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Volume phase transitions of biaxial nematic elastomers

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We present a mean-field theory to describe biaxial nematic phases of side-chain liquid crystalline elastomers. Novel biaxial nematic phases are theoretically predicted in a side-chain liquid crystalline polymer and gel, where side chains (mesogens) and rigid-backbone chains favor mutually perpendicular orientations. We calculate uniaxial and biaxial orientational order parameters and examine deformations of the gel and stable biaxial nematic phases of the liquid crystalline gel dissolved in isotropic solvents. We predict first-order uniaxial-biaxial nematic phase transitions of the gel and the volume of the gel is discontinuously changed at the phase transition temperature.

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I. INTRODUCTION

Liquid crystalline elastomers (LCEs) [1,2], or gels, dissolved in solvent molecules show volume phase transitions by changing temperature [3–19]. The key point is that the volume change is induced by the orientational ordering of the liquid crystalline gel. Then the liquid crystalline ordering, such as a nematic and and a smectic phase, can be a major cause of in the shape change of LCEs.

When we consider a nematic phase of side-chain LCEs or side-chain LC polymers, there are three possible types in nematic phases, which were first considered by Wang and Warner [20]. 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 which is connected with a flexible spacer. When one order parameter is positive, the other can be positive or negative. Figure 1 shows three principal uniaxial nematic phases for a side-chain LC polymer. 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 chain is perpendicular to the mesogens. The N_2 phase ($S_m < 0$ and $S_b > 0$) is defined as the backbone chain is aligned along to the ordering direction z and the mesogens are 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 to the ordering direction z. 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. The identification of these nematic phases has been based on an examination of the shape of the backbone chain using x-ray diffraction [21,22] and neutron scattering [23,24]. The N_2 phase is unusual because the side chains are not aligned with the director (z axis). Such a polymer requires both mesogenic side groups and a mesogenic rigid backbone chain [25,26], where the backbone chain and side groups simultaneously and independently are ordered.

Recently we have presented a mean field theory to describe volume phase transitions of a side-chain LCE dissolved in a solvent molecule and calculated the swelling behavior and deformations for the three different uniaxial nematic phases (N_1, N_2, and N_3) [27–29]. In these uniaxial nematic phases (N_1, N_2), we can expect biaxial nematic phases. Biaxiality occurs if anisotropic particles orient along a second axis perpendicular to a main director of the particles [30]. Biaxial phases of side-chain LCEs have been discovered in nematic and smectic *A* systems with side-on or end-on attachment of mesogenic group to the polymer backbone [31–34]. Biaxial shape memory effect has also been reported in chiral smectic *C* elastomers [35].

Figure 2 schematically shows novel biaxial nematic phases (N_{1b}, N_{2b}) of a side-chain LCE, where the mesogens and backbone chains favor mutually perpendicular orientations. In the uniaxial nematic N_1 phase, on decreasing the volume of the gel, we can expect additional ordering of backbone chains in the direction **m** (minor director) perpendicular to the director **n** (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 **m** (minor director) perpendicular to the major director **n**. Such mutually perpendicular orientations have been theoretically predicted in mixtures of a liquid crystal and a nanotube [36].

In this paper, we present a mean-field theory to describe the swelling behaviors of the LC gels including the uniaxial and the biaxial nematic phases. We calculate uniaxial and biaxial orientational order parameters and examine stable biaxial nematic phases of the liquid crystalline gel dissolved in isotropic solvents. We predict the first-order uniaxial-biaxial phase transitions of the gels and the volume of the gel is discontinuously changed at the phase transition. We first theoretically predict a stable biaxial phase of the liquid crystalline gels.

II. FREE ENERGY

We consider a side-chain liquid crystalline elastomer (or gel), consisting of liquid crystalline backbone chains and side chains, dissolved in solvent molecules. Let n be the number of segments on a subchain between two crosslinks. The repeating unit on the subchain consists of a mesogen with the axial ratio n_m and a rigid backbone chain of the axial ratio n_b connected by a spacer with the number n_s of the segments. The total number of segments on the subchain is given by $n = (n_m + n_s + n_b)t$,

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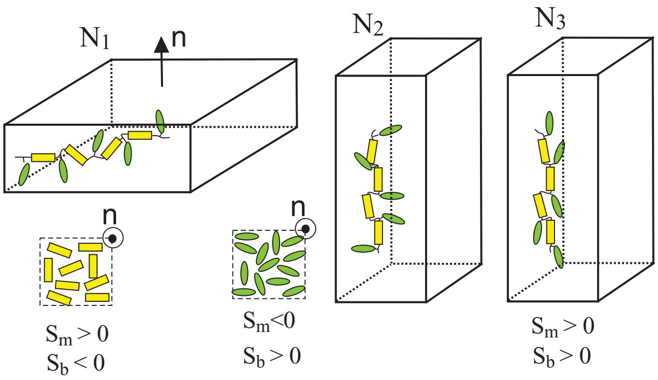

FIG. 1. (Color online) Three possible uniaxial nematic phases of side-chain liquid crystalline elastomers. Depending on two orientational order parameters: one is S_m of a side chain (mesogen) and the other is S_b of a rigid-backbone chain, we can define a nematic N_1 phase with $S_m > 0$ and $S_b < 0$, a N_2 phase with $S_m < 0$ and $S_b > 0$, and a N_3 phase with $S_m > 0$ and $S_b > 0$.

where t is the number of a repeating unit. Let N_g and N_0 be the number of the side-chains ad solvent molecules inside the gel, respectively.

The volume fraction of the gel is given by

$$\phi_g = a^3 n N_g / V, \tag{1}$$

where a^3 is the volume of a unit segment, $V = a^3 N_t$ is the volume of the gel, and $N_t(= nN_g + N_0)$ shows the total number of segments including gel and solvent molecules. The volume of the gel is also given by $V = N_g R_x R_y R_z$, where R_i is the length along the $i(=x,y,z)$ axis between crosslink points of the gel. The volume fraction of the mesogen is given by

$$\phi_m = a^3 n_m t N_g / V = x_m \phi_g, \tag{2}$$

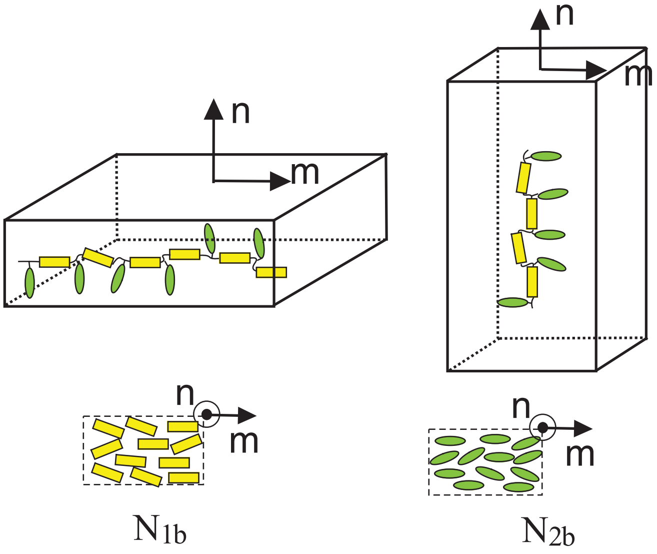

FIG. 2. (Color online) Biaxial nematic phases of side-chain liquid crystalline elastomers. A minor director **m** perpendicular to the major director **n** appears by the additional ordering of backbone chains (N_{1b}) and mesogens (N_{2b}).

