Theory of polar biaxial nematic phases

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A theoretical model is proposed for describing the polar biaxial and uniaxial nematic phases observed in thermotropic liquid crystals formed from rodlike polyester molecules. The polarity and biaxiality are shown to result from the same molecular mechanism, i.e., they are associated with the same critical order parameter which consists of two vectors determining the average molecular orientations in the biaxial and uniaxial phases. The model allows us to determine the critical behavior and electric or magnetic field effects that characterize polar nematic phases and to analyze, at the phenomenological and molecular levels, remarkable properties that have been disclosed experimentally.

Recently, the coexistence of biaxiality and spontaneous macroscopic polarization has been observed experimentally by Watanabe, Takezoe, and co-workers [1–5] in the nematic phase of a thermotropic liquid crystal formed from rodlike aromatic polyester molecules. The two above-mentioned properties—biaxiality and polarity—have been vainly sought independently for many year in thermotropic nematic phases. On the one hand, only centrosymmetric biaxial nematic phases of lyotropic system were previously known [6], since their discovery by Yu and Saupe [7]. On the other hand, although ferroelectricity is known to exist for more than twenty years [8] as a secondary (improper) effect in thermotropic smectic phases, the onset of a spontaneous polarization as a primary mechanism (order parameter) in liquid crystals, was only found recently [9,10] in a uniaxial cholesteric phase formed by a lyotropic mixture of polypeptide polymer and benzyl.

The aim of the present work is to describe theoretically the formation of polar biaxial nematic phases from the isotropic liquid, and to show that the predictions of the theory, in which the molecular symmetry plays an essential role, are consistent with the experimental observations reported in Refs. [1–5]. The polarity and biaxiality are shown to result from the same molecular mechanism, i.e., they are associated with the same critical order parameter, corresponding to the vector representation of the isotropic liquid symmetry group. However, in contrast to the usual theory of polar liquids [11] two vectors are required to stabilize the biaxial phase. This allows us to analyze, at the phenomenological and molecular levels, the remarkable behaviors disclosed experimentally.

The polar biaxial phase found by Watanabe *et al.* [1] is formed from a copolyester based on hydroxybenzoic acid (HBA) and hydroxynaphtoic acid (HNA). The intrinsic symmetry of the polymer molecule, represented in Fig. 1, is monoclinic C_S with the polarity along the rigid polymer chain direction, the molecular plane containing the aromatic groups. The nematic phase appears on heating above the crystal phase at about 280 °C and was identified by optical microscopy and x-ray diffraction. Its polar character was verified by second-harmonic generation (SHG) activity which reveals a monoclinic polar structure corresponding to the same (macroscopic) symmetry C_S as the constituent molecules, with polarization components along—and perpendicular to—the chain direction, i.e., the nematic phase is biaxial.

In a standard nematic phase formed from rodlike molecules of optically uniaxial symmetry, the order parameter of the transition from the isotropic liquid, of O(3) symmetry, is a second rank tensor [12,13]. In the uniaxial nematic phase there is only one effective nonzero component of the order parameter, S_1, which is defined from the probability distribution to find the molecular axis in the spherical (θ, ϕ) direction,

$$P(\theta,\phi) = \frac{1}{4\pi}\left\{ 1 + \frac{S_1}{2}(1 - 3\cos^2\theta) \right\}, \tag{1}$$

the S_1 term in Eq. (1) describes the uniaxial nematic symmetry. Thus, one has $S_1 = 5\langle 1 - 3\cos^2\theta\rangle$ where $\langle\ \rangle$ denotes the average on the P distribution. For a biaxial phase [13,14], there are two effective nonzero order-parameter components, which are: $S_1 = 5\langle 1 - 3\cos^2\theta\rangle$ and $S_2 = \langle\sin^2\theta\cos 2\phi\rangle$. Note that Eq. (1) holds close to the isotropic-liquid to uniaxial nematic transition temperature and that the corresponding (primary) order parameter transforms as the spherical harmonic $Y_0^2 = \frac{1}{2}(1 - 3\cos^2\theta)$. At lower temperatures other spherical harmonics $Y_0^{2L}(\theta,\phi)$ compatible with the uniaxial symmetry become significant. However, they are not symmetry breaking quantities and therefore coincide with secondary order parameters, having no influence on the phase diagram and critical behavior of the system.

