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Reentrant isotropic transition of polypeptide liquid crystal: effect of steric and orientation-dependent interactions

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According to the theoretical model proposed in the previous work (J. Lin, *Polymer*, 1997, **38**, 4837), the dependence of the molecular parameters on the reentrant isotropic transition where the anisotropic–isotropic transition and the intramolecular helix–coil transition are coupled was investigated, and a pronounced effect has been shown. This theory was further improved by taking into account the orientation-dependent interactions, using the orientational energy term prescribed by Flory and Ronca. The calculation carried out shows that the anisotropic phase formation at reentrant region is accelerated due to the presence of the orientation-dependent interactions, while the biphasic region tends to be widened. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: lattice model; liquid crystalline polymer; orientation-dependent interaction)

INTRODUCTION

In 1950s, Flory applied a lattice model treatment to the necessary conditions of polymer solutions capable of forming liquid crystal[1]. Shown by curve a in *Figure 1* is the famous phase diagram calculated for the theoretical rigid, impenetrable rods, which corresponds well in overall appearance to the experimental observations[2]. This phase diagram is characterized as a narrow biphasic region separating the isotropic phase from the liquid crystalline phase, connected to a wide biphasic region in which nearly pure polymer is in equilibrium with nearly pure solvent. Later on this theory was extended considerably to various liquid crystalline systems by Flory and his collaborators[3–11]. However, throughout these theoretical considerations, it has been assumed that the conformations of the polymer chains are the same in both the isotropic and anisotropic phase. It is readily apparent that this assumption must fail if the nematogenic chain molecules are able to adopt a variety of conformations, some more extended and rod-like than others. In the early 1980s, a theoretical approach concerning the system in which polymer chain is able to assume either rod-like or random coil conformation was carried out by Flory and Matheson[12–14]. The two transitions, one conformational exemplified by the coil–helix transition and the other intermolecular isotropic–anisotropic transition, are considered to be coupled and found to be mutually affected.

An experimental example for the coupled intramolecular and intermolecular transitions is the reentrant isotropic phenomenon[15–19]. When poly(γ-benzyl L-glutamate) (PBLG) is dissolved in a binary solvent mixture containing a denaturing component such as dichloroacetic acid (DCA), a pure liquid crystalline phase can be formed at room temperature where PBLG is in the helical state, if the polymer concentration is sufficiently high. As the temperature is decreased, the acid molecules start attacking the hydrogen bond involved in the helical architecture and a helix–coil transition takes place. The random coil form is predominant at lower temperatures where acid molecules are firmly attached to amide linkages. Since the random coil polymer chains are geometrically inconsistent with the long-range orientational order of the liquid crystals, an anisotropic to isotropic transition, reentrant isotropic transition, can be observed at lower temperatures.

Theoretical treatment based on the Flory–Matheson lattice model for the possibility of a reentrant isotropic transition was first proposed by Lin and Abe[18,19]. They rest mainly on the analysis of the effect of different polymer–solvent interaction parameters, χ, in the isotropic and anisotropic phases. Recently, this reentrant isotropic theory was further improved by adopting the following modifications[20]. First, the molecular conformation in the isotropic phase is temperature dependent and follows a modified Zimm and Bragg's notion for the helix–coil transition, in which the effect of acid has been taken into account[21,22]. Second, the χ parameter, which is considered to be negative in the whole temperature range[19], is also regarded as an inverse measure of temperature. A typical result is shown by curve b in *Figure 1* according to [20]. Since the ordinate χ is an inverse measure of temperature, at low temperatures an anisotropic to isotropic reentrant transition caused by intramolecular helix–coil transformation is predicted. In the reentrant isotropic region, the helix anisotropic phase is in equilibrium with an isotropic phase comprising nearly flexible chain molecules. A high temperature anisotropic–isotropic transition which may be related to the enhanced chain flexibility in isotropic phase caused by thermal energy is also shown.

From the comparison of two theoretical calculations in *Figure 1*, it can be seen that the effect of variable chain conformation is significant. The phase diagram calculated for perfectly rigid, impenetrable rods is just an idealized specification. In particular, partial flexibility due to the molecular conformation changes usually plays an important role, and for sufficiently large macromolecules its effects may be dominant. Curve b would be an example which shows the importance of the proper representation of

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molecular conformation in predicting the phase behaviour of liquid crystal polymers.

