Conformational changes coupled with the isotropic–anisotropic transition Part 2. Effect of the external orientational field

Jiaping Lin*, Huaijian Zhou, Dafei Zhou

Department of Polymer Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

Abstract

Under certain conditions, polypeptide liquid crystal may exhibit an isotropic–anisotropic transition coupled with the intramolecular coil–helix changes. Based on the theoretical model that describes this phenomenon well [Lin J, et al. Polymer 2000; Lin J. Polymer 1997, 1998], the influence of external orientational field on such conformationally coupled transition was studied by introducing an energy term related to the quadrupole field. The calculations carried out show that the coupled isotropic–anisotropic and coil–helix transitions are accelerated when an external orientational field is applied. The effect of the external field intensity and molecular parameters of polypeptide has also been studied. The information obtained through the investigation may find important applications, such as envisaging new routes for processing the rigid–flexible block copolymer with better mechanical properties and constructing molecular devices for information storage and processing. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The effect of the external orientational field on the isotropic–anisotropic equilibrium presents an interesting problem in relation to both fundamental studies and fabrication processes [1–4]. As for the theoretical considerations regarding this important issue, limited work has been reported in the literature so far. Marrucci and Ciferri have estimated the excess free energy arising from the external force acting upon individual rigid-rod molecules and introduced an additional term in the Flory "1956" expression [5]. They concluded that the effect of the external orientational field is mainly that of shifting the isotropic–anisotropic separation interval toward smaller values of polymer concentration in the solution. A detailed study of such effect on the phase behavior of a thermotropic liquid crystal polymer containing stiff and flexible fragments has been performed by Shibaev et al. [6] based on the lattice model. The exact form of the orientational distribution function proposed by Flory and Ronca was used in the theory. Phase diagrams for various strengths of the external field and various values of the flexibility parameter of the flexible

fragments were constructed. It turned out that for any flexibility of the polymer chain, a phase transition to anisotropic state induced by the external field is possible. The combined action of the external field and cooperative chain stiffening effect can lead to the formation of a stable liquid crystal phase. Theoretical considerations according to the concept other than lattice model are also available in the literature. For instance, within the framework of the Onsager model [7], Khokhlov and Semenov analyzed the influence of the external orientational field on the solution of rigid-rod molecules [8,9]. Their calculations show that the application of an external field results in narrowing the region of phase separation and shifting the phase transition concentration to a lower value.

As stated in our previous work [10–12], under certain conditions polypeptide liquid crystals may undergo a reentrant isotropic transition where the intramolecular helix–coil transition occurs. Such conformationally coupled transition is of great interest from both theoretical and experimental points of view, since it can pertain to semi-rigid chains in general. The character of the conformationally coupled transition may vary significantly when an external orientational field is applied to the polypeptide system. The fields may arise from uniaxial elongation of polymer solutions due to the application of the external electrical or magnetic fields or due to certain types of flow of polymer

* Corresponding author. Tel.: +86-21-6425-1011; fax: +86-21-6425-3539.

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

solutions. Such external fields can be quadrupole symmetry fields, i.e. fields in which the potential energy of a rectilinear chain fragment is proportional to $-\cos^2 \phi$, where ϕ is the angle between the direction of this fragment and the orientation axis [6].

The purpose of this paper is to evaluate the effect of the external field on the conformationally coupled isotropic–anisotropic transition. On the basis of the previous theoretical model [10–12], an extra term related to the external orientational field of quadrupole type was introduced. The influence of the external field intensity and molecular parameters of polypeptide was studied. The coupled transitions, liquid crystal phase formation and coil–helix transformation were calculated to be accelerated when an external field is applied.

2. Theory

Free energy expression applicable to a conformational variable chain has been prescribed [13]. When an external orientational field of quadrupole type is applied, an additional energy term should be added to the free energy expression. Shibaev et al. [6] have written an expression for such external energy term. It is written to be compatible with the present condition as follows

$$E_{ex}/kT = -\epsilon_0 n_2[(1 - \theta)x\langle\cos^2 \Psi_j\rangle + \theta x\langle\cos^2 \Psi_i\rangle] \qquad (1)$$

where n_2 is the number of the polymer components composed of x segments, θ is the helix fraction of the polypeptide and the dimensionless parameter ϵ_0 defines the intensity of the applied external field. In the above expression, the averaging is performed over all angles Ψ_j between the links of the flexible coil component and the orientation axis and over all Ψ_i between the rigid helix segment and the orientation axis.