where $x_m \equiv n_m/(n_m + n_s + n_b)$ is the fraction of the mesogen segments. The volume fraction of the rigid backbone is given by

$$\phi_b = a^3 n_b t N_g / V = x_b \phi_g, \tag{3}$$

where $x_b \equiv n_b/(n_m + n_s + n_b)$. The volume fraction of the spacer is given by

$$\phi_s = a^3 n_s t N_g / V = x_s \phi_g, \tag{4}$$

where $x_s \equiv n_b/(n_m + n_s + n_b)$ and we have $\phi_g = \phi_m + \phi_b + \phi_s$.

To derive the equilibrium volume fraction ϕ_g of the gel, we consider thermodynamics of our system. The free energy of nematic elastomers consists of three terms

$$F = F_{el} + F_{\rm mix} + F_{\rm nem}, \tag{5}$$

where the first term shows the elastic free energy due to the deformation of nematic gels, the second term shows the free energy for an isotropic mixing of a gel with solvent molecules, and the last term shows the free energy for nematic ordering. In this paper we consider both uniaxial and biaxial nematic elastomers.

A. Elastic free energy

We first consider the elastic free energy due to the deformation of the LC gel, which includes an isotropic, a uniaxial nematic and a biaxial nematic phase. The elastic penalty of the gel is given by the deformation of the backbone chains.

The number of configurations of a subchain of the contour length $L(=a(n_b + n_s)t)$, connecting two crosslinks separated by a distance $\mathbf{R} = (R_x, R_y, R_z)$ in a network, is proportional to the anisotropic Gaussian distribution [1]

$$P(\mathbf{R}) \propto \left(\frac{a^3}{\mathrm{Det}(l_{ij})} \right) \exp\left(-\frac{3}{2L} R_i l_{ij}^{-1} R_j \right), \tag{6}$$

where the effective step length forms a tensor l_{ij} and is given by

$$l_{ij} = \frac{3a}{N} \sum_{i,j}^{N} \langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle, \tag{7}$$

where $N = (n_b + n_s)t$ is the total number of segments on a backbone chain and $\mathbf{u}_i$ is the unit vector along the i-th bond vector of the segment on the backbone chain. The elastic entropy of the polymer chain is given by

$$\mathcal{S}(\mathbf{R}) = k_B \ln P(\mathbf{R}), \tag{8}$$

where k_B is the Boltzmann constant.

In the freely-jointed model [37], there is no correlation between the different bonds and then we have $\mathbf{u}_i \cdot \mathbf{u}_j = u_i^2 \delta_{ij}$. The coordinate projections in the frame where the director is along z axis give $u_x = \sin\theta\cos\varphi$, $u_y = \sin\theta\sin\varphi$, and $u_z = \cos\theta$, where θ $(0 < \theta < \pi)$ is the angle between the bond vector and the z direction and φ is the azimuthal angle $(0 < \varphi < 2\pi)$. Then the effective step length is given by

$$\begin{aligned} l_{xx} &= 3a \sin^2\theta \cos^2\varphi, \\ l_{yy} &= 3a \sin^2\theta \sin^2\varphi, \\ l_{zz} &= 3a \cos^2\theta. \end{aligned} \tag{9}$$

The spontaneous mean-square end-to-end distance $\mathbf{R}_s = (R_{x0}, R_{y0}, R_{z0})$ of the backbone chain is given by

$$\langle R_{i0} R_{j0} \rangle = \tfrac{1}{3} l_{ij} L, \tag{10}$$

and we then obtain

$$\begin{aligned} R_{x0}^2 &= a^2 N \langle \sin^2\theta \cos^2\varphi \rangle, \\ &= \tfrac{1}{3} a^2 N (1 - S_b + \sqrt{3}\Delta_b), \end{aligned} \tag{11}$$

$$\begin{aligned} R_{y0}^2 &= a^2 N \langle \sin^2\theta \sin^2\varphi \rangle, \\ &= \tfrac{1}{3} a^2 N (1 - S_b - \sqrt{3}\Delta_b), \end{aligned} \tag{12}$$

$$\begin{aligned} R_{z0}^2 &= a^2 N \langle \cos^2\theta \rangle, \\ &= \tfrac{1}{3} a^2 N (1 + 2S_b), \end{aligned} \tag{13}$$

where we have used the uniaxial nematic order parameter

$$S_b = \tfrac{3}{2} \left\langle \cos^2\theta - \tfrac{1}{3} \right\rangle, \tag{14}$$

and the biaxial nematic order parameter

$$\Delta_b = \frac{\sqrt{3}}{2} \langle \sin^2\theta \cos(2\varphi) \rangle, \tag{15}$$

of the backbone chain. Using the tensor order parameter $S_{b,\alpha\beta} = (3/2) S_b (n_\alpha n_\beta - \delta_{\alpha\beta}/3)$, $(\alpha,\beta = x,y,z)$, we have $\Delta_b = S_{b,xx} - S_{b,yy}$ and $S_b = S_{b,zz}$. Here $S_{b,zz}$ describes alignment of molecules along the z axis (major director), whereas the nonzero value of Δ_b describes ordering along the x or y axis. When $\Delta_b = 0$, Eqs. (13) and (14) result in the case of the uniaxial nematic phase [27]. When $S_b = 0$ and $\Delta_b = 0$, we have $R_{x0} = R_{y0} = R_{z0} (= R_0)$, where $R_0 \equiv a\sqrt{N}$ corresponds to the ideal chain in an isotropic phase.

