Conformational changes coupled with the isotropic–anisotropic transition Part 1. Experimental phenomena and theoretical considerations

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Abstract

Phase behavior and conformation characteristics were reported for poly(γ-benzyl-L-glutamate) (PBLG) in dichloroacetic acid (DCA) and a mixed solvent of CHCl₃/trifluoroacetic acid (TFA). The anisotropic–isotropic transition, where intramolecular helix–coil transition was coupled, was observed for the PBLG liquid crystal solution prepared, at room temperature, with either a decrease in temperature or an increase in acid content. The information on PBLG molecular conformation provided by IR determinations indicates that in the acid mediated liquid crystal solution, the PBLG side chain may become flexible while the helix backbone remains stable prior to the helix–coil transition. Based on the molecular information gained through the experiments, the reentrant theory previously derived (Lin J. Polymer 1997;38:4837; Lin J. Polymer 1998;39:5495) was further generalized by introducing a temperature-dependent axial ratio of the Kuhn chain. The calculations carried out show an appreciable improvement in the agreement between the theory and the experimental phase diagram. The present theory also accounts, reasonably, for the temperature dependence of the PBLG order parameter observed in the experiments. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid crystalline polymer; Polypeptide; Lattice model

1. Introduction

Conformational changes are an important issue in the formation of an anisotropic phase in real semirigid chains. If the nematogenic chain molecules are able to adopt a variety of conformations, some more extended and rod-like than others, the occurrence of liquid crystallinity in such systems must invariably be accompanied by selective reorganization favoring more extended chain conformations owing to the severe expulsion of randomly arranged chains from the nematic phase. The intramolecular conformational changes can, therefore, be coupled with the isotropic–anisotropic transition and be accelerated by the intermolecular orientational ordering. Such an effect is termed conformational ordering and may be pertain to semirigid chains in general [1,2].

An extreme case of the conformational ordering that has received attention is the reentrant isotropic phase transition in polypeptide liquid crystals. In the presence of a denaturant acid, the polypeptide molecules would tend to be in a random coil state by the lowering of the temperature. An anisotropic–isotropic transition, reentrant transition, occurs at low temperature, as the coil chain is unable to support the liquid crystal ordering. The reentrant isotropic transition has already been reported for poly(γ-benzyl-L-glutamate PBLG/dichloroethane (EDC)/dichloroacetic acid (DCA) liquid crystal solution [5–7]. The conformational information regarding the PBLG main-chain in the EDC/DCA mixed solvent, obtained from NMR determinations, indicates that the helix backbone remains quite stable as long as the PBLG molecule exists in the liquid crystal state. However, in the isotropic phase the molecule is able to assume either a rod-like or a random coil state under different conditions. As for the side chain conformation, it may be also important in determining the phase behavior and order characteristics, but no experimental data have been reported so far.

Regarding the theoretical considerations for the possibilities of a reentrant isotropic phase in the polypeptide liquid crystal, Lin and co-workers have proposed a theory [3,4,7] based on the Flory–Matheson lattice model in which the free energy change for the helix–coil transition has been incorporated into the lattice scheme [2,8]. Some assumptions are also adopted. First, the molecular conformation in the isotropic phase is temperature-dependent and follows a modified Zimm–Bragg notion for the helix–coil transition in which the acid effect has been taken into account [9,10]. Second, the solvent–polymer interaction parameter, χ, is

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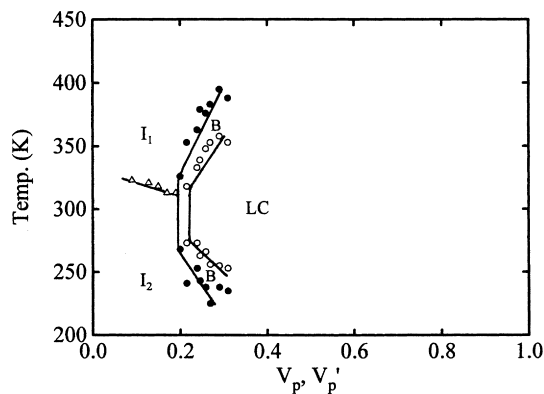*E-mail address:* jplin@mail.online.sh.cn (J. Lin).

