/1 mixture is 218,000, while the molecular weights within conjugate isotropic and anisotropic phases of this solution were 174,000 and 248,000, respectively. For I/II = 1/3 solution, the high-molecular-weight component seems to be rejected from the isotropic phase.

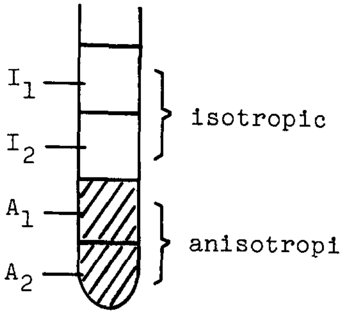

Fig. 3. Separation into isotropic and anisotropic phases.

Boundaries of the biphasic region were widened by mixing I and II samples; the difference $v_2^{**} - v_2^{*}$ is only a few percent for the solution of I or II, while it reaches about 9 % for the solution of 1/1 mixture. By regarding PBLG molecule as a rod with diameter 1.58 nm and the unit height 0.15 nm, molecular weights 347,000 (I) and 99,000 (II) correspond to axial ratios (x) of 150 and 43, respectively. According to the Abe and Flory's method, we have calculated the ternary phase diagram comprising a solvent and two kinds of solutes of x = 150 and 43 with various values of the interaction parameter χ (treated in an expression of the van Laar form). Two diagrams with $\chi = 0$ and -0.4 are drawn in Fig. 4, where oblique light lines are representative tie lines connecting conjugate phases.

PBLG samples used in this work are not monodisperse, and certain kinds of molecular aggregations may persist at 80°C. The observed biphasic gap is much smaller than that expected for the athermal system. It is better to adopt negative χ values in a qualitative comparison of experimental results (Table II) with calculation (Fig. 4). Consideration of chain flexibility (MATHESON and FLORY 1981) may also improve the disagreement between theory and experiment.

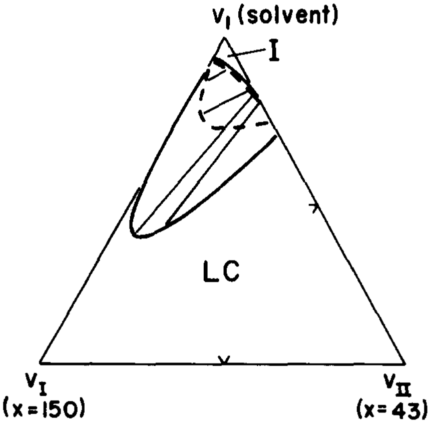

Fig. 4. Ternary phase diagram calculated for solvent and two rodlike solutes. —— $\chi = 0$, --- $\chi = -0.4$.

TABLE II
Composition and Fractionation Data for PBLG/BA Solutions at 80°C

I/II	v_2 [a]	ϕ [a]	isotropic		anisotropic	
			v_2^*	$\bar{M}_v$	v_2^{**}	$\bar{M}_v$
1/0	0.117	0.69	0.109	319,000	0.133	369,000
3/1	0.130	0.68	0.118	256,000	0.157	321,000
1/1	0.158	0.62	0.125	174,000	0.211	248,000
1/3	0.184	0.51	0.159	97,000	0.208	200,000
0/1	0.194	0.54	0.188	85,000	0.202	103,000

[a] ϕ: volume fraction of the isotropic phase in bulk solution with the polymer volume fraction v_2.

REFERENCES

ABE, A. and FLORY, P. J.: Macromolecules 11, 1122 (1978)

AHARONI, S. M. and WALSH, E. K.: Macromolecules 12, 271 (1979)

BALBI, C., BIANCHI, E., CIFERRI, A., TEALDI, A., and KRIGBAUM, W. R.: J. Polym. Sci. Polym. Phys. Ed. 18, 2037 (1980)

BAMFORD, C. H., ELLIOTT, A., and HANBY, W. E.: Synthetic Polypeptides, New York: Academic 1956

CIFERRI, A. and KRIGBAUM, W. R.: Mol. Cryst. Liq. Cryst. 69, 273 (1981)

CONIO, G., BIANCHI, E., CIFERRI, A., and TEALDI, A.: Macromolecules 14, 1084 (1981)

DOTY, P., BRADBURY, J. H., and HOLTZER, A. M.: J. Amer. Chem. Soc. 78, 947 (1956)

FUKUZAWA, T., UEMATSU, I., and UEMATSU, Y.: Polym. J. 6, 431 (1974)

FLORY, P. J.: Proc. R. Soc. London Ser. A 234, 73 (1956)

FLORY, P. J. and FROST, R. S.: Macromolecules 11, 1126 (1978)

ISHIHARA, A.: J. Chem. Phys. 19, 1142 (1951)

MATHESON, R. R. and FLORY, P. F.: Macromolecules 14,954 (1981)

MCKINNON, A. J. and TOBOLSKY, A. V.: J. Phys. Chem. 72, 1157 (1968)

MILLER, W. G., KOU, L., TOHYAMA, K., and VOLTAGGIO, V.: J. Polym. Sci. Polym. Symp. No. 65, 91 (1978)

ONSAGER, L.: Ann. N. Y. Acad. Sci. 51, 627 (1949)

PAPKOV, S. P.: Contemporary Topics in Polymer Science Vol. 2, PEARCE, E. M. and SCHAEFGEN, J. R. Ed., New York: Plenum Press 1977

PARRY, D. A. D. and ELLIOTT, A.: J. Mol. Biol. 25, 1 (1967)

ROBINSON, C.: Tetrahedron 13, 219 (1961); Mol. Cryst. 1, 467 (1966)

SAMULSKY, E. T.: Liquid Crystalline Orders in Polymers, Chap. 5, BLUMSTEIN, A. Ed., New York: Academic 1978

SASAKI, S., HIKATA, M., SHIRAKI, C., and UEMATSU, I.: Polym. J. 14, 205 (1982)

YAHAGI, K. and UEMATSU, I.: unpublished data

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