In the case of a molecular symmetry C_S, the orientation in space of the molecules cannot be described with the (θ, ϕ) coordinates, and requires use of the three Euler angles (α, β,
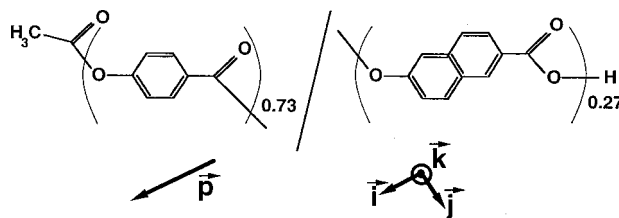

FIG. 1. The HBA-HNA polymer molecule represented within its mirror plane. $\vec{p}$ is the molecular polarization. $\vec{i}$, $\vec{j}$, and $\vec{k}$ are unit vectors in the molecular-vector space.

γ). In this case the probability distribution $P(\alpha,\beta,\gamma)$ has to be expanded into spherical functions $D^L_{mm'}(-L\leqslant m,m' \leqslant L)$ instead of spherical harmonics, giving rise to a wider variety of molecular configurations than those associated with molecular units having a cylindrical symmetry. For this latter symmetry, when going from the isotropic liquid to a polar nematic phase, a single vector can appear in $P(\theta,\phi)$ since there exist only three functions $Y^1_m(-1\leqslant m\leqslant 1)$ trans-

forming as the components of a vector. In contrast, for non-cylindrical molecules there are nine functions $D^1_{mm'}$ in the distribution $P(\alpha,\beta,\gamma)$, which transform as the components of three vectors. The number of allowed vectors depends on the actual molecular symmetry. For molecules with monoclinic symmetry C_S the corresponding probability distribution, restricted to the primary order parameters, reads [16,17]

$$P(\alpha,\beta,\gamma)=1/8\pi^2\{1+[U_x(\cos\alpha\cos\beta\cos\gamma-\sin\alpha\sin\gamma)+U_y(\cos\alpha\cos\beta\sin\gamma+\sin\alpha\cos\gamma)-U_z\sin\beta\cos\alpha$$
$$-V_x(\cos\beta\sin\alpha\cos\gamma+\cos\alpha\sin\gamma)-V_y(\cos\beta\sin\alpha\sin\gamma-\cos\alpha\cos\gamma)+V_z\sin\beta\sin\alpha]\}. \tag{2}$$

(U_x,U_y,U_z) and (V_x,V_y,V_z) are the components of two vectors $\vec{U}$ and $\vec{V}$ representing the six-dimensional order parameter associated with the transition from the isotropic liquid to a polar-biaxial nematic phase of C_S symmetry. Averaging on $P(\alpha,\beta,\gamma)$, one gets $U_x=3\langle\cos\alpha\cos\beta\cos\gamma -\sin\alpha\sin\gamma\rangle$, etc. These expressions provide the average orientation of the molecules in the biaxial nematic phase, which is given by

$$\langle\vec{i}(\alpha,\beta,\gamma)\rangle=\frac{\vec{U}}{3}, \quad \langle\vec{j}(\alpha,\beta,\gamma)\rangle=-\frac{\vec{V}}{3}, \quad \langle\vec{k}(\alpha,\beta,\gamma)\rangle=\vec{0}. \tag{3}$$

$\vec{i}$ and $\vec{j}$ are the unit vectors belonging to the molecular mirror plane, which are, respectively, parallel to the molecular polarization and normal to it, and $\vec{k}=\vec{i}\times\vec{j}$ (Fig. 1). Since the relative directions of the vectors $\vec{U}$ and $\vec{V}$ can be expressed by their moduli U, V and by the angle Φ between them, the order parameter decomposes into three effective (U,V,Φ) and three Goldstone components. These latter components describe the orientation of the $(\vec{U},\vec{V})$ plane which coincides with the macroscopic mirror plane of the biaxial state. Thus, the free energy associated with the isotropic liquid-polar uniaxial-polar biaxial sequence of phase transitions depends only on the effective components (U,V,Φ). Taking into account the transformation properties of these components by the isotropic group O(3) yields the invariant monomials: $I_1=\vec{U}\cdot\vec{U}=U^2$, $I_2=\vec{V}\cdot\vec{V}=V^2$, and $I_3=\vec{U}\cdot\vec{V}=UV\cos\Phi$, which give the following order-parameter (Landau) expansion:

$$F_1(I_1,I_2,I_3)=a_1I_1+a_2I_1^2+\cdots+b_1I_2+b_2I_2^2+\cdots$$
$$+c_1I_3+c_2I_3^2+\cdots+d_{12}I_1I_2+\cdots. \tag{4}$$

Minimization of F_1 with respect to U, V, and Φ leads to three possible stable states.

