Liquid-crystalline properties and reentrance phenomena in PBLG solutions

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In dilute solutions of $poly-\gamma$ -benzyl-L-glutamate (PBLG), the only observable transition is intramolecular helix-coil transition. At higher concentrations, intermolecular correlations become important under suitable conditions resulting in transitions of the system to liquid-crystalline states. We present here a mean-field analysis of combined helix-coil and isotropic-nematic (cholesteric) transitions, taking into account the effect of "induced rigidity" as proposed by de Gennes and Pincus. Coupled self-consistent equations for the orientation and helix-fraction order parameters are derived and solved, a universal phase diagram as well as temperature and density dependence of order parameters calculated, and results compared to actual experimental data. We find qualitative agreement but a poor quantitative fit for PBLG in pure solvents. In solvents containing denaturing agents, we predict an isotropic-nematic-isotropic reentrance phenomenon, and propose experimental conditions under which it can be observed.

I. INTRODUCTION

Liquid-crystalline states in polymers have become of significant interest in polymer physics since the development of Kevlar at Dupont¹ and X-500 at Monsanto.² Fibers spun from mesomorphic states have been found to possess tensile strengths reaching 30×10^9 dyn/cm². Also, biologists have a natural interest in liquid-crystalline states of substances such as polypeptides.

When polypeptides such as poly- γ -benzel-Lglutamate (PBLG) are dissolved in suitable organic solvents such as dioxane, *m*-cresol, methyl chloride, and chloroform, they form α helices. PBLG has a chemical structure

$$\begin{pmatrix} \mathbf{R} & \mathbf{H} \\ | & \mathbf{I} \\ -\mathbf{C} - \mathbf{N} - \mathbf{C} - \\ | & \mathbf{H} \\ \mathbf{H} & \mathbf{O} \end{pmatrix}_{n}, \quad \mathbf{R} = \mathbf{C}\mathbf{H}_{2} - \mathbf{C}\mathbf{H}_{2} - \mathbf{C} \bigvee_{\mathbf{O}^{-}}^{\mathbf{O}}.$$

The hydrogen in the polymer forms hydrogen bonds stabilizing the helical conformation. The latter then behave like rigid rods.³

When the concentration of PBLG is low, the helices assume random orientations and the system as a whole remains isotropic. As the concentration is increased, at a critical value ρ_A domains of liquid-crystalline states begin to appear. As the concentration is further increased, the domains grow and at a second critical value ρ_B the entire sample becomes liquid crystalline.⁴ Thus a two-phase transition is well defined.

II. THEORY OF PHASE TRANSITIONS IN LIQUID CRYSTALS

In the liquid-crystalline phase the helices are orientationally aligned. Their mean direction is represented by a unit vector called the "director." On account of the chiral nature of the molecules, the director rotates about an axis in the sample normal to the directors. This mesophase is called "twisted nematic" or "cholesteric." Cholesteric liquid crystals manifest many unusual properties: high optical rotation, visible optical periodicities, iridescent colors, selective scattering, and transmission of circularly polarized light. The determination of these properties can be used for detecting the presence of the liquid-crystalline phase.

The degree of alignment of the molecules with respect to the director can be measured by the order parameter⁵

$$\sigma_2 = \int P_2 \cos\theta f(\theta) d\hat{\Omega} , \qquad (1)$$

where Ω denotes the orientation of an individual molecule, θ the angle between the molecule and the director, and $f(\theta)$ the normalized distribution of the molecules over various orientations. In the isotropic phase where the molecules point in random directions, $f(\theta)$ is constant $1/4\pi$ and $\sigma_2 = 0$. In a perfectly aligned case $f(\theta) = \delta(\theta)$ and hence $\sigma_2 = 1$.

Experimentally σ_2 can be measured by using NMR, x-ray, and optical techniques. It is often seen to lie in the range 0.3 - 0.7.^{6,7} σ_2 is a function of the concentration of the polypeptides as well as the temperature of the solution. But it appears to be independent of the solvent, provided that the solvent does not interact with the polypeptides. This point will be elaborated further in Sec. III.

In the simplest, mean-field theory of liquid crystals,⁸ we assume the interaction between molecules in the solution to be given pairwise by

$$(1,2) = v_0(r_{12}) + v_2(r_{12})P_2(\hat{\Omega}_1 \cdot \hat{\Omega}_2), \qquad (2)$$

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 $\hat{\Omega}_1$ and $\hat{\Omega}_2$ giving the respective orientations of molecules 1 and 2. We can consider the above potential as the first two terms in an expansion of the potential in terms of Legendre polynomials.⁹ While in general the interaction potential between two cylindrical molecules should be expanded in spherical harmonics and can be very complex, the above potential is seen to suffice to explain certain qualitative features of the liquid-crystalline states.

