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Thermodynamic Properties of Moderately-concentrated Poly(γ-benzyl-L-glutamate) Solutions

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The osmotic pressures for poly(γ-benzyl-L-glutamate) solutions in ethylene dichloride and chloroform were measured at 29 °C in the concentration range of 2—15 vol % polymer. The osmotic pressures increased monotonously with an increase in the concentration. No evidence was found for the coexistence of two phases. The results are compared with the theory of the solutions of rodlike molecules. The values of the thermodynamic interaction parameter, χ, for the systems were found to be 0.44—0.47 in the concentration range lower than 6.5 vol% polymer, where the solutions must be isotropic.

Poly(γ-benzyl-L-glutamate) (PBLG) is in the state of a random coil when it is dissolved at low concentrations in dichloroacetic or trifluoroacetic acid. In other solvents, such as chloroform, ethylene dichloride (EDC), and *N*,*N*-dimethylformamide (DMF), the polymer is α-helical. Below a critical concentration (A-point), these solutions are isotropic, while above another concentration (B-point) they are anisotropic. The coexistence of these isotropic and anisotropic phases occurs in the intermediate concentration range, and these critical concentrations depend on the temperature.

The equilibrium properties of solutions of rodlike molecules have been treated theoretically by Onsager,$^{1)}$ Isihara,$^{2)}$ and Flory.$^{3)}$ These theories predict that, above a critical concentration, rodlike molecules will be packed closely and will all be aligned in one direction, without requiring attraction forces, thus forming a nematic liquid crystal. The molecular distribution methods of Onsager and Isihara have been given for dilute solutions. Flory's lattice theory, however, is regarded as being free from any restriction on the concentration range.

In Flory's theory the enthalpy term in the free energy of mixing is assumed to be of the Van-Laar type and to be characterized by a parameter χ, which is also used in the statistical theory of solutions of randomly-coiled polymers. The phase diagrams are shown for axial ratios of r=50 and 100 in Fig. 1. The differences in the two concentrations corresponding to the A- and B-points are small for χ<*ca.* 0.1. In the range of χ>*ca.* 0.1 for r=100, and χ>*ca.* 0.25 for r=50, the concentrations of the solute in the isotropic phases become extremely low, while the volume fractions of the solute in the anisotropic phase approach unity.

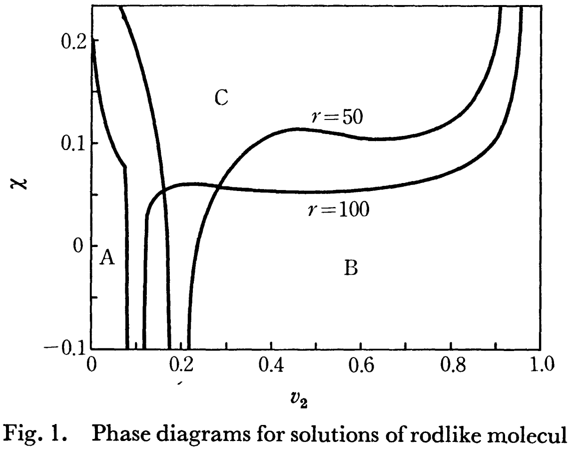

Fig. 1. Phase diagrams for solutions of rodlike molecules: region A, isotropic; B, anisotropic; C, coexistence region; axial ratio (r)=50 and 100.

Robinson *et al.*$^{4)}$ found the A-point and the B-point for PBLG solutions in methylene chloride and dioxane by polarizing microscope measurements. The molecular-weight dependences of the concentrations of these points were in semiquantitative agreement with Flory's lattice theory, provided the value of χ is sufficiently small. Hermans$^{5)}$ found the A-point for PBLG solutions in *m*-cresol from the viscosity methods. Nakajima *et al.*$^{6)}$ discussed the phase diagrams obtained by the observation of the turbidity for the three-component system of the PBLG–DMF–poor solvent, in which the addition of a poor solvent to the polymer-solvent system caused an increase in the thermodynamic parameter, χ. Further, Wee and Miller$^{7)}$ observed the A-point and the B-point as a function of the temperature by polarizing microscope and NMR spectrum measurements respectively; thus they obtained the phase diagram. These diagrams were in semiquantitative agreement with the prediction of Flory's theory. No direct values of χ, however, were given in these experiments.