Then the entropy change per a backbone chain, due to the deformation from the initial spontaneous state $\mathbf{R}_s$ to the current state $\mathbf{R}$, is given by

$$\Delta \mathcal{S} = \mathcal{S}(\mathbf{R}) - \mathcal{S}(\mathbf{R}_s), \tag{16}$$

Substituting Eqs. (11)–(13) into Eq. (16), the elastic free energy F_{el} due to the deformation of the gel, consisting of N_g backbone chains, is given by

$$\begin{aligned} F_{el} &= -N_g T \Delta \mathcal{S}, \\ &= \frac{1}{2} N_g \left[\lambda_{xx}^2 + \lambda_{yy}^2 + \lambda_{zz}^2 - 3 - \ln\left(\frac{a^3}{l_{xx} l_{yy} l_{zz}} \right) \right], \end{aligned} \tag{17}$$

where T is the absolute temperature and we define

$$\begin{aligned} \lambda_{xx}^2 &\equiv \left(\frac{R_x}{R_{x0}} \right)^2, \\ &= \kappa_x^2 (1 - S_b + \sqrt{3}\Delta_b)^{-1}, \end{aligned} \tag{18}$$

$$\begin{aligned} \lambda_{yy}^2 &\equiv \left(\frac{R_y}{R_{y0}} \right)^2, \\ &= \kappa_y^2 (1 - S_b - \sqrt{3}\Delta_b)^{-1}, \end{aligned} \tag{19}$$

$$\begin{aligned} \lambda_{zz}^2 &\equiv \left(\frac{R_z}{R_{z0}} \right)^2, \\ &= \kappa_z^2 (1 + 2S_b)^{-1}, \end{aligned} \tag{20}$$

and $\kappa_i \equiv R_i/R_0, (i = x,y,z)$. The strain λ_{ii} is a function of the order parameters and so it is convenient to use the deformation (κ_i), related to the isotropic Gaussian chain. Substituting Eqs. (18)–(20) into Eq. (20), the elastic free energy can be rewritten as

$$\begin{aligned} \beta F_{el} = \frac{1}{2} N_g \Bigg[& \frac{\kappa_x^2}{1 - S_b + \sqrt{3}\Delta_b} + \frac{\kappa_y^2}{1 - S_b - \sqrt{3}\Delta_b} \\ & + \frac{\kappa_z^2}{1 + 2S_b} - 3 + \ln A \Bigg], \end{aligned} \tag{21}$$

where $\beta \equiv 1/(k_B T)$ and

$$A \equiv (1 - S_b + \sqrt{3}\Delta_b)(1 - S_b - \sqrt{3}\Delta_b)(1 + 2S_b). \tag{22}$$

The volume fraction of the gel is given by

$$\phi_g = \frac{a^3 n}{R_x R_y R_z} = \frac{1}{c_1 \kappa_x \kappa_y \kappa_z}, \tag{23}$$

where $c_1 \equiv (n_b + n_s)^{1.5} \sqrt{t}/(n_m + n_b + n_s)$ and then the κ_x in Eq. (21) is given as a function of ϕ_g, κ_y, and κ_z:

$$\kappa_x = \frac{1}{c_1 \phi_g \kappa_y \kappa_z}. \tag{24}$$

In this subsection we derive the elastic free energy of the LC gel. In the following subsection we obtain the mixing free energy and nematic free energy by taking into account the intermolecular interactions.

B. Free energy of mixing

The second term F_{mix} in Eq. (5) shows the free energy for an isotropic mixing of a gel with a solvent molecule. According to the Flory-Huggins theory [38] for polymer solutions, this free energy is given by

$$\beta F_{\text{mix}}/N_t = (1 - \phi_g)\ln(1 - \phi_g) + \chi \phi_g (1 - \phi_g), \tag{25}$$

where χ shows the isotropic (Flory-Huggins) interaction parameter between a gel and a solvent molecule. In this paper we take that the solvent molecule is a good solvent for the gel: $\chi \simeq 0$.

C. Nematic free energy

The third term F_{nem} in Eq. (5) shows the free energy for nematic ordering. To describe the nematic ordering, we take into account the orientational-dependent (Maier-Saupe) interactions between liquid crystalline molecules [39]. Let $\nu_{mm}(>0)$ be the orientational-dependent (Maier-Saupe) interactions between the mesogens, ν_{mb} be that between the mesogen and the rigid backbone chain, and $\nu_{bb}(>0)$ be that between the rigid backbone chains. These interaction parameters are dimensionless parameters: $\nu_{ij} \equiv U_{ij}/k_B T$, where 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 mesogens on the side chain and the backbone chain with the orientational unit vector $\mathbf{u} = \{\theta,\varphi\}$, defined by a polar angle $(0 \leqslant \theta \leqslant \pi)$ and an an azimuthal angle $(0 \leqslant \varphi \leqslant 2\pi)$, or solid angle $d\Omega = \sin\theta d\theta d\varphi$.

The nematic free energy is given by

$$\beta F_{nem}/N_t = \sum_{i,j=m,b} \frac{\phi_i}{n_i} \int f_i(\mathbf{u}) \ln[4\pi f_i(\mathbf{u})] d\Omega + \frac{1}{2} \sum_{i,j=m,b} \phi_i \phi_j \iint f_i(\mathbf{u}) f_j(\mathbf{u}') \beta_{ij}(\mathbf{u},\mathbf{u}') d\Omega d\Omega', \tag{26}$$

where β_{ij} is the Mayer-Mayer function between two components i and j. For the orientation-dependent interactions, the attractive Maier-Saupe interactions are given by

$$\beta_{mm} = -\nu_{mm} P_2(\cos\gamma), \tag{27}$$

$$\beta_{bb} = -\nu_{bb} P_2(\cos\gamma), \tag{28}$$

$$\beta_{mb} = -\nu_{mb} P_2(\cos\gamma), \tag{29}$$

where γ is the angle between the local orientations $\mathbf{u}$ and $\mathbf{u}'$. We here use the additional theorem of spherical harmonics:

$$P_2(\cos\gamma) = P_2(\cos\theta) P_2(\cos\theta') + 2 \sum_{k=1}^{2} \frac{(2-k)!}{(2+k)!} \times P_2^k(\cos\theta) P_2^k(\cos\theta') \cos[k(\varphi - \varphi')], \tag{30}$$

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

$$S_i = \int P_2(\cos\theta) f_i(\theta,\varphi) d\Omega, \tag{31}$$

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

$$\Delta_i = \int D(\theta,\varphi) f_i(\theta,\varphi) d\Omega, \tag{32}$$

where $D(\theta,\varphi) \equiv (\sqrt{3}/2)\sin^2\theta\cos(2\varphi)$. Then Eq. (30) can be given by

$$P_2(\cos\gamma) = P_2(\cos\theta) P_2(\cos\theta') + D(\theta,\varphi) D(\theta',\varphi'). \tag{33}$$

Substituting Eqs. (31)–(33) into Eq. (26), the nematic free energy is given by

$$\beta F_{\mathrm{nem}}/N_t = \sum_{i,j=m,b} \frac{\phi_i}{n_i} \int f_i(\mathbf{u}) \ln[4\pi f_i(\mathbf{u})] d\Omega - \frac{1}{2}\nu_{mm}\phi_m^2 (S_m^2 + \Delta_m^2) - \nu_{mb}\phi_m\phi_b(S_m S_b + \Delta_m \Delta_b) - \frac{1}{2}\nu_{bb}\phi_b^2 (S_b^2 + \Delta_b^2). \tag{34}$$

The free energy F in Eq. (5) is given by the sum of Eqs. (21), (25), and (34). In the next section, we derive the deformation κ_α, the order parameters S_i and Δ_i, and the volume fraction ϕ_g of the gel in a thermal equilibrium state.