Fig. 1. Experimental phase diagram for the PBLG/DCA system: I_1, isotropic phase of orientationally disordered helices; I_2, isotropic phase of random coils; B, biphasic region; LC, liquid crystalline phase.

considered to be negative in the whole temperature range and is regarded as an inverse measure of temperature. The reentrant isotropic phase observed in the polypeptide liquid crystal solution is predicted well by the theoretical calculations. The influence of the molecular parameters and intermolecular orientation-dependent interaction on the reentrant isotropic transition has also been studied; the effect is appreciable. Although a good qualitative agreement of the theory with the experimental observations was achieved, further development of the theory is still needed for a more reasonable interpretation of the observed phenomenon. For instance, in theory, the relaxation of the chain rigidity upon heating which leads to the curvature of the biphasic chimney towards high concentrations is artificially described by a helix–coil transition. However, in the real case, the polypeptide helix is usually stable up to very high temperatures. Also, the theoretically predicted critical volume fractions, v_p and v_p', are too high with respect to the experimental observations.

In this study, the phase behavior of PBLG/DCA and PBLG/CHCl$_3$/trifluoroacetic acid (TFA) was investigated using a polarizing microscope. The liquid crystal solutions formed at room temperature were found to undergo a reentrant isotropic transition in addition to that of the PBLG/EDC/DCA system. IR studies were carried out in order to elucidate the conformational characteristics of the PBLG molecules in the anisotropic–isotropic transition. Based on the molecular information gained through the experiments, the previously derived reentrant theory was further generalized by introducing a temperature-dependent axial ratio of the Kuhn chain. The phase diagrams calculated on this basis show an improvement in the agreement between the theory and the experimental observations.

2. Experimental

The PBLG sample was prepared by a standard *N*-carboxy-γ-benzyl-L-glutamate anhydride (NCA) method.

The polypeptide formed was purified by repeated precipitation from a chloroform solution in a large volume of methanol. The molecular weight of the PBLG sample was estimated from the intrinsic viscosity measured in DCA using the relation of Doty et al. [11] $[\eta] = 2.78 \times 10^{-5} M_v^{0.87}$. The molecular weight of the samples used in the experiments is 9.6×10^4. The PBLG solutions were prepared by dissolving the polymer sample in DCA or in the mixed solvent of CHCl$_3$/TFA over 1–2 days. The polymer volume fraction, v_p and v_p' were estimated from the density (1.27 g/cm^3) of PBLG [11].

Phase transitions were observed using a Leitz-Ortholux II polarized light microscope that was provided with a hot stage. The IR spectra were measured at room temperature using a Nicolet Manga-IR 550 spectrometer. The ^{1}H NMR spectra were recorded on a JEOL JNM-GSX-500 spectrometer with a variable temperature controller operating at 500 MHz.

3. Results

3.1. Optical observations

It is well known that PBLG molecules favor the random coil conformation in dilute DCA solution at room temperature [7,12]. In the present work, when the PBLG concentration is increased above a critical value of $v_p = 0.190$, the formation of the liquid crystal phase was observed using a microscope. On further increasing the concentration, a uniform cholesteric mesophase eventually forms. Since the random coil structure is inconsistent with the liquid crystal ordering, a coil–helix intramolecular conformational transformation is expected in the isotropic–anisotropic transition. On cooling the formed PBLG/DCA liquid crystal solution, the flexible random coil conformation may become stable at lower temperature. A reentrant isotropic phase induced by the helix–coil transition was also viewed. On the other hand, with increasing temperature, the PBLG helical chain also becomes flexible due to the thermal energy, and thus the liquid crystal phase tends to be less stable. An anisotropic–isotropic transition takes place eventually at the point where the free energy of the ordered phase becomes equivalent to that of the conjugated isotropic phase.