The mean-field free-energy functional for such a system of N molecules in volume V is given by⁸

$$\mathfrak{F}(f(\theta)) - \mathfrak{F}_0 = NkT \int f(\theta) \ln[4\pi f(\theta)] d\hat{\Omega} + \frac{1}{2} N \rho \gamma_2 \sigma_2^2, \quad (3)$$

where $\gamma_2 = \int v_2(r) d\vec{r}$, \mathfrak{F}_0 is the free energy of the isotropic states, and $\rho = N/V$. The derivation of free energy beyond the mean-field approximation has been given elsewhere.¹⁰

To find the equilibrium distribution function $f(\theta)$ free energy is minimized, subject to the constraint that $f(\theta)$ is normalized to unity. This yields^{5,8,10}

$$f(\theta) = \frac{1}{Z} \exp\left(-\frac{\gamma_2 \rho}{kT} \sigma_2 P_2(\cos\theta)\right) ,$$

$$Z = \int \exp\left(-\frac{\gamma_2 \rho}{kT} \sigma_2 P_2(\cos\theta)\right) ,$$
 (4)

with σ_2 as defined in Eq. (1).

The above equations can be used to dermine order parameter σ_2 as a function of the thermodynamic variable $B = \rho \gamma_2 / kT$. Comparison with experimental measurements of the order parameter as a function of the concentration ρ and the temperature T will indicate that the mean-field theory gives qualitatively the right trend but quantitatively rather poor fit.

Furthermore, potentials of the form (2) do not include chiral terms. Hence they are expected to give rise to the nematic rather than the cholesteric phase. This point can, however, be easily rectified,¹¹ since the chiral part of the interaction is but a weak perturbation of the orientation alignment force.

III. HELIX-COIL TRANSITION

Throughout the above discussion we have assumed that the PBLG molecules are in their helical state. Since only helical molecules can take part in the formation of the liquid-crystalline state, the number of molecules in the helicial state is an important variable.

It is seen that molecules in neutral solvents become susceptible to transition from helical to coiled state upon heating. But even at rather high temperatures (353 K, for PBLG in dioxane, to 473 K in *m*-cresol) the fraction of molecules in the coiled state remains small.¹² The polymer dissociates before reaching a sufficiently high temperature to complete the helix-coil transition. Estimates of the latter range from 700 to 1000 K, too high to be observed experimentally.

Experiments show that the addition of a small quantity of a second solvent such as dichloroacetic acid (DCA) or trifloroacetic acid (TFA) to the solution of PBLG tends to encourace the formation of coils.¹²⁻¹⁴ These solvents produce radicals in the solution which tend to form hydrogen bonds with the PBLG molecules, thus breaking the intramolecular hydrogen bonds required for helix formation and helping to stabilize the coiled state. These solvents are not neutral, as they interact with the molecules. In the presence of such nonneutral solvents, PBLG molecules undergo helix-coil transition when temperature is varied. For polypeptide solutions such as poly-L-glutamic acid in 0.2 M aqueous NaCl + dioxane (2:1) or poly-L-lysine in water, the helical state remains stable at lower temperatures and the coiled state gains stability when the temperature is elevated. For PBLG, however, the reverse is true. PBLG is in the coiled state at lower temperatures and undergoes a transition to the helical state as temperature is raised.^{3,12-14}

Under such circumstances it should be possible for an intramolecular helix-coil transition to be partially complete. That is, in a long polymer it should be possible for some series of monomers to be in the helical state and others in coiled states. However, one expects that free-energy barriers would exist, to discourage helical and coiled monomers from being adjacent. Hence in polypeptides the molecules generally tend to be nearly all helical or coiled.

