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Comparison of Osmotic Pressures for the Poly(γ-benzyl-L-glutamate) Solutions with the Theories for a System of Hard Spherocylinders

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Osmotic pressures for the poly(γ-benzyl-L-glutamate)-dimethylformamide system were obtained over the concentration range covering the isotropic and anisotropic phases. Three samples were examined at three temperatures. The system was athermal for the isotropic phase. The equation of state (the concentration dependence of osmotic pressures) was compared with the existing theories of liquid of rigid spherocylinders. The equation of state for the isotropic phase was reasonably satisfied by the modified Cotter theory if the decreased axial ratio was assumed for the polymer. The difference of the equation of state between the isotropic and anisotropic phases was not so large as predicted from its theory. The phase transition concentrations were observed using a polarizing microscope. The transition points were in rough agreement with its theory for shorter rods; for longer rods, they were much higher than predicted. It was deduced that the flexibility of the polymer softens the phase transition.

INTRODUCTION

It is known that poly(γ-benzyl-L-glutamate) (PBLG) in solution exists as a stiff chain or rodlike chain particle. As the polymer concentration is increased the solution undergoes a phase transition from an isotropic phase to an anisotropic phase (liquid crystalline).[1,2] This phenomenon was predicted on the basis of molecular asymmetry alone by Onsager[3] and Ishihara.[4] The theoretical results indicated that the concentration dependence of osmotic pressure in the anisotropic phase is distinct from that in the isotropic phase. Their theories which treat the first and second virial coefficients only as to the translational entropy of a system are essentially restricted to a low concentration range. The various types of theory for rigid rods which are applicable to higher concentrations were proposed thereafterwards.[5-9] Among these the lattice treatment of Flory has been frequently used as a basic theory to examine experimental results.[10-13] However, Straley[14] has indicated that the quantitative predictions of the Flory theory are in error. He has also examined the dependence of transition points on the axial ratio for PBLG solutions determined by the other researchers.[2,15] He has indicated that it is in rough agreement with the Onsager theory for short rods and that the discrepancy between the experiments and theory for sufficiently long rods may be attributed to the flexibility of PBLG.

There have been only a few studies on the thermodynamic properties of PBLG solutions in the moderately concentrated range.[12,13,16] The present work was undertaken to compare equations of state (concentration dependence of osmotic pressures) determined experimentally both in the isotropic and anisotropic phases with those predicted by the various theories.

EXPERIMENTAL

Materials

PBLG was prepared by polymerization of γ-benzyl-L-glutamate-*N*-carboxy anhydride and then refluxing with hot ethanol to remove low molecular weight impurities. To obtain the samples covering a wide molecular weight range, three kinds of initiator were chosen. The samples coded as PBLG-A, -B, and, -C and -D were respectively obtained using *n*-hexylamine, diethylamine, and triethylamine as initiators. Dimethylformamide (DMF) was selected as a solvent because of a minor association of PBLG in it.[17] After DMF was dried over calcined calcium sulfate, it was purified by vacuum distillation.

Osmometry

Osmotic pressures were determined in the concentration range up to volume fraction of 0.02 by employing a High-Speed Membrane Osmometer (Hewlett-Packard Co., Model 503). An osmometer[18] described previously was used for solution in the range above volume fraction of 0.04. The solution charged in a solution cell was stirred as little as possible to avoid air-bubble formation in a solvent cell.[19] The rate of movement of solvent in a capillary was observed under a selected pressure. Osmotic pressure was determined by interpolating the relation between the pressure and the rate of meniscus movement to the null rate. The pressure was read using a manometer; mercury and silicone were used as the manometric fluids. An equilibrium pressure was ordinarily attained within 5 hr. The volume fraction was determined after each run, assuming no volume change of mixing. Specific volumes of polymer were respectively taken as 0.785, 0.790, and 0.795 g/cm^2 at 15, 30, and 45°C.[20] Semipermeable membranes were prepared from regenerated cellulose membranes (Zartius-Membranefilter Co.). Solvent removed from a solvent cell contained no measurable amount of polymer.

Accuracy of the method is estimated as 0.02 g/cm^2 for osmotic pressures at low concentrations. The error may be larger for the more viscous solutions of higher concentrations. The major error in osmotic pressures is believed to arise from the possible effects of dilution or concentration of the solvent through it. In order to maintain a high level of accuracy, it is necessary to adjust the pressure to keep the capillary meniscus as far as possible stationary. The resulting errors should not exceed 2 and 3% of the osmotic pressures for the solutions of PBLG-A and -B, and -C, respectively.

Determination of transition points

Polymers and solvents weighed were charged in glass tubes (i.d. 5 mm). After the solvents were frozen using liquid nitrogen and most of air was evacuated, all tubes were sealed. The tubes were stood for at least 3 weeks at 45°C, and then the states of the solutions were observed between crossed polars using a polarizing microscope at various temperatures.

THEORY OF LIQUID OF RIGID RODS

The theories of liquid of rigid rods were presented on the basis of interaction alone through the repulsion which prevents their overlapping. According to the theories of Onsager,[3] Lasher,[6] Alben,[7] and Cotter,[8,9] the Helmholtz free energy F and configurational entropy S_c for a collection of N rigid spherocylinders at the number density ρ are given by the realtion

$$\frac{F}{NkT} = -\frac{S_c}{Nk} + \ln \Lambda = \int f(\Omega)\ln\{4\pi f(\Omega)\}\, d\Omega + A(\rho) + \left\{\frac{B(\rho)}{2}\right\} \iint \sin \gamma(\Omega, \Omega') f(\Omega) f(\Omega')\, \mathrm{d}\Omega\, \mathrm{d}\Omega' \qquad (1)$$

where Λ^{-1} is the kinetic energy contribution to the single-particle partition function, $\gamma(\Omega, \Omega')$ is the angle between the axes of two rods, and $f(\Omega)$ is the normalization distribution function. There is a normalization condition

$$\int f(\Omega)\, \mathrm{d}\Omega = 1. \qquad (2)$$

The two functions of the density, $A(\rho)$ and $B(\rho)$ are not the same in each theory. The first term on the right-hand side of Eq. (1) represents the orientational entropy, and the second and the third terms are the entropy due to the translational degrees of freedom of rods with a distribution of orientations. A competition exists between the tendencies to maximize the two different kinds of entropy. To determine the most probable distribution function $\bar{f}(\Omega)$, F must be minimized with respect to f under the constraint (2). Applying the Euler-Lagrange equation, the integral equation is straightforwardly derived as