Based on the optical observations, a phase diagram of the PBLG/DCA which is divided into several characteristic zones as described in Fig. 1 was constructed. The boundary of the isotropic phase of helices and random coils was obtained by monitoring the helix–coil transition, through the measurements of the chemical shifts of amide hydrogen, by ^{1}H NMR. The transition temperature was taken as the inflection point on the δ_{NH} vs. temperature curve. As shown by the phase diagram, two anisotropic–isotropic transitions occur at high and low temperatures, with the latter being a result of the helix–coil transition.
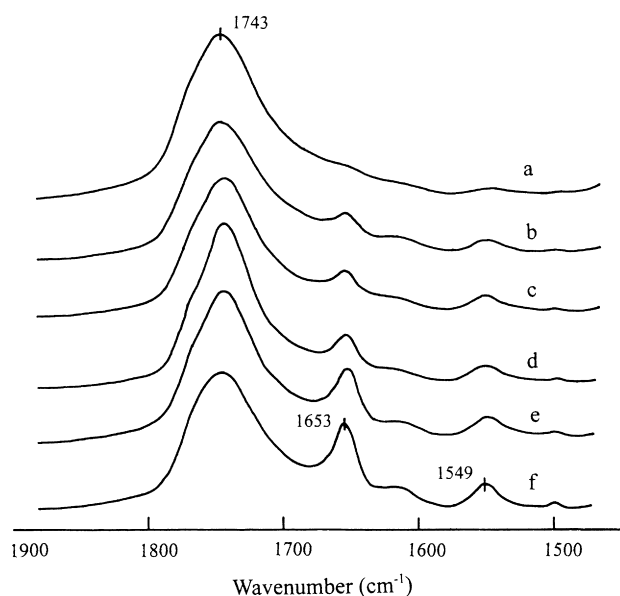
Fig. 2. Infrared spectra of PBLG/DCA solutions with various polymer volume fractions: (a) $v_p = 0.05$; (b) 0.123; (c) 0.184; (d) 0.229; (e) 0.266; and (f) 0.309. (a)–(c): isotropic solution; and (d)–(f): liquid crystal solution.
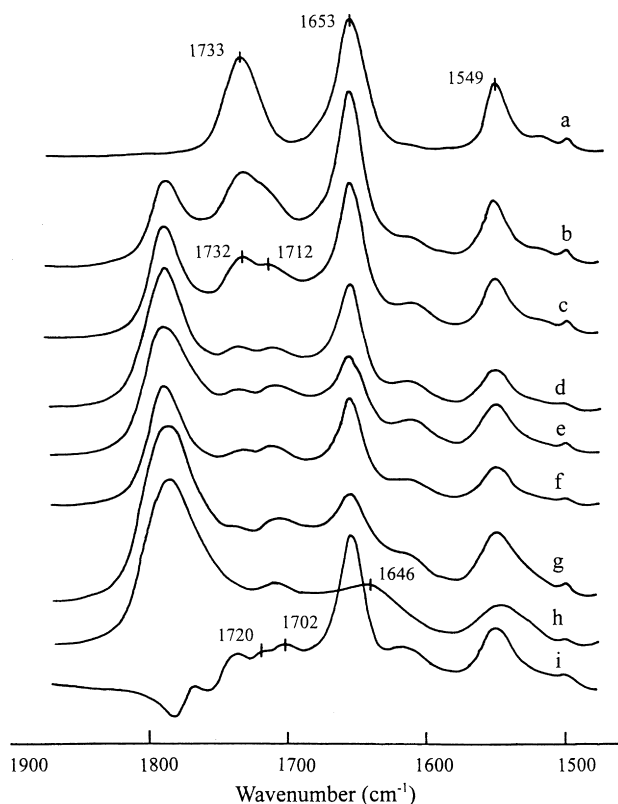

Fig. 3. Infrared spectra of PBLG/CHCl$_3$/TFA solutions of $v_p = 0.20$ with various TFA mole fractions: (a) $f_{TFA} = 0$; (b) 0.104; (c) 0.155; (d) 0.264; (e) 0.328; (f) 0.351; (g) 0.463; and (h) 0.639. (a)–(d): liquid crystal solution; (e)–(f): biphasic solution; and (g)–(h): isotropic solution. Shown in (i) is the difference spectra between PBLG/DCA and DCA.