Let us consider here a simple model of the helix-coil transition. Assume that there are g_h degenerate helical states with energy ϵ_h and g_c degenerate coiled states with energy ϵ_c , for each individual molecule. Furthermore, let us assume the molecules to be in either the helical state or a coiled state. Let N be the total number of molecules, N_h of them being in the helical state, and $N - N_h$ in coiled states. The free-energy functional is given simply as

$$\mathfrak{F}(N_{h}) = N_{h}\epsilon_{h} + (N - N_{h})\epsilon_{c} + NkT \left(g_{h}\frac{N_{h}}{g_{h}N}\ln\frac{N_{h}}{g_{h}N} + g_{c}\frac{N - N_{h}}{g_{c}N}\ln\frac{N - N_{h}}{g_{c}N}\right).$$
(5)

The equilibrium distribution can be obtained by minimizing \mathfrak{F} with respect to N_h :

$$0 = \frac{\delta \mathfrak{F}}{\delta N_h} = \epsilon_h - \epsilon_c + kT \left(\ln \frac{N_h}{g_h} - \ln \frac{N - N_h}{g_c} \right) \,.$$

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$$\frac{N_h}{N - N_h} = \frac{g_h}{g_c} \exp\left(\frac{\epsilon_c - \epsilon_h}{kT}\right)$$
$$= \exp\left(\frac{(\epsilon_c - \epsilon_h)}{kT} - \ln\frac{g_c}{g_h}\right)$$

If $x \equiv N_h/N$ denotes the fraction of molecules in the helical state, we find

$$x/(1-x) = \exp A \quad , \tag{6}$$

where $A = (\epsilon_c - \epsilon_h)/kT - \ln(g_c/g_h)$. We can determine $\Delta \epsilon \equiv \epsilon_c - \epsilon_h$ and $\ln(g_c/g_n)$ by fitting them to the experimental temperature dependence of x. First, the point at which x = 0.5 determines the "transition" temperature T_{hc} . At $T = T_{hc}$, A = 0 or $\Delta \epsilon = kT_{hc} \ln(g_c/g_h)$. Next, the slope of the x(T) is from Eq. (6),

$$\frac{d}{dT} x(T) = \frac{d}{dT} \frac{e^{A}}{1 + e^{A}} = -\frac{e^{A}}{(1 + e^{A})^{2}} \frac{dA}{dT},$$
at $T = T_{hc},$

$$\left(\frac{dx}{dT}\right)_{T = T_{hc}} = -\frac{\Delta\epsilon}{4kT_{hc}^{2}}.$$
(7)

Thus

$$\Delta \epsilon = -4kT_{hc}^2 \left(\frac{dx}{dT}\right)_{T=T_{hc}},\tag{7'}$$

$$\ln\left(\frac{g_c}{g_h}\right) = -4T_{hc} \left(\frac{dx}{dT}\right)_{T_{hc}}.$$
 (7")

Thus our simple two-parameter model takes on some semblance of reality when the two parameters are fitted to the transition temperature and the slope at transition.

Some experimenters³,¹³ use a more general theory to fit their experimental results. They assume each monomer in choosing between helical or coil states to encounter a difference in energy ΔH and a difference in entropy ΔS . However, they associate an additional free-energy contribution with the formation of a boundary or "wall" between a helical section. This free energy $F_{\rm int}$, or the parameter $\Sigma = \exp(-F_{\rm int}/kT)$, measures the tendency of neighboring monomers to settle down in the same state. Thinking of the molecule as a set of individual monomers, ΔH and ΔS characterize single-monomer properties, while Σ represents an intermonomer correlation effect. According to this theory,³

$$x = (\lambda - 1)/(2\lambda - 1 - \xi) \tag{8}$$

where $\lambda = \frac{1}{2}(1+\xi) + [\frac{1}{4}(1-\xi)^2 + \Sigma\xi]^{1/2}$ and $\xi = \exp[(\Delta H/kT) - \Delta S]$. For polypeptides, Σ is usually small ($\approx 10^{-4}$), indicating a tendency for the molecules to be internally uniform, i.e., nearly all helix or all coiled.

In this theory, at $T = T_{hc}$ each monomer should show no individual preference for the helical or coiled state. Thus $\Delta H = kT_{hc}\Delta S$ or $\xi = 1$; $\lambda = 1$ $+\sqrt{\Sigma}$. At $T = T_{hc}$, then, $x(T_{hc}) = 0.5$, and

$$\left(\frac{dx}{dT}\right)_{T=T_{hc}} = \frac{1}{4\sqrt{\Sigma}} \left(\frac{d\xi}{dT}\right)_{T=T_{hc}} = \frac{1}{-4\sqrt{\Sigma}} \frac{\Delta H}{kT_{hc}^2}.$$

To make contact between this model and our simple two-parameter model, we compare Eqs. (7) and (8), and find the relations

$$\Delta \epsilon = \Delta H / \sqrt{\Sigma} \tag{8'}$$

and

$$\ln(g_c/g_h) = \Delta H/kT_{hc}\sqrt{\Sigma}.$$
 (8")

Since tables of T_{hc} , ΔH , and Σ are available for some polypeptides in various solvents, we can use this result and Eq. (7) to obtain $\Delta \epsilon$ and $\ln(g_c/g_h)$, as shown in Table I. In the future we hope to employ such data on monomers and effects of walls to make the theory more quantitative.

