on the branches. If two polymers entangle each other on their parent backbones, the entanglement cannot be removed so easily. However, if the molecular weight dependence of the viscosity of a star-shaped polymer also has a power higher than 3.4 as was reported in the literatures,[6] this may not be the main reason. Another reason may be that, while linear polymer coils may be assumed to overlap each other extensively in undiluted polymers, the assumption cannot be justified for branched polymers. Because of the small radius of gyration and the high segment density of branched polymers, the coils cannot overlap extensively but must contact each other at the surfaces of the polymer coils.

It is observed in Figure 7 that the viscosity of a branched polymer becomes equal to the viscosity of the parent polymer at $M_b = 3.5–4.0 \times 10^4$. If M_b is smaller than the value, there may be no effective entanglement on branches. In other words, there may be a critical molecular weight for the entanglement of branches as predicted by Berry and Fox.[9] To confirm this speculation, however, further investigations are surely required.

Finally, it should be noted that the steady-state compliance J_e of a branched polymer calculated from eq 2 is much higher than the value estimated from the quasi-equilibrium relaxation modulus, E_e, at the plateau zone. If we apply the theory of rubber elasticity to the relaxation modulus of a chain between two entanglement points, that is

$$J_e = ({}^1/_3E_e) = M_e/pRT \qquad (12)$$

we have $M_e = 2.4 \times 10^5$ from J_e in Table II and $M_e = 2.2 \times 10^4$ from E_e. This big difference may be understood if we accept the explanation of Ferry, *et al.*,[38,39] on the physical meaning of J_e, in which J_e is assumed to be the sum of two terms—the contribution of entanglement networks $J_{e,n}$ and that of the entanglement network slippage $J_{e,l}$. An increase in J_e may be caused by polydispersity of the samples used, but the increase in J_e observed in this work appears to be much higher than the increase in J_e of linear polymers due to polydispersity.[40] It is our opinion that this remarkable increase in J_e due to branching may be caused by the effect of network slippage. The branched polymers would have higher entanglement densities than linear polymers, but only at the surfaces of the polymer domains.

Acknowledgment. We wish to thank Mr. Y. Shin and Mr. M. Kawahashi for their assistance in making the samples and also Dr. T. Kato and Mr. K. Miyaso for their aid in determining the molecular weights of the samples by light scattering and osmotic pressure measurements.

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Dilute Solution Thermodynamic Properties of Poly(γ-benzyl L-glutamate) in N,N-Dimethylformamide

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ABSTRACT: Osmotic pressures of dilute, isotropic solutions of fractionated poly(γ-benzyl L-glutamate) in N,N-dimethylformamide have been measured both as a function of temperature and of solute molecular weight. The osmotic second virial coefficient is found to have a temperature dependence similar to that of dilute solutions of random coils in poor solvents. A Θ temperature of *ca.* 22° is observed. The experimental data indicate that at certain temperatures the polymer–solvent system may be characterized by a χ value of up to 0.5 even though a single isotropic phase is present. This is at variance with lattice theory for rigid, impenetrable rods which predicts that any appreciable enthalpic contribution to the free energy of mixing will cause the system to separate into two phases, an isotropic phase of vanishingly small solute concentration and a concentrated anisotropic phase. Studies of phase equilibria as a function of temperature, solute concentration, and molecular weight are reported. At low solute concentrations a low-temperature gel phase is formed which does not show optical properties characteristic of the anisotropic phase that has been observed at higher concentrations.

The solution properties of synthetic polypeptides have been most frequently investigated in which these biologically important macromolecules assume randomly coiling conformations, or else the rodlike, α-helical conformation depending on the choice of solvent.[1-3] Typical is poly(γ-benzyl L-glutamate) (PBLG) which exists in the random coil state in dilute solution in dichloroacetic or trifluoroacetic acid; in other solvents such as dioxane, *m*-cresol, or N,N-dimethylformamide (DMF) the polymer is α-helical. The

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polypeptide solutions are isotropic at sufficiently low solute concentrations. At higher concentrations in both classes of solvents liquid–crystalline or anisotropic phases have been observed.[3–7]

The thermodynamic properties of solutions of polymer random coils have been examined extensively both experimentally and theoretically.[8–11] In contrast the corresponding behavior of solutions of highly asymmetric particles is less well established, at least experimentally. Theoretical treatments of solutions of coherent rods have been most readily developed wherein the rods are considered to be rigid and impenetrable. Molecular distribution treatments have been given for very dilute athermal solutions.[12–14] More general lattice treatments have been given by Flory[15,16] and by DiMarzio and Gibbs.[17] The lattice treatment of Flory includes enthalpic contributions introduced in the van Laar approximation through the familiar χ parameter from random coil solution thermodynamics.