$$\ln 4\pi\bar{f}(\Omega) + B(\rho)\int \sin\gamma(\Omega, \Omega')\bar{f}(\Omega')\,\mathrm{d}\Omega' = C \tag{3}$$

where C is independent of Ω. This equation cannot be analytically solved, but it has been numerically solved for various values of B by Lasher.[6] He found that for small B (low density) the only solution of Eq. (3) corresponds to the isotropic distribution

$$\langle \ln 4\pi\bar{f}(\Omega)\rangle_{\text{iso}} = 0 \tag{4a}$$

and

$$\langle\!\langle \sin\gamma(\Omega, \Omega')\rangle\!\rangle_{\text{iso}} = \frac{\pi}{4} \tag{4b}$$

and for large B (high density) there exists a different kind of solution

$$\langle \ln 4\pi\bar{f}(\Omega)\rangle_{\text{aniso}} > 0 \tag{5a}$$

and

$$\langle\!\langle \sin\gamma(\Omega, \Omega')\rangle\!\rangle_{\text{aniso}} < \frac{\pi}{4} \tag{5b}$$

where

$$\langle \ln 4\pi\bar{f}(\Omega)\rangle = \int \bar{f}(\Omega)\ln 4\pi\bar{f}(\Omega)\,\mathrm{d}\Omega \tag{6a}$$

and

$$\langle\!\langle \sin\gamma(\Omega, \Omega')\rangle\!\rangle = \iint \sin\gamma(\Omega, \Omega')\bar{f}(\Omega)\bar{f}(\Omega')\,\mathrm{d}\Omega\,\mathrm{d}\Omega'. \tag{6b}$$

The solution for large B indicates that the anisotropic state is thermodynamically stable compared to the isotropic state and that it represents a nematic liquid crystal.

The pressure P is given using the thermodynamical relation as

$$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = kT\rho^2\left\{\left(\frac{\partial A}{\partial \rho}\right) + \langle\!\langle \sin\gamma \rangle\!\rangle\left(\frac{\partial B}{\partial \rho}\right)\right\}. \tag{7}$$

The chemical potential of the liquid is given as

$$\mu = \frac{F(\rho)}{N} + \frac{P(\rho)}{\rho}. \tag{8}$$

Onsager first treated Eq. (1) as a form of expansion of virial series in density, and then neglected the terms of higher order than the second. He found the equation of state for liquid of spherocylinders of length L and diameter D as

$$\frac{Pv_0}{kT} = v + (4 + 2r\langle\!\langle \sin\gamma \rangle\!\rangle)v^2 \tag{9}$$

where v_0 is the volume of a rigid spherocylinder, $v = \rho v_0$ is a dimensionless density, and r is given by $6(x-1)^2/\pi(3x-1)$; x is the axial ratio i.e. $L/D + 1$. Lasher gave the equation of state on the basis of the scaled particle method as

$$\frac{Pv_0}{kT} = \{1 + (2 + 2rv\langle\!\langle \sin\gamma \rangle\!\rangle\}\frac{v}{(1-v)^2}. \tag{10}$$

The scaled particle theory was presented in a more rigorous manner by Cotter and the equation is

$$\frac{Pv_0}{kT} = \left[1 + v + \frac{2}{3}\left(1 + q - \frac{1}{2}q^2\right)v^2 + 2rv\{1 + (1+q)v\}\langle\!\langle \sin\gamma \rangle\!\rangle\right]\frac{v}{(1-v)^3} \tag{11}$$

where q is $2/(3x-1)$. Lately Cotter has somewhat modified this equation of state as

$$\frac{Pv_0}{kT} = \left\{1 + v + \frac{2}{3}\left(1 + q - \frac{1}{2}q^2\right)v^2 + 2rv\left(1 + \frac{1+2q}{3}v\right)\langle\!\langle \sin\gamma \rangle\!\rangle\right\}\frac{v}{(1-v)^3} \tag{12}$$

The last two equations for the isotropic state reduce to the expression of Reiss *et al.*,[21] when the axial ratio of the spherocylinder decreases to unity. Cotter has indicated that Eq. (12) is somewhat better agreement with the Monte Carlo computation of Vieillard-Baron[22] than Eq. (11). In contrast to the cluster expansion approach and scaled particle methods, Alben has reworked the Flory method for construction of the partition function and finds the equation of state

$$\frac{Pv_0}{kT} = -\ln(1-v) + (7 + 4r\langle\!\langle\sin\gamma\rangle\!\rangle)\left\{\frac{v}{(1-v)} + \ln(1-v)\right\}. \quad (13)$$

Eqs. (10)–(13) can be expressed as a series in v. The coefficients to the second term agree with those of Onsager's approximation i.e., Eq. (9).

Lasher has given $\langle\!\langle\sin\gamma\rangle\!\rangle$ and $\langle\ln 4\pi f\rangle$ for twelve different values of B to 10.6, which give the respective twelve values of v at a given axial ratio for the various theories. We can determine the corresponding pressures in the anisotropic phase by substituting the values of v and $\langle\!\langle\sin\gamma\rangle\!\rangle$ in Eqs. (9)–(13), and can determine the corresponding chemical potentials by substituting the values of v, P, and $\langle\ln 4\pi f\rangle$ in Eqs. (1) and (8) when the functions $A(\rho)$ and $B(\rho)$ are given. The equations of state and chemical potentials in the isotropic phase can be easily obtained by replacing $\langle\!\langle\sin\gamma\rangle\!\rangle$ with $\pi/4$ and $\langle\ln 4\pi f\rangle$ with zero. The two dimensionless densities (v and v') at the transition points can be determined using the thermodynamic equilibrium conditions

$$P(v)_{\mathrm{iso}} = P(v')_{\mathrm{ansio}} \quad (14a)$$

and

$$\mu(v)_{\mathrm{iso}} = \mu(v')_{\mathrm{aniso}} \quad (14b)$$

Unfortunately the values of $\langle\!\langle\sin\gamma\rangle\!\rangle$ for B to 10.6 give the behavior only near the transition density. The following procedure to obtain $\langle\!\langle\sin\gamma\rangle\!\rangle$ for larger B (high density) was employed. When no free volume in liquid is left i.e., $v \rightarrow 1$, the rods would be perfectly aligned along the preferred direction and then $\langle\!\langle\sin\gamma\rangle\!\rangle$ approaches to zero. The reciprocal of $B(v)$ for each theory except the Onsager method becomes zero in $v = 1$. A curve was drawn by extrapolating the twelve points of $\langle\!\langle\sin\gamma\rangle\!\rangle$ for B^{-1} to the origin. The value of $\langle\!\langle\sin\gamma\rangle\!\rangle$ for a given larger B was read off the curve. The various equations of state with the coexisting dimensionless densities for $x = 22.8$ are shown in Figure 1. Figure 1 indicates that the transition densities are lower the greater the estimation of drop in entropy due to the excluded volume effect of rods with a distribution of orientations.

