Novel biaxial nematic phases of side-chain liquid crystalline polymers

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We present a mean field theory to describe biaxial nematic phases of side-chain liquid crystalline polymers, in which rigid side-chains (mesogens) and rigid-backbone chains favor mutually perpendicular orientations. Taking into account both excluded volume and attractive interactions between rigid rods, novel biaxial nematic phases are theoretically predicted. We calculate uniaxial and biaxial orientational order parameters as a function of temperature and the length of backbone chains. We find a first-order biaxial-biaxial phase transition and a first (or second)-order uniaxial-biaxial one, depending on the length of mesogens and backbone chains. © *2012 American Institute of Physics.*
[http://dx.doi.org/10.1063/1.4771592]

I. INTRODUCTION

Biaxial nematic phase has been first theoretically predicted by Freiser.[1] Since then, it has been the subject of much experimental,[2–10] computational,[11–13] and theoretical[13–22] work. Biaxiality occurs if anisotropic particles orient along a second axis perpendicular to a main director of the particles.[23,24] Such biaxiality is expected significant advantages in display applications with a fast response.[25] Biaxial phases of side-chain liquid crystalline polymers (LCPs) have been studied in nematic and smectic A phases with side-on or end-on attachment of mesogenic group to the polymer backbone.[26–30]

When we consider a nematic phase of side-chain LCPs, there are three uniaxial nematic phases, which were first considered by Wang and Warner.[31] The three nematic phases can be defined by two orientational order parameters: one is S_m of nematogenic side-chains (mesogens) and the other is S_b of a rigid-backbone chain. When one order parameter is positive, the other can be positive or negative.[32,33] Figure 1 shows three principal uniaxial nematic phases for a side-chain LCP. The N_1 phase ($S_m > 0$ and $S_b < 0$) is defined as that the mesogens are aligned along to the ordering direction (z) and the backbone chains are randomly distributed on the plane perpendicular to the director $\mathbf{D}_m$. The N_2 phase ($S_m < 0$ and $S_b > 0$) is defined as the backbone chain is aligned along to the ordering direction $\mathbf{D}_b$ and the mesogens are randomly distributed on the plane perpendicular to the backbone chain. The third N_3 phase is defined by $S_m > 0$ and $S_b > 0$, where the backbone and mesogens are oriented along to the ordering direction $\mathbf{D}_{mb}$. In the N_1 phase, the backbone chain adopts an oblate shape. In the N_2 and N_3 phases, a prolate shape of the backbone is obtained.[34–40]

In these uniaxial nematic phases (N_1, N_2), we can expect biaxial nematic phases. Figure 1 schematically shows novel biaxial nematic phases (N_{1b}, N_{2b}) of side-chain LCPs, where the mesogens and backbone chains favor mutually perpendicular orientations.[41] In the uniaxial nematic N_1 phase, we can expect additional ordering of backbone chains in the direction $\mathbf{d}_b$ (minor director) perpendicular to the director $\mathbf{D}_m$ (major director). This corresponds to biaxial ordering (N_{1b}). In the N_2 phase, we may have a biaxial nematic (N_{2b}) phase, where the additional ordering of mesogens appears in the direction $\mathbf{d}_m$ (minor director) perpendicular to the major director $\mathbf{D}_b$. Recently, such mutually perpendicular orientations have been theoretically predicted in mixtures of a liquid crystal and a nanotube,[32,42] in liquid crystalline elastomers,[43,44] and in combined main-chain/side-chain liquid crystalline polymers using the self-consistent field theory.[45]

In this paper, we present a mean field theory to describe the biaxial nematic phases of side-chain LCPs. Taking into account both excluded volume and attractive interactions between rigid rods, the novel biaxial nematic phases are theoretically predicted in side-chain LCP melts, where side-chains (mesogens) and rigid-backbone chains favor mutually perpendicular orientations. We calculate uniaxial and biaxial orientational order parameters and find first (or second)-order uniaxial-biaxial phase transitions, depending on the length of the mesogen and of the backbone chain.