Applied to solutions of rigid rods Flory's lattice theory predicts the phase equilibrium behavior shown in Figure 1. As the solute volume fraction v_2 is increased a point is reached at which the solution separates into two phases. The more dilute phase is isotropic containing randomly oriented rods. The more concentrated phase is anisotropic containing partially ordered rods. As long as $\chi <$ *ca.* 0.1 the concentration difference between the two phases is small and insensitive to changes in temperature. When $\chi >$ *ca.* 0.1 the concentration of solute in the isotropic phase becomes vanishingly small while the volume fraction of solute in the anisotropic phase approaches unity. When two phases coexist in equilibrium one is always isotropic and the other is always anisotropic. The shallow minimum in the phase diagram at $\chi \sim {}^1/_{20}$ probably is not significant.[16] In contrast solutions of random coils in poor solvents are predicted to separate into two isotropic phases when χ exceeds a critical value $\geqslant 0.5$, depending on the molecular weight. The behavior for random coils is quite generally verified experimentally.

Experimental studies of solutions of α-helical polypeptides are only in partial agreement with the theoretical models. In their studies of PBLG in dioxane and methylene chloride at ambient temperature, Robinson and coworkers found the polymer concentration in the isotropic phase to be only slightly more dilute than that found in the anisotropic phase.[5,6] Although their observations were in semiquantitative agreement with the lattice treatment, provided there is no resultant attraction between solute particles relative to interactions between like and unlike species,[18] no direct knowledge of χ was available. They reported similar behavior in other helicogenic solvents and in dichloroacetic acid suggesting that the phase separation does not depend appreciably on the nature of the polymer–solvent system. In *m*-cresol the volume fraction at which PBLG first forms the anisotropic phase is also found to be in semiquantitative agreement with theory.[19]

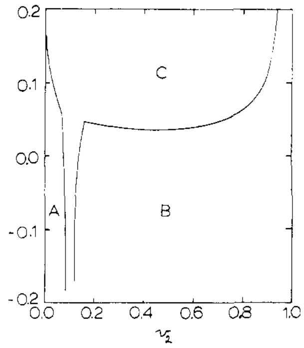

Figure 1. Phase diagram for solutions of rigid, impenetrable rods:[16] region A, isotropic; B, anisotropic; C, biphasic region; axial ratio (x) = 100.

Thermodynamic properties of the systems PBLG–pyridine, PBLG–dichloroethane, and poly(β-benzyl L-aspartate)–chloroform were investigated by Flory and Leonard in the concentration range 60–100 vol % polymer.[20] Their data could not be explained on the basis of the lattice theory for solutions of impenetrable rods,[16] but could be explained if solvent–polymer side chain mixing with the side chains in a disordered state was considered. The experimental data were found to fit reasonably a modified lattice model taking into account solvent–side chain mixing and interactions if χ values of 0.35 and 0.20 were assumed for PBLG in pyridine and dichloroethane, respectively, and a χ value of zero for poly(β-benzyl L-aspartate) in chloroform. On the other hand X-ray data indicate that the side chains are ordered in a 50% solution of PBLG in DMF.[21]

For solutions of random configuration polymers the χ parameter is sometimes increased by adding a nonsolvent to the polymer–solvent system. Nakajima, Hayashi, and Ohmori[22] have investigated solutions of PBLG in DMF using this approach. Using water or methanol as the nonsolvent, they determined the χ value necessary to give agreement between the lattice theory of rods for anisotropic phase formation and the observed point of phase separation. A linear dependence of χ on volume per cent nonsolvent was found with $\chi \sim 0.17$ at the highest nonsolvent concentration.