In contrast to Lasher's numerical calculation method, Eq. (3) can be analytically solved using some approximation. A closed form expression for $f(\Omega)$ is obtained by replacing $\sin\gamma$ in Eq. (3) with $A\sin^2\gamma$.[7] If one chooses $3\pi/8$ for A, the equation of state is identical to the strict equation for isotropic phase. Another expression is obtained by expanding $\sin\gamma$ in Legendre polynominals and then by truncating the series after its second term (Cotter's approximation).[9] The two independent approaches were applied to the

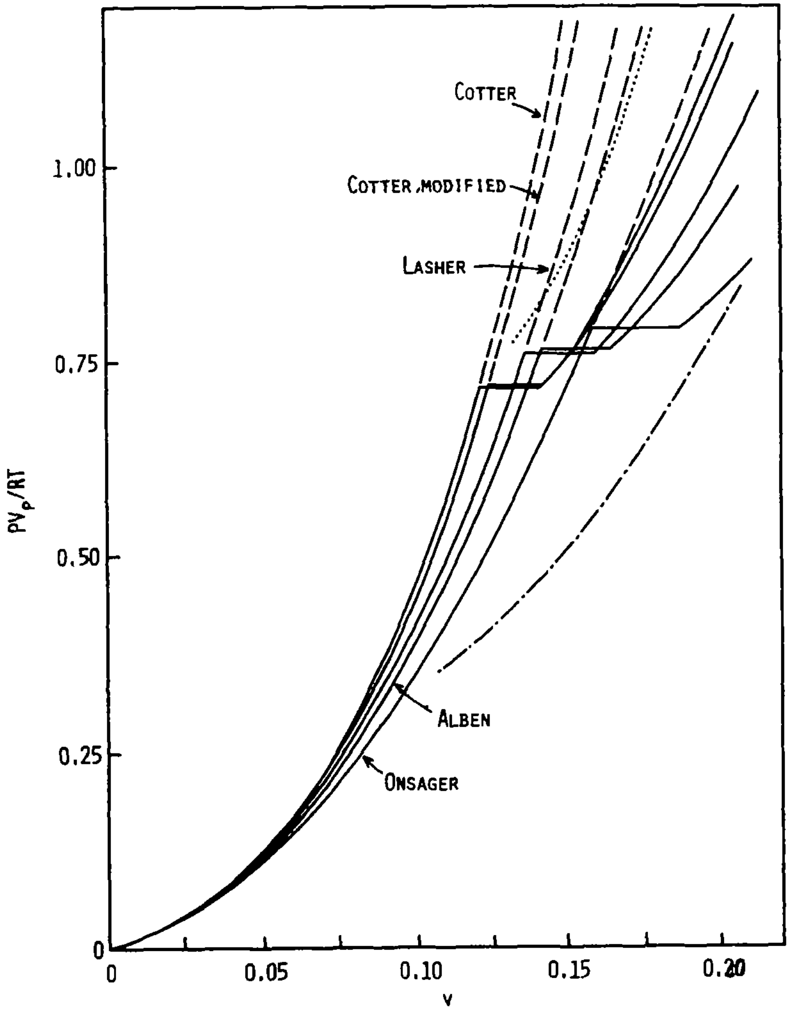

FIGURE 1 Comparison of various equations of state for $x = 22.8$. The solid lines correspond to the equilibrium states predicted using Lasher's treatment from the theories indicated; the dashed lines to locally stable isotropic states. The solid and dotted line corresponds to the approximate behavior for the anisotropic phase obtained from the modified Cotter theory in which $\sin \gamma$ is replaced by $3\pi \sin^2 \gamma/8$; the dotted line to the behavior obtained with Cotter's approximation.

modified Cotter theory. The respective equations of state with $x = 22.8$ for the anisotropic phase obtained by using a table of order parameter for B given by Wojtowicz[23] are shown in Figure 1. The differences between the approximate equations of state and the equation obtained by Lasher's strict treatment are more marked. We feel that the approximations are not applicable to express the equation of state for the anisotropic liquid of the spherocylinders.

Applying the theory of liquid of long rods to the system of rod and solvent, the free energy of Eq. (1) can be treated as the excess free energy over that of solvent. Then 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 rigid rods have no free volume themselves.

The PBLG liquid crystal is not really nematic, but rather cholesteric. Straley[14] has suggested that the forces giving rise to the twist represent a very small perturbation on the local structure; his conception is derived from that one full rotation of the direction of alignment is several thousand times the average intermolecular distance. In the present report, we consider that the difference of the free energy between the two phases is very small and is therefore neglected.

RESULTS

Osmotic pressure π is usually shown by a power series in volume fraction of polymer v,

$$\frac{\pi}{v} = RT(B_1 + B_2 v + B_3 v^2 + \cdots) \tag{15}$$

where B_1, B_2, B_3, etc. are the osmotic virial coefficients, the first term of them being equal to V_p^{-1}; V_p is the molar volume of the polymer, and is related to the molecular weight M_n and the specific volume $\bar{v}$ by $M_n \bar{v}$.