In this work, the influence of the molecular parameters on the reentrant isotropic transition was studied on the basis of the reentrant isotropic theory. This theory was further improved by taking into account the orientation-dependent interactions. The intermolecular attractive forces were found to accelerate the isotropic–anisotropic transition in the reentrant isotropic region.

THEORY

Short description of the reentrant isotropic theory

In this section a brief description is given of the theoretical model describing the observed reentrant isotropic behaviour. This theory is discussed in more detail in Ref. 20. Theoretical treatment for the possibility of a liquid crystal formation coupled with the coil–helix transition of polymeric molecules in solution has been prescribed by Flory and Matheson[14]. According to their model, the free energy change for the coil–helix transition has been incorporated into the lattice scheme by adopting an expression

$$-\sum mx_i(\theta \ln s - \rho \ln \sigma) \tag{1}$$

where x is the number of segments comprising polymer component, s and ρ denote, respectively, the statistical weight for a unit in the helical state relative to the coil state and the weighting factor for initiation of a helical sequence, m represents the number of repeat units involved in a helical sequence, θ is the fraction of polymer units in the helical conformations and ρ is the fraction of units that mark the beginning of a helical sequence. As the polymer component is assumed to occur in a helical form in the anisotropic phase (see Ref. 20), the resulting equations for the fully helical, anisotropic phase in equilibrium with the isotropic phase are

$$\ln(1-v_\mathrm{p}) + (1-1/x)v_\mathrm{p} + \chi v_\mathrm{p}^2 - \ln(1-v_\mathrm{p}{}') - v_p{}'(y-1)/x + \ln[1-v_\mathrm{p}'(1-y/x)] - \chi v_\mathrm{p}'^2 = 0 \tag{2}$$

and

$$\ln v_\mathrm{p} + (x-1)v_\mathrm{p} + \chi x(1-v_\mathrm{p})^2 - \ln v_\mathrm{p}' - v_\mathrm{p}'(y-1) + \ln f_1 - \chi x(1-v_\mathrm{p}{}')^2 + mx\ln[1-\rho/(1-\theta)] + mx\ln s + \ln\sigma = 0 \tag{3}$$

where v_p is the volume fraction of the polymer component, y is the disorientation index and prime symbol (′) is appended to denote the anisotropic phase. Auxiliary relations that complete specification of the equilibrium conditions are

$$f_\mathrm{p} = \int_0^{x/2} \sin^\mathrm{p}\Psi \exp(-\alpha \sin\Psi)\,\mathrm{d}\Psi \tag{4}$$

$$\alpha = -(4/\pi)x \ln[1-v_\mathrm{p}'(1-y/x)] \tag{5}$$

$$y = (4/\pi)x(f_2/f_1) \tag{6}$$

$$s = (1-\rho/\theta)/[1-\rho/(1-\theta)] \tag{7}$$

$$\sigma = \rho^2/(\theta-\rho)(1-\theta-\rho) \tag{8}$$

The extension of the Flory–Matheson model to the polypeptide liquid crystal solutions exhibiting reentrant transition is performed by taking the molecular conformation changes occurring in the isotropic phase into account by using a modified Zimm and Bragg's notion for the helix–coil transition[21,22]. According to Zimm and Bragg, the statistical weight of s can be related to a change in the Gibbs free energy ΔG_0 for the helix formation

$$s = \exp(-\Delta G_0/RT) = \exp(-\Delta H_0/RT + \Delta S_0/R) \tag{9}$$

where ΔG_0 is broken up into an intrinsic enthalpy and entropy change, ΔH_0 and ΔS_0. For high molecular weight polypetides, the helix fraction θ is given by

$$\theta = 1/2 + (s-1)/2[(1-s)^2 + 4\sigma s]^{1/2} \tag{10}$$

To properly account for the helix–coil transitions in acid-mediated solutions of polypeptides, the factor of s should be replaced by[22]

$$s_c = s/(1+Ka) \tag{11}$$

where a is the acid activity, K is the equilibrium constant due to the binding which occurs through H bonding to exposed amide linkages in the coiled state. K is written in an expression form

$$K = \exp(-\Delta G_c/RT) = \exp(-\Delta H_c/RT + \Delta S_c/R) \tag{12}$$

where $\Delta H_c < 0$, $\Delta S_c < 0$. After considering the effect of molecular conformation changes, two anisotropic–isotropic transitions are predicted to occur at high and low temperatures.