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Table I

Sample	$10^{-5}\bar{M}_n$, g/mol	$10^{-5}\bar{M}_w$, g/mol	$\bar{M}_w/\bar{M}_n$
PBLG-1B	0.274	0.34	1.24
PBLG-2	1.40	2.68	1.91
PBLG-3	2.12	3.71	1.75
PBLG-4	3.0	3.59	1.2
PBLG-5	3.4	3.47	1.02
PBLG-6	3.6	3.90	1.08
PBLG-7	4.4	4.69	1.07
PBLG-8	4.9	5.3	1.08

Apart from phase equilibrium studies χ values may also be obtained for random coil solutions from the virial coefficients and their temperature coefficients evaluated from light scattering or osmotic pressure measurements near the Θ temperature.[8] In comparison only a few virial coefficient determinations have been reported for polypeptides in helicogenic solvents.[1,23-26] In no case has the temperature dependence of the virial coefficients been investigated.

The experimental results to date indicate that the formation of the anisotropic phase is primarily entropic. An enthalpic contribution is also indicated. Its importance is not particularly clear. This investigation was undertaken to elucidate further enthalpic contributions to the thermodynamic properties of rod-shaped polymers in helicogenic solvents. DMF was chosen as the solvent primarily because it is one of the few helicogenic solvents in which PBLG exhibits no tendency to associate.[1] The temperature and molecular weight dependence of the osmotic second virial coefficient and phase equilibria were examined. The system PBLG–DMF is shown to be more complicated thermodynamically than anticipated from theory.

Experimental Section

Materials. PBLG was prepared by polymerization of γ-benzyl L-glutamate N-carboxyanhydride in dioxane–benzene (1:4, v/v) with diisopropylamine initiator. The resulting polymer was fractionated on a Baker and Williams column[27] 4.5 cm in diameter and 75 cm long with an 18–35° linear temperature gradient along the column. The column support was 125–177 μ glass beads (LaPine Scientific Co.). After deposition of a 1–2-g sample at the top of the column, the polymer was eluted with an exponential gradient of increasing solvent power[28] utilizing the nonsolvent–solvent pair methanol–methylene chloride. Fractions were reprecipitated from DMF and lyophilized from dioxane. Number average molecular weights were determined from osmotic pressure measurements in DMF at 35 ± 0.1°. Weight average molecular weights were determined from viscosity measurements in dichloroacetic acid in Cannon–Ubbelohde dilution viscometers (solvent flow times of *ca.* 150 sec) at 25 ± 0.02°. The calibration curve of Fujita, Teramoto, and coworkers[24,29] was utilized. Polydispersity corrections to the $\bar{M}_w$'s so obtained were considered and found to be less than the discrepancies among the published calibration curves.[1,24,29,30] The molecular weights of the fractions chosen for this study are given in Table I along with the polydispersity in molecular weight as given by the ratio $\bar{M}_w/\bar{M}_n$. All solvents were purified by fractional distillation at reduced pressure.

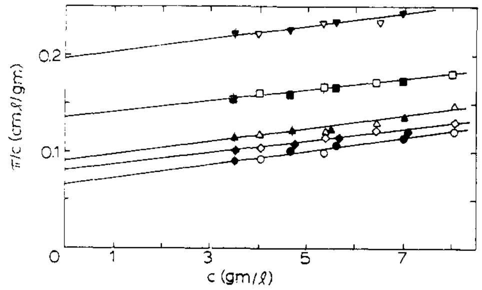

Figure 2. π/c *vs.* c for PBLG in DMF at 45.0°: PBLG-2, run 1, ▽, run 2, ▼; PBLG-3, run 1, □, run 2, ■; PBLG-4, run 1, △, run 2, ▲; PBLG-6, run 1, ◇, run 2, ◆; PBLG-7, run 1, ○, run 2, ●. Vertical bars indicate error estimate when error exceeds size of symbol.

Osmotic Pressures. A Mechrolab Model 503 high-speed membrane osmometer (Hewlett-Packard Co.) equipped with a variable-temperature controller was employed. Regenerated cellulose membranes (Schleicher and Schuell Co.) types 07 and 08 suitable for organic solvents were used. The membranes were conditioned immediately before use by soaking them in 100% acetone for 4 hr, followed by soaking in 50% acetone–50% DMF 4 hr and finally soaking in 100% DMF 4 hr. The membranes were degassed by vacuum aspiration at 60°. In general equilibrium was slow, apparently a result of the transport properties of DMF through the membrane. At the higher temperatures equilibration times of 1–3 hr were typical. At lower temperatures up to 12 hr per measurement were required, especially for the 08 membranes. The stability of the membrane in DMF increased as the temperature was lowered with lifetimes of 1–7 days. Osmotic pressures were reproducible typically to ±0.02 cm of solvent and were measured at temperatures from 15 to 55 ± 0.1°. At a given temperature samples were run in random sequence.