The plots of π/v vs. v for four samples at low concentrations are shown in Figure 2 and are slightly curved upward, respectively. From the linear part of the plot, V_p and B_2 were respectively determined as intercept and slope. The results are summarized in Table I. The osmotic pressure data for PBLG-A, -B, and -C above $v = 0.04$ are summarized in Table II. The value of y in column 3 is defined by

$$y = \frac{(\pi/v - RTB_1)}{RTv}. \tag{16}$$

This value is considered as an apparent second virial coefficient. Considering that the value of y for the isotropic phase increases with an increase in concentration, we found that the virial coefficients of higher order than the

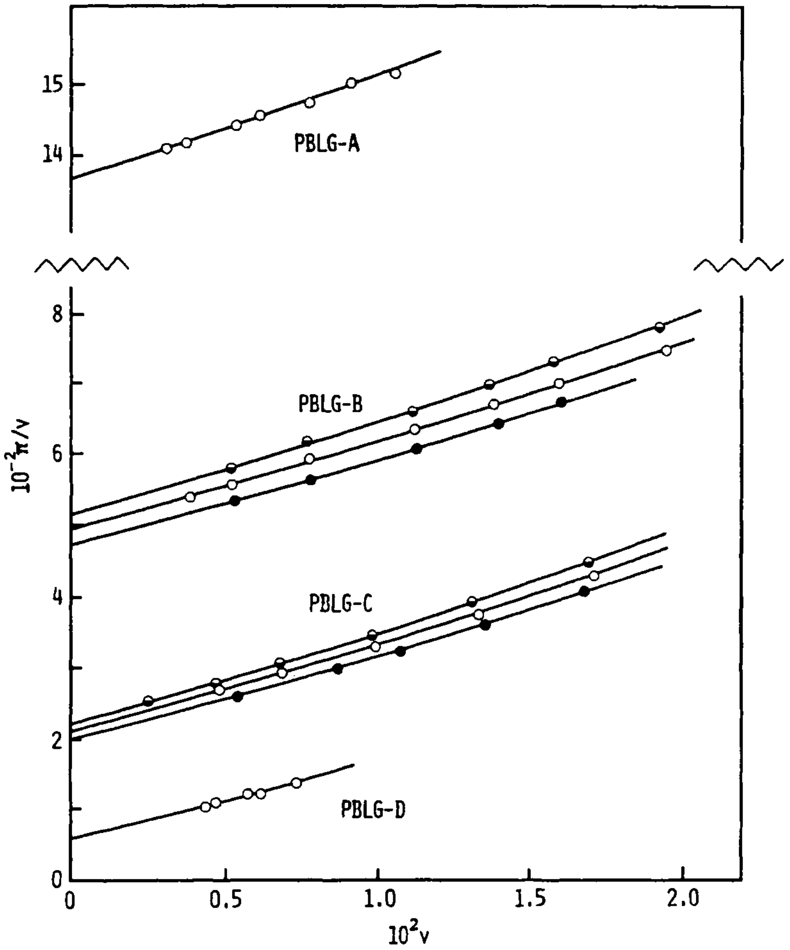

FIGURE 2 Experimental results of π/v plotted against v at low concentrations for the system indicated: (●) at 15°C; (○) at 30°C; (◒) at 45°C.

second are not negligible. The plots of π vs. v at 30°C for the isotropic phase are shown in Figures 3–5. In Figures 6 and 7, the plots of π vs. v at 30°C for solutions of PBLG-B and -C are shown over the concentration range covering two different phases. The experimental data for PBLG-C solutions at 15 and 45°C except the results at 15°C for the anisotropic phase are reduced to the positions at 30°C (see Discussion). The positions of the transition concentrations found by using a polarizing microscope are shown by the vertical dotted lines. Equation (14a) predicts that the biphasic region would show a region of a constant osmotic pressure, yet the present results contradict this prediction. This may be due partly to the polydispersity of the polymer used.

TABLE I

Osmotic pressure data for PBLG in DMF at low concentrations

Temperature °C	$M_n \times 10^{-4}$	$V_p \times 10^{-4}$ cm^3/mol	$B_2 \times 10^4$ cm^3 mol/g	Apparent axial ratio	Axial ratio in solid
		PBLG-A			
30	2.38	1.88	5.21	7.40	10.9
		PBLG-B			
15			4.74		
30	6.60	5.21	4.84	22.8	30.1
45			4.82		
		PBLG-C			
15			4.66		
30	15.5	12.3	4.65	54.4	70.8
45			4.59		
		PBLG-D			
30	57	45	4.1	182	260

DISCUSSION

Heat of dilution

Osmotic pressure is related to the chemical potential of solvent μ_1 by

$$\mu_1 - \mu_1^0 = -V_1\pi \tag{17}$$

where μ_1^0 is the chemical potential of pure solvent and V_1 is the molar volume of the solvent. Therefore, the osmotic pressure includes usually the term due to the heat of dilution as well as the increment in entropy. In order to compare the osmotic pressure data with the theories the heat of dilution must be first examined. By studying the temperature dependence of the osmotic pressure, the partial molar heat of dilution Δh_1 at a given weight fraction of polymer w can be determined using the well known thermodynamic relation by

$$\Delta h_1 = \frac{-\partial(V_1\pi/T)}{\partial(1/T)}. \tag{18}$$

The plots of $V_1\pi/T$ vs. w for the solutions of PBLG-B and -C were independently examined at different temperatures for two concentration ranges below volume fraction of 0.02 and above 0.04. The respective plots were nearly fitted by smooth curves in the isotropic phase within the experimental error. This demonstrates that the PBLG-DMF system is athermal in this phase. In the anisotropic phase no available difference of $V_1\pi/T$ at a weight fraction

