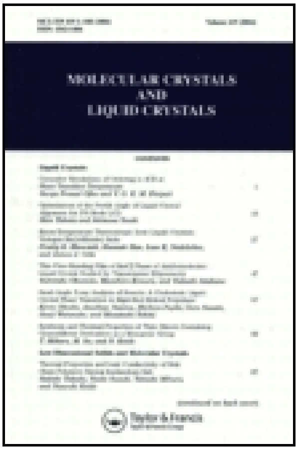

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Thermodynamic Properties of Poly(γ-benzyl-*L*-glutamate) Solutions over Entire Concentration Range†

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The solvent activities for the poly(γ-benzyl-*L*-glutamate)-dimethylformamide system were obtained from isothermal distillation and vapor pressure measurements in the concentration range 15–100 vol % of polymer at 30° C. Three samples were studied. The results were combined with osmotic pressure data obtained previously. The solvent activities at comparatively low concentrations were compared with the Cotter modified theory. The solvent activity behavior of the lower molecular weight sample ($M = 23{,}800$) is in rough agreement with that predicted by the theory over both isotropic and anisotropic regions, provided that the polymer with some amount of solvent acts as a kinetic unit. The results at higher concentrations are reasonably explained by the Flory-Leonard model of mixing of polymer side-chain with solvent. The solution process is discussed over a wide concentration range.

INTRODUCTION

Most polymers behave as random flexible chains in solution. The thermodynamic properties of the solution have been extensively investigated over a wide concentration range and understood both experimentally and theoretically.[1] Certain classes of polymers exist as rodlike chain particles in solution. Among them are synthetic polypeptides such as poly(γ-benzyl-*L*-glutamate) (PBLG). The concentration dependence between the flexible and stiff chains is different. The latter solution may undergo a phase transition from an isotropic phase to an anisotropic phase (liquid crystal) as the polymer concentration is increased. The theoretical treatments of the solution of rods have been developed wherein the rods are considered to be rigid. The phase transition phenomenon was first predicted on the basis of the cluster expansion ap-

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†Presented at the Eighth International Liquid Crystal Conference, Kyoto, July 1980.

proaches by Onsager[2] and Ishihara.[3] The lattice treatments for the equilibrium properties of the solutions of rods have been presented by Flory,[4] Dimarzio,[5] and Cotter and Martire.[6] In general, the results are similar to those arising from the cluster expansion approaches.

Flory[7] analyzed the axial ratio dependence of concentration at the phase transition for PBLG solutions found by Robinson and coworkers[8] and suggested that their data are qualitatively agreement with his lattice treatment. Straley[9] reexamined their data together with the data of other workers on the basis of the cluster expansion approach of Onsager. He suggested that the experiments and theory are in rough agreement for shorter rods and that the discrepancy for sufficient longer rods may be attributed to the flexibility of alpha-helices.

The thermodynamic properties of the systems of synthetic polypeptides and solvents in a concentration range of 60–100 vol % of polymer were measured by Flory and Leonard.[10] The data were beyond possibility of reconciliation with Flory's lattice theory. To account for the discrepancy, they considered that mixing of flexible side chains of polymer with solvent dominates thermodynamic behavior at high concentrations. Rai and Miller[11,12] found in the similar study for the systems of several synthetic polypeptides including PBLG and dimethylformamide (DMF) that DMF soluble polymers show the sorption thermodynamics explained by Flory-Leonard model and that non-DMF-soluble polymers show the thermodynamics explained by BET sorptions isotherms.

In contrast to the theories of solution properties, the statistical mechanics of the dense liquid of rigid rods have been developed with a view to examine the thermodynamic behavior of thermotropic liquid crystal by Lasher,[13] Alben,[14] and Cotter.[15,16] If their theories can be applied to the system of rod and solvent, they are preferable to the cluster expansion approaches and lattice treatments for examining the solution properties of PBLG, because they are free from the inherent limitation in the lattice model, in which the breadth of rod and the diameter of spherical solvent are assumed equal, and they are applicable to the moderately-concentrated solutions unlike the cluster expansion methods. Detailed osmotic pressure measurements for the PBLG-DMF system have been recently performed in the concentration range to about 20% of polymer.[17] The temperature dependence data of osmotic pressures indicated that the heat of dilution for the isotropic phase is nearly zero within some experimental error. Hence, we considered that the polymer may behave as a hard-core particle in the solvent. The osmotic pressure data for the isotropic phase were reasonably satisfied by the Cotter modified theory among the above theories if the decreased axial ratio is assumed for the polymer, whereas the difference in osmotic pressure behavior below and above the transition concentrations was not so much as that predicted by the theory.

In this paper, we report the results of solvent activity data for the same system evaluated from the vapor pressure and isothermal distillation methods in the concentration range of 15–100 vol % of polymer. The results are combined with the osmotic pressure data and compared with the existing theories. The solution process is investigated over the entire concentration range.

EXPERIMENTAL

Materials

Three samples of PBLG employed are the same as those used previously.[17] The molecular weights M, molar volumes V_p, and apparent axial ratios x determined previously from the osmotic pressure measurements at dilute solutions are:

	M	V_p	x	x in solid
PBLG-A	23,800	18,800	7.40	10.3
PBLG-B	66,000	52,100	22.8	28.3
PBLG-C	155,000	123,000	54.4	66.8

The fifth column represents the axial ratios of polymer in the solid state estimated using the length of the α-helix of 1.5 A per residue and its mean breadth, as calculated for a spherocylinder having a specific volume of 0.790 cm^3/g. After DMF and di (octyl phthalate) (DOP) were respectively dried over calcined calcium sulphate and magnecium sulphate, they are purified by vacuum distillation.

