Physical Properties

Phase Behavior of the Ternary System Solvent: Poly(γ-Benzyl L-Glutemate) and Polystyrene

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SUMMARY
       Phase equilibria were investigated at 80°C for a ternary system involving a solvent benzyl alcohol, a rodlike polymer poly(γ-benzyl L-glutamate) (PBLG), and a flexible polymer polystyrene (PS). The fairly dilute solution of the two polymers was isotropic and monophasic. At greater concentrations, it was separated into two isotropic phases. Above an even higher critical concentration of the two polymers, three phases, a cholesteric (A_1) and two isotropic phases (I_1 and I_2), coexisted at equilibrium. PBLG was contained exclusively in the phases A_1 and I_1, while PS was in the phase I_2. The more concentrated solution was separated into a cholesteric phase and an isotropic phase. The latter contained PS but excluded PBLG. These features were discussed on the ground of the Flory theory by considering the polymer compatibility.

INTRODUCTION
       The molecule of poly(γ-benzyl L-glutamate) (PBLG) assumes the rodlike α-helical conformation. Its solution in benzyl alcohol (BA) forms a thermoreversible gel. The phase behavior of the BA/PBLG binary system was described in previous papers [1,2]. The gel network comprises fairly crystalline fibrillar aggregates, for which two different structures depending upon the gelation condition are observed by X-ray diffraction. Melting temperatures of these gels are in the range of 62–70°C. Above the transition temperature, the solution exceeding a critical concentration forms a cholesteric liquid crystal. As is well known for binary systems involving rodlike solutes [3–9], there is a narrow concentration range, where an iso-tropic and a slightly denser anisotropic phases coexist at equilibrium.
       The earlier theories [3–5] were developed for the system with a monodisperse rodlike solute. Flory and his co-workers extended the lattice theory for the polydisperse system [10–13]. Abe and Flory described the phase behavior of ternary systems involving a solvent and two rodlike solutes of differ-ent lengths [11]. They predicted (1) the widening of the biphasic region by mixing the two solutes and (2) the parti-tion of the high molecular weight fraction into the anisotrop-ic phase. This tendency has been observed qualitatively for several systems [2,14–16].

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It is predicted from the lattice theory that two aniso-
tropic phases possibly coexist at equilibrium in binary and
ternary systems [4,11,17]. This has been claimed for the
solution of PBLG in dimethylformamide [18] and also for the
ternary aqueous solution of a polysaccharide schizophyllan
[16]. There are still some controversial points on this
subject [19, 20].
    Flory described furthermore the phase equilibrium in a
ternary system consisting of a solvent, a rodlike solute, and
a randomly coiled polymer [21]. The phase diagram comprises
an isotropic, monophasic region and a biphasic region at
greater concentrations, where the random-coil component is
expelled from the anisotropic phase into the coexisting iso-
tropic phase. This prediction was confirmed for several
systems, for instance, poly(isocyanate)s/polystyrene/tetra-
chloroethane [22], poly(p-benzamide)/X-500 (or polyacryloni-
trile)/dimethylacetamide (DMAc) + 3 % LiCl [23,24], and so on
[25]. Phase behavior was also investigated for ternary
systems involving two (semi)rigid polymers and a solvent, such
as cellulose acetate/hydroxypropyl'cellulose/DMAc [26] and
PBLG/poly(hexyl isocyanate)/chloroform [27].
    The Flory treatment for the solvent/rod/coil system is
restricted to athermal mixtures. In experimentally accessible
systems, however, the rodlike and flexible polymers may have
quite different chemical constitution. Therefore, the enthal-
py parameter reflecting interactions between molecules may
play an important role. In the present paper, we describe the
phase behavior of the system BA (component 1) + PBLG (compo-
nent 2), to which a typical flexible polymer polystyrene (PS)
is added as the third component. The experiments were carried
out at 80°C. At this temperature, BA is not so volatile, PS
is well soluble in BA (the solubility limit was higher than 40
wt %), and the solution is presumably free from the aggregation
of PBLG molecules associated with the gelation.