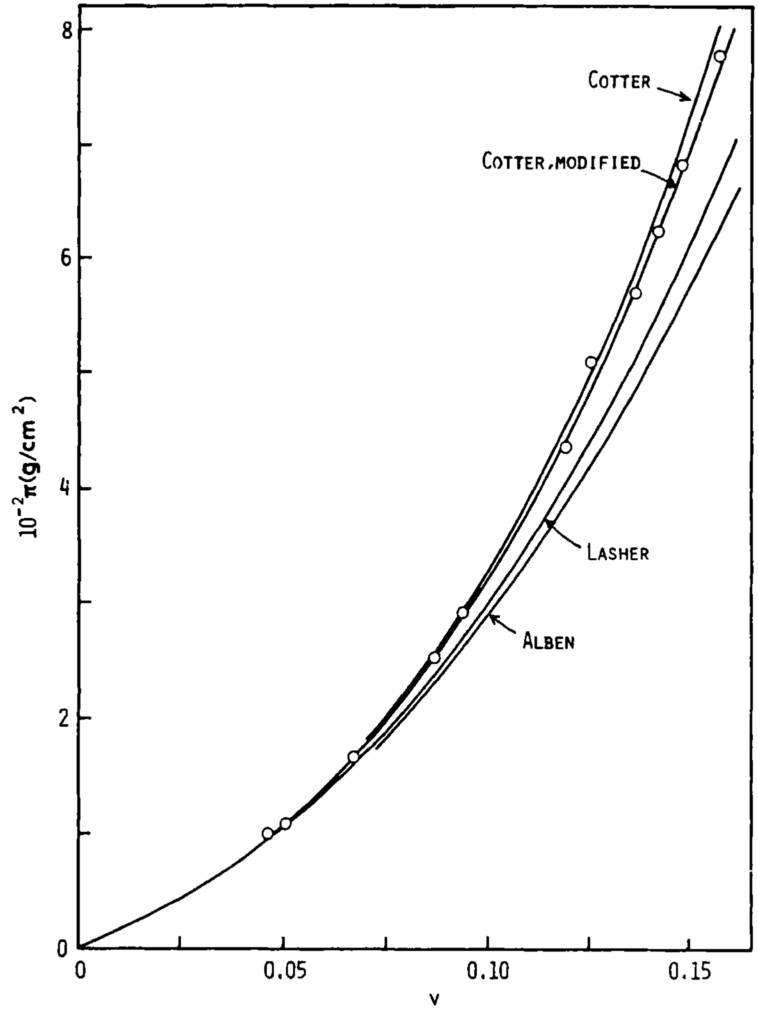

FIGURE 3 Comparison of equation of state for PBLG-A solution obtained experimentally at 30°C for the isotropic phase with the theories indicated.

concentration was found between temperatures of 30° and 45°C. However, when the respective plots at 15°C were literally compared with the plots at 30° and 45°C, the difference between the two curves was appreciated. Considering approximately the derivatives of $V_1\pi/T$ to be the corresponding quotient of difference between the values at 15° and 30°C, Δh_1 is found to be about 1 cal/mol, and to be nearly insensitive of concentration and molecular weight.

In view of the experimental error in the osmotic pressure measurements (see EXPERIMENTAL), a maximum variation in Δh_1 is 0.0015 cal/mol for

TABLE II

Osmotic pressure data for PGLG in DMF at moderately concentrated range

$v \times 10^2$	π g/cm^2	$y \times 10^4$ cm^3 mol/g
PBLG-A at 30°C		
4.68	100	6.39
5.03	109	6.18
6.73	166	6.35
8.65	252	6.95
9.38	291	7.19
11.91	436	7.48
12.54	510	8.37
13.60	569	8.05
14.21	624	8.27
14.78	683	8.56
15.70	777	8.87
PBLG-B at 15°C		
8.11	148	6.82
8.51	155	6.48
10.70	252	7.20
13.22	371	7.22
16.21	495	
16.86	511	
17.43	532	
18.13	591	
18.93	623	
PBLG-B at 30°C		
6.23	86	5.53
7.84	135	6.09
10.08	222	6.58
12.20	324	6.89
12.42	341	7.05
13.76	421	7.25
13.90	434	7.35
14.77	458	
16.20	531	
17.39	576	
18.09	636	
19.39	692	
19.81	714	
PBLG-B at 45°C		
9.74	223	6.74
10.20	241	6.71
12.17	352	7.24
13.75	460	7.63
16.68	584	
17.01	605	
17.58	631	
18.82	702	

TABLE II (*continued*)

$v \times 10^2$	π g/cm^2	$y \times 10^4$ cm^3 mol/g
	PBLG-C at 15°C	
5.96	60	5.54
7.73	100	5.79
8.16	111	5.82
9.70	154	5.85
10.51	168	
11.16	191	
14.06	243	
14.59	272	
15.91	311	
17.82	366	
	PBLG-C at 30°C	
13.63	266	
15.80	343	
16.49	358	
18.82	449	
	PBLG-C at 45°C	
5.60	59	5.52
6.42	78	5.74
7.07	93	5.74
8.00	116	5.70
8.68	139	5.90
8.84	143	5.86
9.83	176	5.92
10.37	197	
11.53	237	
11.65	239	
13.18	265	
14.65	317	
15.53	343	
17.94	427	

the solution at low concentrations. This variation is larger for the high concentration range, and is about 0.3 cal/mol in the concentration of $v = 0.1$, and is about 0.7 cal/mol in $v = 0.2$.

Goebel and Miller[24] found that the temperature dependence of osmotic pressures for the same system is exceedingly large in the concentration range to $v = 0.005$. The value of heat of dilution is estimated as 0.1 cal/mol for $v = 0.005$ from analysis of their data at 15° and 30°C. This exceeds by far the maximum variation of the heat estimated here. We have no way of accounting for this discrepancy. Miller *et al.*,[11,16] have reported differential scanning calorimetry experiments for the same system in the concentration range of