The liquid crystal phase was also observed above a critical volume fraction when the PBLG was dissolved in a CHCl$_3$/TFA mixture. For instance, a PBLG solution with $v_p = 0.20$ and TFA mole fraction $f_{TFA} = 0.104$ showed uniform cholesteric striations at room temperature. If the acid content, f_{TFA}, was increased to 0.328, the isotropic phase separation of a small portion of an isotropic phase appeared. Further increase in f_{TFA} resulted in a complete extinction of the anisotropic phase at $f_{TFA} = 0.463$. The anisotropic–isotropic transition is believed to be induced by the helix–coil transition in the PBLG molecules. On cooling the formed PBLG/CHCl$_3$/TFA liquid crystal solution, a reentrant isotropic phase was also observed. The reentrant isotropic transition temperature tends to be higher as the acid content in the solution is increased. For instance, the extinction temperature of the anisotropic phase increased from -41 to -36 to $-6°$C, as the acid content, f_{TFA}, was increased from 0.104 to 0.155 to 0.264. Such an observed dependence is well in line with the theoretical calculation result that the reentrant isotropic transition temperature increases as the acid activity increases [3]. The higher temperature transition was not observed because of the instability of the CHCl$_3$/TFA solvents.

3.2. Infrared studies

IR studies were carried out in order to examine the PBLG conformational changes in DCA solution, as the liquid crystal phase is formed with increasing polymer concentration (Fig. 2). The peak at 1743 cm^{-1} is contributed by DCA. The peaks at 1653 and 1549 cm^{-1} are the amide I and amide II band of the PBLG α-helix structure, respectively [13]. Fig. 2a–c are the IR spectra of the PBLG/DCA isotropic solution with $v_p = 0.05$, 0.123 and 0.184, respectively. Random coil structures are dominant in the dilute DCA solution as revealed by NMR, but the IR study is not sensitive to the coil form in the dilute solution. As the concentration is increased, the amide I and II bands that are characteristic of the helix form become evident, suggesting the winding up of PBLG molecules. When the polymer concentration is above a critical value, i.e. $v_p = 0.190$, according to the optical observation, liquid crystal formation occurs. Strong amide I and II bands of PBLG can be noted in Fig. 2d–f for the IR spectra of the liquid crystal solutions with $v_p = 0.229$, 0.266 and 0.309, respectively, indicating that the PBLG molecules take a helix conformation when they enter the anisotropic state. This result agrees well with the conclusion derived from the ^{2}H NMR measurement [7].

Molecular conformational changes in the concentrated PBLG/CHCl$_3$/TFA solutions accompanying the anisotropic–isotropic transition with increasing acid content were also followed by IR detection. A series of IR spectra for PBLG solutions with various acid contents is shown in Fig. 3. In the liquid crystal state, the PBLG backbone remains in the helix conformation as strong amide I and II

bands appear for the IR spectra of liquid crystal solutions (Fig. 3a–d). TFA causes no change in these bands as the acid content increases, until the formation of the isotropic phase occurs. Information of the side chain conformation is also provided by these IR spectra. The peak at 1733 cm^{-1} is assigned to the ester carbonyl of the PBLG side chain in free state. Hydrogen bonding of the acid with the ester carbonyl causes an additional band with frequency slightly lower than 1733 cm^{-1} [14,15]. Shown in Fig. 3a is the spectrum for PBLG/CHCl$_3$ liquid crystal solution. The ester carbonyl band is at 1733 cm^{-1}, indicating that the side chain is in a free state. When the TFA acid is added, a shoulder peak appears at 1712 cm^{-1} for the solution with $f_{TFA} = 0.155$ (Fig. 3c). This peak shifts to lower frequency and increases in intensity with further addition of the acid. The association of the acid with the PBLG side chain prior to the backbone helix–coil transition was also observed for the PBLG/DCA liquid crystal solution. Although the side chain ester carbonyl band is overlapped by the DCA solvent band, the information obtained from the subtraction of the DCA background spectrum still shows two separate peaks of the ester carbonyl band, which indicates that the acid is hydrogen bonded with the PBLG side chain in the liquid crystal state prior to the helix–coil transition. A typical result of such a curve is given in Fig. 3i. On further increasing the acid content to $f_{TFA} = 0.328$ (Fig. 3e), the helix–coil transition begins to take place. The PBLG chain becomes flexible and unable to support the orientational ordering, and an anisotropic–isotropic transition was accordingly viewed through the microscope. After passing a biphasic zone, a uniform isotropic phase is formed. The random coil structure of PBLG in the isotopic phase is evident by the amide I band at 1646 cm^{-1} (Fig. 3h). The vibrational frequency of the random coil conformation of polypeptide has been reported to be 1646 cm^{-1} [15]. In the dilute PBLG/DCA solution where the random coil conformation is dominant, the IR technique is not effective in detecting the coil structure. This may be because of the lower PBLG concentration and the overlapping of the solvent band as shown by Fig. 2a. Moreover, with an increase in the polymer concentration, some winding up of PBLG to the helix form may take place, which could also hinder the IR detection of the coil structure in the dilute PBLG/DCA solution. But, in the case of the concentrated situation of the PBLG/CHCl$_3$/TFA system, PBLG has a high enough concentration to be detected. At higher TFA content, PBLG transforms into the coil structure completely, and the amide I band characteristic of the coil structure can easily be found.