IV. LIQUID -CRYSTAL-INDUCED HELIX-COIL TRANSITION

Throughout Sec. III we dealt with dilute solutions of polypeptides, so that each molecule acted in-

Material	Solvent	Number of monomers	$\Delta \epsilon = \frac{\Delta H}{\sqrt{\Sigma}}$ (K)	T _{hc} (K)	$\ln(g_c/g_h)$
$PBLG^3$	DCA + DCE 4:1	1600	-35000	312.5	-112
poly-L- glutamic acid ³	0.2 M aqueous NaCl + dioxane 2:1	260	2500	304	8.3
$poly-L-lysine^3$	water, pH 10.1	1500	2667	300	8.9
PBLG ¹³	DCA + DCE 70%:30%		-20700	287	-72.2
PBLG ¹³	DCA + DCE 82%:18%		-12800	318	-40.3

TABLE I. Values for $\Delta \epsilon$ and $\ln(g_c/g_h)$ calculated from Eqs. (7) and (8).

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dependently. As the concentration of polypeptides is increased interactions between molecules become important. As was pointed out by de Gennes and Pincus,¹⁵ certain correlation-induced phenomena begin to surface.

The helical molecules are expected to experience interacting forces like those described in terms of the anisotropic potential introduced in Sec. II. If enough of these rigid helices are present, a liquid-crystalline phase may emerge. Since the free energy of the system can be lowered in a transition from the isotropic to nematic phase, and since only helical molecules can participate in such a transition, the transition may actually induce helix formation. This "induced-rigidity" effect was first noted by de Gennes and Pincus.¹⁵ The free energy required for increasing the helix fraction *above* the low-density equilibrium value is supplied by the formation of nematic droplets from an isotropic medium.

The total free energy of the system is given by

$$\begin{aligned} \mathfrak{F} - \mathfrak{F}_{0} &= N_{h}kT \bigg(\int f(\theta) \ln 4\pi f(\theta) d\widehat{\Omega} \bigg) + \frac{1}{2} N_{h} \frac{N_{h}}{V} \gamma_{2} \sigma_{2}^{2} + N_{h} \epsilon_{h} \\ &+ (N - N_{h}) \epsilon_{c} + NkT \bigg(g_{h} \frac{N_{h}}{g_{h} N} \ln \frac{N_{h}}{g_{h} N} \\ &+ g_{c} \frac{N - N_{h}}{Ng_{c}} \ln \frac{N - N_{h}}{g_{c} N} \bigg) . \end{aligned}$$

$$(9)$$

This result comes from combining Eq. (3) with Eq. (5), now that intramolecular helix-coil and intermolecular isotropic-nematic transitions are allowed to take place simultaneously. At equilibrium, we have first of all

$$0 = \frac{\delta(\mathfrak{F} - \mathfrak{F}_0)}{\delta f(\theta)} = N_h k T [\ln f(\theta) + 1] + \frac{N_h^2}{V} \gamma_2 \sigma_2 P_2(\cos \theta).$$

Hence

$$f(\theta) = \exp[-Bx\sigma_2 P_2(\cos\theta)]/Z, \qquad (10)$$

with $Z = \int d\hat{\Omega} \exp[-Bx\sigma_2 P_2(\cos\theta)]$ and $B \equiv N\gamma_2/VkT$. Similarly,

$$\begin{split} 0 &= \frac{\delta(\mathfrak{F} - \mathfrak{F}_0)}{\delta N_h} \\ &= kT \bigg(\int f(\theta) \ln 4\pi f(\theta) d\widehat{\Omega} \bigg) + \frac{N_h \gamma_2 \sigma_2^2}{V} \\ &+ (\epsilon_h - \epsilon_c) + NkT \bigg(\frac{1}{N} \ln \frac{N_h}{g_h N} - \frac{1}{N} \ln \frac{N - N_h}{g_c N} \bigg) \;. \end{split}$$