II. FREE ENERGY

We consider a melt of a side-chain LCP, consisting of a liquid crystalline backbone chain and rigid side-chains (mesogens). The repeating unit on the side-chain LCP consists of a mesogen with the axial ratio $n_m (= L_m/d)$ and a rigid-backbone chain of the axial ratio $n_b (= L_b/d)$, where L_m and L_b are the lengths and d is the diameter of the mesogen and the backbone chain on the repeating unit. The total number of segments on the polymer is given by $n = (n_m + n_b)t$, where t is the number of a repeating unit on the LCP. The volume of the mesogen and that of the backbone chain are given by $v_m = (\pi/4)d^2 L_m$ and $v_b = (\pi/4)d^2 L_b$, respectively. The volume per polymer molecule is given by $V = (v_m + v_b)t = (\pi/4)d^3 n$ and the number density of mesogens and backbone chains is given by $c = t/V$.
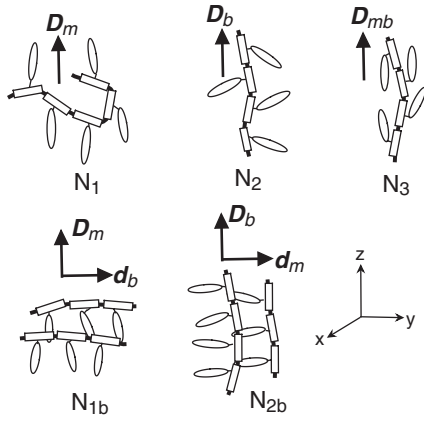
a)Electronic mail: matuyama@bio.kyutech.ac.jp. URL: http://iona.bio.kyutech.ac.jp/~aki/.

FIG. 1. Three possible uniaxial nematic phases (N_1, N_2, N_3) and two biaxial nematic phases (N_{1b}, N_{2b}) of side-chain liquid crystalline polymers. Depending on two orientational order parameters: one is that S_m of a side-chain (mesogen) and the other is S_b of a rigid-backbone chain, we can define a nematic N_1 phase with $S_m > 0$ and $S_b < 0$, a N_2 phase with $S_m < 0$ and $S_b > 0$, and a N_3 phase with $S_m > 0$ and $S_b > 0$. Biaxial nematic N_{1b} phase is defined as a minor director $\mathbf{d}_b$ appears perpendicular to the major director $\mathbf{D}_m$. Biaxial nematic N_{2b} phase is defined as a minor director $\mathbf{d}_m$ appears perpendicular to a major director $\mathbf{D}_b$.

The volume fraction of the mesogens is given by

$$x_m = n_m/(n_m + n_b), \tag{1}$$

and that of the backbone chain is $x_b = n_b/(n_m + n_b)$.

To describe the nematic ordering, we take into account both the excluded volume interactions[47] and the orientational-dependent anisotropic interactions between liquid crystalline molecules.[48] Let $v_{mm}(>0)$ be the anisotropic (Maier-Saupe) interactions between the mesogens, v_{mb} be that between the mesogen and the rigid-backbone chain, and $v_{bb}(> 0)$ be that between the rigid-backbone chains. These anisotropic interaction parameters are dimensionless parameters: $v_{ij} \equiv U_{ij}/k_B T$, where T is the absolute temperature, k_B is the Boltzmann constant, U_{ij} is the interaction energy between the components i and j ($i, j = m, b$). Let $f_m(\mathbf{u})$ and $f_b(\mathbf{u})$ be the orientational distribution function of the mesogen and the backbone chain with the orientational unit vector $\mathbf{u} = \{\theta, \varphi\}$, defined by a polar angle ($0 \le \theta \le \pi$) and an azimuthal angle ($0 \le \varphi \le 2\pi$), or solid angle $d\Omega = \sin\theta d\theta d\varphi$. The nematic free energy is given by[46]

$$\beta F_{nem}/V = \sum_{i,j=m,b} c \int f_i(\mathbf{u}) \ln[4\pi f_i(\mathbf{u})] d\Omega$$
$$+ \frac{1}{2} \sum_{i,j=m,b} c^2 \iint f_i(\mathbf{u}) f_j(\mathbf{u}') \beta_{ij}(\mathbf{u}, \mathbf{u}') d\Omega d\Omega', \tag{2}$$

where β_{ij} is the Mayer-Mayer function between two components i and j. For the interaction between rigid rods, we take into account both the excluded volume and the attractive interaction:[46–50]

$$\beta_{ij} = v_{ij} \left[\frac{8}{\pi} |\mathbf{u} \times \mathbf{u}'| - v_{ij} P_2(\cos\gamma) \right], \tag{3}$$