EXPERIMENTAL
    A sample of PBLG was synthesized by the N-carboxy anhy-
dride method using triethylamine as the initiator in dioxane.
The low molecular weight fraction was considered to be cut off
by reprecipitating the crude sample from the dichloroethane
solution with a relatively small amount of methanol. It was
previously shown that the PBLG sample with $\overline{M}_w/\overline{M}_n < 1.2$ could
be obtained in this way [28]. The molecular weight was esti-
mated to be about 350,000 from the intrinsic viscosity mea-
sured in dichloroacetic acid at 25°C in terms of the viscos-
ity—molecular weight relationship given by Doty et al. [29].
A sample of PS (Pressure Chemical Co.) with $\overline{M}_w = 233,000$
($\overline{M}_w/\overline{M}_n < 1.06$) was used. The solvent was analytical grade BA.
    Weighed amounts of samples and solvent (ca. 2 ml in
total) were mixed with a magnetic stirrer bar at about 100°C
for a few days. The homogeneous mixture was quenched to 20°C
to form a gel, and then transferred to a calibrated stoppered
tube (7 mm diameter, 80 mm long). It was centrifuged at about
600 rpm at 80°C for 10h a day to accelerate the separation of
coexisting phases, and allowed to stand overnight in an air
bath thermostated at 80°C. This procedure was repeated for

several days. After the conjugate phases were separated by a narrow boundary, the volume of each phase was determined from its column height. The lower anisotropic layer was observed to be a cholesteric mesophase with a polarizing microscope.

By quenching from 80°C to 20°C, the cholesteric layer and/or the lower isotropic layer gelled, while the uppermost isotropic layer did not. This suggests that PBLG was almost excluded from the uppermost layer. The conjugate phases were easily isolated owing to the gelation of the lower layer (or layers). A weighed amount of each isolated phase was dried in vacuo at high temperature to determine the total polymer concentration. The small content of PS in the lower layer (or layers) was determined by extracting the dried and weighed film using a Soxhlet's extractor with carbon tetrachloride. The latter is a good solvent for PS, but does not dissolve PBLG (a test was performed for a known mixture).

Infrared spectroscopic analysis of the composition was attempted as Marsano made for the ternary system involving PBLG [27]. But, the results were not reproducible, probably due to the unavoidable orientation of PBLG molecules.

The composition of the uppermost isotropic layer was calculated according to the lever rule. It was considered to be reliable, since the calculated total polymer content agreed with the observed one.

The volume fraction of each component was calculated assuming additivity from the corresponding weight fraction by using the specific volumes of 1.001 mL/g for BA, 0.813 mL/g for PBLG [30,31], and 0.965 mL/g for PS [32].

RESULTS AND DISCUSSION

The phase separation data are collected in Table 1. The volume of each phase relative to the total solution volume is denoted by ϕ. The concentrations given in volume fraction with a prime and a double prime refer to the isotropic and anisotropic phases, respectively, and those without a prime, to the original solution. These data are plotted in Figure 1, where each cross indicates an original solution and a pair of circles connected with a tie line (broken line) indicates its conjugate phases.

The binary solution in the biphasic region, no. 1, was separated into the lower anisotropic (A_0) and the upper isotropic (I_0) phases. It was already shown that the critical concentrations, v_2' (I_0) and v_2'' (A_0), are not constant and depend upon ϕ [12,15,16]. Therefore, the present values are not considered to be specific. The PBLG molecule with a molecular weight 350,000 is geometrically a rod with an axial ratio $x_2 = 150$, for which v_2' is predicted to be about 0.05 from the lattice theory [4,5]. The observed critical concentrations corresponds to those predicted for $x_2 = 94$. Such a deviation has often been observed for the system with sufficiently long rods [16], and may partly be due to the molecular flexibility.

Two dilute ternary solutions, no. 2 and 3, were separated into two isotropic phases. The lower phase contained more PBLG than the upper one. The no. 4 and 5 solutions were separated into three phases, the lowest cholesteric (A_1), the middle isotropic (I_1) and the uppermost isotropic phases (I_2).

Table 1

Phase Separation Data for the system BA(1)/PBLG(2)/PS(3) at 80°C

Soln No.	Original		Anisotropic			Isotropic 1			Isotropic 2[a]		
	v_2	v_3	ϕ	v_2''	v_3''	ϕ	v_2'	v_3'	ϕ	v_2'	v_3'
1	.112	-	.36	.139	-	.64	.086	-	-	-	-
2	.025	.025	-	-	-	.74	.03	.02	.26	.01	.04
3	.040	.040	-	-	-	.55	.06	.02	.45	.016	.064
4	.075	.055	.16	.128	.007	.46	.116	.003	.38	.003	.138
5	.085	.041	.11	.123	.008	.61	.114	.003	.27	.007	.137
6	.085	.080	.54	.153	.008	-	-	-	.46	.005	.165
7	.127	.127	.47	.27	.005	-	-	-	.53	0	.235
8	.175	.175	.48	.37	.006	-	-	-	.52	0	.33