Using expression (9) for $f(\theta)$, we obtain

$$\frac{\delta(\mathfrak{F}-\mathfrak{F}_0)}{\delta N_h} = kT \left(-\frac{N_h \gamma_2 \sigma_2^2}{V kT} - \ln \frac{Z}{4\pi} \right) + \frac{N_h \gamma_2 \sigma_2^2}{V} + (\epsilon_h - \epsilon_c) + kT \left(\ln \frac{N_h g_c}{(N-N_h)g_h} \right) = 0.$$

Thus

$$\ln \frac{g_c N_h}{g_h (N-N_h)} = \frac{\epsilon_c - \epsilon_h}{kT} + \ln \frac{Z}{4\pi},$$

 \mathbf{or}

$$\frac{x}{1-x} = \exp\left(\frac{\epsilon_c - \epsilon_h}{kT} - \ln\frac{g_c}{g_h} + \ln\frac{Z}{4\pi}\right) = \exp\left(A + \ln\frac{Z}{4\pi}\right),$$
(11)

with $A = (\epsilon_c - \epsilon_h)/kT - \ln(g_c/g_h)$. The free energy at equilibrium is given by

 $\frac{F - F_0}{NkT} = \frac{N_h}{N} \left(-\frac{N_h}{N} \frac{\gamma_2 \rho}{kT} \sigma_2 - \ln \frac{Z}{4\pi} \right) + \frac{1}{2} \frac{N_h}{N} \frac{N_h}{N} \frac{N}{V} \frac{\gamma_2 \sigma_2^2}{kT} + \frac{\epsilon_c}{kT}$ $-\frac{N_h}{N}\frac{\epsilon_c-\epsilon_h}{kT}+\frac{N_h}{N}\ln\frac{N_h}{g_hN}+\frac{N-N_h}{N}\ln\frac{N-N_h}{g_hN}.$

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$$\frac{N_h}{N}\ln\frac{N_h}{g_hN} + \frac{N-N_h}{N}\ln\frac{N-N_h}{g_cN}$$

$$= x\ln\frac{x}{g_h} + (1-x)\ln\frac{1-x}{g_c}$$

$$= x\ln\frac{x}{1-x} + x\ln\frac{g_c}{g_h} + \ln(1-x) - \ln g_c$$

$$= x\left(A + \ln\frac{Z}{4\pi}\right) + x\ln\frac{g_c}{g_h} - \ln\left[1 + \exp\left(A + \ln\frac{Z}{4\pi}\right)\right]$$

$$- \ln g_c,$$

one finds in a few lines

$$\frac{F - F_0}{NkT} = -\frac{1}{2}Bx^2\sigma_2^2 - \ln\left[1 + \exp\left(A + \ln\frac{Z}{4\pi}\right)\right] - \ln g_c + \frac{\epsilon_c}{kT}.$$
(12)

Thus the set of coupled self-consistent equations

$$\sigma_2 = \int f(\theta) P_2(\cos\theta) d\Omega ,$$

$$f(\theta) = \exp[-Bx\sigma_2 P_2(\cos\theta)]/Z ,$$

$$Z = \int \exp[-Bx\sigma_2 P_2(\cos\theta)] d\Omega ,$$

$$x/(1-x) = \exp[A + \ln(Z/4\pi)] ,$$

determine the stable and metastable configuration of the system under the thermodynamic condition (P, T), or alternatively (A, B), and Eq. (12) for $F - F_0$ gives the free energy associated with each configuration.

Under suitable conditions there can be two solutions to the self-consistent equations:

(i) Isotropic configuration: $\sigma_2 = 0$ or $f(\theta) = 1/Z$ $=1/4\pi$.

In this case $x/(1-x) = \exp A$, and $(F_I - F_0)/NkT$ $= -\ln(1 + \exp A) - \ln g_c + \epsilon_c / kT.$

(ii) Nematic configurations:

TABLE II. Calculated values of A and B along the transition curve and order parameters at transition for nematic (N) and isotropic (I) phases.

A	В	x _I	x _N	σ_{2N}
-1.5	-9.96	0.182	0.976	0.875
-1.0	-8.91	0.269	0.965	0.855
-0.5	-7.93	0.378	0.943	0.824
0.0	-7.05	0.500	0.917	0.778
0.5	-6.30	0.622	0.896	0.714
1.0	-5.72	0.731	0.893	0.636
1.5	-5.30	0.818	0.910	0.569
2.0	-5.02	0.881	0.931	0.505
2.5	-4.83	0.924	0.953	0.474
3.0	-4.72	0.953	0.969	0.456
3.5	-4.65	0.971	0.980	0.440
4.0	-4.61	0.982	0.988	0.437

$$\sigma_2 \neq 0 ,$$

$$f(\theta) = \exp[-Bx\sigma_2 P_2(\cos\theta)]/Z ,$$

$$Z = \int \exp[-Bx\sigma_2 P_2(\cos\theta)]d\Omega ,$$

$$x/(1-x) = \exp[A + \ln(Z/4\pi)],$$

and

$$\frac{F_N - F_0}{NkT} = -\frac{1}{2}Bx_N^2\sigma_2^2 - \ln\left[1 + \exp\left(A + \ln\frac{Z}{4\pi}\right)\right]$$
$$- \ln g_c + \frac{\epsilon_o}{kT}.$$