Isothermal distillation

In the intermediate concentration range, isothermal distillation measurements were performed using DOP as a reference solute at 30° C. The apparatus is consisted of a glass vessel. Three glass tubes (6 mm i.d.) were prepared. Weighed amounts (about 15 mg) of polymer were put into the two tubes, and the weighed reference solute was put into the third tube. After they were placed into the apparatus, a certain amount of solvent was poured with a syringe into the glass tube containing the reference solute. Most of the air was removed, and the apparatus was sealed off, after the solution was frozen in liquid nitrogen. The apparatus was then immersed in a thermostated bath. At the end of the experiment, it was removed from the bath and cut off with a flame. The three tubes removed were weighed quickly. The volume fraction of polymer was determined, assuming no volume change of mixing. Apparent equilibrium was reached in 14 days even for the run in which large amounts of solvent were transferred into the higher-molecular-weight sample (PBLG-C). This was confirmed by the results that the curve of volume fraction of polymer vs. mole fraction of solute evaluated by the run extending over 14 days was not changed by the points evaluated after the days more than 14 days within the experimental error. To determine whether the curve found by this method indicates true equilibrium curve, for the several cases solvent was added to the polymer in one glass tube as well as the reference solute; comparatively low concentrated polymer solutions (7–8%) were prepared. Then the isothermal distillation was performed. The results are discussed later.

Vapor pressure

Prior to the isothermal distillation measurements, the activity coefficient of DMF was measured in the solution of reference solute DOP. The basic part of the apparatus was composed of the Baratron pressure gauge (Type 220, MKS Instruments, Inc.) and two sealed tubes storing respectively solvent and solute degassed thoroughly. The tubes were immersed in a bath at 30°C, and the pressure gauge was maintained at 31°C to prevent condensation of solvent. After the system including the pressure gauge was evacuated to 10^{-5}mm, it was first confirmed that no apparent increase of pressure higher than 10^{-3} mm was found over the solute. Once again the gauge and solute reservoir were evacuated and then they were isolated from each other. Then solvent vapor was admitted into the pressure gauge and the vapor pressure was read. The solvent was subsequently added into the solute by breaking the break seal and the solution was mixed while stirring using a magnet. Once again solvent vapor pressure was read over the solution. At the end of the experiment the air was admitted into the apparatus. The solution was removed to a weighing bottle and the concentration was determined gravimetrically. The mole fraction activity coefficient γ_1 was calculated from the vapor pressure lowering ΔP_1 by

$$\gamma_1 = (1 - \Delta P_1/P_1^\circ)/(1 - x_2) \tag{1}$$

where P_1° is the vapor pressure of pure solvent and x_2 is the mole fraction of solute. These values appear in Figure 1 plotted as $(\gamma_1 - 1)/x_2^2$ vs. x_2. Expression for the activity coefficient determined from these data is

$$\gamma_1 = 1 + 5.31x_2^2 - 13.4x_2^3. \tag{2}$$

The apparatus for determining directly vapor pressure over polymer solution was basically a chamber for housing a quartz spring balance, the abovementioned pressure gauge, and a sealed tube storing solvent degassed. Weighed sample (about 40 mg) of the polymer was placed on a thin glass basket and the basket was suspended from the calibrated spring. Solvent vapor was admitted from the solvent reservoir into the chamber and the pressure gauge, after they were evacuated and the system was isolated. The increase in weight owing to sorption of solvent by the polymer was obtained from the elongation of spring. When no further weight increase was detectable over an extended period of time, sorption equilibrium was assumed to have been obtained. The equilbrium was usually reached in at least 12 hr. To obtain the desorption data, the system was evacuated quickly and isolated again.

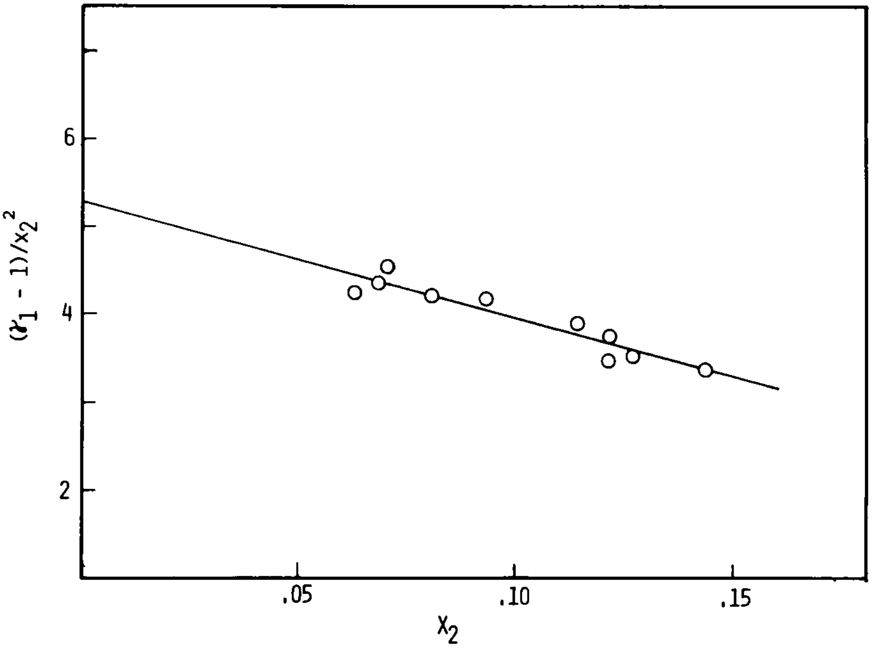

FIGURE 1 Activity coefficient of DMF in solutions of DOP at 30°C.