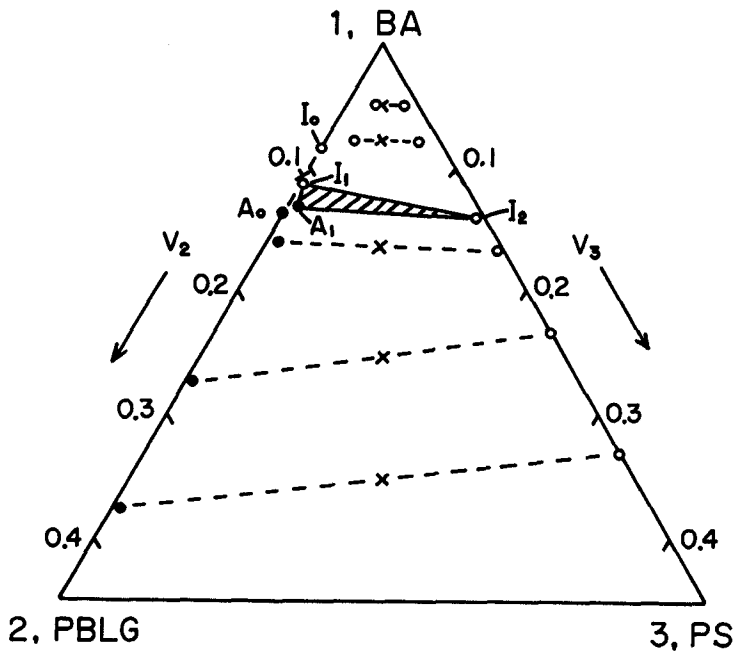[a] Calculated from the data for the original and conjugate phases according to the lever rule.

Figure 1. Ternary phase diagram observed for the system BA/PBLG/PS at 80°C (cf. Table 1). Hatched triangle, region for the triphase separation; (o), conjugate isotropic phase; (●), cholesteric phase; (X), original mixture; broken line, tie line.

PBLG was contained substantially in the phases A_1 and I_1, but almost excluded from the phase I_2. The compositions of these three phases are almost invariant in spite of the variation of their volumes. The concentrated solutions with total polymer concentrations higher than v_2'' (A_0), no. 6, 7, and 8, were separated into two phases, the lower anisotropic and the upper isotropic phases.

The equilibria involving two isotropic phases (region II) and three phases (region AII) have been reported for ternary systems involving two (semi)rigid polymers and a solvent [26, 27]. The regions II and AII in the solvent/rod/coil system are not predicted from the Flory theory [21], which offers only the anisotropic-isotropic equilibrium (region AI). They may arise from the incompatibility of the PBLG-PS pair.

The interaction parameter χ_{23} is estimated according to

$$\chi_{23} = \frac{V_R}{RT}(\delta_2 - \delta_3)^2$$

where V_R is a reference volume taken as 100 mL/mol, and the Hildebrand solubility parameter δ is given by referring to the Small's table [33]. The calculated value of χ_{23} was about 0.6 at 80°C, suggesting that PBLG and PS are incompatible and should demix at greater concentrations in a common solvent.

The phase diagram was calculated according to the Flory theory [21] by introducing the enthalpy term associated with
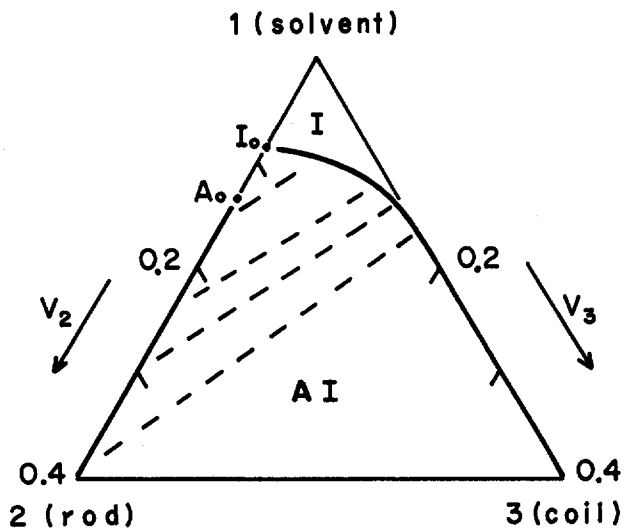

(a)

Figure 2. Ternary phase diagram calculated for the system solvent/rodlike solute ($x_2 = 94$)/random-coil polymer ($x_3 = 500$). (a) $\chi_{23} = 0$, (b) $\chi_{23} = 0.2$, and (c) enlargements in the vicinity of I_0 and A_0 in Figure 2b.