Orientation-dependent interactions

In the theoretical treatment carried out by Flory and Matheson[12–14], only steric interactions between the helices have been represented in the lattice model, the orientation-dependent interactions are ignored. However, such attractive interaction energies would have an influence on the stability of the liquid crystalline phase addition to that of molecular shape. Flory and Ronca[10,23] have prescribed an orientation-dependent interaction term for rigid rods, based on the form derived by Maier and Saupe[24,25]. This energy term is written to be compatible with the lattice model as follows

$$E_\mathrm{orient} = -1/2(xn_\mathrm{p}kT^* v_\mathrm{p}S^2) \tag{13}$$

where n_p is the number of rod-like molecules, k is the Boltzmann's constant, T^* is the characteristic temperature that measures the strength of the orientation-dependent interaction and S is the order parameter defined by

$$S = 1 - 3/2\langle\sin^2\Psi\rangle \tag{14}$$

The direct contribution of the orientation-dependent interactions to the reduced free energy, obtained by division of equation (13) by kT, is $-1/2(xn_\mathrm{p}v_\mathrm{p}{}'\mathrm{S}^2/\Theta)$ where $\Theta = T/T^*$. The relations for the fully helical anisotropic phase in equilibrium with the isotropic phase, therefore, should be revised by adding terms of $-v_p'^2S^2/2\Theta$ and $(xv_p'S/\Theta)(1 - v_\mathrm{p}{}'S/2)$ to equations (2) and (3), respectively[10,23]. The orientational energy also affects the orientational distribution, and makes a further contribution to the reduced free energy. Accordingly, the f_p is redefined by[10,23]

$$f_\mathrm{p} = \int_0^{\pi/2} \sin^\mathrm{p}\Psi \exp[-\alpha\sin\Psi - (3xv_\mathrm{p}'S/2\Theta)\sin^2\Psi]\,\mathrm{d}\Psi \tag{15}$$

Numerical calculations

Following the assumptions adopted in the previous work[20], the solvent–polymer interaction parameter, χ, is

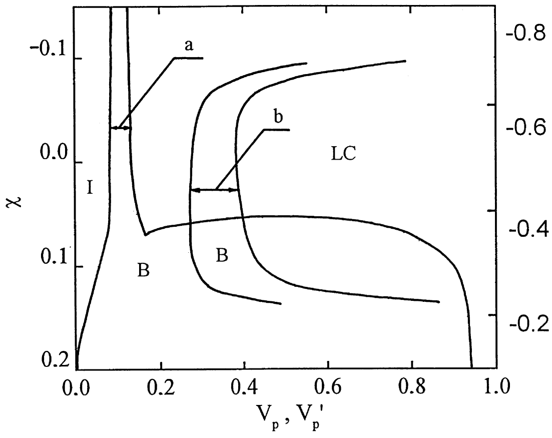

Figure 1 (a) Calculated phase diagram for impenetrable molecules of $x =$ 100 according to Ref. 1 (left-hand ordinate scale). (b) Calculated phase diagram for conformational variable molecules of x=100 in which the thermodynamic parameters used in calculation are similar to that of curve a of *Figure 2* in Ref. 2 (right-hand ordinate scale). I: isotropic phase, B: biphasic region, LC: liquid crystalline phase

considered to take negative values in the whole temperature range employed, and corresponds to a good solvent. The χ parameter which is usually regarded as an inverse measure of temperature is also taken to be of the form $A + B/T$, with A and B specified arbitrarily as -1.667 and 352. The relationships that determine the conditions for stable coexistence of fully helical anisotropic phase in equilibrium with conformational variable isotropic phase can be obtained by equations (2) and (3) with auxiliary relations of equations (4)–(8). The molecular conformations of isotropic phase as manifested by the degree of helicity θ are followed by equations (9)–(12). As for the studies on the effect of orientation-dependent interactions, equation (4) is replaced by equation (15), and two terms of $-v_p'^2S^2/2\Theta$ and $(xv_p'S/\Theta)(1 - v_p'S/2)$ are added to equations (2) and (3), respectively. Results of numerical solutions of these relationships are shown in *Figures 2–5* in which both χ and temperature are plotted against the volume fractions v_p and v_p' in the coexisting phase.