III. EQUILIBRIUM SWELLING OF LIQUID CRYSTALLINE GELS

A. Deformation of LC gels

The deformation of LC gels at a thermal equilibrium state can be determined by the

$$(\partial F/\partial \kappa_z)_{\{\kappa_y, S_i, \Delta_i, \phi_g\}} = 0, \tag{35}$$

$$(\partial F/\partial \kappa_y)_{\{\kappa_z, S_i, \Delta_i, \phi_g\}} = 0, \tag{36}$$

where κ_x is given as a function of κ_y and κ_z as shown in Eq. (24). The derivatives of the free energies F_{mix} and F_{nem} with respect to the deformation κ_α become zero since the free energies F_{mix} and F_{nem} do not include the variables κ_α. Using Eq. (21), Eqs. (35) and (36) lead to

$$\kappa_z^4 = \frac{1 + 2S_b}{c_1^2 \kappa_y^2 \phi_g^2 (1 - S_b + \sqrt{3}\Delta_b)}, \tag{37}$$

and

$$\kappa_y^4 = \frac{1 - S_b - \sqrt{3}\Delta_b}{c_1^2 \kappa_z^2 \phi_g^2 (1 - S_b + \sqrt{3}\Delta_b)}, \tag{38}$$

respectively. Combining Eqs. (37) and (38), we obtain

$$\kappa_x = \left[\frac{(1 - S_b + \sqrt{3}\Delta_b)^2}{(c_1\phi_g)^2 (1 - S_b - \sqrt{3}\Delta_b)(1 + 2S_b)} \right]^{1/6}, \tag{39}$$

$$\kappa_y = \left[\frac{(1 - S_b - \sqrt{3}\Delta_b)^2}{(c_1\phi_g)^2 (1 - S_b + \sqrt{3}\Delta_b)(1 + 2S_b)} \right]^{1/6}, \tag{40}$$

and

$$\kappa_z = \left[\frac{1 + 2S_b}{c_1\phi_g (1 - S_b + \sqrt{3}\Delta_b)^{1/2} (1 - S_b - \sqrt{3}\Delta_b)^{1/2}} \right]^{1/3}. \tag{41}$$

When $\Delta_b = 0$, Eqs. (39)–(41) result in the deformation of the gels in a uniaxial nematic phase: $\kappa_x = \kappa_y$. When $\Delta_b = 0$ and $S_b = 0$, we have an isotropic deformation: $\kappa_x = \kappa_y = \kappa_z$.

Substituting Eqs. (39)–(41) into Eq. (21), the elastic free energy of the gel is given by

$$\beta F_{el}/N_t = \frac{3}{2n} \left[\left(\frac{\phi_g}{c_1^2 A} \right)^{1/3} - \phi_g + \frac{\phi_g}{3} \ln A \right]. \tag{42}$$

In the next subsection we derive the orientational order parameters.

B. Equilibrium values of orientational order parameters

The orientational distribution functions $f_m(\theta,\varphi)$ of the mesogen and $f_b(\theta,\varphi)$ of the backbone chain are determined by the free energy (5) with respect to these functions:

$$(\delta F/\delta f_m(\mathbf{u}))_{\{\kappa_\alpha, S_i, \phi_g, f_b\}} = 0, \tag{43}$$

$$(\delta F/\delta f_b(\mathbf{u}))_{\{\kappa_\alpha, S_i, \phi_g, f_m\}} = 0 \tag{44}$$

with the normalization conditions for the distribution function:

$$\int f_i(\theta,\varphi) \sin\theta d\theta d\varphi = 1. \tag{45}$$

These lead to the orientational distribution function

$$f_m(\theta,\varphi) = \frac{1}{W_0}\exp[\Gamma_{m,1}P_2(\cos\theta) + \Gamma_{m,2}D(\theta,\varphi)], \qquad (46)$$

$$\Gamma_{m,1} \equiv n_m(\nu_{mm}\phi_m S_m + \nu_{mb}\phi_b S_b), \qquad (47)$$

$$\Gamma_{m,2} \equiv n_m(\nu_{mm}\phi_m \Delta_m + \nu_{mb}\phi_b \Delta_b), \qquad (48)$$

for the mesogens and

$$f_b(\theta,\varphi) = \frac{1}{Z_0}\exp[\Gamma_{b,1}P_2(\cos\theta) + \Gamma_{b,2}D(\theta,\varphi)], \qquad (49)$$

$$\Gamma_{b,1} \equiv B\left(S_b(1-S_b) + \Delta_b^2\right) + n_b(\nu_{bb}\phi_b S_b + \nu_{mb}\phi_m S_m), \qquad (50)$$

$$\Gamma_{b,2} \equiv -B(1+2S_b)\Delta_b + n_b(\nu_{bb}\phi_b\Delta_b + \nu_{mb}\phi_m\Delta_m), \qquad (51)$$

$$B \equiv \frac{3n_b}{n\phi_b A}\left[\phi_g - \left(\frac{\phi_g}{c_1^2 A}\right)^{1/3}\right], \qquad (52)$$

for the backbone chain. The constants W_0 and Z_0 are determined the normalization condition (45). Substituting Eqs. (46) and (49) into Eq. (45), we obtain

$$W_0 = 4\pi I_m[0,0], \qquad (53)$$

and

$$Z_0 = 4\pi I_b[0,0], \qquad (54)$$

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

$$I_i[q,r] \equiv \iint d\Omega[P_2(\cos\theta)]^q[D(\theta,\varphi)]^r \times \exp[\Gamma_{i,1}P_2(\cos\theta) + \Gamma_{i,2}D(\theta,\varphi)], \qquad (55)$$

for $q,r = 0,1,2,\ldots$. Using $x \equiv \cos\theta$ and $y \equiv \varphi/(2\pi)$, Eq. (55) can also be rewritten as

$$I_i[q,r] \equiv \int_0^1\int_0^1 dxdy[P_2(x)]^q[D(x,y)]^r \exp\left[\Gamma_{i,1}\frac{3}{2}\left(x^2 - \frac{1}{3}\right) + \Gamma_{i,2}\frac{\sqrt{3}}{2}(1-x^2)\cos(4\pi y)\right]. \qquad (56)$$