The free-energy difference between these two configurations is thus



FIG. 1. Phase diagram of PBLG, showing regions where isotropic (I) and nematic (N) phases are stable. $A = (\Delta \epsilon/kT) - \ln(g_c/g_b)$ and $B = \gamma_2 \rho/kT$.

A transition occurs at $F_I = F_N$. The isotropic phase is stable if $F_1 < F_N$, and the nematic phase is stable if $F_N < F_I$. For given model parameters $\Delta \epsilon = \epsilon_c$ $-\epsilon_n$, $\ln(g_c/g_h)$, and γ_2 , A and B are more convenient thermodynamic variables than ρ and T. Table II lists the calculated value of A and B along the transition curve. Also shown are the order parameters at transition for both nematic and isotropic phases. Note that $\sigma_{2I} \equiv 0$. The difference $x_N - x_I$ shows the induced-rigidity effect noted by de Gennes and Pincus.¹⁵ Figure 1 shows a calculated phase diagram in the AB space.

V. PBLG IN NEUTRAL SOLVENTS: ANALYSIS OF EXPERIMENTAL DATA

As mentioned in Sec. II, the mean-field theory fails to fit the temperature- and density- (concentration) dependent properties of PBLG in dioxane. It might be hoped that the induced-rigidity theory of de Gennes and Pincus could account for the discrepancy.

To apply the induced-rigidity model, one needs first to determine the three physical parameters $\Delta \epsilon$, $\ln(g_c/g_h)$, and γ_2 . The experimental measurement⁶ of $\sigma(T)$ gives us the information that the transition takes place at $\rho = 0.161$ and $T_1 = 65 \text{ °C}$ = 338 K. Hence, once $\Delta \epsilon$ and $\ln(g_c/g_h)$ are specified, we can determine γ_2 from the *AB* phase diagram. In Fig. 2 we plot $\sigma(T)$ for (i) experimental; (ii) mean field; (iii) $\Delta \epsilon = 100.5 \times 338 \text{ K} = 33 970 \text{ K}$,



FIG. 2. Order parameter σ_2 as a function of temperature for PBLG in solvent. \odot : experimental results (Ref. 6); ——: mean-field result; ----: $\Delta \epsilon = (100.5)$ 338 = 33 970 K; $\ln(g_c/g_h) = 98.0$; $\gamma_2 = -10140$ K at transition A = 2.5 and B = -4.831; ——: $\Delta \epsilon = (20.5)$ 338 = 6929 K; $\ln(g_c/g_h) = 18.0$ and $\gamma_2 = -10140$ K at transition A = 2.5and B = -4.831; --: $\Delta \epsilon = (28.5)$ 338 = 9633 K, $\ln(g_c/g_h)$ = 24.0, $\gamma_2 = -9615$ at transition A = 4.5 and B = -4.58. Arrow indicates transition temperature (338 K).



FIG. 3. Order parameter σ_2 as a function of density (concentration) for PBLG in neutral solvent: \odot : experimental results (Ref. 7); — : mean-field result; ----: result for A = 2.5. Arrow indicates assumed transition density (0.085).

$$\begin{split} &\ln(g_c/g_h) = 98.0, \ \gamma_2 = -10\ 140\ \text{K}, \ A_{\rm tr} = 2.5, \ \text{and}\ B_{\rm tr} \\ &= -4.831; \ (\mathrm{iv})\ \Delta \epsilon = 20.5 \times 338\ \mathrm{K} = 6929\ \mathrm{K}, \ \ln(g_c/g_h) \\ &= 18.0, \ \mathrm{and}\ \gamma_2 = -10\ 140\ \mathrm{K}, \ A_{\rm tr} = 2.5, \ \mathrm{and}\ B_{\rm tr} \\ &= -4.831; \ (\mathrm{v})\ \Delta \epsilon = 28.5 \times 338\ \mathrm{K} = 9633\ \mathrm{K}, \ \ln(g_c/g_h) \\ &= 24.0, \ \gamma_2 = -9615\ \mathrm{K}, \ A_{\rm tr} = 4.5, \ B_{\rm tr} = -4.58. \end{split}$$

In Fig. 3, we plot $\sigma_2(\rho)$. The experimental measurement⁷ shows a transition at $\rho = 0.085$ and T = 300 K. In Fig. 3 we plot (i) experimental points; (ii) mean-field; (iii) result for A = 2.5, $\gamma_2 = -1704$ K. At a fixed temperature A remains constant all along the curve.