Temperature-Phase Studies. Samples (4 ml) of each of nine solutions ranging from 1 to 5 wt % polymer were placed in capped vials and stored at −15° for at least 12 hr. The vials were transferred to a constant-temperature bath and held at −17° for at least another 12 hr. The temperature was then raised at a rate of either 0.5 or 1°/hr. Every half-hour the appearance of the solutions was noted. After the solutions had been warmed to ambient temperature they were diluted with DMF and the above procedure was repeated. The solutions were carried through two dilutions, the final observations being made 7–8 days after the initial solutions were prepared. Aliquots of the solutions stored at −15° were also viewed in a polarizing microscope as they warmed to ambient temperature in an unthermostated environment.

Results

Typical osmotic pressure data are shown in Figures 2–5. The data are summarized in Figure 6 and in Table II in terms of the coefficients relating osmotic

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TABLE II
SECOND VIRIAL COEFFICIENTS (10^4A_2) FOR PBLG SAMPLES AS A FUNCTION OF TEMPERATURE[a]

	t, °C					
Sample	15.0	20.0	24.0	30.0	45.0	55.0
PBLG-1B	−6 ± 1.3	−0.5 ± 0.13	1.0 ± 0.25		3.0 ± 0.36	2.5 ± 0.27
PBLG-2		−0.9 ± 0.44	0.3 ± 0.45	1.2 ± 0.35	2.2 ± 0.23	2.6 ± 0.15
PBLG-3					2.0 ± 0.12	
PBLG-4					2.3 ± 0.21	2.4 ± 0.12
PBLG-5			−0.1 ± 0.52		1.8 ± 0.17	
PBLG-6					2.1 ± 0.17	
PBLG-7			0.0 ± 0.47		2.4 ± 0.17	2.06 ± 0.076
PBLG-8					2.0 ± 0.12	

[a] Units are cm³ mol/g².

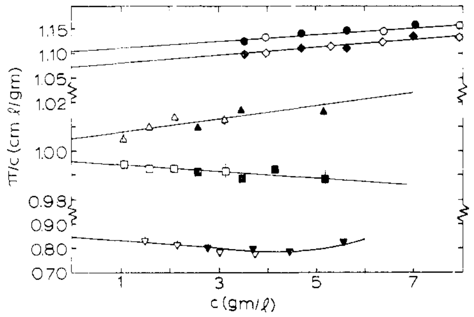

Figure 3. π/c *vs.* c for PBLG-IB in DMF: 15.0°, run 1, ▽ run 2, ▼; 20.0°, run 1, □, run 2, ■; 24.0°, run 1, △, run 2, ▲; 45.0°, run 1, ◇, run 2, ◆, ; 55.0°, run 1, ○, run 2, ●.

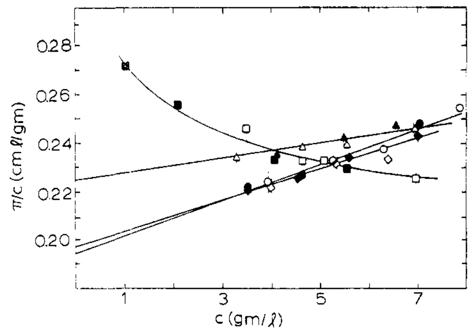

Figure 4. π/c *vs.* c for PBLG-2 in DMF: 20.0°, run 1, □, run 2, ■; 30.0°, run 1, △, run 2, ▲; 45.0°, run 1, ◇, run 2, ◆; 55.0°, run 1, ○, run 2, ●.