RESULTS

Osmotic pressure π is related to solvent activity a_1 by

$$RT\ln a_1 = -\pi V_s + \pi^2 V_s \kappa \tag{3}$$

where V_s is the molar volume of solvent and κ is the isothermal compressibility of solvent. Since κ is the order of 10^{-5} atm^{-1}, the second term of the right-hand side of Eq. (3) is negligibly small compared to the first term, even if π attains to considerable degree such as 10^2 atm. Hence, the second term was ignored in this work, when it is required to convert π into a_1 or vice versa. In Figure 2, the isothermal distillation data for PBLG-A solution in the concentration range to 45 vol % of polymer at 30° C are shown in the form of π vs. volume fraction of polymer v_2 with the osmotic pressure data determined previously.[17] The isothermal distillation data for PBLG-B and -C solutions below 30 vol % of polymer are shown in Figure 3. The thermodynamic behavior obtained from the isothermal distillation and vapor pressure measurements is shown in Figure 4 of the form of π vs. v_2 in the intermediate concentration range, and is shown in Figures 5-7 of the form of a_1 vs. v_2 at high concentrations. Most of the isothermal distillation data were due to the absorption method, and the desorption data for the PBLG-C are also indicated in Figures 3, 4, and 7. Most

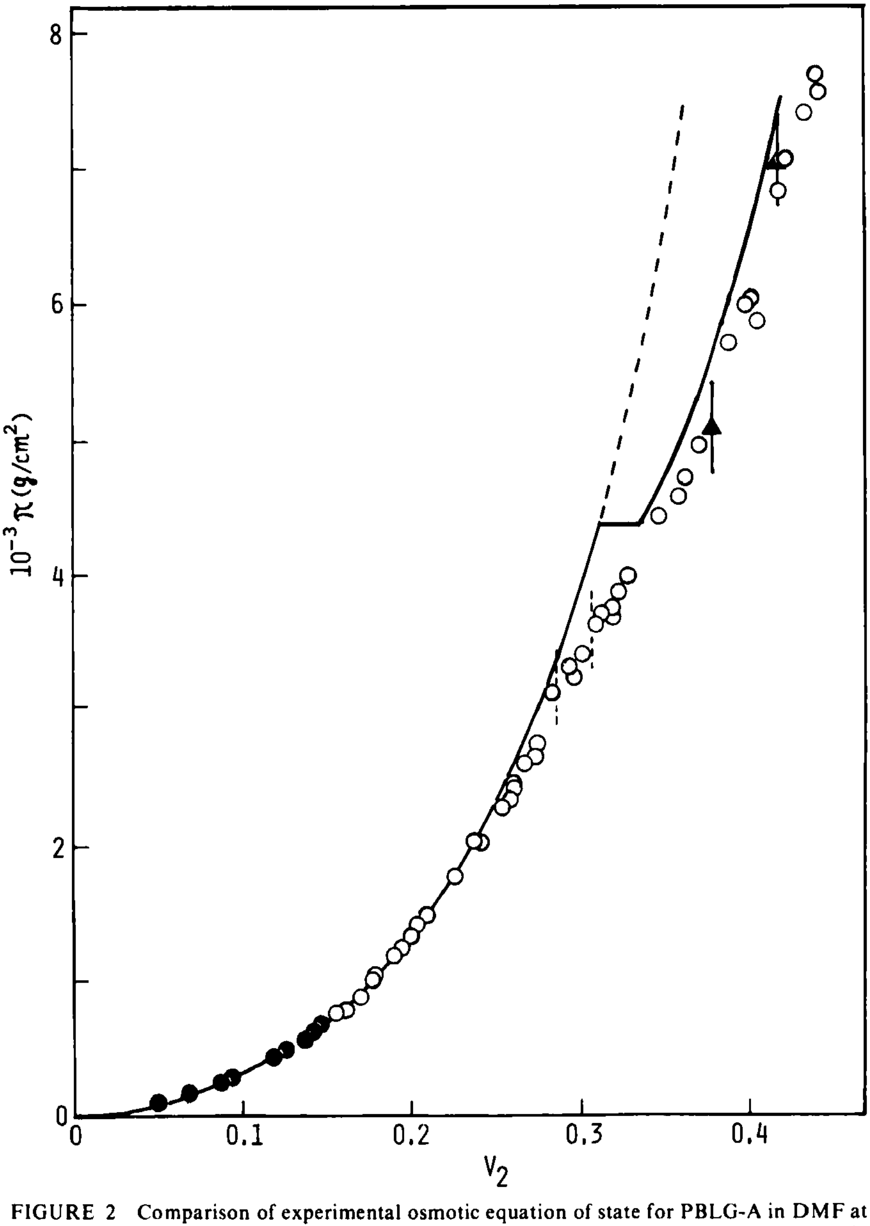

FIGURE 2 Comparison of experimental osmotic equation of state for PBLG-A in DMF at 30° C with theoretical equation: ●, osmotic pressure; ○, isothermal distillation (absorption); ▲, vapor pressure (desorption from low concentration); solid line calculated according to Cotter's modified theory. Dashed line corresponds to locally stable isotropic state. Vertical dashed lines indicate positions of phase boundaries found experimentally.