χ_{23}. A value of the axial ratio $x_2 = 94$ was used so as to fit the data of the I_0 and A_0 points. The PS molecule with a molecular weight 233,000 has a contour length of 5600 Å. The degree of polymerization of PS in terms of the lattice unit was set at $x_3 = 500$ (a greater value produced no significant variation). The phase diagram calculated with χ_{23} smaller than 0.1 exhibited the features described by Flory. Figure 2a
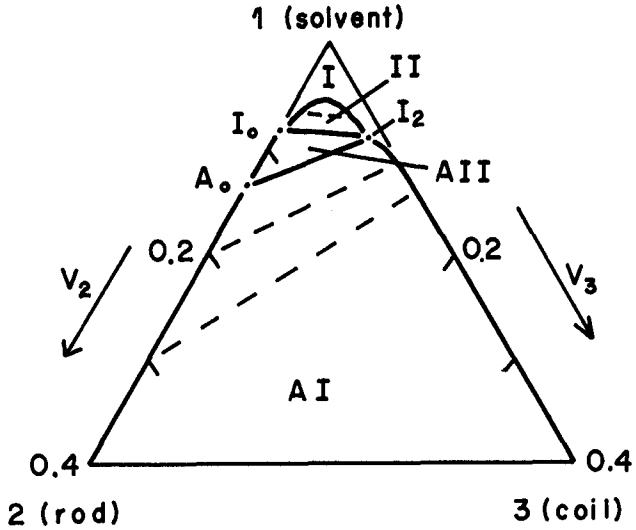
(b)
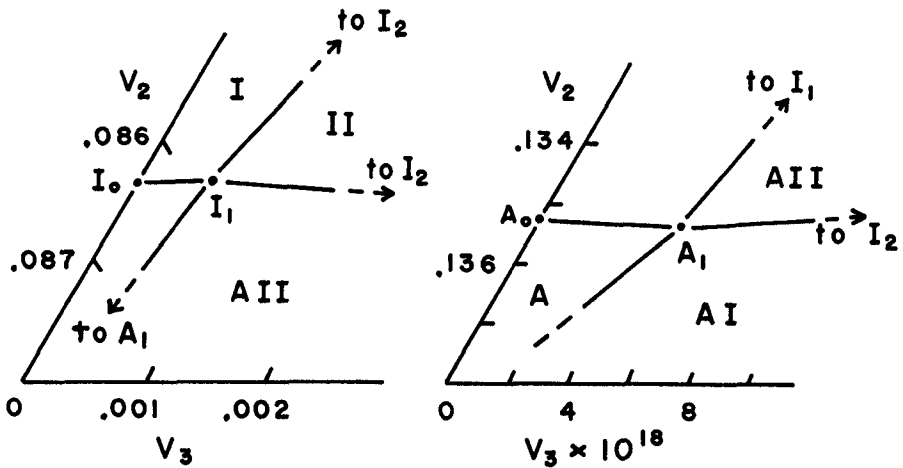
(Figure 2)   (c)

shows the theoretical diagram with $X_{23} = 0$, consisting of the isotropic, monophasic region (I) and the biphasic region (AI). In the phase diagram calculated with X_{23} larger than 0.2, the regions II and AII newly appeared, as is shown in Figure 2b. The details in the vicinity of I_0 and A_0 are illustrated in Figure 2c.

Major discrepancies between the experimental (Figure 1) and theoretical phase diagrams (Figure 2b) may be summarized as follows.

(1) The points I_0 and A_0 are theoretically very close to I_1 and A_1, respectively (Figure 2c). But, a considerable deviation was observed. Since the triphase separation needed much time, the composition was analyzed after two weeks. It is not certain whether the separation was completely achieved.

(2) In the biphasic AI region, the random-coil component should be almost excluded from the anisotropic phase. However, a small amount of PS was contained in the anisotropic phase. This may also reflect the incomplete separation of conjugate phases.

(3) The experimental tie lines are more nearly parallel to the base line than theoretically expected. This tendency has been reported for poly(p-benzamide) systems [23, 24].

Allowing for the experimental difficulties associated with the high viscosity of the systems, we consider that the observed results are in satisfactory agreement with the theory. It may be necessary to improve the separation technique and the method of determination of the composition. The effects of polydispersity and molecular weight are worth further investigation and will be published elsewhere.

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