Substituting Eqs. (46) and (49) into Eq. (31), the uniaxial orientational order parameter for the mesogen and the backbone chain are determined by the self-consistency equation

$$S_m = I_m[1,0]/I_m[0,0], \qquad (57)$$

and

$$S_b = I_b[1,0]/I_b[0,0], \qquad (58)$$

respectively. Similarly, substituting Eqs. (46) and (49) into Eq. (32), the biaxial order parameters are determined by

$$\Delta_m = I_m[0,1]/I_m[0,0], \qquad (59)$$

and

$$\Delta_b = I_b[0,1]/I_b[0,0], \qquad (60)$$

The order parameters are determined by solving numerically these four coupled equations as a function of a temperature.

C. Equilibrium swelling of LC gels

In this subsection we derive the volume fraction ϕ_g of the gel at a thermal equilibrium state. Substituting Eqs. (46) and (49) into Eq. (34), the nematic free energy is given by

$$\begin{aligned}\beta F_{\text{nem}}/N_t = {} & \frac{3}{nA}\left[\phi_g - \left(\frac{\phi_g}{c_1^2 A}\right)^{1/3}\right]\left[S_b^2(1-S_b) - (1+S_b)\Delta_b^2\right] + \frac{1}{2}\nu_{mm}\phi_m^2\left(S_m^2 + \Delta_m^2\right) \\ & + \nu_{mb}\phi_m\phi_b(S_m S_b + \Delta_m\Delta_b) \\ & + \frac{1}{2}\nu_{bb}\phi_b^2\left(S_b^2 + \Delta_b^2\right) \\ & - \frac{\phi_m}{n_m}\ln I_m[0,0] - \frac{\phi_b}{n_b}\ln I_b[0,0]. \qquad (61)\end{aligned}$$

Then the free energy (5) is given by the sum of Eqs. (25), (42), and (61). The chemical potential μ_0 of the solvent molecules inside the gel s given by

$$\begin{aligned}\beta\left(\mu_0 - \mu_0^\circ\right) &= \beta(\partial F/\partial N_0)_{N_g} \\ &= f - \phi_g(\partial f/\partial\phi_g) \\ &\quad + \frac{1}{n}\left(\frac{\phi_g}{c_1^2 A}\right)^{1/3} + \ln(1-\phi_g) + \phi_g + \chi\phi_g^2 \\ &\quad + \frac{1}{2}\nu_{mm}\phi_m^2\left(S_m^2 + \Delta_m^2\right) \\ &\quad + \nu_{mb}\phi_m\phi_b(S_m S_b + \Delta_m\Delta_b) \\ &\quad + \frac{1}{2}\nu_{bb}\phi_b^2\left(S_b^2 + \Delta_b^2\right), \qquad (62)\end{aligned}$$

where $f \equiv \beta F/N_t$ and μ_0° is the chemical potential of the pure solvent molecules outside the gel.

The equilibrium volume fraction ϕ_g of the gel can be determined from the balance among the solvent molecules existing outside and inside the gel

$$\mu_0 - \mu_0^\circ = 0. \qquad (63)$$

When the osmotic pressure $\Pi(=\mu_0^\circ - \mu_0)$ plotted against ϕ_g contains the van der Waals loops, the equilibrium value of ϕ_g can be determined by $\Pi = 0$. The stability conditions of the gel are determined by using the Maxwell construction and

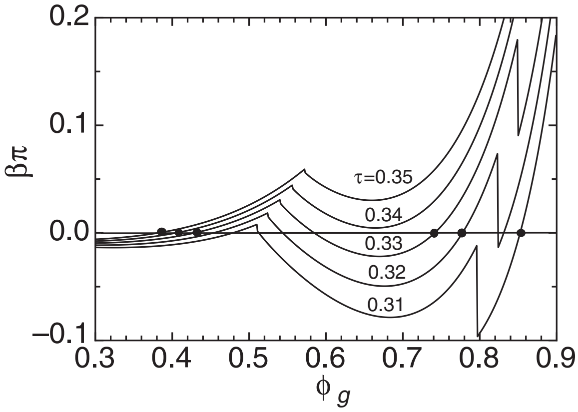

FIG. 3. Osmotic pressure Π plotted against ϕ_g for $c_{mb} = -1$ with $n_m = 2$ and $n_b = 2$. The reduced temperature τ is changed.

the region $(\partial\Pi/\partial\phi_g)_T < 0$ corresponds to unstable spinodal regions (see Fig. 3).

IV. VOLUME PHASE TRANSITIONS

We here define the reduced-temperature $\tau \equiv 4.54 n_m/\nu_{mm}$, which is proportional to temperature, and defined the anisotropic interaction parameters

$$c_{mb} = \nu_{mb}/\nu_{mm}, \tag{64}$$

and

$$c_b = \nu_{bb}/\nu_{mm}, \tag{65}$$

where c_{mb} and c_b are constants. The larger values of a_{mb} shows 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 $c_{mb} < 0$ the backbone chains favor to be perpendicular to the mesogens [27–29]. In the following we set $c_b = 1, n_s = 2, t = 10$, and $\chi = \nu_{mm}/10$.

Figure 3 shows the osmotic pressure plotted against ϕ_g for $c_{mb} = -1$ with $n_m = n_b = 2$, which are the same values with Fig. 6. The reduced temperature τ is changed from $\tau = 0.35$ to 0.31. The closed circles show the equilibrium volume fraction of the gel at the each temperature. At $\tau = 0.33$, we have the first-order phase transition from a condensed gel to a swollen gel. Figure 4 shows the order parameters plotted against ϕ_g at $\tau = 0.31$ in Fig. 3. At $\phi_g \simeq 0.52$, we have the first-order phase transition from an isotropic phase to a uniaxial nematic N_2 phase with $S_b > 0$, $S_m < 0$, and $\Delta_b = \Delta_m = 0$. We also have the first-order phase transition from a uniaxial nematic N_2 phase to a biaxial nematic N_{2b} phase with $S_b > 0$, $S_m < 0$, $\Delta_b > 0$, and $\Delta_m < 0$. The equilibrium volume fraction for $\tau = 0.31$ is given by $\phi_g \simeq 0.85$. As shown in Fig. 3, the osmotic pressure jumps at the first-order phase transitions. The equilibrium volume fraction of the gel can be obtained by solving $\Pi = 0$ as a function of the temperature. In the following we show some numerical results of the swelling behavior of the gel and the deformations as a function of temperature.