where $v_{ij} = (\pi/4) L_i L_j d$ is the average excluded volume between the molecules i and j in an isotropic phase, γ is the angle between the local orientations $\mathbf{u}$ and $\mathbf{u}'$. Here we use the additional theorem of spherical harmonics:

$$P_2(\cos\gamma) = P_2(\cos\theta) P_2(\cos\theta') + 2 \sum_{k=1}^{2} \frac{(2-k)!}{(2+k)!}$$
$$\times P_2^k(\cos\theta) P_2^k(\cos\theta') \cos[k(\varphi - \varphi')], \tag{4}$$

where the terms proportional to the associated Legendre polynomials (P_2^k) will vanish in a uniaxial nematic phase, which does not depend on the azimuthal angle. In a biaxial nematic phase, however, the terms of the Legendre polynomials (P_2^2) have a finite contribution.

The orientational order parameters S_i ($i = m, b$) of a uniaxial nematic phase is given by

$$S_i = \int P_2(\cos\theta) f_i(\theta, \varphi) d\Omega, \tag{5}$$

where $P_2(\cos\theta) = (3/2)(\cos^2\theta - 1/3)$ and the biaxial order parameter is given by

$$\Delta_i = \int D(\theta, \varphi) f_i(\theta, \varphi) d\Omega, \tag{6}$$

where $D(\theta, \varphi) \equiv (\sqrt{3}/2) \sin^2\theta \cos(2\varphi)$. Using the tensor order parameter $S_{i,\alpha\beta} = (3/2) S_i (n_\alpha n_\beta - \delta_{\alpha\beta}/3)$, ($\alpha, \beta = x, y, z$), we have $\Delta_i = S_{i,yy} - S_{i,xx}$ and $S_i = S_{i,zz}$. Here $S_{i,zz}$ describes alignment of molecules along the z axis (major director), whereas the nonzero value of Δ_i describes ordering along the x or y axis. Then Eq. (4) can be given by

$$P_2(\cos\gamma) = P_2(\cos\theta) P_2(\cos\theta') + D(\theta, \varphi) D(\theta', \varphi'). \tag{7}$$

Substituting Eqs. (5)–(7) into (2), the nematic free energy is given by

$$\beta F_{nem}/n = \sum_{i,j=m,b} \frac{x_i}{n_i} \int f_i(\mathbf{u}) \ln[4\pi f_i(\mathbf{u})] d\Omega$$
$$- \frac{1}{2}(v_{mm} + 5/4) x_m^2 (S_m^2 + \Delta_m^2)$$
$$- (v_{mb} + 5/4) x_m x_b (S_m S_b + \Delta_m \Delta_b)$$
$$- \frac{1}{2}(v_{bb} + 5/4) x_b^2 (S_b^2 + \Delta_b^2), \tag{8}$$

where the term 5/4 corresponds to the excluded volume interactions.

Minimizing (8) with respect to $f_i(\mathbf{u})$ with the normalization condition $\int f_i(\mathbf{u}) d\Omega = 1$, we obtain the orientational distribution functions,

$$f_m(\mathbf{u}) = \frac{1}{Z_m} \exp[\Gamma_{m,u} P_2(\cos\theta) + \Gamma_{m,b} D(\mathbf{u})], \tag{9}$$

for a mesogen and

$$f_b(\mathbf{u}) = \frac{1}{Z_b} \exp[\Gamma_{b,u} P_2(\cos\theta) + \Gamma_{b,b} D(\mathbf{u})], \tag{10}$$

for a backbone chain, where we define

$$\Gamma_{m,u} \equiv n_m[(v_{mm} + 5/4) x_m S_m + (v_{mb} + 5/4) x_b S_b], \tag{11}$$

$$\Gamma_{m,b} \equiv n_m[(v_{mm} + 5/4) x_m \Delta_m + (v_{mb} + 5/4) x_b \Delta_b], \tag{12}$$

$$\Gamma_{b,u} \equiv n_b[(v_{bb} + 5/4)x_b S_b + (v_{mb} + 5/4)x_m S_m], \quad (13)$$

$$\Gamma_{b,b} \equiv n_b[(v_{bb} + 5/4)x_b \Delta_b + (v_{mb} + 5/4)x_m \Delta_m]. \quad (14)$$

The constants Z_m and Z_b can be obtained by the normalization condition: $\int f_i(\mathbf{u})d\Omega = 1$, as

$$Z_i = 4\pi I_i[0, 0], \quad (15)$$

where the function I_i ($i = m, b$) is defined as

$$I_i[p, q] \equiv \int_0^1 dx \int_0^1 dy [P_2(x)]^p [D(x, y)]^q$$
$$\times \exp\left[\Gamma_{i,u}\frac{3}{2}\left(x^2 - \frac{1}{3}\right) + \Gamma_{i,b}\frac{\sqrt{3}}{2}(1-x^2)\cos(4\pi y)\right], \quad (16)$$

with $p, q = 0, 1, 2, \ldots$.