Application of the external field on the polypeptide solution may induce a small order in the isotropic phase. This effect appears to be small, and in the present study it is neglected for simplicity, as in the work of Marrucci and Ciferri [5]. The polypeptide is assumed to take helical conformation as long as it enters the anisotropic phase. The relations for the fully helical anisotropic phase in equilibrium with the conformational variable isotropic phase prescribed in the previous work should be revised by adding the contribution from the external field. The reduced chemical potentials of the components in an anisotropic phase are given by

$$(\mu'_s - \mu_s^{0'})/RT = \ln(1 - v'_p) + v'_p(y - 1)/x$$
$$- \ln[1 - v'_p(1 - y/x] + \chi v'_p 2 \qquad (2)$$

$$(\mu'_p - \mu_p^{0'})/RT = \ln v'_p + v'_p(y - 1) - \ln f_1 + \chi x(1 - v'_p)^2$$
$$- mx \ln s - \ln \sigma - \epsilon_0 x\langle\cos^2 \Psi_i\rangle \qquad (3)$$

where v_p is the volume fraction of polymer component, y is the disorientation index, the prime denotes the anisotropic phase, s is the statistical weight for the helical state relative to the coil, σ is the weight factor for the initiation of a helical sequence and m represents the number of repeat units involved in a helical sequence. The last term in Eq. (3) is the contribution from the external orientational field, obtained by partial differentiation of E_{ex}/kT under anisotropic condition in which Eq. (1) is reduced to $E_{ex}/kT = -\epsilon_0 n_2 x\langle\cos^2 \Psi_i\rangle$.

In the isotropic state, the orientational order parameter, $S = 1/2 - 3/2\langle\cos^2 \Psi_i\rangle = 0$, thus $\langle\cos^2 \Psi_i\rangle = 1/3$. The $\langle\cos^2 \Psi_j\rangle$ term is also equal to 1/3, as the links of the flexible sequences can acquire only three orientations [6]. Therefore Eq. (1) appears to be $E_{ex}/kT = -\epsilon_0 n_2 x/3$. The obtained chemical potentials for the isotropic phase are

$$(\mu_s - \mu_s^0)/RT = \ln(1 - v_p) + (1 - 1/x)v_p + \chi v_p^2 \qquad (4)$$

$$(\mu_p - \mu_p^0)/RT = \ln v_p + (x - 1)v_p + \chi x(1 - v_p)^2$$
$$+ mx \ln[1 - \rho/(1 - \theta)] - \epsilon_0 x/3 \qquad (5)$$

where ρ is the fraction of units that marks the beginning of a helical sequence in the polypeptide chain.

The external field energy should also affect the orientational distribution which, in turn, alters the orientational factor Z_{orient} in the partition function and, hence, makes a further contribution to the reduced free energy [6]. According to Shibaev et al., f_p should be redefined by

$$f_p = \int_0^{\pi/2} \sin^p \Psi \exp(-\alpha \sin \Psi + \epsilon_0 x \cos^2 \Psi)\, d\Psi \qquad (6)$$

$$\alpha = -(4/\pi)x \ln[1 - v'_p(1 - y/x)] \qquad (7)$$

$$y = (4/\pi)x(f_2/f_1) \qquad (8)$$

3. Numerical calculations

3.1. Effect of the external orientational field

The relations governing the biphasic equilibrium can be obtained by equating Eq. (2) to Eq. (4) and Eq. (3) to Eq. (5) with auxiliary relations of Eqs. (6) and (8). The molecular conformations in the isotropic phase as manifested by the degree of the helicity θ are followed by Eqs. (9)–(12) of Ref. [12]. In the calculations, the relation between χ and temperature takes the same form of that in Ref. [10]. To properly account for the phase behavior, especially the high temperature anisotropic–isotropic transition, the axial ratio x is replaced by a temperature-dependent Kuhn chain axial ratio $x_k = 27300/T$, according to Ref. [10].