Figure 5 shows the swelling curve of the gel (a) and the order parameters (b) plotted against the reduced temperature τ for $c_{mb} = 1$ with $n_m = 2$, $n_b = 2$. The larger (smaller) values of ϕ_g corresponds to a condensed (swollen) gel. At high temperatures, the gel is swollen and is in an isotropic (I) state. On decreasing temperature we find the first-order volume phase transition from a swollen gel to a condensed state. As shown in Fig. 5(b), the condensed gel is in the nematic N_3 phase, where the order parameters have $S_m > 0$, $S_b > 0$, and $\Delta_m = \Delta_b = 0$. When $c_{mb} > 0$, the mesogens and backbone chains favor to be mutually parallel and then we have the uniaxial N_3 phase at lower temperatures. The shape of the gel is elongated parallel to the nematic director as shown in Fig. 1.

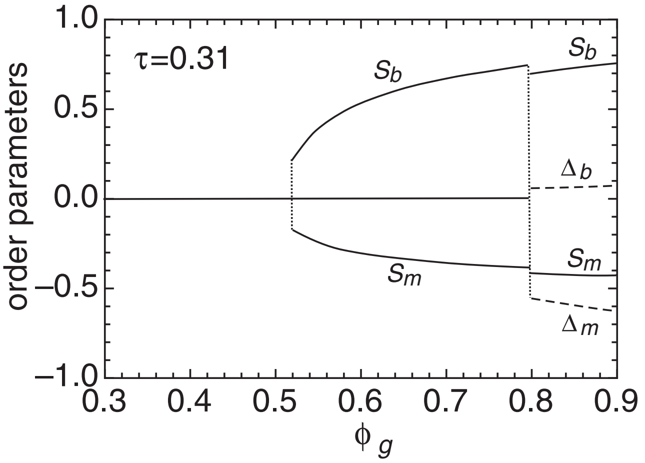

FIG. 4. Order parameters plotted against ϕ_g at $\tau = 0.31$ in Fig. 3.

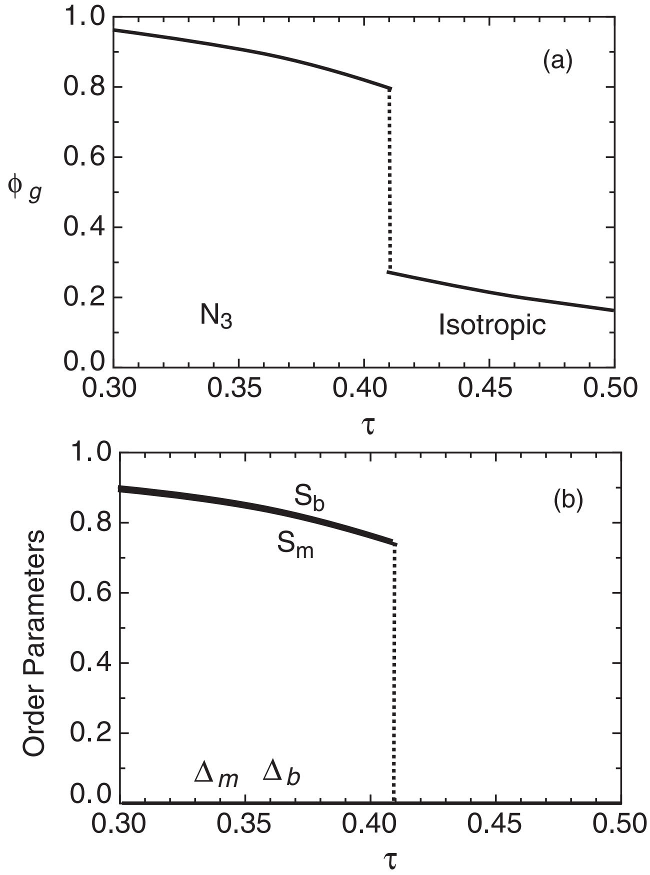

FIG. 5. Swelling curve of the gel (a) and the order parameters (b) plotted against the reduced temperature τ for $c_{mb} = 1$ with $n_m = 2$ and $n_b = 2$.

Figure 6 shows the swelling curve of the gel (a) and the order parameters (b) plotted against the reduced temperature τ for $c_{mb} = -1$ with $n_m = 2$ and $n_b = 2$. When $c_{mb} < 0$, the mesogens and backbone chains favor to be mutually perpendicular orientation. On decreasing temperature, we find the first-order phase transition from an isotropic to a uniaxial N_2 phase with $S_b > 0$ and $S_m < 0$. Further decreasing temperature, we have the first-order phase transition from the N_2 phase to a biaxial N_{2b} phase, where we have $\Delta_m < 0$ and $\Delta_b > 0$ [Fig. 6(b)]. We find the discontinuous volume phase transitions of the gel at the isotropic (I)-uniaxial nematic (N_2) phase transition and at the uniaxial (N_2)-biaxial (N_{2b}) phase transition. We here emphasize that the biaxial nematic phase of the gel can be stabilized at lower temperature side of the uniaxial nematic phase.

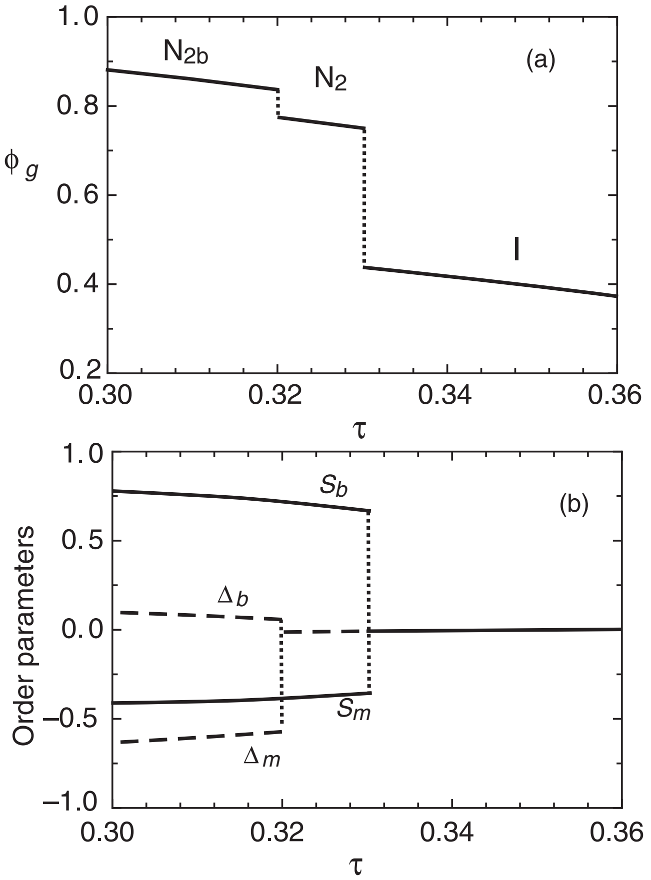

FIG. 6. Swelling curve of the gel (a) and the orientational order parameters S_b, S_m, Δ_b, and Δ_m (b) plotted against the reduced temperature τ for $c_{mb} = -1$ with $n_m = 2$ and $n_b = 2$.