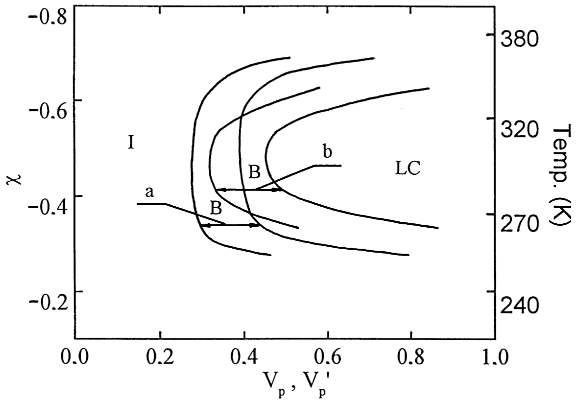

Figure 3 Phase diagrams calculated for (a) $\Delta S_0 = -2.45$ cal/mol K and (b) $\Delta S_0 = -2.55$ cal/mol K. Invariant parameters used in the calculations are $\Delta H_0 = -1000$ cal/mol, $\Delta H_c = -3000$ cal/mol, $\Delta S_c = -6.67$ cal/mol K, $\sigma = 10^{-4}$, $a = 0.085$ and $x = 100$. I: isotropic phase, B: biphasic region, LC: liquid crystalline phase

Shown in *Figure 2* are the calculated results for the effect of intrinsic enthalpy for the helix formation. Phase diagrams have been calculated for (a) $\Delta H_0 = -980$ cal/mol and (b) -1020 cal/mol. Other thermodynamic parameters applied in the numerical calculations are indicated in the caption. Of particular interest here is the region associated with the low temperature reentrant isotropic transition. A slight increase in the absolute value of ΔH_0, which is the manifestation of greater rigidity of the molecular chain, could give rise to a dramatic shift of reentrant zone to lower temperatures. It is also of interest to note the effect of ΔH_0 on the critical volume fractions and the high temperature anisotropic–isotropic transformation. With increasing the absolute value of ΔH_0, both v_p and v_p' are found to move to lower concentrations in the whole temperature range, and the liquid crystalline phase at high temperatures tends to be stabilized.

The role of intrinsic entropy change for the helix formation, ΔS_0, which is also associated with the flexibility of molecular chain-like ΔH_0, is illustrated in *Figure 3*. The binodals shown have been calculated for (a) $\Delta S_0 =$ -2.45 cal/mol K and (b) -2.55 cal/mol K. Relaxation of chain rigidity in the isotropic phase, as manifested in larger absolute value of ΔS_0, induces the reentrant isotropic transition occur at higher temperatures. The liquid crystal–isotropic miscibility gap is simultaneously shifted to higher concentrations in both high and low temperature transition zones. The influence on the high temperature anisotropic–isotropic transition is similar to to that of ΔH_0, i.e. higher molecular rigidity leads to higher anisotropic–isotropic transition temperatures.

The parameter σ, which is variously referred to as a nucleation or cooperativity parameter, is related to the