The orientational order parameters can be numerically calculated from Eqs. (5) and (6), using the distribution functions (9) and (10):

$$S_m = I_m[1, 0]/I_m[0, 0], \quad (17)$$

$$\Delta_m = I_m[0, 1]/I_m[0, 0], \quad (18)$$

$$S_b = I_b[1, 0]/I_b[0, 0], \quad (19)$$

$$\Delta_b = I_b[0, 1]/I_b[0, 0]. \quad (20)$$

Substituting Eqs. (9) and (10) into Eq. (8), the nematic free energy is given by

$$\beta F_{nem}/n = \frac{1}{2}(v_{mm} + 5/4)x_m^2(S_m^2 + \Delta_m^2)$$
$$+ (v_{mb} + 5/4)x_m x_b(S_m S_b + \Delta_m \Delta_b)$$
$$+ \frac{1}{2}(v_{bb} + 5/4)x_b^2(S_b^2 + \Delta_b^2)$$
$$- \frac{x_m}{n_m}\ln I_m[0, 0] - \frac{x_b}{n_b}\ln I_b[0, 0]. \quad (21)$$

III. PHASE DIAGRAMS

For numerical calculations of Eqs. (17)–(20), we here defined the anisotropic interaction parameters

$$c_{mb} = v_{mb}/v_{mm}, \quad (22)$$

and

$$c_b = v_{bb}/v_{mm}, \quad (23)$$

where c_{mb} and c_b are constants. The larger values of c_{mb} show the stronger attractive interaction between the mesogen and the backbone chain. When $c_{mb} > 0$, the backbone chains favor to be parallel to the mesogens, while when $c_{mb} < 0$ the backbone chains favor to be perpendicular to the mesogens.[32,33,43] The positive and negative values of v_{mb} are related to the attractive and repulsive anisotropic interactions, respectively,
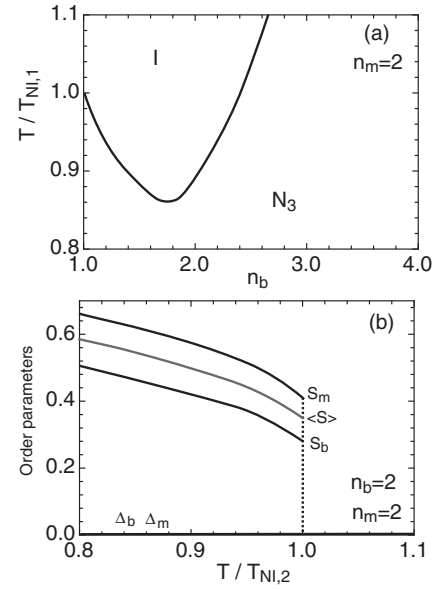

FIG. 2. (a) Phase diagram on $(T/T_{NI, 1}, n_b)$ plane for $c_{mb} = 0.1$ and $n_m = 2$. (b) The orientational order parameters plotted against the temperature $T/T_{NI, 2}$ for $n_m = n_b = 2$.

which eventually lead to the parallel or perpendicular orientations. In the following, we set $c_b = 0.5$. The reduced temperature is defined as $\tilde{T} = 1/v_{mm}(= k_B T/U_{mm})$. When $x_m = 1$, the nematic-isotropic phase transition (NIT) of a pure mesogen takes place at $n_m(v_{mm} + 4/5) = 4.54$,[49,50] and then the NIT temperature is given by

$$\tilde{T}_{NI} = \frac{n_m}{4.54 - 1.25n_m}, \quad (24)$$

where the term $1.25n_m$ corresponds to the excluded volume effect between mesogens. The NIT temperature increases with n_m and diverges to the high temperatures at $n_m > 3.64$ because of the excluded volume interactions.[50]