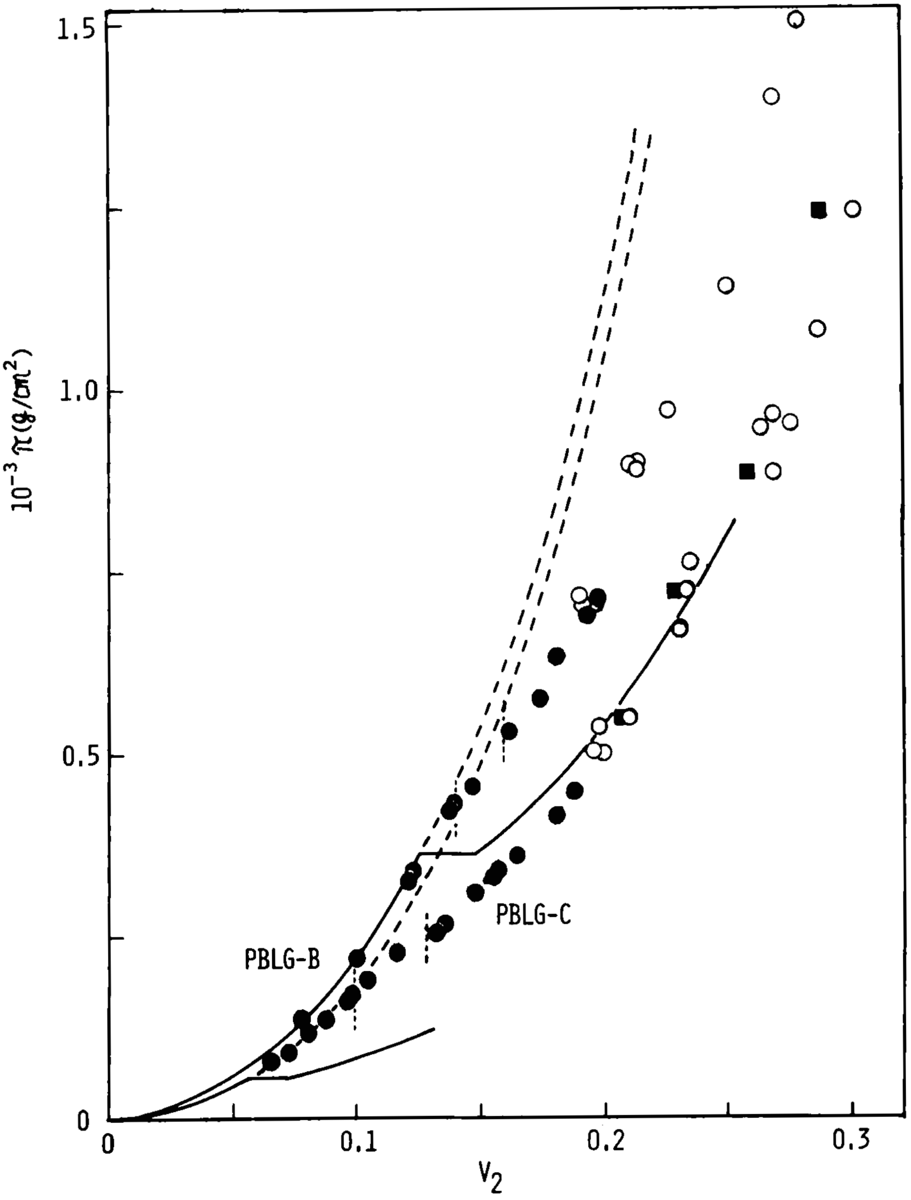

FIGURE 3 Comparison of experimental osmotic equations of state for PBLG in DMF at 30°C with theoretical equations: ●, osmotic pressure; ○, isothermal distillation (absorption); ■, isothermal distillation (desorption from low concentrations); upper and lower solid lines for PBLG-B and -C calculated respectively according to Cotter's modified theory. Dashed lines correspond to locally stable states. Vertical dashed lines indicate positions of phase boundaries found experimentally.

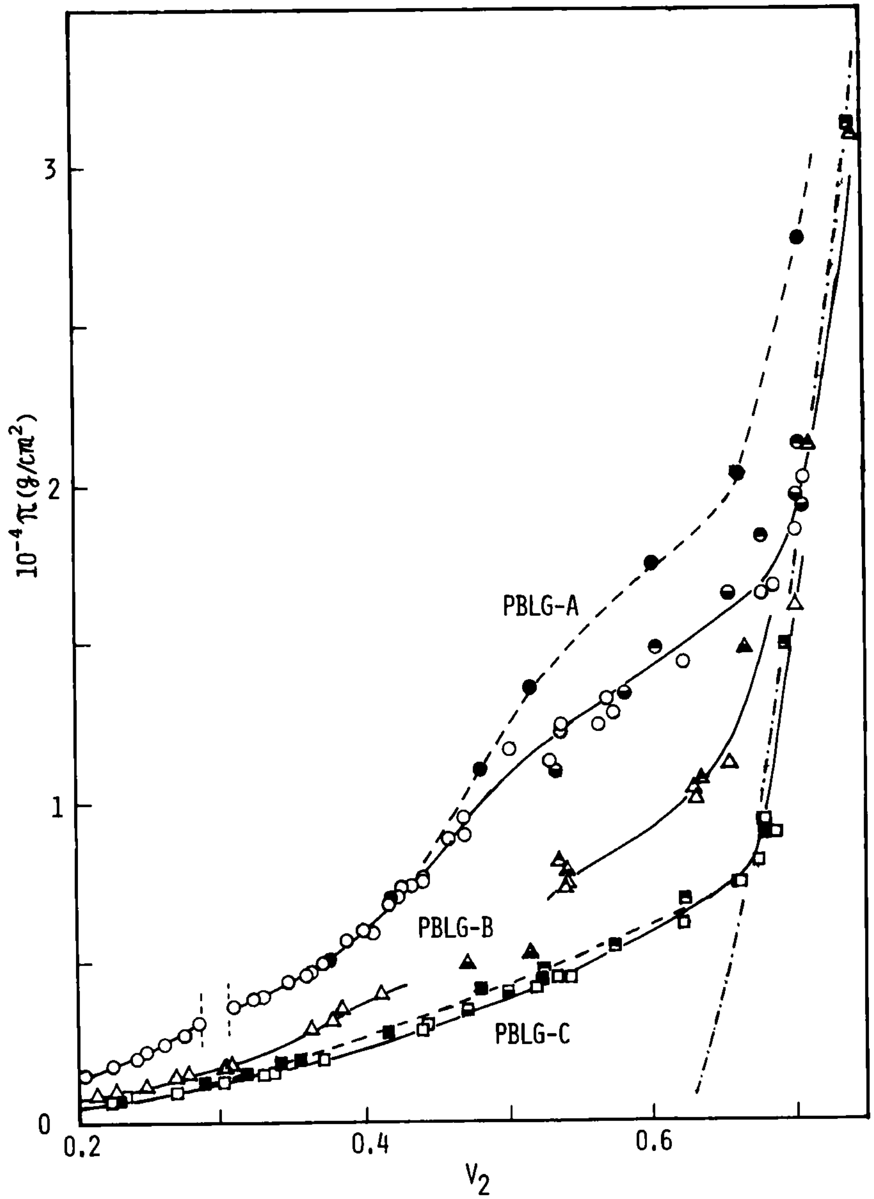

FIGURE 4 Activity data for PBLG-DMF in intermediate concentration range at 30° C: (——), absorption process; (----), desorption process. Circles, triangles, and squares indicate the results for PBLG-A, -B, and -C, respectively: (○, △, □), isothermal distillation (absorption); (◓, ▲, ⬒), vapor pressure (absorption); (⊖, ▲, ⊟), vapor pressure (desorption); (●, ■), desportion from low concentrations; (–·–·), Flory-Leonard side-chain mixing model with $\chi = 0.69 + 0.30\nu_1'$.