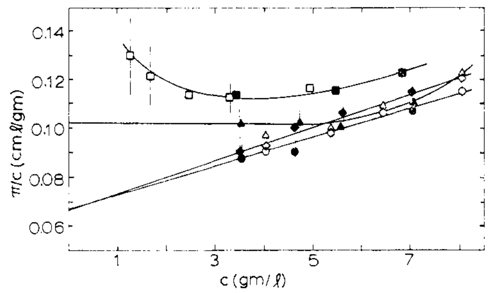

Figure 5. π/c *vs.* c for PBLG-6 and PBLG-7, in DMF: PBLG-6 at 20.0°, run 1, □, run 2, ■; PBLG-7 at 24.0°, run 1, △, run 2, ▲; PBLG-7 at 45.0°, run 1, ◇, run 2, ◆; PBLG-7 at 55.0°, run 1, ○, run 2, ●.

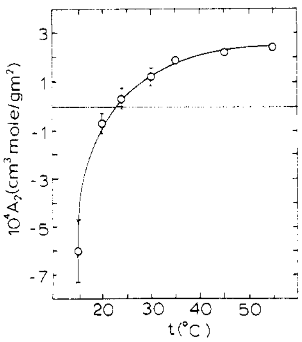

Figure 6. Second virial coefficient *vs.* temperature for PBLG in DMF.

pressure to concentration as given in eq 1. At 45°

$$\pi/c = RT(\bar{M}_n^{-1} + A_2c + A_3c^2 + \ldots) \qquad (1)$$

the plots for the various molecular weights are linear and parallel within experimental error up to a concentration of *ca.* 0.8 wt %. For a fixed molecular weight A_2 decreases as the temperature is lowered and eventually becomes negative. It was exceedingly difficult to obtain reliable data for the higher molecular weight samples at both low concentration and low temperature, as can be seen from the error bars in Figures 4 and 5. In such instances A_2 is not reported.

We thus find that the osmotic second virial coefficient for PBLG in DMF has a positive temperature coefficient, and a molecular weight dependence smaller than our experimental error. At approximately 22° A_2 vanishes, *i.e.*, a Θ temperature exists.

Phase equilibria in the subambient temperature, low concentration region were studied by the procedure outlined in the experimental section. Typical results are shown in Figures 7–9 and are qualitatively described as follows: at the lower temperatures the solutions were rather rigid or gellike (Figure 8, region A); as a solution was warmed a temperature was reached, indicated by a square in Figures 7–9, at which a less viscous solution appeared; as a solution was further warmed the less viscous portion increased in volume at the expense of the more rigid portion (Figure 8, region B); above the temperature indicated by a circle the rigid portion was no longer observable (Figure 8, region C). The boundary between rigid and fluid regions was rather diffuse, and not sharp as between two immiscible liquids. The temperature at which a "phase" was observed to appear or disappear was the same for both rates of heating. However, if a solution was observed during a 1°/hr cooling mode the "biphasic" region was depressed a few degrees, indicating that equilibrium is attained by a kinetically slow process.

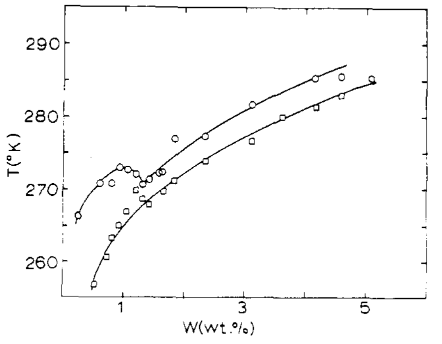

Figure 7. Temperature–composition diagram for PBLG-2 in DMF.

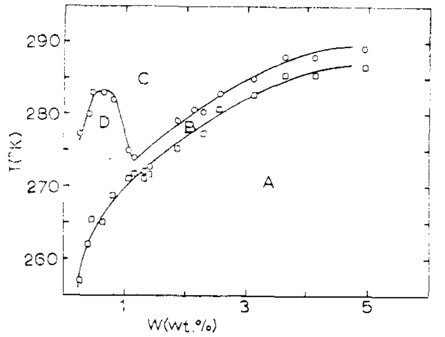

Figure 8. Temperature–composition diagram for PBLG-4 in DMF.