In Fig. 4 we plot $T(\rho)$. The experimental result¹⁶ shown by a continuous line shows the coexistence region. The mean-field result is a straight line, as shown in the figure. For a given $\Delta \epsilon$ we chose $\ln(g_c/g_h)$ and γ_2 such that it passes through two points (a) $\rho_1 = 0.0975$, $T_1 = 313$ K and (b) $\rho_2 = 0.1225$, $T_2 = 353$ K. Thus we show results (i) $\Delta \epsilon = 20.5 \times 313$ K = 6416.5 K; $\ln(g_c/g_h) = 16.36$, $\gamma_2 = -14753$ K and (ii) $\Delta \epsilon = 5.0 \times 313$ K = 1565 K, $\ln(g_c/g_h) = 3.948$, and $\gamma_2 = -18220$ K.

The theoretical estimate for the helix-coil transition is from 700 to 1000 K. Hence in our results it should be

$$\frac{\Delta\epsilon}{\ln(g_c/g_h)} \simeq (700 - 1000) \,\mathrm{K} \; .$$

As can be seen from the figures, while it is possible to obtain slightly better fit to experimental data than the straightforward mean-field theory, the quantitative fit is still not good. The large difference in order parameter at transition can be accounted for by the addition of a $P_4(\hat{\Omega}_1 \cdot \hat{\Omega}_2)$ term in the potential. However, the overall fit would remain poor.

There are several possible explanations. First, the region of validity of mean-field approximation is too limited. A more general theory which in-



FIG. 4. Phase diagram of PBLG in neutral solvents showing regions where isotropic (I) and nematic (N) phases are stable. Continuous line gives the experimental result (Ref. 16). In the region between two continuous lines the isotropic and nematic phases coexist; ----: mean-field result (straight line); $- \cdot - \cdot - \cdot \cdot \cdot \Delta \epsilon = (20.5)$ 313 = 6416.5, $\ln(g_c/g_h) = 16.36$; $\gamma_2 = -14753$ K; ----: $\Delta \epsilon = (5.0)$ 313 = 1565 K, $\ln(g_c/g_h) = 13.948$, and $\gamma_2 = -18220$ K; \odot indicates the two points used to fit the theory.

cludes the effect of spatial correlations between molecules¹⁰ and anisotropic steric effects⁹ is necessary. Second, the present model is too crude. And third, the experimental data still contain uncertainties, some of which are due to analyses which are highly model dependent.

VI. PBLG IN MIXTURE OF SOLVENTS: PREDICTION OF REENTRANCE PHENOMENA

In Sec. V we assumed that no denaturing agent was present in the solvent. Experimentally it is seen (Sec. III) that in the presence of denaturing agents such as DCA and TFA, the helices tend to degenerate to random coils at low temperatures. If the concentration of PBLG is large enough to form a nematic phase, then we should observe a nematic isotropic transition as temperature decreases.

Thus we expect the occurrence of the reentrance phenomena. At high temperature (~373 K) a large fraction of the molecules are in helical state, giving rise to a concentration high enough for a nematic phase. However, the latter is not stable against thermal fluctuations. Thus the system finds itself in the isotropic phase. As the temperature is lowered an isotropic nematic transition takes place—as discussed in Sec. II. As the temparature is further lowered the helices would tend to coil (Sec. III). However, the possibility of the system remaining in the nematic phase induces rigidity, thus sppressing at least temporarily helix-coil transitions (Sec. IV). Finally, when the system is cooled to a sufficiently low temperature, the helix-coil transition can no longer be held back. The molecules coil, causing the solution to return to the isotropic phase.