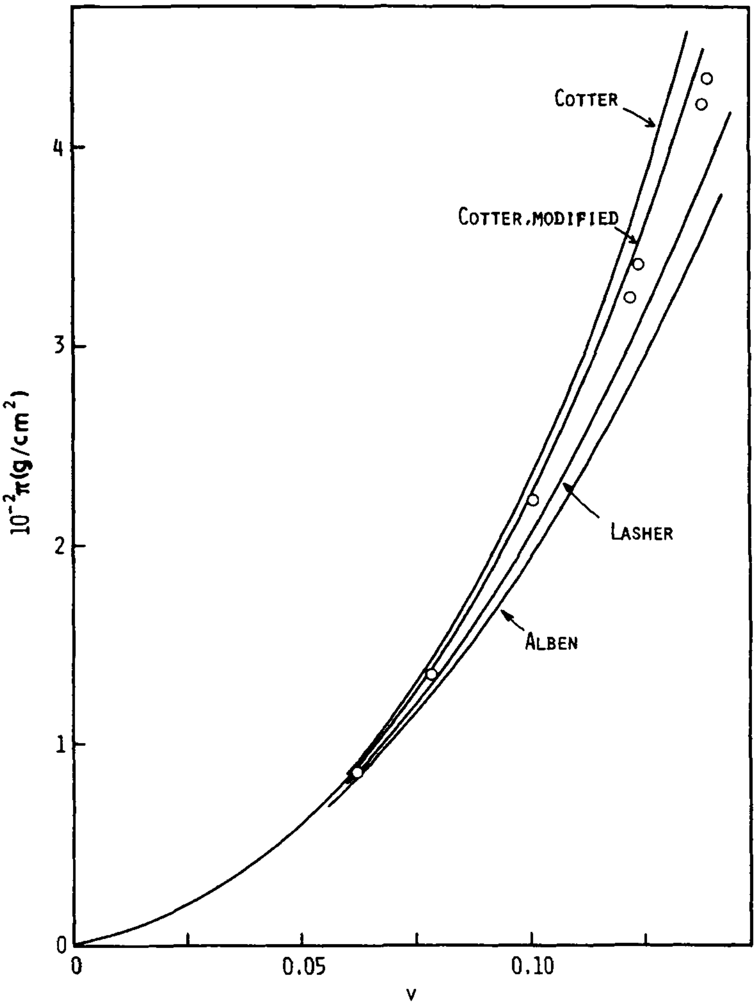

FIGURE 4 Comparison of equation of state for PBLG-B solution obtained experimentally at 30°C for the isotropic phase with the theories indicated.

$v = 0.02$–0.3. The heat due to a thermal transition was detected and was treated as the heat of mixing of nearly pure solvent and highly concentrated polymer phase in equilibrium. The heats of dilution were estimated as 3 cal/mol in $v = 0.1$ (for the isotropic phase) and as 17 cal/mol in $v = 0.2$ (for the anisotropic phase). There exists a large discrepancy between these values and the heats estimated here. We may be able to explain this discrepancy. PBLG solutions become gel at low temperatures of 0–10°C.[24] The heat

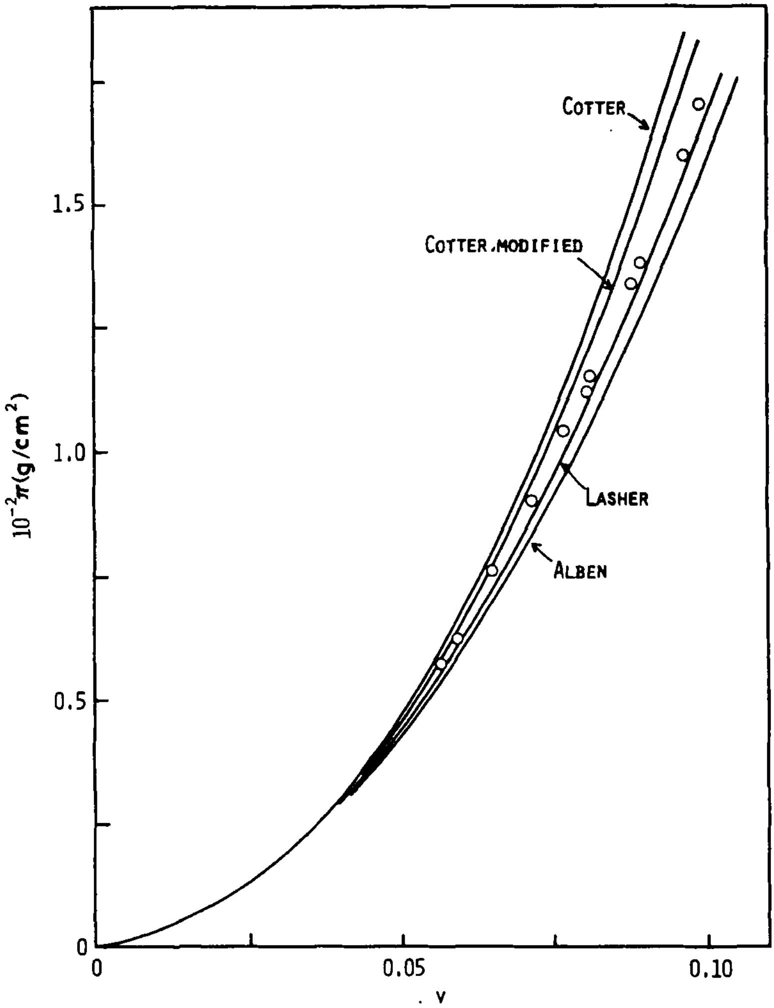

FIGURE 5 Comparison of equation of state for PBLG-C solution reduced to positions at 30°C for the isotropic phase with the theories indicated.

detected by Miller *et al.*, does not correspond to the heat of mixing, but to the heat of fusion, which is required for melt of gel.

Equation of state in the isotropic phase

It is known that PBLG exists in the form of α-helical configuration; the length of the helix is 1.5 A per residue. By means of analysis of X-ray scattering Arndt and Riley[25] found the diameter to be 15 A in the solid state. PBLG can