Figure 2(a) shows the phase diagram on $(T/T_{NI, 1}, n_b)$ plane for $c_{mb} = 0.1$ and $n_m = 2$. The temperature is normalized by the NIT temperature $T_{NI, 1}$ of $n_b = 1$. The solid line shows the first-order phase transition (N$_3$IT) between an isotropic and a nematic N$_3$ phase. The N$_3$IT temperature has a minimum as a function of n_b. For large n_b, the anisotropic coupling between mesogens and backbone chains prevails and we have N$_3$ phase. Figure 2(b) shows the orientational order parameters S_m and S_b plotted against the temperature $T/T_{NI, 2}$ for $n_m = n_b = 2$, where $T_{NI, 2}$ is the N$_3$IT temperature of $n_b = 2$ in Fig. 2(a). The orientational order parameters S_m and S_b jump from zero to positive values at the N$_3$IT temperature, while the biaxial order parameters Δ_m and Δ_b are zero. This corresponds to the uniaxial nematic N$_3$ phase, where the mesogens and backbone chains are parallel to each other. The orientational order parameter S_b of the backbone chain is smaller than S_m, because we take $c_b = 0.5$, which means the attractive interaction v_{bb} between backbone chains is weaker than the v_{mm} between mesogens. When $c_b = 1$ and $n_m = n_b$, we have $S_m = S_b$. The mean value of the uniaxial order parameters is given by

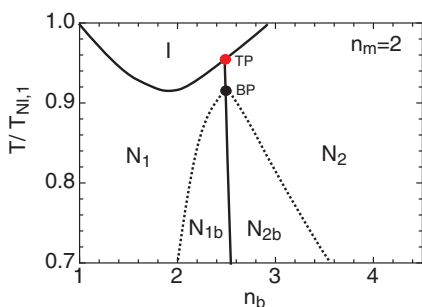$$\langle S \rangle = x_m S_m + x_b S_b \quad (25)$$

FIG. 3. Phase diagram of a side-chain LCP, plotted against the axial ratio n_b of the backbone chain with $c_{mb} = -1.5$ and $n_m = 2$. The solid (dotted) lines show first (second)-order phase transitions. The red closed circle shows a triple point (TP), where there phases coexist. The black closed circle shows a bicritical point (BP), where two distinct second-order lines meet at the first-order line.

and the mean value of the biaxial order parameters is

$$\langle \Delta \rangle = x_m \Delta_m + x_b \Delta_b. \tag{26}$$

Figure 3 shows the phase diagram on the $(T/T_{NI,1}, n_b)$ plane for $n_m = 2$ and $c_{mb} = -1.5$. The solid (dotted) lines show first (second)-order phase transitions. The red closed circle shows a triple point (TP), where I, N_1, and N_2 phases coexist. The black closed circle shows a bicritical point (BP), where two distinct second-order lines meet at the first-order line.[51] For short backbone chains of $n_b < 2.5$, we find the first-order nematic N_1-isotropic phase transition (N_1IT) and the second-order uniaxial N_1-biaxial N_{1b} phase transitions ($N_1 N_{1b}$T). For long backbone chains of $n_b > 2.5$, we find the first-order nematic N_2-isotropic phase transition (N_2IT) and the second-order uniaxial N_2-biaxial N_{2b} phase transitions ($N_2 N_{2b}$T). At $n_b \simeq 2.5$ we have the first-order $N_1 N_2$T and $N_{1b}N_{2b}$T. The biaxial nematic phases N_{1b} and N_{2b} appear between the N_1 and N_2 phases and are broadened with decreasing temperature. A similar phase diagram has been predicted by Rusakov and Shliomis.[40]

Figure 4 shows the orientational order parameters plotted against n_b at $T/T_{NI,1} = 0.8$ in Fig. 3. The solid curves show the uniaxial order parameters S_m and S_b and the broken curves are the biaxial order parameters Δ_m and Δ_b. We have the first-order $N_{1b}N_{2b}$T at $n_b \simeq 2.5$, where the order parameters jump. We also find the second-order $N_1 N_{1b}$T at $n_b \simeq 2.2$ and $N_2 N_{2b}$T at $n_b \simeq 3$, where the order parameters Δ_m and Δ_b are continuously changed. The N_1 and N_2 phases are differ-
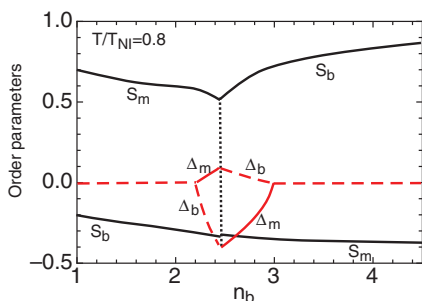