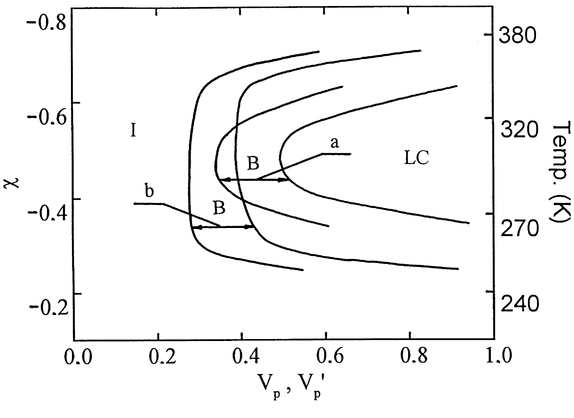

Figure 2 Phase diagrams calculated for (a) $\Delta H_0 = -980$ cal/mol and (b) $\Delta H_0 = -1020$ cal/mol. Invariant parameters used in the calculations are $\Delta S_0 = -2.5$ cal/mol K, $\Delta H_c = -3000$ cal/mol, $\Delta S_c = -6.67$ cal/mol K, $\sigma = 10^{-4}$, $a = 0.085$ and $x = 100$. I: isotropic phase, B: biphasic region, LC: liquid crystalline phase

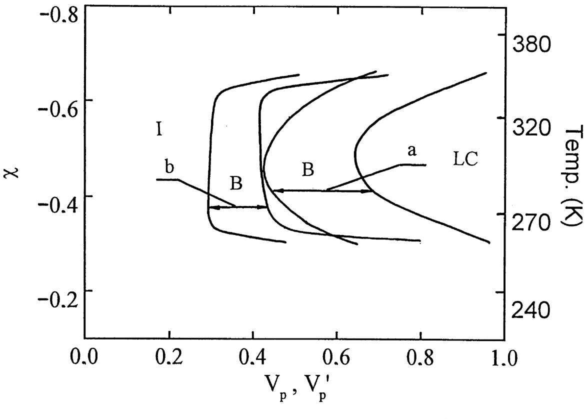

Figure 4 Phase diagrams calculated for (a) $\sigma = 10^{-3}$ and (b) $\sigma = 10^{-5}$. Invariant parameters used in the calculations are $\Delta H_0 = -1000$ cal/mol, $\Delta S_0 = -2.5$ cal/mol K, $\Delta H_c = -3000$ cal/mol, $\Delta S_c = -6.67$ cal/mol K, $a = 0.085$ and $x = 100$. I: isotropic phase, B: biphasic region, LC: liquid crystalline phase

length of the helical sequences, i.e. the smaller σ, the longer the rigid sequence in the molecular chain[26]. *Figure 4* illustrates the influence of σ on the biphasic equilibrium. Two cases are shown for the molecules with σ values of (a) 10^{-3} and (b) 10^{-5}. A binodal pair calculated for $\sigma = 10^{-4}$ can be found in curve a of *Figure 5*. The onset of biphasic stability receives an appreciable influence from the length of the helical sequences. The binodal curves shift to much higher concentrations from the high temperature transition region to the reentrant zone as the σ is so changed (from 10^{-5} to 10^{-3}) to deplete the population of the long rigid sequences. As a result, the reentrant transition takes place at higher temperatures and becomes gradual when σ is larger. Concomitantly with the shift of critical volume fractions, v_p and v_p', a significant broadening of the biphasic gap is also noted with increasing the value of parameter σ.

The effect of T^* which serves as a measure of the strength of the orientation-dependent interaction is shown in *Figure 5* for (a) $T^* = 0$ K, (b) 50 K and (c) 100 K. The introduction of the orientational interaction does not change the general feature of the phase diagram, i.e. the biphasic chimney formed at intermediate χ values or temperatures curves gradually toward higher concentrations when the temperature increases or goes down. However, the liquid crystalline phase tends to be stabilized in both high and low temperature transition regions as T^* increases from null to 100 K. It is also noted that with increasing T^*, the biphasic gap widens, and the critical volume fraction v_p shifts faster to lower concentrations than v_p' does. The broadening of the biphasic gap due to the introduction of orientational interaction in lyotropic liquid crystal system has also been reported by Warner and Flory for impenetrable rods at athermal conditions[11].