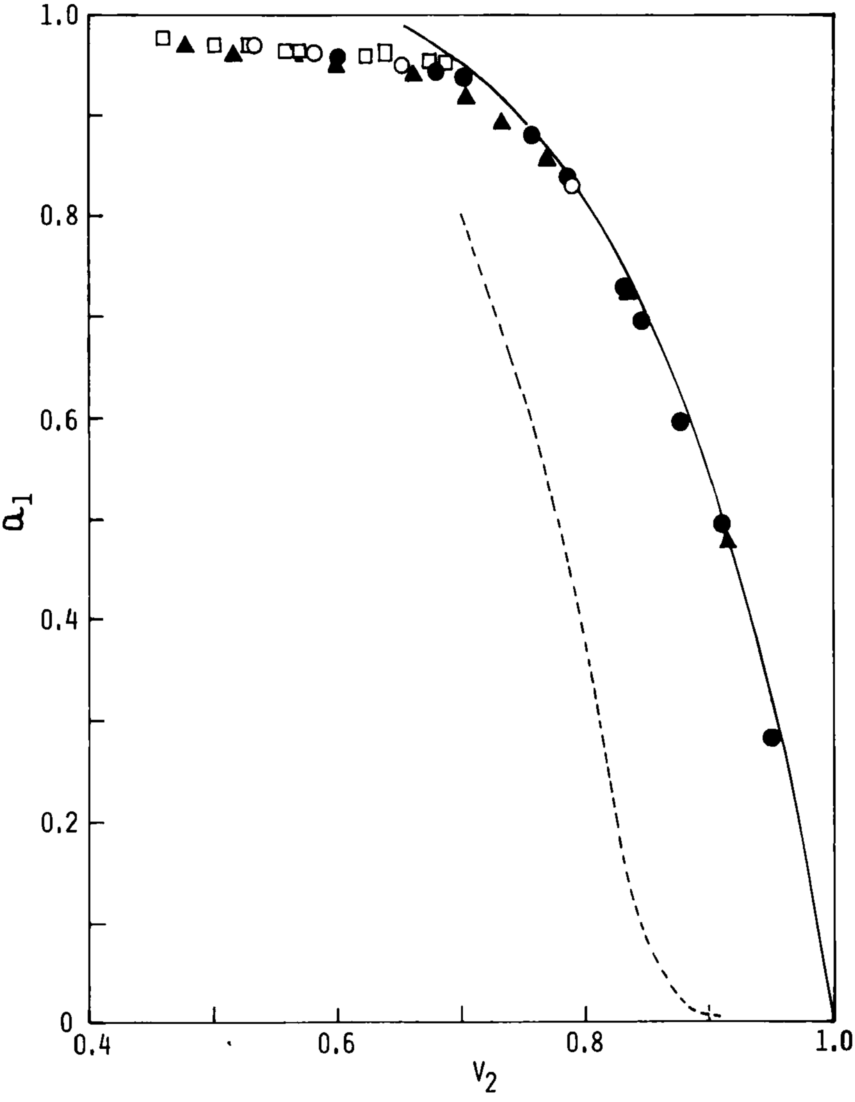

FIGURE 5 Comparison of experimental solvent activities for PBLG-A in DMF at 30°C with theoretical curves: ○, vapor pressure (absorption); ●, vapor pressure (desorption); ▲, vapor pressure (desorption from low concentrations); □, isothermal distillation (absorption); (——), Flory-Leonard side-chain mixing model with $\chi = 0.69 + 0.30\nu_1'$, (----), Cotter's modified theory with $\ll \sin\gamma \gg = 0$.