The effect of the external field intensity is illustrated in Fig. 1. The binodals shown have been calculated for (a) $\epsilon_0 = 0$ and (b) $\epsilon_0 = 0.05$. Other parameters used in the
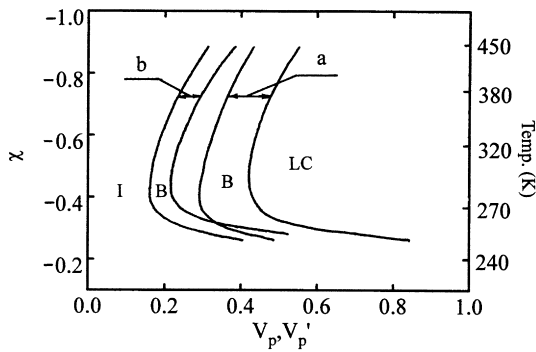
Fig. 1. Effect of the external field on the binodal curves for the isotropic–anisotropic equilibria calculated at: (a) $\epsilon_0 = 0$; and (b) $\epsilon_0 = 0.05$. Invariant parameters used in the calculations are $\Delta H_0 = -1500$ cal/mol, $\Delta S_0 = -1.2$ cal/mol K, $\Delta H_c = -2000$ cal/mol, $\Delta S_c = -3.0$ cal/mol K, $a = 0.84$, $m = 10$, $\sigma = 10^{-4}$. I: isotropic phase, B: biphasic region, LC: liquid crystalline phase.

numerical calculations can be found in the caption. The pair of binodals ($\epsilon_0 = 0$) is identical with that previously calculated for the system without the application of the external field. The existence of the external field rends the isotropic–anisotropic interval shift toward the lower values of polymer concentrations. Accordingly the biphasic region tends to be narrow in the presence of the external field.

The role of the external field can also be seen in Fig. 2 where the external field intensity ϵ_0 is plotted against χ and T. At low values of ϵ_0, an isotropic phase is calculated to be stable. As the value of ϵ_0 is increased, an external field-induced isotropic–anisotropic transition is shown. It should be noted that within the low-temperature range, the intramolecular coil–helix changes are coupled with the intermolecular isotropic–anisotropic transition. The conformationally coupled transition is induced by the external field.

Illustrated in Fig. 3 is the relationship between the external field intensity and the critical volume fractions v_p and v'_p at a given χ where the polymer chain takes random coil conformation in the isotropic phase. Two pairs of the calculated binodals are shown for (a) $\chi = -0.287$ where
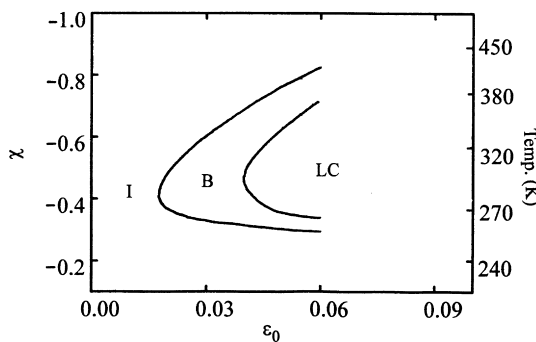

Fig. 2. Variation of χ values and phase transition temperatures as a function of the external field at a given polymer concentration of $v_p = 0.25$. Invariant parameters used in the calculations are similar to those in Fig. 1. I: isotropic phase, B: biphasic region, LC: liquid crystalline phase.
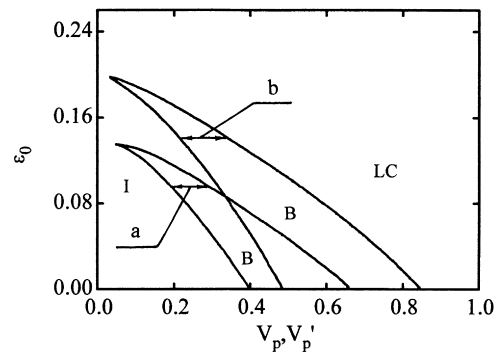

Fig. 3. Volume fraction v_p and v'_p in the isotropic and anisotropic phase, respectively, coexisting at equilibrium as a function of the external field at: (a) $\chi = -0.287$ where $\theta = 0.367$; and (b) $\chi = -0.259$ where $\theta = 0.165$. Invariant parameters used in the calculations are similar to those in Fig. 1. I: isotropic phase, B: biphasic region, LC: liquid crystalline phase.