DISCUSSION

Effect of steric interactions

The reentrant isotropic transition is an interesting phenomenon to support the idea of 'induced rigidity' or 'conformational ordering', i.e. intermolecular orientational order promoting intramolecular conformational changes[23,27]. Within the reentrant region, the coil–helix conformational transition is accelerated by the formation of the anisotropic phase. The equilibrium anisotropic phase contains chains that are substantially more rigid than those inhabiting the isotropic phase. The coil–helix transition may then acquire the character of a first-order phase transition, due to the generation of the liquid crystal phase. The studies in the present work show that the molecular structures have a pronounced influence on the equilibrium between conformational variable isotropic phase and fully helical anisotropic phase. These influences could come from the rigidity of molecular chains and the length of rigid sequences which are associated with the intrinsic enthalpy and entropy changes for the helix formation, and the σ parameter. The liquid crystalline phase within the reentrant region is stabilized by higher rigidity of molecular chains and longer length of the rod sequences.

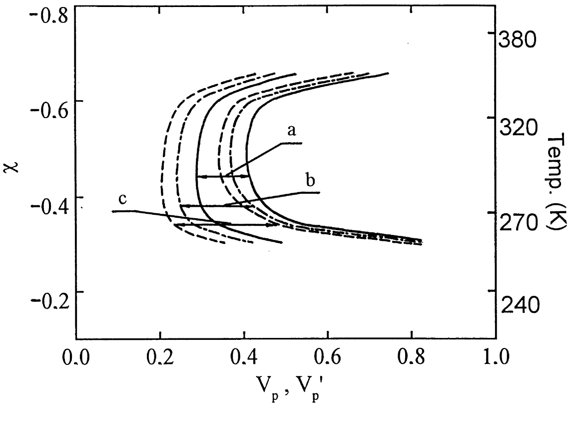

Figure 5 Phase diagrams calculated for (a) $T^* = 0$ K, (b) $T^* = 50$ K and (c) $T^* = 100$ K. Invariant parameters used in the calculations are $\Delta H_0 = -1000$ cal/mol, $\Delta S_0 = -2.5$ cal/mol K, $\Delta H_c = -3000$ cal/mol, $\Delta S_c = -6.67$ cal/mol K, $\sigma = 10^{-4}$, $a = 0.085$ and $x = 100$

The results obtained through the analysis carried out on the reentrant isotropic transition could apply with appropriate adaptations to other systems consisting of long chain molecules that may take alternative conformations, one rigid and rectilinear in form and the other a random coil. Occurrence of the liquid crystalline phase in such systems must invariably be accompanied by selective reorganization favouring more extended, rod-like conformations. The equilibria of the helix–coil type are also not unlike the case of alternating rigid–flexible block copolymers which have received interest widely due to their potential applications[28,29]. Qualitatively this is not surprising as the helix–coil sequence can be described in terms of a rigid–flexible sequence. Formation of a liquid crystalline phase in such copolymers could be accompanied by the stiffening of the flexible segments if the allowance is made for the conformation changes. The flexible blocks would become oriented and contribute to the overall anisotropy of the liquid crystalline polymer. Since the physical meanings of the intrinsic enthalpy change, ΔH_0, and entropy change, ΔS_0, can be further interpreted as the parameters associated with the rigidity of the helical sequences, and the flexibility of the random coils[26], i.e. the larger the absolute value of ΔH_0 the higher rigidity of helical rods, the larger absolute value of ΔS_0 the higher flexibility of random coils, it appears from the calculations that higher rigidity and longer length of the rod blocks would favour the liquid crystalline formation, while an increase in the flexibility of the coil blocks can hinder the entrance of the flexible chain into the anisotropic phase. Moreover, the existence of the orientation-dependent interactions especially for those containing high anisotropic groups may facilitate the formation of liquid crystals in such systems.

The effect of the orientation-dependent interactions

The importance of the orientation-dependent interaction in the reentrant isotropic transition has been shown by Pincus and de Gennes[30]. They relied on the Maier–Saupe