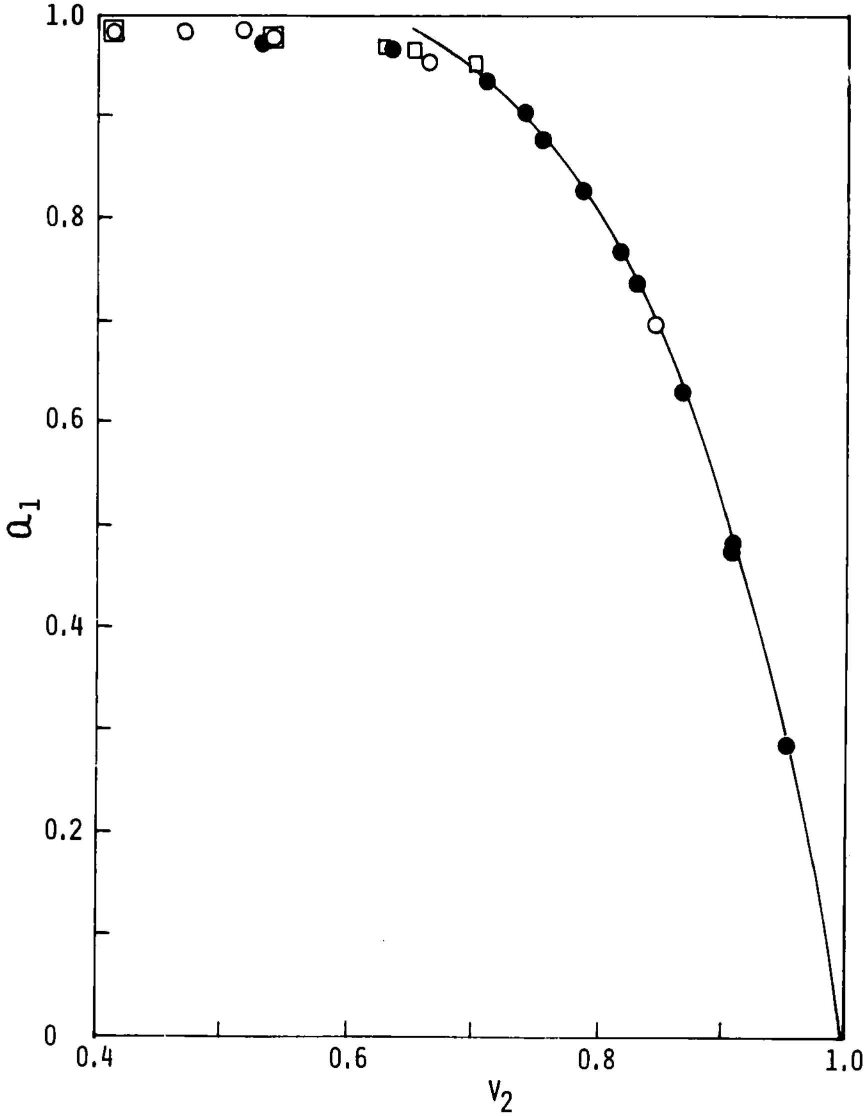

FIGURE 6 Comparison of experimental solvent activities for PBLG-B in DMF at 30°C with theoretical curve. The symbols and curve indicated are the same as described in Figure 5.

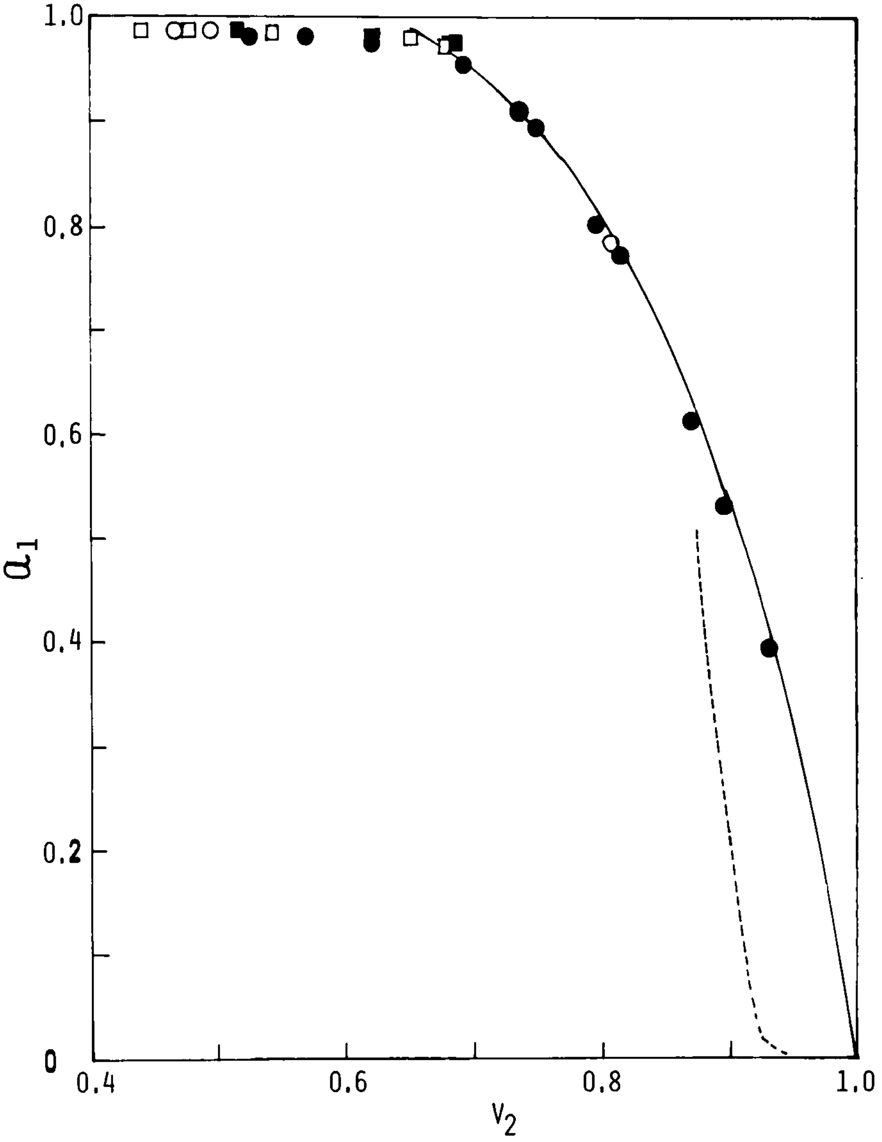

FIGURE 7 Comparison of experimental solvent activities for PBLG-C in DMF at 30° C with theoretical curves. Filled squares indicate the results measured by the isothermal distillation method (desorption from low concentrations). The other symbols and curves indicated are the same as described in Figure 5.

of the vapor pressure data were obtained from the absorption of solvent by the solid polymer within the concentration range of about 50% of solvent and from the subsequent desorption of solvent. For the PBLG-A solution, desorption data of the vapor pressure measurements which were started from a sufficiently low concentration (about 8%) are also indicated in Figures 2, 4, and 5. From the features of the experimental data and curves, the true equilibrium data are considered to be obtained over most of the concentration range, except in the intermediate range, where somewhat hysteresis is observed. Miller *et al.*[11] observed no hysteresis for the same system over the concentration range below 30 vol % of solvent and we also observed no hysteresis for the PBLG-chloroform system over the wide concentration range,[18] whereas Flory *et al.*[10] observed a considerable hysteresis above about 20% of solvent in the PBLG-pyridine and PBLG-ethylene dichloride systems.