$\theta = 0.367$, and (b) $\chi = -0.259$ where $\theta = 0.165$. At the low value of the external field intensity, an isotropic–anisotropic transition occurs as the concentration of the solution increases. With increasing ϵ_0, the biphasic region becomes narrower and shifts toward lower concentrations. Finally at a certain critical value of the external field intensity, the polymer chains are oriented even in the dilute solution and the region of the phase separation disappears. It is also noted from the comparison between curves a and b that the biphasic region turns broader when the chain rigidity in the isotropic phase, as manifested in θ, becomes flexible. This effect is due to the free energy penalty related to the winding up of the random coil to the rigid helix conformation upon liquid crystal formation. A higher chain flexibility in the isotropic phase corresponds to a larger free energy change in the transition, which gives rise to higher values of v_p and v'_p.

3.2. Effect of the molecular parameters

Fig. 4 gives the relation between ΔH_0 and the external field intensity at which the conformationally coupled isotropic–anisotropic transition occurs. The transition temperature is 255 K. As stated in the previous work [12], ΔH_0 is the intrinsic enthalpy change for the helix formation, and can be further interpreted as a parameter associated with the polymer chain rigidity, i.e. the larger the absolute value of ΔH_0 the higher rigidity of the helical rods. It can be seen that the required external field intensity for inducing an isotropic–anisotropic transition increases with decreasing chain rigidity in the isotropic phase. Anisotropic phase can be formed even for the polymer chain with very high flexibility as long as enough strong external field is applied. For instance, when $\Delta H_0 = -1342$ cal/mol, the helix conformation of the polypeptide is no longer stable in the isotropic phase. However, an isotropic–anisotropic transition where the coil–helix transition is coupled can still be induced by an external field with $\epsilon_0 = 1.9$.

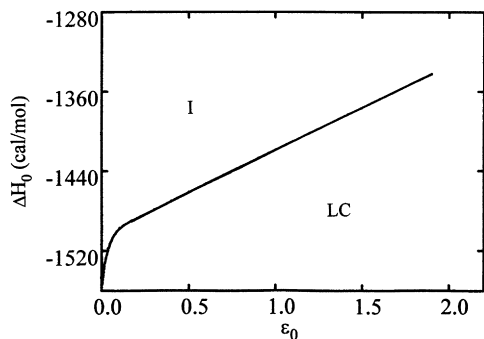ΔS_0 is the intrinsic entropy change for the helix formation

Fig. 4. Plot of ΔH_0 vs. the external field required for inducing an anisotropic phase at $v_p = 0.25$. Invariant parameters used in the calculations are $\Delta S_0 = -1.2$ cal/mol K, $\Delta H_c = -2000$ cal/mol, $\Delta S_c = -3.0$ cal/mol K, $a = 0.84$, $m = 10$, $\sigma = 10^{-4}$ and $T = 255$ K. I: isotropic phase, LC: liquid crystalline phase.
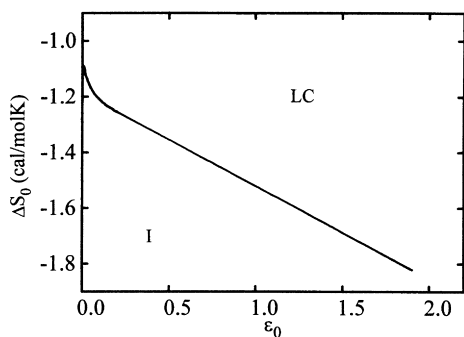

Fig. 6. Plot of σ vs. the external field required for inducing an anisotropic transition at $v_p = 0.25$. Invariant parameters used in the calculation are $\Delta H_0 = -1500$ cal/mol, $\Delta S_0 = -1.2$ cal/mol K, $\Delta H_c = -2000$ cal/mol, $\Delta S_c = -3.0$ cal/mol K, $a = 0.84$, $m = 10$, and $T = 255$ K. I: isotropic phase, LC: liquid crystalline phase.