The thermodynamic properties of the PBLG–pyridine, PBLG–EDC, and poly(β-benzyl-L-asparatate)–chloroform systems investigated by Flory and Leonard$^{8)}$ in the concentration range of 60—100 vol% polymer. Their data could not be explained on the basis of Flory's lattice theory, but they could be explained if the mixing of a flexible side chain of the polymer with a solvent was considered. Their data were found to fit reasonably well a modified lattice model if χ_s values of 0.35, 0.20, and zero were assumed for the PBLG–pyridine, PBLG–EDC, and poly(β-benzyl-L-glutamate)–chloroform systems respectively, in which χ_s is a thermodynamic interaction parameter between the solvent and the side chain of the polymer.

There have been reported only a few studies aimed at evaluating the χ parameter in PBLG solutions from thermodynamic experiments. Goebel and Miller$^{9)}$ obtained 0.5 for χ in dilute solutions of PBLG in DMF

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at 22 °C from osmotic-pressure measurements. Rai and Miller[10] obtained 0.8 for χ in the same system in the concentration range of 0—30 vol% polymer from differential scanning calorimetric measurements on the assumption that χ is independent of whether the system is an isotropic or an anisotropic phase, and of the composition.

In this report, we will discuss the results of osmotic-pressure measurements on the PBLG–chloroform and PBLG–EDC systems in moderately concentrated regions and will attempt to obtain A- and B-points thermodynamically and to determine the χ value directly. The results are compared with those of Flory's theory.

Experimental

Materials. Three samples of PBLG (PBLG-A, -B, and -C) different in molecular weight were used. These were prepared by polymerzing γ-benzyl-L-glutamate-*N*-carboxy anhydride in dioxane, with triethylamine as an initiator. The molecular weights of PBLG-A, -B, and -C were found to be 1.88×10^5, 1.78×10^5, and 0.98×10^5 respectively by osmometry in DMF solutions. A high-speed membrane osmometer (Hewlett-Packard Co., Model 501) was employed. The axial ratios of PBLG-A, -B, and -C are 85, 81, and 45 respectively. After DMF was dried over $MgSO_4$ for 2 or 3 days, it was purified by vacuum distillation. The chloroform and EDC were dried over $CaCl_2$ and then distilled.

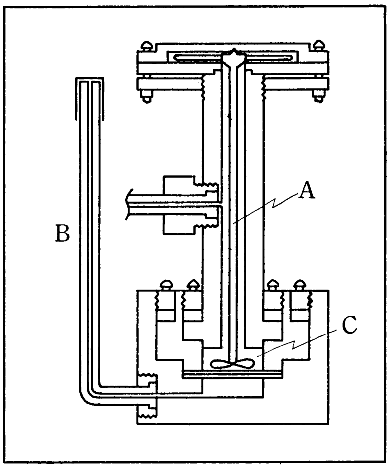

Fig. 2. Osmometer: A, stirrer; B, capillary; C, solution cell.

Osmotic-pressure Measurements. A high-pressure osmometer of the Flory[11]–Kuwahara[12] type was constructed (Fig. 2). It was designed so that highly viscous polymer solutions were stirred thoroughly without a leak in the applied pressure. The stirrer, A, was rotated by means of the outer magnet.

The osmotic pressures were measured at 29 °C by a compensation method. The solution was stirred in an Erlenmeyer flask for 24 hr; then it was put into a solution cell. After the solution had been stirred for 4—6 hr, it took 4—6 hr more until the equilibrium pressure was attained. No significant drift in this pressure was observed for a period of 24 hr. It was found that the polymer did not measurably leak into the solvent cell. In a few instances the pressure was reduced slightly after 30—40 hr; then leakages of the polymer were observed. The concentration of the polymer was estimated after each run. The volume fraction of the polymer, v_2, was obtained on the assumption that no volume change occurred on mixing. The semipermeable membranes used were degenerated cellulose membranes (Schleicher & Schuell Co., Type 08).