DISCUSSION

The theories of liquid of rigid spherocylinders were presented on the basis of interaction alone through the repulsion which prevents their overlapping. According to the theories of Onsager,[2] Lasher,[13] Alben,[14] and Cotter,[15,16] the Helmholtz free energy F for a collection of N rigid spherocylinders at the number density ρ are given by the relation

$$F/NkT = \langle \ln 4\pi\bar{f}(\Omega)\rangle + A(\rho) + \{B(\rho)/2\} \ll \sin\gamma(\Omega,\Omega') \gg \tag{4}$$

where $\gamma(\Omega,\Omega')$ is the angle between the long axes of particles, $\bar{f}(\Omega)$ is the most probable orientational distribution function,

$$\langle \ln 4\pi f(\Omega)\rangle = \int \bar{f}(\Omega) \ln 4\pi\bar{f}(\Omega)d\Omega \tag{5a}$$

and

$$\ll \sin\gamma(\Omega,\Omega') \gg = \iint \sin\gamma(\Omega,\Omega')\bar{f}(\Omega)\bar{f}(\Omega')d\Omega d\Omega'. \tag{5b}$$

The two functions of density, $A(\rho)$ and $B(\rho)$ are not the same in each theory. From the statistical mechanical point of view, Cotter's recent scaled particle approach[16] is considered to be the most promising. The equation of state obtained for liquid of the spherocylinders of length L and diameter D is

$$\frac{Pv_0}{kT} = \left\{1 + \rho v_0 + \frac{2}{3}\left(1 + q - \frac{1}{2}q^2\right)\rho^2 v_0^2 + 2r\rho v_0\left(1 + \frac{1+2q}{3}\rho v_0\right) \ll \sin\gamma \gg \right\} \frac{\rho v_0}{(1-\rho v_0)^3} \tag{6}$$

where v_0 is the hard-core volume of particle, q is $2/(3x-1)$, and r is $6(x-1)^2/\pi(3x-1)$: x is the axial ratio; $L/D + 1$. By expanding this equation in ρv_0 and then truncating the resulting series after its second term, Onsager's equation of state is obtained

$$\frac{Pv_0}{kT} = \rho v_0 + (4 + 2r \ll \sin \gamma \gg)\rho^2 v_0^2. \tag{7}$$

Lasher has given $\ll \sin \gamma \gg$ and $\langle \ln 4\pi \bar{f} \rangle$ for twelve values of B to 10.6 for the anisotropic phase. Since we draw a curve by extrapolating the twelve points of $\ll \sin \gamma \gg$ vs. B^{-1} to the origin, we can evaluate the equation of state to high density. Two dimensionless densities (ρv_0 and $\rho' v_0$) at the transition points depend on the axial ratio alone.

Applying the theory of liquid of rods to the system of rod and solvent, the free energy of Eq. (4) can be treated as the excess free energy over that of solvent. The pressure P becomes the osmotic pressure π. The dimensionless density can be replaced by the volume fraction of rod in solution, provided that the rods themselves have no free volume.

Considerable experimental evidence indicating that PBLG has some flexibility in dilute solutions has been accumulated.[19] Miller and Flory[20] suggested that this flexibility may be attributed to the fact that the helix contains a small number of defects in which a few monomer units are not hydrogen-bonded with the neighboring units. In the range of low molecular weight, molecule is consisted of a single helical section and some flexible units in two ends of it. On further increase in chain length, the molecule acquires an average of more than one helical sequence. According to the results of ORD measurements by Matsumoto and Teramoto,[21] the average numbers of helical sections in the PBLG-A, -B, and -C molecules are considered to be about 1.0, 1.3, and 1.7, respectively. In veiw of the data of second virial coefficients, the PBLG-A seems to be more flexible than the higher molecular weight samples contrary to the expectation. However, we assume that this fact is attributed to a somewhat molecular association of side-by-side type in the PBLG-A solution. The molecular association of this type is frequently observed in benzene and dioxane.[22]

In any event, first we consider that PBLG behaves over the concentration range studied here as an equivalent spherocylinder with an apparent axial ratio determined from the osmotic pressure data at low concentrations. In Figures 2 and 3, the experimental results are compared with the equations of state predicted from the Cotter modified approach. The experimental equations of state for the isotropic phase are in fairly good agreement with the theory over most of concentration range, except at the range near the transition points (detailed comparison for the PBLG-B and -C solutions should be referred to Figures 4 and 5 in Ref. 17). The values of $\partial \pi / \partial v_2$ obtained experimentally for the three samples below and above the transition points do not change so abruptly as the predicted (detailed comparison for the PBLG-B and

-C solutions should be referred to Figures 6 and 7 in Ref. 17). However, an important feature of Figure 2 is that the experimental equation of state is roughly similar to the predicted equation of state over the concentration range covered.

In the previous paper,[17] the dependence of A-point (concentration where the ordered phase first appears) on an apparent axial ratio was compared with that predicted from the Cotter modified approach. The results indicated that the locus of A-point is in rough agreement with the theory for shorter rods and that the concentrations of A-point are much higher than the predicted for longer rods. The explanation may be that the feature and degree of interruptions of the helix depend on the chain length. When a molecule is consisted of a single helical sequence and some flexible units in two ends of it, the effect of this flexibility on the free energy adds merely a constant term to Eq. (4), if the degree of the flexibility due to the tail segments is independent of concentration and phase. This situation would be in the case of the PBLG-A solution. When a molecule has a possibility of an average of more than one helical sequence, Eq. (4) would be considerably altered. However, the influence of the modification on the osmotic pressure is almost included in the value of a decreased axial ratio for the isotropic phase (whereas the modification contributes to the solute activity), provided that the flexibility of the molecule is retained independent of concentration. The situation in the anisotropic phase is distinct from that in the isotropic phase. Since the number of intermolecular conformations arising from the inner defects of the helix decreases with an increase in orderliness of alignment, loss in entropy on entering the aligned phase causes the resulting osmotic pressure to be higher than the rigid behavior and causes the phase transition concentrations to be higher.

It is interesting that the experiments are compared with the Cotter modified theory at sufficiently high concentrations. When no free volume in liquid is left i.e. $\rho v_0 \rightarrow 1$, the rods would be perfectly aligned along the preferred direction and then $\langle\!\langle \sin \gamma \rangle\!\rangle$ approaches zero. In Figures 5 and 7, the experimental solvent activities are compared with Cotter's equation with $\langle\!\langle \sin \gamma \rangle\!\rangle = 0$. A considerable discrepancy is found. If a value of $\langle\!\langle \sin \gamma \rangle\!\rangle$ larger than zero by a small order is employed (such a procedure is reasonable from the physical point of view), theoretical curves depart increasingly from the experiments. If the experimental rods have a somewhat free volume, the experiments may approach the predicted curves to some extent. However, important features of Figures 5–7 are that the data above about 70% of polymer are insensitive to the axial ratio of samples used; yet the theory has the axial ratio dependency.