FIG. 4. Orientational order parameters plotted against n_b at $T/T_{NI,1} = 0.8$ in Fig. 3.
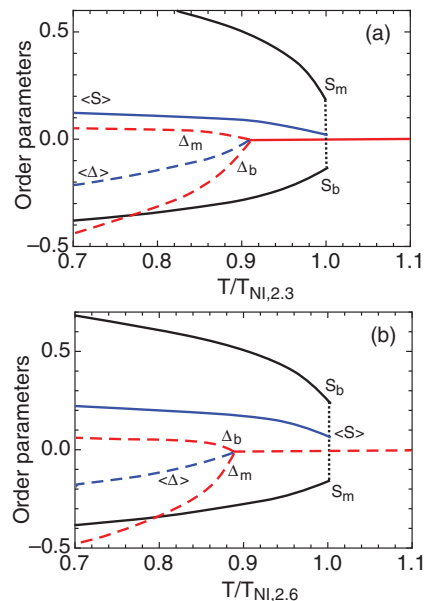

FIG. 5. (a) Order parameters plotted against temperature for $n_b = 2.3$ (b) $n_b = 2.6$ in Fig. 3.

ent in a sign of order parameters S_m and S_b and have the same symmetry, or uniaxial nematic phase. However, the biaxial nematic phase is less symmetric than the uniaxial phase and the transition form the uniaxial to the biaxial state is of second order.[1, 15] The biaxial N_{1b} and N_{2b} phases are also different in a sign of order parameters and have the same symmetry, resulting the first-order phase transition.

Figure 5 shows order parameters plotted against temperature for $n_b = 2.3$ (Panel (a)) and $n_b = 2.6$ (Panel (b)) in Fig. 3. The temperature is normalized by the NIT temperature (T_{NI,n_b}) of $n_b = 2.3$ (Panel (a)) and $n_b = 2.6$ (Panel (b)). The uniaxial order parameters S_m and S_b jump at the first-order N_1IT (Panel (a)) and N_2IT (Panel (b)) temperatures. The mean value of the uniaxial order parameters is small, however, the S_m and S_b have large values. The absolute value of the biaxial order parameter is determined by the difference between the two elements of the tensor order parameters: $|\langle \Delta \rangle| = |S_{xx} - S_{yy}|$, and the biaxial order parameter $|\langle \Delta \rangle|$ continuously increases at the second-order $N_1 N_{1b}$T (Panel (a)) and $N_2 N_{2b}$T (Panel (b)). In the N_{1b} (Panel (a)), the biaxial order parameter Δ_m is almost zero and the $|\Delta_b|$ increases with decreasing temperature, because the backbone chains start to orient along to the second director. On the other hand, in the N_{2b} (Panel (b)), the biaxial order parameter Δ_b is almost zero and the $|\Delta_m|$ increases with decreasing temperature, because the mesogens start to orient along to the second director.

Figure 6 shows the phase diagram on the $(T/T_c, n_b)$ plane for $n_m = 4$ and $c_{mb} = -1.5$. The temperature is normalized by the temperature T_c at the BP. As discussed in Eq. (24), when $n_m > 3.56$, the NIT temperature disappears, or an isotropic phase disappears, because of the excluded volume interactions between long mesogens, and then we have the uniaxial N_1 and N_2 phases at high temperatures. On decreasing temperature we have the second-order uniaxial-biaxial phase transitions: $N_1 N_{1b}$T and $N_2 N_{2b}$T. We also find
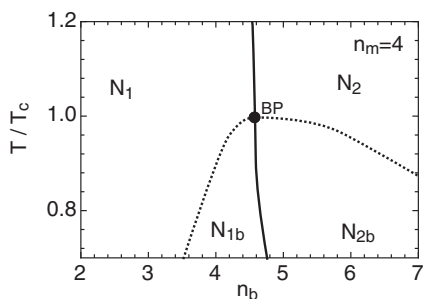
FIG. 6. Phase diagram for $c_{mb} = -1.5$ and $n_m = 4$. The solid (dotted) lines show first (second)-order phase transitions.