Results and Discussion

Table 1 shows the results of the osmotic-pressure measurements. In Fig. 3 the dependence of the osmotic pressure on the concentration is shown for PBLG-A in EDC. No data in the concentration region higher

Table 1. Osmotic pressure data and values of χ

$10^2 v_2$	π(g/cm^2)	χ
	PBLG-A in EDC	
2.09	18	
3.47	36	0.44
4.90	58	0.45
7.62	138	0.46
7.82	130	0.47
	PBLG-A in chloroform	
2.25	24	
4.90	49	0.46
5.67	70	0.46
5.74	76	0.46
8.88	110	0.49
10.50	158	0.498
	PBLG-B in chloroform	
2.29	16	0.44
4.42	41	0.46
5.23	64	0.46
6.44	99	0.46
7.43	120	0.47
9.57	193	0.474
14.36	425	0.493
	PBLG-C in chloroform	
3.11	26	0.46
3.96	40	0.46
5.71	70	0.47
7.52	120	0.47
9.95	200	0.483
11.13	279	0.479
15.17	533	0.491

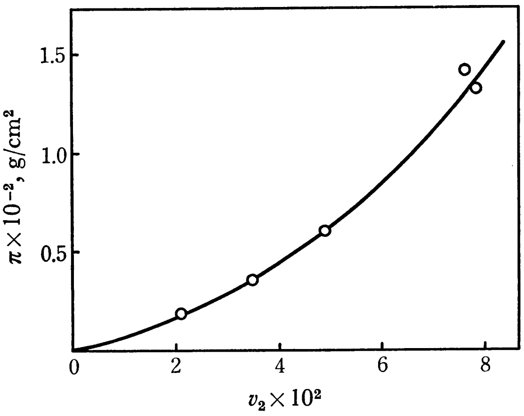

Fig. 3. Experimental values of π plotted against v_2 for solutions of PBLG-A in EDC at 29 °C.

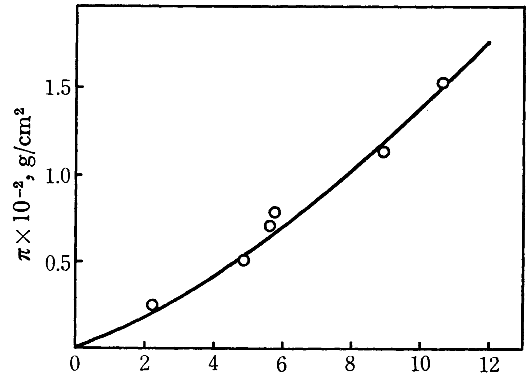

Fig. 4. Experimental values of π plotted against v_2 for solutions of PBLG-A in chloroform at 29 °C.

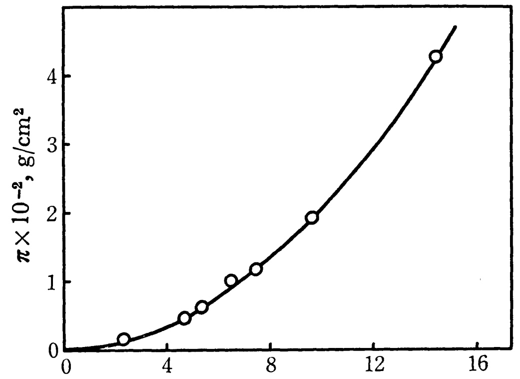

Fig. 5. Experimental values of π plotted against v_2 for solutions of PBLG-B in chloroform at 29 °C.