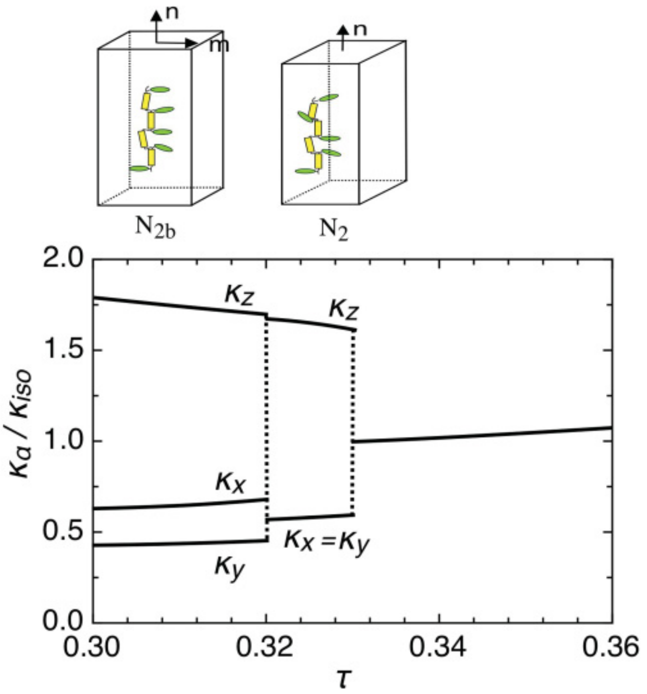

FIG. 7. (Color online) Deformation $\kappa_\alpha/\kappa_{\text{iso}}$ ($\alpha = x,y,z$) plotted against the reduced temperature τ for $c_{mb} = -1$ with $n_m = 2$ and $n_b = 2$.

Figure 7 shows the deformation $\kappa_\alpha/\kappa_{\text{iso}}$ of the gel plotted against the temperature for Fig. 6. The value of κ_α is normalized by the deformation κ_{iso} in the isotropic phase at the I-N_2 phase transition. In the N_2 phase, we have $\kappa_z > \kappa_x = \kappa_y$ and the gel is a cylindrical symmetry, or a uniaxial nematic phase, where the backbone chains are elongated along to the director, while the mesogens are randomly distributed on the plane perpendicular to the director. In the biaxial N_{2b} phase, we have $\kappa_z > \kappa_x > \kappa_y$, where the κ_z corresponds to the deformation along to the main director **n** and κ_x shows the elongation along to the minor director **m**. At the uniaxial-biaxial phase transition, the values of κ_x and κ_y split.

Figure 8 shows the swelling curve of the gel (a) and the order parameters (b) plotted against the reduced temperature τ for $c_{mb} = -1$ with $n_m = 3$ and $n_b = 2$. On decreasing temperature, we find the first-order phase transition from an isotropic (I) to a uniaxial N_1 phase with $S_b < 0$ and $S_m > 0$. Further decreasing temperature, the firs-order phase transition from the N_1 phase to the biaxial N_{1b} phase takes place, where we have $\Delta_m > 0$ and $\Delta_b < 0$ [Fig. 8(b)]. We also find the discontinuous volume phase transition of the gel at the I-N_1 phase transition and at the uniaxial (N_1)-biaxial (N_{1b}) phase transition temperature. When the length of mesogen is slightly larger than that of backbone ($n_m = 3$, $n_b = 2$), the main director is given by the orientational ordering of mesogens and the minor director of the biaxial N_{1b} phase is given by orientational ordering of the backbone chain. The deformation of the gel is shown in Fig. 9. In the biaxial N_{1b} phase, the gel has a rectangular shape with $\kappa_y > \kappa_x > \kappa_z$.

When $n_m = n_b = 3$, we have the first order phase transition from an isotropic to a biaxial N_{1b} phase and the volume of the gel is discontinuously changed at the phase transition temperature as shown in Fig. 10. The long backbone chains stabilize the biaxial N_{1b} phase and the uniaxial N_1 phase in Fig. 8 disappears. The biaxial nematic phase is strongly dependent on the length of a mesogen and a rigid-backbone chain. If the backbone chain is short ($n_b < n_m$), we only have the uniaxial N_1 or N_3 phase. In order to form a stable biaxial nematic phase, we need the condition $n_s \simeq n_m \simeq n_b$.

We emphasize that the idea of these biaxial nematic phases is important to reconsider the structure of nematic phases of LC polymers and elastomers. Such biaxial nematic phases may be hidden at the lower temperature sides of a uniaxial nematic phase. The mutually perpendicular orientation between mesogens and backbone chains can be a major cause of the novel biaxial nematic phases. Such attachment geometries can be achieved by side-chain side-on elastomers. Biaxiality of nematic polymers and elastomers sets in when the rotational diffusion around the long axis gets hindered enough to allow biaxial nematic phase. Recent experiments have suggested that the side-on attachment of the mesogens hinders the rotation of the molecules around their long axes more than the other geometries, such as end-on and main-chain attachment [34].