4. Discussion

4.1. PBLG molecular conformation

^{2}H NMR studies on the PBLG conformation suggest that the helical structure remains quite stable in the acid-mediated solution as long as the molecule exists in the liquid crystalline phase [7]. The evidence of the rigid backbone in the anisotropic phase is also provided by the present IR measurements. Further information gained from the IR studies shows that in the liquid crystalline state the acid could associate with the polypeptide by hydrogen bonding to the caboxyl groups of the side chain ester much before the occurrence of the helix–coil transition in the backbone. Additional information regarding the PBLG chain conformation comes from the study by Duke et al. on the pretransition phenomena in the PBLG liquid crystal phase [16]. The results obtained from the measurements of the diamagnetic susceptibility and the subsequent calculation of the side chain orientation function demonstrate that the PBLG side chain becomes flexible much before the helix–coil transition as the acid such as TFA is introduced into the liquid crystal solution. Although the experimental measurements do not give the information about the association model of TFA with the PBLG side chain, it presents strong evidence for the disruption of the PBLG side chain structure by the acid. Such a disruption of the side chain was also found for PBLG in the isotropic solution before the helix–coil transition [17].

Accumulation of the experimental results suggests that in the acid mediated liquid crystal solution, the PBLG backbone prefers to take a nearly perfect helical arrangement prior to a sharp helix–coil transition, while the side chain may have considerable mobility owing to the association with the acid molecules. Such a change in the mobility of the PBLG side chain must give rise to an increase in overall chain flexibility [16,18].

4.2. Phase diagram

The PBLG phase diagram shown in Fig. 1 is characterized as a narrow biphasic region separating the isotropic phase from the liquid crystal phase. The chimney-like biphasic region is gradually bent towards higher concentrations as the temperature is increased, leading to a high-temperature anisotropic–isotropic transition. The bending is believed to be because of the enhanced chain flexibility caused by the thermal energy and is widely observed for the real semirigid polymers [19]. In our previous theoretical work, [3,4] such a relaxation of the chain rigidity is artificially described by a helix–coil transition at higher temperatures. Actually, the polypeptide α-helix itself is generally stable at very high temperatures to undergo a helix–coil transition (above 500 K), while the molecular chain itself could tend to be quite flexible prior to the intramolecular transition.

For the semirigid polymer chains, Flory [20] has proposed a simple model in which the tendency to induce the formation of a nematic phase is controlled by the Kuhn segment of the chain. The axial ratio x_k of the Kuhn segment is given by
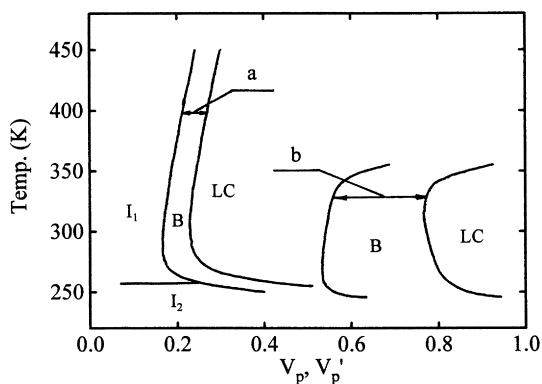
$$x_k = 2q/d \qquad (1)$$