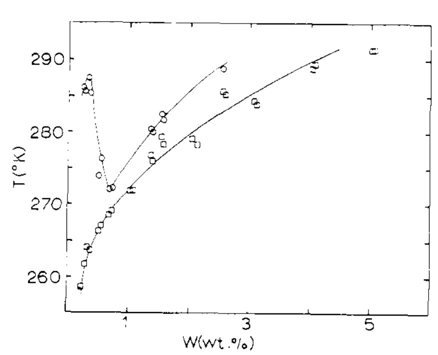

Figure 9. Temperature–composition diagram for PBLG-8 in DMF.

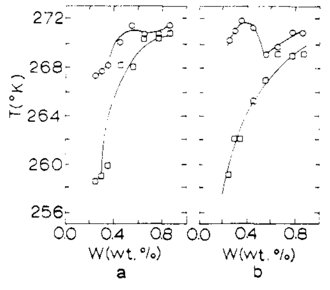

Figure 10. Temperature–composition diagram for PBLG-7 in DMF: a, in absence of filter paper fibers; b, in presence of fibers.

In the concentration region 0–1 wt % a hump exists in the upper boundary in the phase diagrams qualitatively reminescent of the biphasic region frequently observed with solutions of random coil polymers. Studies in this concentration region were repeated. The experimental procedure was altered in that the solutions were prepared directly at the desired concentration rather than by dilution. Consequently the polymer in these solutions had not been through previous heating and cooling cycles. The results are shown in Figure 10a. The hump is barely evident. This same procedure was repeated except the solutions upon preparation were "seeded" or contaminated with a few filter paper fibers. The hump, as seen in Figure 10b, is now more pronounced. These observations again indicate that equilibrium is difficult to achieve and that the past history of the solution may influence the ease of attaining equilibrium.

Low-temperature, low-concentration rigid solutions placed between glass plates and viewed through crossed polars in a polarizing microscope gave no evidence of the brilliantly colored regions observed with higher concentration solutions known to be anisotropic. With the insertion of a first-order red filter, red, blue and darkened areas were evident in contrast to the homogeneous, pink field observed when only solvent was viewed. Upon rotating the microscope stage the red and blue areas interchanged with an extinction angle of 89 ± 2°. Upon warming to room temperature the red, blue, and darkened areas eventually coalesced into one homogeneous, pink field. Some samples containing less than 1 wt % polymer exhibited formation of random-shaped droplets during warming, indicative of a well-defined phase boundary. Solutions 1–2 mm thick viewed at low temperature did not generally exhibit any significant color patterning, indicating perhaps that some order was extraneously introduced in assembling the parallel plate cell.

Discussion

Independent of any assumed model the virial coefficients of eq 1 may be equated to the excess chemical potential of mixing of the solvent as shown in eq 2[8,31] where $\bar{V}_1$ is the partial molar volume of the solvent. For sufficiently dilute solutions in which A_3 and higher

$$(\mu_1 - \mu_1^0)^E = -c\bar{V}_1RT(A_2c + A_3c^2 + \ldots) \qquad (2)$$

coefficients are of no consequence A_2 can therefore be written as

$$A_2 = \frac{\Delta s_1^E}{R\bar{V}_1c^2}\left[1 - \frac{(\Delta h_1^E)}{(\Delta s_1^E)}\frac{1}{T}\right] \qquad (3)$$

where Δs_1^E and Δh_1^E are the excess partial molar entropy and enthalpy of mixing, respectively. Consequently we might suspect quite generally that A_2 may have a temperature dependence and even vanish at some temperature, provided of course that Δh_1^E and Δs_1^E both have the same sign and Δh_1^E has a substantial value relative to $T\Delta s_1^E$. The ratio $\Delta h_1^E/\Delta s_1^E$ can be identified with the Flory Θ temperature at which A_2 vanishes for solutions of random coils.[32]

From the lattice model for rigid, impenetrable rods[16]

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(31) H. Tompa, "Polymer Solutions," Butterworth and Co., Ltd., London, 1956.