[12]. It is also associated with the rigidity of the polymer chain. A larger absolute value of ΔS_0 corresponds to a higher flexibility of the random coil segments in the polymer chain. The effect of ΔS_0 can be seen from Fig. 5. The relationship between ΔS_0 and the external field intensity, which is needed for inducing an anisotropic phase at $v_p = 0.25$ is shown. The calculation was performed for the isotropic–anisotropic transition occurring at 255 K where the intramolecular transformation is coupled. The value of ϵ_0 is increased with the increase in the chain flexibility. Theoretically, an anisotropic phase can be induced for random coil chain as long as the allowance is made for the coil–rigid conformational changes.

The parameter σ, usually called cooperativity parameter, is related to the length of the helical and random coil sequences in the polypeptide chain. A smaller value of σ means longer rigid and coil sequences in the polymer chain [12]. Fig. 6 shows the relationship between σ parameter and the intensity of the external field required for inducing an anisotropic phase at $v_p = 0.25$. The phase transition temperature is 255 K. ϵ_0 was calculated to be increased with increasing σ, which implies that the longer random

coil sequence is, the more external energy is needed for winding the random coils up to helix rods to form liquid crystal phase.

3.3. Effect of the external field on the order parameter

The effect of the external field on the orientational order parameter was also examined according to Eq. (3) in Ref. [10] (Fig. 7). In the calculations, f_p was given by Eqs. (6)–(8) and x was replaced by $x_k = 27300/T$. The results of the S vs. v_p plot at 298 K are shown for several discrete values of (a) $\epsilon_0 = 0$, (b) 0.05 and (c) 0.08. The variations of S in the anisotropic phase are illustrated by the solid curves, and the broken curves indicate the results of calculations extended over the concentration range where the biphasic equilibrium should be expected. As can be seen from these plots, the orientational ordering is promoted appreciably when the external field is applied.

4. Discussion

The experimental results that are available in the literature

Fig. 5. Plot of ΔS_0 vs. the external field required for inducing an anisotropic phase at $v_p = 0.25$. Invariant parameters used in the calculation are $\Delta H_0 = -1500$ cal/mol, $\Delta H_c = -2000$ cal/mol, $\Delta S_c = -3.0$ cal/mol K, $a = 0.84$, $m = 10$, $\sigma = 10^{-4}$ and $T = 255$ K. I: isotropic phase, LC: liquid crystalline phase.
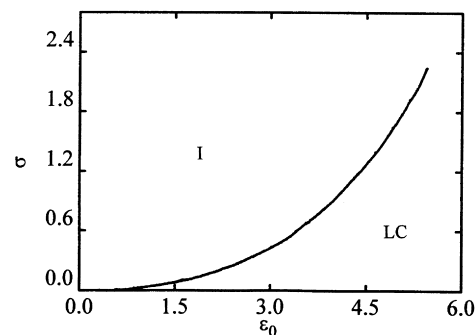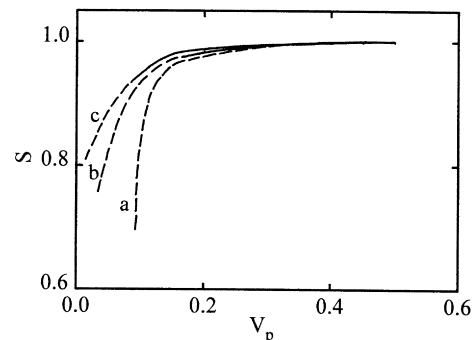

Fig. 7. Calculated order parameter S as a function of temperature on variation of an external applied field: (a) $\epsilon_0 = 0$; (b) $\epsilon_0 = 0.05$; and (c) $\epsilon_0 = 0.08$. The broken curves indicate the results of the calculations extended over the concentration range where the biphasic equilibrium should be expected.