Fig. 4. (a) Phase diagram calculated for the PBLG in the acid-mediated solution. The parameters used in the calculations are $\Delta H_0 = -1500$ kcal/mol, $\Delta S_0 = -1.2$ cal/mol K, $\Delta H_c = -2000$ cal/mol, $\Delta S_c = -3.0$ cal/mol K, $a = 0.84$, $m = 10$, $\sigma = 10^{-4}$, $q_0 = 1500$ Å and $d = 15.6$ Å. (b) Phase diagram calculated according to the previous theoretical model [3,4]. The parameters used in the calculations are $\Delta H_0 = -1000$ cal/mol, $\Delta S_0 = -2.5$ cal/mol K, $\Delta H_c = -3000$ cal/mol, $\Delta S_c = -6.667$ cal/mol K, $a = 0.075$, $m = 10$, $\sigma = 10^{-4}$ and $x = 48$. I_1: isotropic phase of the orientationally disordered helices; I_2: isotropic phase of random coils; B: biphasic region; and LC: liquid crystalline phase.

where q is the familiar persistence length and d, the lateral dimension of the polymer.

The persistence length q is reported to further decrease with increasing temperature. According to Sixou et al. [21] such a temperature dependence can be described by

$$q = q_0 T_0 / T \qquad (2)$$

where q_0 is the value of the persistence length at room temperature T_0. Since the PBLG molecular chain becomes flexible in the acid-mediated solution owing to the association of the side chain with the acid, and since its rigidity may also decrease with increasing temperature, it is reasonable to use a temperature-dependent x_k for explaining the formation of the mesophase replacing the axial ratio of the rigid rod adopted in our previous work.

The relationships that determine the conditions for the stable coexistence of the fully helical anisotropic phase in equilibrium with the conformation variable isotropic phase can be obtained from Eqs. (2) and (3) with the auxiliary relations Eqs. (4)–(8) of Ref. [4]. In the numerical calculation, x is replaced by x_k, which is governed by Eqs. (1) and (2). For the PBLG sample, $q = 1500$ Å and $d = 15.6$ Å were adopted according to the literature [19]. The molecular conformations of the isotropic phase, as manifested by the degree of the helicity θ, are given by Eqs. (9)–(12) of Ref. [4]. In order to properly simulate the helix–coil transition at higher temperatures, some parameter values of Eqs. (9)–(12) in Ref. [4] that were used in the previous calculations were adjusted to render the helix–coil transition that took place above 500 K. The relation between parameter χ and temperature follows the same equation adopted in Ref. [4], i.e. $\chi = -1.667 + 352/T$.

The calculated phase diagram is shown in Fig. 4a, where the temperature is plotted against the volume v_p and v_p' in the

coexisting phase. The parameters applied in the numerical calculations are indicated in the caption. An isotropic phase is shown in lower polymer concentrations. The low and high-temperature isotropic phases are conformationally different. The line to the left of the phase diagram separates the isotropic phase of macromolecular helices (I_1) from the isotropic phase of random coils (I_2). The boundary was obtained by designating $\theta = 0.5$ as the transition point. A helix anisotropic phase is formed when the polymer concentration is increased. Since the random coil conformation becomes stable with decreasing temperature, a reentrant isotropic phase (I_2) is predicted to appear at lower temperatures. At higher temperatures, an anisotropic–isotropic transition caused by enhanced chain flexibility is shown. In the present work, the relaxation of the chain rigidity is manifested by the decrease in the x_k value upon increasing the temperature. In the higher temperature biphasic zone, the molecules assume the same conformation in the coexisting phase, which is in accordance with that observed in the experiments. Shown in Fig. 4b is the PBLG diagram calculated according to the previous theoretical model [3,4]. The PBLG sample used in the present experiment corresponds to $x = 48$. The other parameters used in the calculation are the same as those adopted in our previous work and are listed in the caption of Fig. 4. Comparison of these two calculated results with the experimental results in Fig. 1 illustrates an appreciable improvement in the agreement between the theoretical and the experimental observations. The present theoretical calculation predicts an anisotropic–isotropic transition induced by increasing chain flexibility at higher temperatures, while in the previous work such a transition is artificially explained by a helix–coil conformational change. The improved theory not only provides a reasonable picture for the anisotropic–isotropic transition at higher temperatures, but also rationalizes the predicted volume fractions v_p and v_p' in the whole temperature range.