"Reentrant" transitions have been observed before in liquid crystals under pressure.¹⁷ The mechanisms are totally different. To observe the phenomenon in the present case, no pressurization is necessary. As a matter of fact, since the liquid-crystalline phase can be detected opticallyunder crossed polarization microscope⁵-the experiment can be performed easily. We suggest mixing 30% dichloroethane (DCE) with 70% DCA. Add PBLG until the liquid-crystalline phase is observed at room temperature (about 10-20%PBLG). Cool the system to about 280 K to observe a transition to the isotropic phase. Heating the system to about 330 K should result in another transition, also to the isotropic phase. There have been some experiments on helix-coil transitions in these mixtures; hence information is available on $\Delta \epsilon$ and $\ln(g_c/g_h)$ as required by our model (see Table I). Unfortunately, there is no experiment on the liquid-crystal transition in such mixed solvents; hence at this time we do not have a way of determining γ_2 —the anisotropic interaction between helices in the solution. Assuming γ_2 independent of the solvent and only a property of the helices, we can obtain γ_2 from experiment on PBLG in pure dioxane.⁶ This assumption is not unreasonable, as it is seen from the critical concentration of PBLG at which the system becomes



FIG. 5. Phase diagram of PBLG in 70% DCA and 30% DCE. T: temperature; ρ : the volume fraction of PBLG in the solution; I: regions where isotropic phase is stable; N: regions where twisted nematic (cholesteric) phase is stable; —: result without taking into account coil-coil interaction; ----: result including first-order effect of coil-coil interaction.



FIG. 6. Order parameter σ_2 of PBLG in 70% DCA and 30% DCE as a function of temperature; volume fraction of PBLG=0.161.

liquid crystalline; i.e., the boundaries of the coexistence region are independent of the solvent provided that the solvent is neutral.⁴ Thus at least the neutral solvent does not change the anisotropic interaction $v_2(r)$ hence γ_2 . We have to assume further that the only effect of denaturing agents such as DCA or TFA is to induce coiling. As a consequence of this assumption they do not change the interaction between helices.

From γ_2 determined from PBLG in dioxane and $\Delta \epsilon$ and $\ln(g_c/g_h)$ determined from experiment,^{3,13} we can obtain a phase diagram. Assuming 100% helices in dioxane (corresponding to $A \rightarrow \infty$ in Fig. 1), the mean-field result $B_{IN} = -4.54$, with $\rho_{IN} = 0.161$, $T_{IN} = 338$ K, implies $\gamma_2/k = (-4.54 \times 338 \text{ K})/0.161 = -9.53 \times 10^3$ K. $\Delta \epsilon$ and $\ln(g_c/g_h)$ are ob-



FIG. 7. The fraction of helices x of PBLG in 70% DCA and 30% DCE as a function of temperature. ——: volume fraction of PBLG=0.161; ——: volume fraction of PBLG less than 0.14 (no liquid-crystalline phase).

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tained from Table I with the help of Eqs. (7'), (7''), and (8'). The resulting phase diagram showing reentrance is shown in Fig. 5 and $\sigma_2(T)$ and $x_2(T)$ are plotted in Fig. 6 and Fig. 7, respectively, for one particular solution. For comparison x(T) for a dilute solution is also shown. Note the effect of induced rigidity.

In our model, we could have included a firstorder estimate of coil-coil interaction, by adding a term $(\lambda/N)(N - N_h)^2$ to Eq. (9). Here λ is the average coil-coil interaction. We can obtain the equilibrium configuration by minimizing \mathcal{F} with respect to N_h and $f(\theta)$. Thus in place of Eq. (11) we obtain

$$\frac{x}{1-x} = \exp\left(A + \ln\frac{Z}{4\pi} + \frac{2\lambda\rho}{kT}(1-x)\right), \qquad (14)$$

and in place of Eq. (13)

$$\frac{F_N - F_I}{NkT} = -\frac{1}{2} B x^2 \sigma_2^2 + \ln \frac{1 - x_N}{1 - x_I} - (x_N^2 - x_I^2) \frac{\lambda \rho}{kT}.$$
 (15)

In dilute solutions we have no liquid-crystalline

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state, and from Eq. (14) we can show that

$$T_{hc} = (\Delta \epsilon + \lambda \rho) / k \ln(g_c/g_h)$$
.

Experiments show that in dilute solutions of PBLG in DCA:DCE mixture, the helix coil transition temperature decreases by 1 K when concentration is increased by 4%.¹³ Therefore $\lambda = 72.2/0.04 = 1805$ K. The new phase diagram appears as the dashed curve in Fig. 5. As can be seen, there is a quantitative difference, but no qualitative change.

Reentrant phases are rare in nature and are of special interest to physicists. Since the experiment proposed is rather simple, we hope to see experimental verification of this prediction.

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