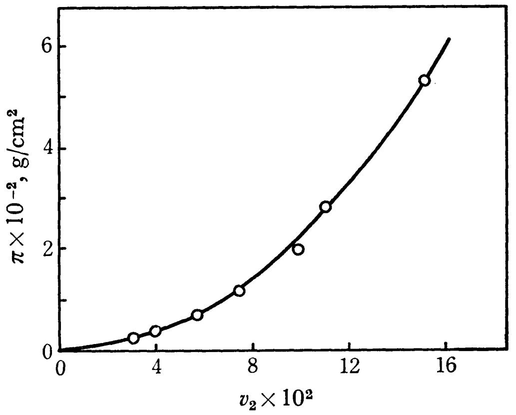

Fig. 6. Experimental values of π plotted against v_2 for solutions of PBLG-C in chloroform at 29 °C.

than the concentration of 8 vol% polymer were obtained, because this system causes gelation at higher concentrations before the attainment of the equilibrium pressure. The data for PBLG-A, -B, and -C in chloroform are shown in Figs. 4, 5, and 6 respectively.

According to the lattice theory of Flory,[3] the free energy of mixing ΔG_m for the system consisting of n_1 mol of a solvent and n_2 mol of a rodlike polymer with an axial ratio, r, is given by:

$$\begin{aligned}\Delta G_m/RT = {} & n_1 \ln v_1 + n_2 \ln v_2 - (n_1+yn_2) \\ & \times \ln\{1-v_2(1-y/r)\} - n_2\{\ln(ry^2)-y+1\} \\ & + \chi r n_2 v_1 \end{aligned} \tag{1}$$

where v_1 and v_2 are the volume fractions of the solvent and the polymer respectively, and y is a orientation parameter. This equation gives the chemical potentials of the solvent both in the isotropic phase and in the anisotropic phase. The relation for the isotropic phase is:

$$(\mu_1-\mu_1{}^0)/RT = \ln(1-v_2) + (1-1/r)v_2 + \chi v_2{}^2 \tag{2}$$

and that for the anisotropic is:

$$(\mu_1-\mu_1{}^0)/RT = \ln(1-v_2) + \{(y-1)/r\}v_2 + 2/y + \chi v_2{}^2 \tag{3}$$

where y is given as the solution of the following equation:

$$v_2 = \{r/(r-y)\}\{1-\exp(-2/y)\} \tag{4}$$

The plots of $\Delta\mu_1(=\mu_1-\mu_1{}^0)$ *versus* v_2, as calculated from Eqs. (1)—(4) for $\chi=0$ with $r=45$ and 85, are shown in Fig. 7. The straight lines parallel to the absissa show that there is no net change in $\Delta\mu_1$ when the isotropic and anisotropic phases co-exist. The rate of change in the chemical potential for the anisotropic phase is much less than for the isotropic phase.

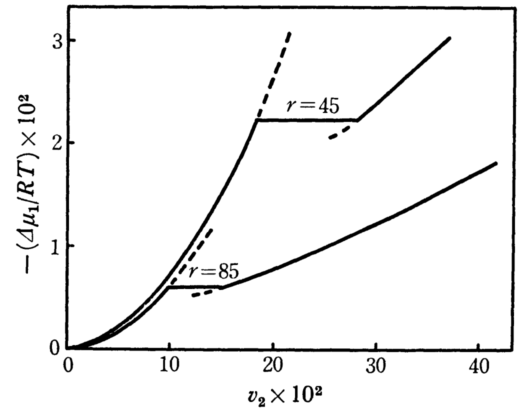

Fig. 7. Calculated curves of $\Delta\mu_1/RT$ plotted against v_2 for solutions of rodlike molecules: axial ratio $(r)=45$ and 85; thermodynamic parameter $(\chi)=0$.

The chemical potential, μ_1, of the solvent is related to the osmotic pressure, π, of the solution by:

$$\mu_1 - \mu_1{}^0 = -\pi V_1 \tag{5}$$

where V_1 is the molar volume of the solvent. Therefore, Fig. 7 also represents the relation between π and v_2.