4.3. Orientational order parameter

Another aspect of the polypeptide liquid crystal that merits investigation is the degree of order in the anisotropic phase. The order parameter of the Kuhn segment can be calculated as a function of temperature after introducing the temperature-dependent x_k. According to Flory and Ronca [22,23], the order parameter S is expressed explicitly as

$$S = 1 - (3/2)(f_3/f_1) \qquad (3)$$

where f_3 and f_1 are given by Eqs. (4)–(6) of Ref. [4]. Shown in Fig. 5 are the calculated values of S as a function of temperature at a given concentration $v_p = 0.32$. Values of $q = 1500$ Å and $d = 15.6$ Å were adopted for PBLG in the calculations. ^{2}H NMR technique has been used to report the experimental data of the order parameter for the PBLG/EDC/DCA liquid crystal solution [7]. The result replotted
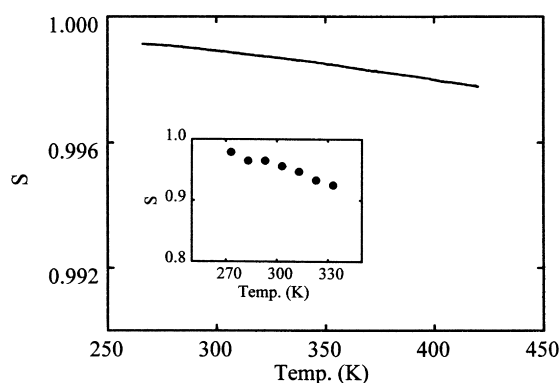
Fig. 5. Variation of the order parameters as a function of temperature determined with Eq. (3). Shown in the inset is the experimental results obtained by ^{2}H NMR measurements [7].

in the inset of Fig. 5 shows that the order parameter tends to decrease with increasing temperature. A comparison between the theory and the result indicates that the temperature dependence of the order parameter is well predicted. However, the calculated S values are appreciable high. As indicated by Abe [24], such a discrepancy may arise in part from an overestimation of the orientational free energy in the lattice theory. A direct experimental elucidation has been suggested.

5. Conclusions

The conformation changes accompanied by the intermolecular phase transition may be dominant in some semi-rigid situations. This effect, as exemplified by the reentrant isotropic transition, was further studied in this work. The obtained results are summarized as follows.

1. Reentrant isotropic transitions were observed in the PBLG/DCA and PBLG/CHCl$_3$/TFA liquid crystal solutions in addition to that previously found in the PBLG/EDC/DCA system. Such conformationally coupled anisotropic–isotropic transition was also observed in the PBLG/CHCl$_3$/TFA liquid crystal solutions with an increase in the acid content.
2. Molecular information gained through the IR measurements indicates that in the PBLG liquid crystal solution where an acid exists, the side chain can associate with the acid while the helix backbone remains quite stable. This effect would undoubtedly increase the overall PBLG chain flexibility. Such a conclusion obtained from the acid induced anisotropic–isotropic transition may also apply to the situation of the low temperature reentrant

transition. In the acid mediated polypeptide liquid crystal solution, when the temperature is decreased, the acid molecules start attacking the helical architecture and a reentrant isotropic transition takes place. The association of the acid with the polypeptide side chain in the reentrant transition may also lead to an increase in the chain flexibility and contribute to the helix–coil conformational-induced anisotropic–isotropic transition at low temperature.
3. The reentrant theory derived previously was further generalized by introducing a temperature-dependent Kuhn chain axial ratio x_k. The phase behavior including both high and low-temperature anisotropic–isotropic transitions is reasonably reproduced. The improved theory is also able to predict the dependence of the order parameter on temperature, which is in line with the experimental observations.

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