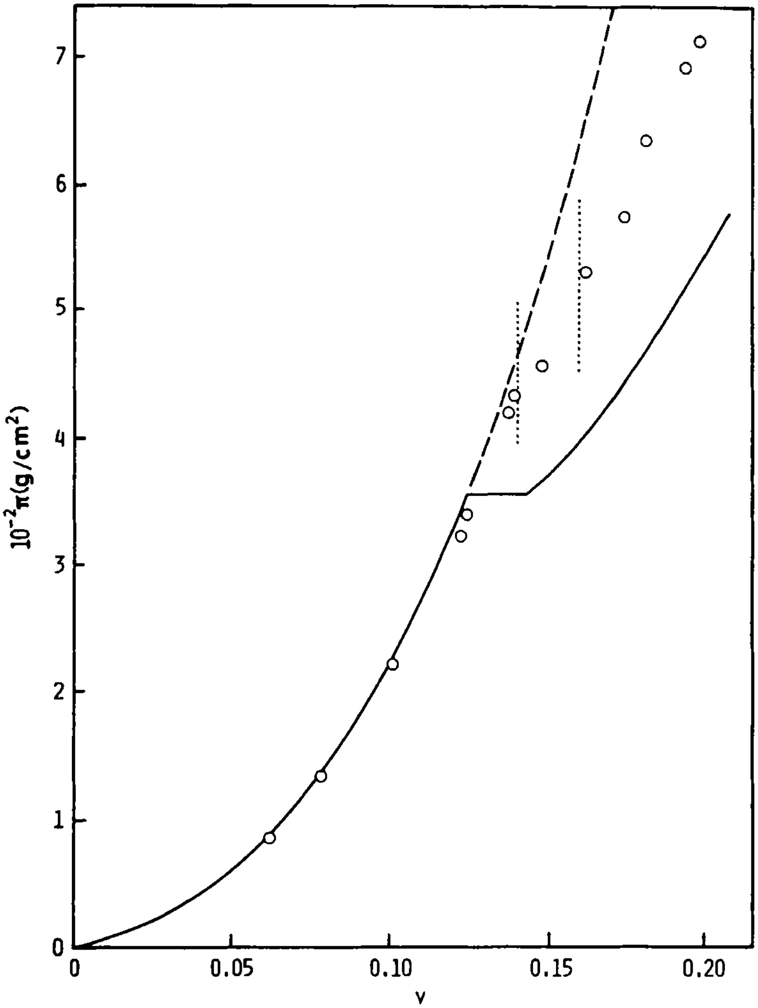

FIGURE 6 Comparison of equation of state for PBLG-B solution obtained experimentally at 30°C with the modified Cotter theory. The dashed line corresponds to locally stable isotropic state. The dotted vertical lines indicate positions of phase boundaries found experimentally.

retain its molecular order in DMF to a considerable extent. Using Eqs. (9) and (15), the second coefficients B_2 is related to the axial ratio of polymer x by

$$B_2 = \left\{\frac{4 + 3(x - 1)^2}{(3x - 1)}\right\} V_p^{-1}. \tag{19}$$

The apparent axial ratios required to produce the values of B_2 estimated from the osmotic pressure data at low concentrations are summarized in column 5

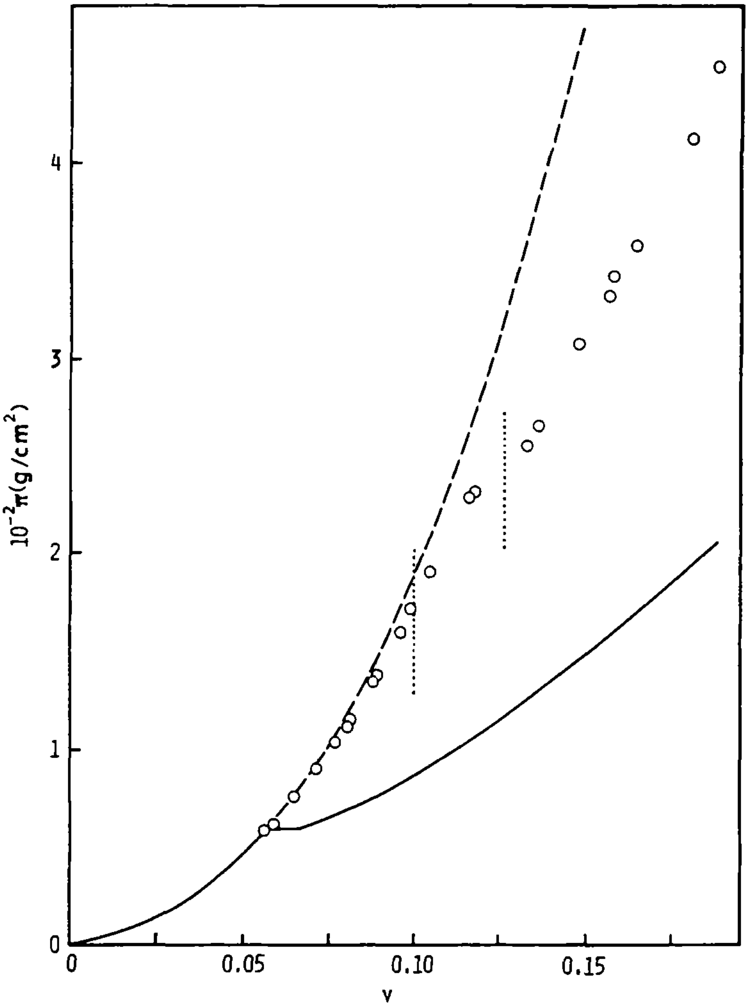

FIGURE 7 Comparison of experimental equation of state for PBLG-C solution reduced to positions at 30°C with the modified Cotter theory. The dashed line corresponds to locally stable isotropic state. The dotted vertical lines indicate positions of phase boundaries found experimentally.

in Table I. These values are considerably smaller than the corresponding values in the solid state, which are listed in column 6 in Table I. In view of the results that the PBLG-DMF system is athermal, this suggests that PBLG does not behave as a perfectly rigid rod in solution. Considerable experimental evidence has been accumlated which indicates that PBLG has some flexibility in dilute solution.[26,27] Inasmuch as there exists no significant theory to express the thermodynamic behavior of liquid (or solution) of semi rod, it is not easy to interpret the experimental result. Nevertheless we considered that PBLG behaves over the concentration range studied here as an equivalent spherocylinder with a reduced axial ratio determined from the osmotic pressure data at low concentrations. In Figures 3–5 the equations of state for the isotropic phase estimated from the various theories are contrasted with the experimental data. The dependence of osmotic pressures on concentration and axial ratio are reasonably satisfied with modified Cotter theory among these. From the physical point of view, we consider that this agreement is not accidental, but is significant. This is because the changes of intramolecular energy and entropy accompanied by some bent of molecules do not contribute to the osmotic pressure (whereas they affect the free energy of mixing considerably), provided that the flexibility is retained independent of concentration in the isotropic phase,[28] and this is because the osmotic pressure would be determined approximately by the entropy term alone due to the translational degrees of freedom of polymers with averaged conformations, provided that the net energetic interaction between the polymers are ignored. The two assumptions are not contrary to the experimental results that the PBLG-DMF system is athermal.

Flory[5] has derived a partition function of a collection of rods on the basis of a lattice model. The chemical potential of solvent in the isotropic phase is given by

$$\mu_1 - \mu_1^0 = RT\left\{\ln(1 - v) + \left(1 - \frac{1}{x}\right)v + \chi v^2\right\} \tag{20}$$

where χ is a thermodynamic interaction parameter. The expression is identical with that for solution of randomly-coiled polymers. To apply the theory to the actual solution, it is assumed to replace x with the ratio of the molar volume of polymer to that of solvent. The experimental results at three temperatures can be fitted by Eq. (20) using values of χ of 0.47–0.50. However, we feel that the agreement would be accidental, because χ should be primarily regarded as a value related to the heat of dilution in Flory's treatment and because the value of χ postulated for fitting is too large compared with the value of $\chi = 0$ determined from the results of temperature dependence of osmotic pressures.