In Flory's lattice theory of solutions of rodlike molecules, the concentrations corresponding to A-points for $r=45$ and 85 are respectively given as $v_2=0.18$ and 0.095 for $\chi=0$, as are shown in Fig. 7. The experimental investigations of Robinson *et al.*[4] for the PBLG–methylene chloride and PBLG–dioxane systems showed that the concentrations observed as the A-points are lower than the predicted concentrations when they are compared on the same axial ratios, provided a value of χ is sufficiently small. The concentrations of the A-points corresponding to the axial ratios of the samples used in this work are obtained on the basis of their data as follows:

	PBLG–methylene chloride	PBLG–dioxane
	$v_2 \times 10^2$	
$r = 45$	9	8
$r = 81$	8	8
$r = 85$	8	8

It was shown in our previous paper[13] that the PBLG-A (r=85)-chloroform system separated into phases at equilibrium in the concentration 8 vol% polymer and at 30 °C.

In the concentration range where a solution is biphasic, some parts of the sample transmit light when placed between crossed polars, while others do not. Although it was difficult to determine clearly the point when no light parts remained in an Erlenmeyer flask, the A-points for the solutions of PBLG-B (r=81) and -C (r=45) in chloroform were found to be at $v_2 \approx$ 0.065—0.070 at 29 °C. The A-points are satisfactorily within the range of the present osmotic-pressure measurements except for the measurements of the PBLG-A solutions in EDC (see Figs. 3—6).

The osmotic pressures for the solutions of PBLG in EDC and chloroform increase monotonously with an increase in the concentration, as are shown in Figs. 3—6. The existence of explicit phase boundaries was not found from the dependence of the osmotic pressure on the concentration.** The reason for this may be considered to be as follows. Since the biphasic region was too narrow to be detected experimentally, and since the difference between the chemical potentials for the isotropic and the anisotropic states was not so much as that predicted by Flory's theory (see Fig. 7), we might have drawn a smooth curve over the region of the two phases in the osmotic *vs.* concentration diagram.

For isotropic solutions, the values of χ are calculated by the substitution of the osmotic-pressure data into these two relations:

$$\chi = -\{\pi V_1/RT + \ln(1-v_2) + (1-1/x)v_2\}/v_2^2 \qquad (6)$$

and:

$$x = V_2/V_1$$

where V_1 and V_2 are the molar volumes of the solvent and the solute respectively. Equation (6) is derived from Eqs. (2) and (5) by replacing r by x. The x thus defined allows the theory to be applied to actual solutions. An idealization adopted in the Flory model for theoretical derivation stipulates that the solvent molecule should be of such a diameter as to be replaceable by a segment of the rodlike solute. This condition is not fulfilled in general; hence, we adopt the definition of x given above in order to permit application to actual solutions. By the use of x, the chemical potential of a solvent at an infinitely dilute solution is of an acceptable form. If we assume that Eq. (2) can also be used in the high concentration region, the values of χ can be similarly obtained from Eq. (6).

The results are shown in Table 1. The values of χ in the concentration range lower than 6.5 vol% polymer, where the solution is isotropic, are found to be 0.44—0.47 for either EDC or chloroform. The values of χ in the concentration range higher than 6.5 vol% polymer are found to be 0.46—0.50. The set of the latter values is slightly larger than that of the former values, on the average. The experimental values of χ for solutions of randomly-coiled polymers have been found to be dependent on the concentration.[11,12,14,15] The assumption of a χ value independent of the concentration is not justified in general for polymer solutions. Therefore, it can not be concluded on the basis of the χ values that the higher concentration region with the slightly larger values of χ is not an isotropic phase.

Flory's lattice theory predicts that a system with a large value of χ will be biphasic at extremely low concentrations. The concentration corresponding to the A-point is given as $v_2 \approx 5 \times 10^{-4}$ for r=45 and χ=0.45; the polymer concentration becomes even lower for higher axial ratios. Since the experimental results are very different from the predictions, it can not be assumed that the phase separation of solutions of rodlike molecules occurs primarily because of the entropic contribution originating from an extremely assymmetric shape of the molecules. We are forced, therefore, to conclude that it is necessary to modify the lattice theory of rodlike molecules.

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** The biphasic region for the PBLG-A–chloroform system is lying near the concentration of 8 vol% polymer. Although the osmotic pressures, as are shown in Fig. 4, were not measured for the concentration range of 6—9 vol% polymer in this experiment, we dared to draw the smoothed curve over the entire region of the measurements for the system.