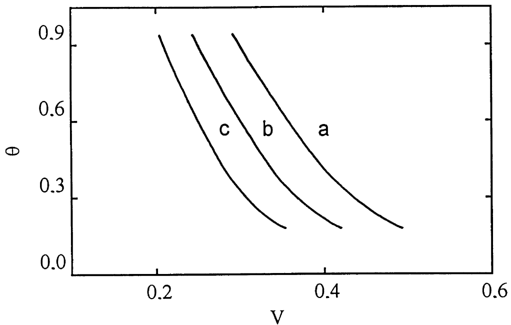

Figure 6 Dependence of the incipient volume fraction v_p on the helix fraction of isotropic phase in reentrant region at characteristic temperatures: (a) $T^* = 0$ K, (b) $T^* = 50$ K and (c) $T^* = 100$ K

theory for representation of the interactions between rod-like particles. However, the universally important steric interactions between the hard rods are not included in the theory, and such treatment is essentially a one-component development and does not take into account the possibility of two phases in equilibrium with one another at certain conditions of polymer concentration, temperature that the phase rule allows for the lyotropics. Therefore, it is quite reasonable to study the effect of the orientation-dependent interactions within the framework of the lattice model as those results revealed in *Figure 5*. Moreover, it is instructive to look at a further plot, *Figure 6*, where the incipient volume fractions v_{p} for stability of the anisotropic phase containing fully helical chains are plotted against the helix fractions of the isotropic phase in the reentrant zone. With decreasing the molecular helicity, the v_{p} shifts to higher concentrations. This shift is the impact of the conformational free energy penalty associated with the transition to helix conformation in the anisotropic phase. Such an energy penalty is partially compensated by the presence of the orientation-dependent interactions which favour the anisotropic phase, as it can be seen that v_{p} becomes smaller when T^* increases from 0 K to 100 K.

The anisotropic to isotropic transitions upon heating are widely observed for lyotropic liquid crystalline solutions. Various explanations have been proposed to interpret such a thermotropic effect based on either steric or orientation-dependent interactions[31]. In spite of its artificiality, the curvature of the biphasic chimney toward high concentrations at high temperatures observed in the polypeptide lyotropics containing a non-helicogenic component is well explained in terms of temperature variation of conformation by the present theoretical work. Here, the relaxation of chain rigidity upon heating is described by a helix–coil transition. The performance of this interpretation can be seen in Ref. 20 where a comparison between theory and experiment has been made. An assessment of the role of orientation-dependent interaction in the high temperature anisotropic–isotropic transitions is made along the lines of present theory. As shown in *Figure 5*, the introduction of the orientation-dependent interactions not only contributes to the stabilization of the liquid crystalline phase but also renders the biphasic region to widen. So far less attention has been paid to the effect of orientation-dependent interactions on the lyotropic polymers, the above arguments indicate that although the dominant factor responsible for the liquid crystal state appears to be the asymmetry of the molecular shape, intermolecular attractive forces also contribute to the liquid crystallinity in lyotropics.

The comparisons of theoretical calculations and experimental results made in previous work[20] indicate that a good qualitative agreement is achieved, although the predicted volume fractions v_{p} and v_{p}' in the whole temperature range seem too high. The performance of the reentrant theory is only in part rationalized in terms of v_{p} and v_{p}' which are moved to lower concentrations after introduction of the orientation-dependent interactions. However, the wider biphasic gaps obtained concomitantly with respect to the experimental observations become somewhat unrealistic.

Another possible explanation for the high critical volume fractions predicted is that the present theory underestimates the helicity in the isotropic phase. Subramanian *et al.*[16] have noted that the helix–coil transition temperature in PBLG/DCA/dichloroethane (EDC) isotropic solutions moves to lower temperatures with an increase in polymer concentration. The effects of enhanced helical fractions upon increasing polymer concentration in isotropic solutions were also reported in Ref. 32. Since the ratio of DCA to helicogenic solvent was kept constant in these experiments, the possibility of the decrease in DCA mole fraction which accompanies the increase in polymer concentration may contribute mainly to the enhancement of helical contents[32]. However, in the present theory such effect has not been considered. The acid mole fraction is maintained invariant throughout the polymer concentration employed. A better agreement between theory and experiments needs either improvement of the experimental procedure or to take the effect of changing acid ratio into account. On the other hand, the contributions from polymer–polymer interactions could also play a role in stiffening the chain rigidity in the isotropic phase especially at high polymer concentrations. Theory and experiments do bear some evidences of this effect[33,34]. It could be a further topic in the development of theory.

In the arguments given above, the conformation changes accompanied by the intermolecular phase transition could be dominant in some kind of semiflexible situation. More theoretical and especially experimental work on this interesting and important subject is desired to be forthcoming.

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