(32) G. C. Berry, *J. Chem. Phys.*, **44**, 4550 (1966).

the chemical potentials of the solvent and the solute in the isotropic phase are, respectively

$$(\mu_1 - \mu_1^0)/RT = \ln(1 - v_2) + (1 - 1/x)v_2 + \chi v_2^2 \quad (4)$$

and

$$(\mu_2 - \mu_2^0)/RT = \ln(v_2/x) + (x - 1)v_2 - \ln x^2 + \chi x(1 - v_2)^2 \quad (5)$$

where x is the axial ratio of the solute, v_2 the volume fraction of solute, and χ the polymer–solvent interaction parameter introduced through the van Laar enthalpy of mixing. For the anisotropic phase

$$(\mu_1 - \mu_1^0)/RT = \ln(1 + v_2) + [(y - 1)/x]v_2 + 2/y + \chi v_2^2 \quad (6)$$

and

$$(\mu_2 - \mu_2^0)/RT = \ln(v_2/x) + (y - 1)v_2 + 2 - \ln y_2 + \chi x(1 - v_2)^2 \quad (7)$$

where y is the equilibrium degree of disorientation. When $y = 1$ the equations become those expected for ideal mixing of parallel rods with solvent.[16] When $x = 100$ and $\chi = 0.25$ the lattice theory predicts the system should be biphasic with the isotropic phase containing only 3×10^{-6} and the anisotropic phase 0.963 volume fraction polymer. At higher χ values the polymer concentration in the isotropic phase is even smaller with only a small dependence on x, unless x is very small.

By the lattice approach the chemical potentials for a random coil polymer are identical with eq 4 and 5.[8] From eq 1 and 4 the second virial coefficient may be connected with the χ parameter. Expansion of ln $(1 - v_2)$ of eq 4 and collection of coefficients of c^2 leads to $A_2 = (\bar{v}^2/\bar{V}_1)(0.5 - \chi)$ where $\bar{v}$ is the partial specific volume of the solute. In terms of the partial molar quantities of eq 3, $RT\bar{v}^2c^2(\chi - {}^1/_2) = \Delta h_1^E - T\Delta s_1^E$ for very dilute solutions. Hence, at the temperature where A_2 vanishes $\chi = 0.5$ for isotropic solutions of impenetrable, rigid rods as well as for isotropic solutions of random coils. However, the connection between A_2 and χ at temperatures other than the Θ temperature will not be the same for dilute solutions of rigid rods as for dilute solutions of random coils.

Since we find A_2 vanishes and hence $\chi = 0.5$ at temperatures slightly less than 25°, we are forced to conclude that there is a substantial enthalpic contribution to the solution thermodynamics and a need to alter the lattice theory of rigid, impenetrable rods. The studies on phase equilibria also indicate that the dilute polymer solutions at low temperatures are more complicated than had been anticipated.

For random coil polymers the appearance of a gel or rigid phase is indicative of covalent crosslinking,[8] hydrogen or hydrophobic bonding,[33] entrapment of chains in two or more crystalline regions producing a noncovalent network,[34] or the appearance of intramolecular order in the polymer molecules.[35] None of these appear to offer an appropriate explanation of our observations. Some kind of order, however, is indicated by the appearance of the rigid phase. This order must be intermolecular in nature as the chains already have maximum intramolecular order. Our inability to observe it in the polarizing microscope could be due to its structure. In the higher concentration anisotropic solutions the twist between ordered layers is known to have a temperature, solvent, and concentration dependence and is unobservable under some conditions.[6] Our gel phase could be similar to the well-characterized anisotropic phase but may have a twist making it unobservable in the polarizing microscope.

The phase diagrams are equally confusing in that the area bounded by the "hump" (Figure 8, region D) must by thermodynamic arguments consist of two isotropic solutions in equilibrium. A phase separation has been reported[36] for PBLG in the solvent system CH_2Cl_2–CH_3OH, although the solutions have not been investigated with respect to order. Attempts to have the PBLG–DMF system split into two phases were unsuccessful. A solution of concentration appropriate to put it in region D was prepared at room temperature, and upon lowering the temperature to put it in region D observed for several weeks. The system gave no visual evidence of separating into two phases distinguished by a sharp phase boundary. It is, however, sometimes difficult to get a solution of a random coil polymer to separate into two phases even though that is the thermodynamically stable state. By the lattice model for rigid, impentrable rods two isotropic solutions in equilibrium will never be stable relative to equilibrium between an isotropic and an anisotropic phase. Modification of the theory to allow for side chain and main chain flexibility can be made to account for these observations.[37] We feel, however, that the phase diagrams (Figures 7–9) and the low-concentration, low-temperature gel phase should be better characterized before proposing any new model.

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