Thermodynamic properties of the PBLG-pyridine, PBLG-ethylene dichloride, and poly(β-benzyl-L-aspartate)-chloroform systems were investigated by Flory and Leonard in the concentration range of 60–100 vol % of polymer.[10] They considered in the region of small composition of solvent that the translational and rotational motions of the helical core of the studied polypeptides are frozen in, but that the side chains of them, which constitute a considerable sizable fraction, are sufficiently disordered and flexible. Assuming that mixing of the flexible side chains with solvent dominates the concentrated solution thermodynamics, their data were compared with the expression

$$a_1 = v_1' \exp(v_2' + \chi v_2'^2) \tag{8}$$

where v_1' is the volume fraction of solvent calculated on the basis of mixing being confined to the side chain domains and χ is the thermodynamic interaction parameter. The relation of v_1' and v_2' to v_1 and v_2 is given by

$$v_2'/v_1' = (M_s/M_u)(v_2/v_1) \tag{9}$$

where M_s and M_u are the molecular weights of side chains and entire peptide unit, respectively. The absorption data of them were found to fit Eq. (8) if the χ values of 0.35, 0.2, and zero were respectively assumed for the above-mentioned systems. Rai and Miller[11] found in the similar study for the PBLG-DMF system in the concentration range below 30% of solvent that the predicted values and experiments were in reasonable agreement by assuming $\chi = 0.6$ below 13% of solvent. The curves of solvent activity a_1 vs. v_2 calculated from Eqs. (8) and (9) with $\chi = 0.69 + 0.30v_1'$ are shown in Figures 4–7. Aside from the special desorption data for the PBLG-A, a reasonable agreement is found between the predicted values and experimental data below about 30% of solvent. Although this value of χ is slightly larger than that of Rai and Miller, general features of the experimental curves of Figures 5–7 are similar to the curve of them.

The solution process of PBLG may be elucidated over the wide concentration range by extending the arguments presented until now. The molecule are quasicrystalline in the solid state; of course the structures depend microscopically on the procedure obtaining the samples.[23] The translational and rotational motions of the main chain backbone are frozen in the field due to the considerable intermolecular attractions between the molecules. However, the long side chains are sufficiently disordered and flexible.[24,25] Since the helical core will not participate in the mixing process, the side chains mix with the first solvent absorbed by the polymer. The side chains being limited in length, the χ value evaluated here by fitting the experimental data to the predicted curve includes the term of the increase of the free energy owing to the extension of them as well as the terms of the polymer-polymer, polymer-solvent, solvent-solvent interactions. The solvent entering the side chain domains produces the reduction of the actual intermolecular attraction between the polymers due to the shielding of the main chain backbone. The translational and rotational motions of the main chains of the polymers initiate locally as more solvent is absorbed. The deviation from Eq. (8) below $v_2 \approx 0.7$ as shown in

Figures 4-7 would demonstrate such a situation. The collection of molecules approaches gradually to such a liquid crystal state as determined by the thermodynamical equilibrium condition. Further addition of solvent leads the system to the isotropic state through the biphasic region.

Some portion of the amounts of solvent entered first the side chain domains may be sufficiently considered to constitute a part of the polymer which acts as a kinetic unit in solution. This seems to require a modification of the experimental and theoretical curves to be compared in the comparatively low concentration range. The basic point of this modification is that the core volume fraction of solute ρv_0 in solution must be larger than the volume fraction v_2 determined by weighing out as two pure components. In order to discuss this problem, we remove the foregoing assumption that the polymers have no free volume and assume completion of mixing with the side chains. The core volume v_0 of polymer with saturated amounts of solvent in solution will be given by

$$v_0 = v^* + A^* \tag{10}$$

where v^* is the core volume of dry solute and A^* is the total core volume of N_s solvents travelling apparently with the solutes divided by the number of the existing solutes N_p. The quantity of v^* is related to the volume per solute v_p by v_p/α and A^* is given by $N_s v_s/N_p\beta$: v_s is the volume per solvent. The quantities α and β are larger than 1. When we express v_0 as Kv_p, the core volume fraction ρv_0 is given by Kv_2. Hence, the experimental osmotic pressure at a given v_2 should be compared with the theoretical value at a Kv_2. Since the osmotic pressure data at low concentrations plotted as $\pi/\mathrm{RT}v_2$ vs. v_2 give the first virial coefficient V_p^{1} ($V_p = N_A v_p$ is the molar volume of polymer) and the second virial coefficient $\{4 + 3(x-1)^2/(3x-1)\}KV_p^{1}$, the apparent axial ratios x of equivalent spherocylinder swollen in solution are estimated depending upon choices of the value of K. The different curves based on Cotter's modified approach are drawn according to the assumed values of K. The theoretical curves as shown in Figures 2 and 3 correspond to those with $K = 1$. The experimental equations of state for the PBLG-B and -C solutions in the isotropic phase seem to be respectively explained more reasonably by the curves with $K = 0.9$ and $K = 0.8$. However, the absorption data do not indicate such an information as the degree of saturation decreases with an increase in chain length. The explanation may be offered by examining the original assumption that the polymer behaves as a rigid spherocylinder with the decreased axial ratio over the entire isotropic region. The disadvantage in this assumption may become stronger with departure from the rigidity of polymers.

Since the experimental equation of state for the PBLG-A, which is considered to be sufficiently rigid, appears to be in fairly good agreement with the curve of $K = 1$, the saturated amounts of solvent may be evaluated, if α and β are known. Although α for PBLG and β for DMF have not been found, a rough method is to adopt the value of 1.15 for polystyrene in non-glassy state as α and the value of 1.3 for benzene as β at ambient temperature.[26] Using these values, the number of saturated solvents per residue is 0.39. This gives 0.85 as the value of $N_p v_p / N_p v_p + N_s v_s)$. This value does not contradict the statement mentioned in the solution process.

Acknowledgments

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