and ready for the comparison with our theory are the studies reported by Toyoshima et al. [14]. In their work, the effect of the external electrical field on the high-temperature anisotropic–isotropic transition in the dioxane solution of PBLG was examined using a microscope. The results show that within the polymer solubility, the high-temperature anisotropic–isotropic transition temperature increases with the strength of the applied electrical field. Such observations are consistent with our theoretical calculations of Fig. 2, in which the high-temperature anisotropic–isotropic transition temperature is shown to increase with the strength of the external field. Due to the difficulty in relating some lattice-dependent parameters to the conventional measurements of quantities, such as $\chi - T$ relationships, a quantitative comparison between the theory and experiment is hindered; however, the qualitative situation seems satisfactory. Regarding the low-temperature anisotropic–isotropic transition, no experimental results are available so far, and the observations are being expected.

The concept of conformational ordering as manifested by the conformational-coupled liquid crystal formation may pertain to semi-rigid chains in general. Occurrence of anisotropic phase in such systems must invariably be accompanied by the flexible–rigid chain conformational changes. The principal general result of this study is that the conformational ordering effect may be accelerated by the application of an external orientational field. It turns out, from the calculations, that the isotropic–anisotropic phase transition induced by an external field is possible for chains even with very high flexibility as long as the flexible–rigid chain conformational changes are allowed. The external orientational field promotes the combined action of the chain-stiffening and liquid crystal formation. The results obtained through the analysis carried out on the equilibria of the helix–coil type in the present work may apply with appropriate adaptations to other systems consisting of long chain molecules that can adopt alternative conformations, one rigid and rectilinear in form and the other random coil.

The equilibria of the helix–coil type are not unlike the case of alternating rigid–flexible block copolymers that have received interest widely due to their potential applications [15–17]. Qualitatively it is not surprising as the helix–coil sequence can be described in terms of a rigid–flexible sequence. As confirmed by our previous work [10–12], the liquid crystal phase can be formed in the conformational variable rigid–flexible system as long as the polymer concentration is high enough. But, in the real case, simply increasing v_p to compensate the free energy penalty associated with the coil–rigid conformational changes could be limited by the polymer solubility. Pure liquid crystal phase may not be obtained within the soluble range for the copolymer having long and flexible coil blocks. However, according to the present study, such energy needed for stiffening the flexible chain segments to contribute to the anisotropy may also be provided by the external orientational field. As shown in Fig. 1, the anisotropic phase can be formed at lower v_p when an external field is applied. The

results obtained in the present work can provide a possible way to process the rigid–flexible block copolymers in liquid crystal state by imposing an external field, such as a longitudinal shear flow. Through this technique, high strength materials may be obtained and in these materials the flexible coil segments take rigid chain conformation to contribute to the mechanical properties.

Another possible application of the conformationally coupled isotropic–anisotropic transition could be the molecular information storage and processing [18,19]. For instance, when a concentrated isotropic solution of polypeptide in which the molecules exists in a random coil fashion is subjected to an external field, a coil–helix conformational change accompanied by the liquid crystal formation takes place. Thus a certain piece of information is recorded at the molecular level. The information recorded may also be easily wiped off by removing the applied field. This reversible transition is manifested by the transition between I and LC at low temperatures in Fig. 1. Since the intermolecular isotropic–anisotropic transition and intramolecular coil–helix transitions are a highly cooperative process, it amounts to a macroscopic reading of the molecular information via phase changes, i.e. the information recorded at the molecular level can be expressed at the macroscopic level by the mesophase. Such cooperativity exhibited in the conformationally coupled transition of polypeptides may lead to molecular amplification devices, and it can also be considered to present the feature of an error filter device as only the molecules with the helix conformation can enter the anisotropic phase [20].

5. Conclusions

1. For the conformationally coupled isotropic–anisotropic transition, the application of the external orientational field can accelerate the transformation. Liquid crystal phase may be formed for the conformational variable chains as long as the applied external field is strong enough.
2. The parameters governing the polypeptide molecular structure, such as ΔH_0, ΔS_0 and σ, have an appreciable influence on the field-induced isotropic–anisotropic transitions where the coil–helix conformational changes are coupled.
3. The results obtained in the present work may find some potential application, for instance, processing the rigid–coil block copolymers under the external field to get a high performance materials and making molecular amplification and error filter devices for the information storage and processing.

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