In this paper we neglect excluded volume interactions between rigid molecules because the mesogens and backbones are short chains. To study biaxiality in elastomers containing long rigid rods [40], such as carbon nanotube, it is important to consider the steric interactions between rods. In this paper

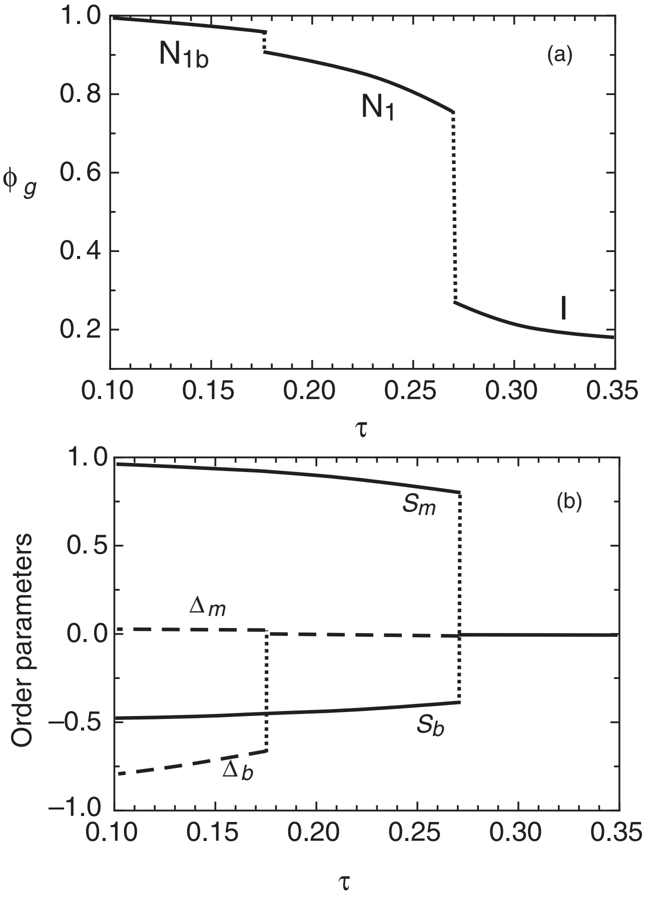

FIG. 8. Swelling curve of the gel (a) and the orientational order parameters S_b, S_m, Δ_b, and Δ_m (b) plotted against the reduced temperature τ for $c_{mb} = -1$ with $n_m = 3$ and $n_b = 2$.

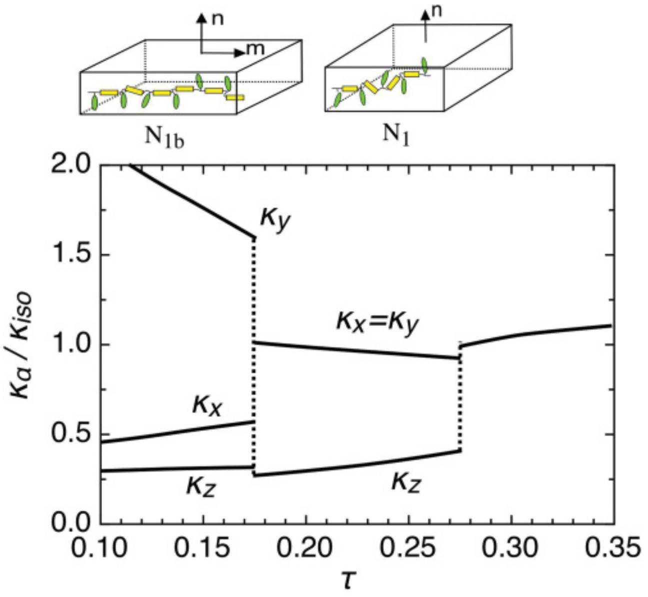

FIG. 9. (Color online) Deformation $\kappa_\alpha/\kappa_{\text{iso}}$ ($\alpha = x,y,z$) plotted against the reduced temperature τ for $c_{mb} = -1$ with $n_m = 3$ and $n_b = 2$.

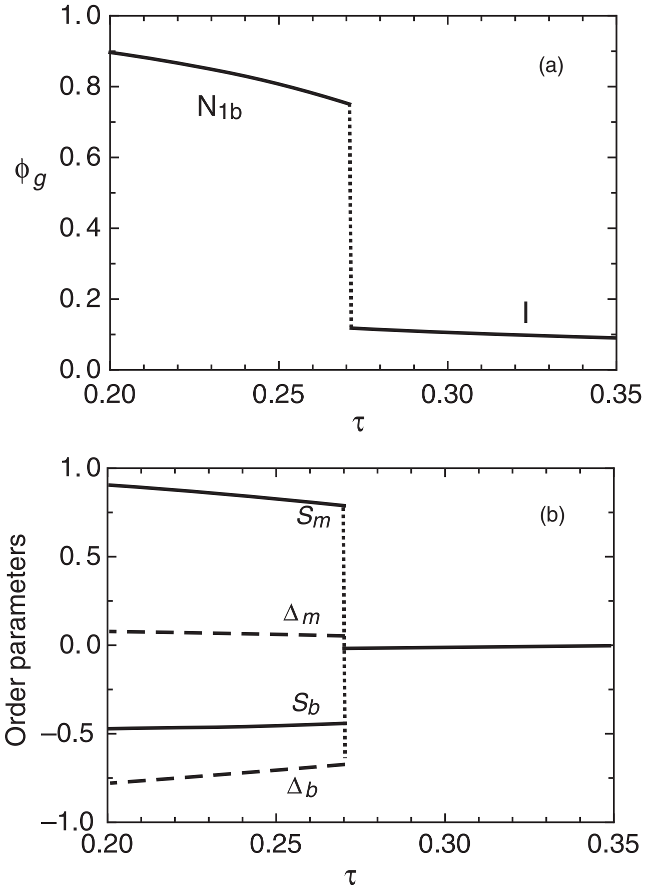

FIG. 10. Swelling curve of the gel (a) and the orientational order parameters S_b, S_m, Δ_b, and Δ_m (b) plotted against the reduced temperature τ for $c_{mb} = -1$ with $n_m = 3$ and $n_b = 3$.

we obtain the first-order volume phase transitions, where the volume, or shape, of the gel is discontinuously changed. Our model corresponds to monodomain LCEs. Either the continuous or discontinuous volume change may depend on the other factors, such as quenched disorder in LCEs [41], polydomain LCEs [42], and polydispersity of chain lengths, etc., however, our theory presented in this paper predicts novel biaxial nematic phases of LCEs.

V. SUMMARY

We have presented a theory to describe novel biaxial nematic phases of a side-chain liquid crystalline gel dissolved in an isotropic solvent and considered three different uniaxial nematic phases (N_1, N_2, and N_3) and two biaxial nematic phases (N_{1b} and N_{2b}). We calculate uniaxial and biaxial orientational order parameters and examine swelling behavior of the LCEs dissolved in isotropic solvents, depending on temperature. We predict the first-order uniaxial-biaxial phase transitions, N_1-N_{1b},N_2-N_{2b}, and the isotropic-biaxial phase transition of the gel. The volume of the gel is discontinuously changed at the phase transition temperature. 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 LCEs.

ACKNOWLEDGMENTS

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