FIG. 8. Order parameters plotted against temperature for $n_m = 6$ and $n_b = 11$ in Fig. 7.

the first-order N_1N_2T and $N_{1b}N_{2b}T$. The region of the biaxial phases is broadened on decreasing temperature.

Figure 7 shows the phase diagram on the $(T/T_c, n_b)$ plane for $n_m = 6$ and $c_{mb} = -1.5$. On increasing the length of the mesogen, the uniaxial nematic N_3 phase appears between N_1 and N_2 phases. The black closed circle shows a tricritical point (TCP), where the first-order phase transition line meets the second-order one. The first-order N_1N_3T and N_2N_3T lines terminate at a liquid-gas like critical point (CP). We also find three TPs, where three different nematic phases coexist. For the long mesogens, we find many multi-critical points appear on the phase diagram. In Figs. 6 and 7, we calculate for $n_m = 4$ and $n_m = 6$, respectively. The lengths of mesogens are larger than 3.64 and then the isotropic phase disappears due to the excluded volume effects. In the nematic phase, however, the anisotropic interaction terms ν_{ij} exist and then the phase diagrams depend on temperature.

Figure 8 shows order parameters plotted against temperature for $n_m = 6$ and $n_b = 11$ in Fig. 7. We have two first-order phase transitions: N_3N_2T and $N_2N_{2b}T$, at $T/T_c = 0.99$ and 0.95, respectively, where the value of S_m and the biaxial order parameters jump. In the N_{2b}, the biaxial order parameter Δ_b is almost zero and the $|\Delta_m|$ increases with decreasing temperature, because the mesogens start to orient along to the second director. The mean value $\langle S \rangle$ of the uniaxial order parameter decreases with decreasing temperature, because the mesogens align perpendicular to the first director.

In this paper we have calculated four order parameters as a function of temperature. To observe such uniaxial and biaxial nematic phases introduced here, we need to experimentally determine orientational order parameters of mesogen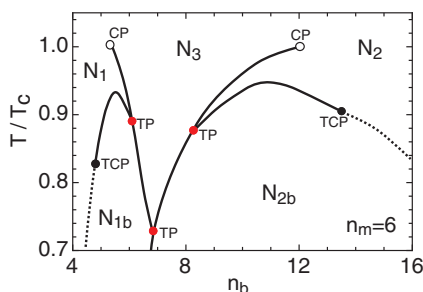s and backbone chains, individually. The perpendicular orientations may be realized side-on side-chain liquid crystalline polymers. Our results demonstrate that the combinations of a long mesogen and a backbone chain are capable of forming biaxial nematic phases. We here focus on biaxial nematic phase. Biaxiality in smectic A phase will also be discussed by applying our model.

IV. SUMMARY

We have presented a theory to describe novel biaxial nematic phases of a side-chain liquid crystalline polymer by taking into account both excluded volumes and attractive interactions between rigid rods. We calculate uniaxial and biaxial orientational order parameters, depending on temperature and the length of mesogens and backbone chains. Three different uniaxial nematic phases (N_1, N_2, and N_3) and two biaxial nematic phases (N_{1b} and N_{2b}) are predicted. For short mesogens and backbone chains, we predict the first-order uniaxial-biaxial phase transitions: $N_1N_{1b}T$ and $N_2N_{2b}T$. For long mesogens with excluded volume effects, uniaxial-biaxial phase transitions can be a first or a second-order phase transitions, depending on the length of backbone chain. The mutually perpendicular alignment between mesogens and backbone chains can be a major cause of the novel biaxial nematic phases. We hope that these results encourage further experimental and theoretical studies for biaxial nematic phases of liquid crystalline polymers.

ACKNOWLEDGMENTS

FIG. 7. Phase diagram $c_{mb} = -1.5$ and $n_m = 6$. The solid (dotted) lines show first (second)-order phase transitions.

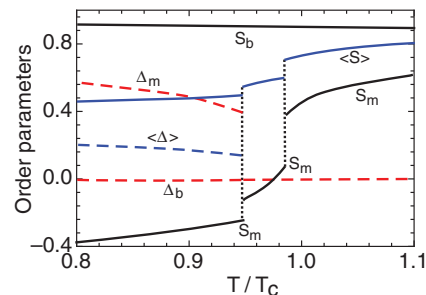[1] M. J. Freiser, Phys. Rev. Lett. **24**, 1041 (1970).
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