Stlaley[14] examined theoretically the partition function derived by Flory and the approximation in it. He gave a distribution function by which the free energy will be minimized, and indicated that the function cannot be isotropic, in contrast to the results of Onsager *et al.* He indicated that Flory's approximation breaks down except at sufficiently concentrated range. Consequently, we abandoned an approach based on the theory of Flory.

Equation of state in the anisotropic phase and phase transition concentrations

The agreement between the experimental results and the modified Cotter theory in the isotropic phase encourages us to compare the experiments with its theory in the anisotropic phase. The equations of state calculated from the theory are shown in Figures 6 and 7. The results propose that values of $\partial\pi/\partial v$ (rate of change of osmotic pressure to change in volume fraction) in the anisotropic phase are much less than for the extrapolation of the curves for the isotropic phase. However, the values of $\partial\pi/\partial v$ obtained experimentally below and above the transition concentrations do not change so abruptly as predicted. In Figure 8, the dependence of A-point (concentration where the ordered phase first appears) an apparent axial ratio is compared with that predicted by the modified Cotter theory. The part for very large axial ratios of theoretical curve was extrapolated from the values for smaller axial ratios. For shorter rods, the locus of A-points is in rough agreement with its theory.

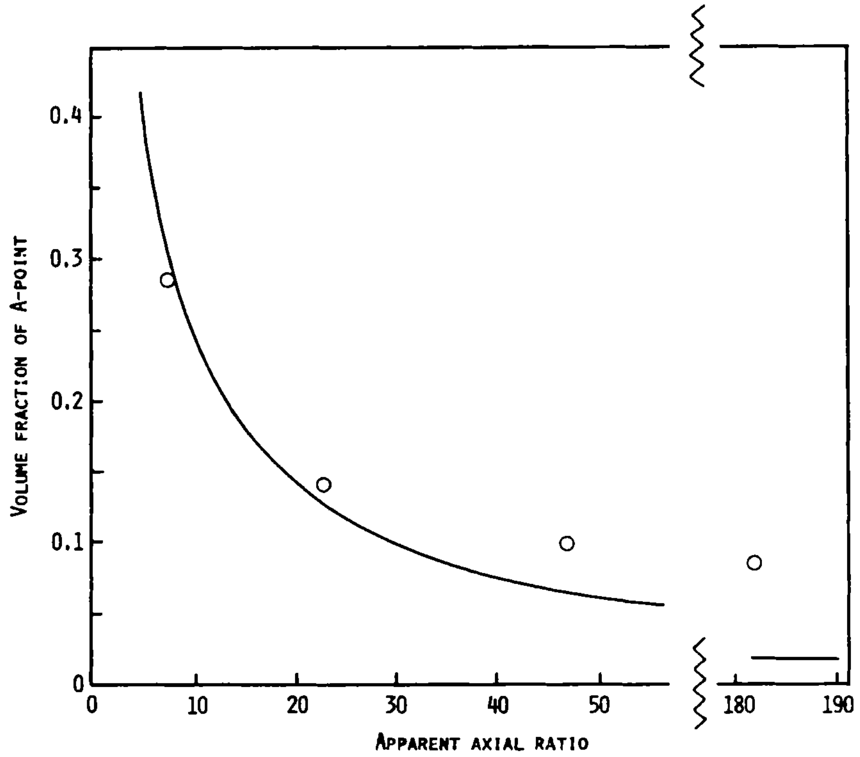

FIGURE 8 Volume fractions at A-point for PBLG solutions plotted against the apparent axial ratio at 30°C. Curve is calculated from the modified Cotter theory.

However, the behavior for the longer rods is anomalous. The concentrations of A-points are much higher than expected. There would appear to be a possible explanation for the results. Miller and Flory[29] suggested that the flexibility of PBLG may be attributed to the fact that the helix contains a small number of defects in which a few monomer units are not completely hydrogen-bonded with the neighboring units. In the range of low molecular weight, molecule is consisted of a single helical sequence and some flexible units in two ends of it. The flexibility due to tail segments would be independent of phase and concentration, and the phase transition concentrations would be approximately determined on the basis of the modified Cotter theory if the decreased axial ratio is assumed for rod. On further increase in chain length, the molecule acquires an average of more than one helical sequence and is allowed to bend. The flexibility in the anisotropic phase decreases with an increase in orderliness of alignment, and such loss in entropy on entering the aligned phase causes the resulting osmotic pressure to be higher than the rigid behavior. We consider that the flexibility softens partly the phase transition and increases the concentration for the ordered phase to form. According to this conception, the heat required for the increase of flexibility may be expected on dilution in the anisotropic phase. This heat may correspond to small heat of dilution found from the study of temperature dependence of osmotic pressures.

Wulf and De Rocco have derived a partition function for a collection of semiflexible molecules on the basis of lattice treatment.[30] This has been done by assuming the molecules to consist of x segments connected by $x - 1$ bonds such that the bonds may lie along 3 mutually perpendicular directions and by requiring a positive energy w for each junction joining two orthogonal bonds. Inasmuch as the PBLG-DMF system is, perhaps, beyond the applicability of lattice model because of the large difference between the breadths of rodlike polymer and solvent, it is difficult to examine quantitatively the experiments using its theory. This model is different from our model for PBLG. However, the theory includes the important results. They are that the increase of flexibility (decrease of w) causes the difference of the free energy between the two phases to be small and then causes the phase transition densities (or concentrations) to become high. This may support our foregoing considerations.

We have implicitly assumed up to now PBLG to be impenetrable rod. We have not taken account of the behavior of side chains of it, which constitute a considerable sizable fraction. Evidence has indicated that the side chains have some flexibility.[31,32] This flexibility can be clearly distinguished from the flexibility of main chain. This may influence the equation of state for the anisotropic phase to some extent in addition to the effect of flexibility of main chain. For the reason, the equation of state obtained experimentally leaves a complicated problem for theoretical considerations.

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