(i) The isotropic liquid for $U=V=0$.

(ii) A *uniaxial polar nematic phase* of $C_{\infty v}$ symmetry, for $U\neq0$, $V\neq0$, and $\Phi=0,\pi$. In this phase $\vec{U}$ and $\vec{V}$ are parallel

and one has $\langle\vec{i}\rangle=(\vec{U}/V)\langle\vec{j}\rangle=\vec{U}/3$, $\langle\vec{k}\rangle=\vec{0}$. It means that although $\vec{i}$ and $\vec{j}$ are perpendicular at the molecular level, their average values are parallel in the uniaxial phase.

(iii) A biaxial polar nematic phase of symmetry C_S for $U\neq0$, $V\neq0$, and $\Phi\neq0,\pi$.

A polar uniaxial nematic phase with $C_{\infty v}$ symmetry was observed by Watanabe *et al.* [1–3] in another polymer formed by HBA, HNA, and meta-hydroxy benzoic acid (m-HBA) as a third comonomer. In this phase the SHG activity shows that the polarity perpendicular to the molecular chain is cancelled. Using 4-hydroxy 4-biphenil carboxylic acid (HBCA) instead of HBA. Furukawa *et al.* [3] could also observe a crossover from biaxial to uniaxial regime in a crystalline film of HBCA-HNA by changing the molar ratio of HBCA with respect to HNA.

The most representative theoretical phase diagrams associated with the Landau free-energy F_1 are shown in Fig. 2. A fourth-degree expansion of F_1 in U and V is assumed in the phase diagram of Fig. 2(a). It shows a sequence of two second-order transitions isotropic→uniaxial nematic →biaxial nematic. A sixth degree expansion is considered for the phase diagram of Fig. 2(b) which exhibits a direct first-order isotropic→biaxial nematic transition. The biaxial phase separates two regions of stability for the uniaxial phase. It has to be stressed that the second-order character
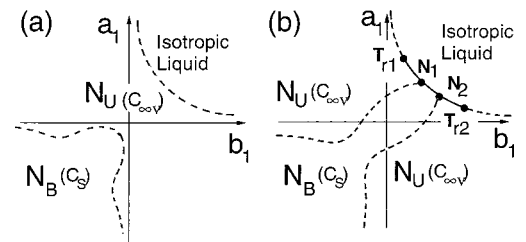

FIG. 2. Theoretical phase diagrams in the (a_1,b_1) plane corresponding to the Landau expansion defined by Eq. (4), and truncated either at the fourth degree (a), or at the sixth degree (b). Dashed and full lines are, respectively, second-order and first-order transition lines. In (b) N_1 and N_2 are three-phase points; T_{r1} and T_{r2} are tricritical points.
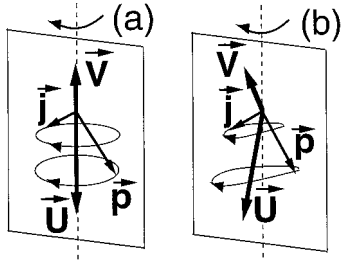
FIG. 3. Schematic representation of the molecular structure in the uniaxial (a) and biaxial (b) polar nematic phases. In both cases the molecular plane rotates about an axis parallel to the plane. The molecular vectors $\vec{i}$ (parallel to $\vec{p}$) and $\vec{j}$ (normal to $\vec{p}$) are within this plane. In the uniaxial phase (a) $\vec{p}$ processes isotropically, then $\langle \vec{i} \rangle = \vec{U}/3$, $\langle \vec{j} \rangle = -\vec{V}/3$, and the single optical axis is parallel to the rotation axis. In the biaxial phase (b) the rotation is anisotropic, then $\langle \vec{i} \rangle$, $\langle \vec{j} \rangle$, and the two optical axes are not parallel to the rotation axis.

predicted in the two phase diagrams for the isotropic liquid $\rightarrow$polar uniaxial nematic is in contrast with the situation found for the isotropic liquid$\rightarrow$centrosymmetric uniaxial nematic transition [6,13]. This latter transition is always first order due to the existence of a cubic invariant of the corresponding tensor order parameter, which is absent for the vector order parameter used in our approach. In the polymer mixtures investigated in Refs. [1–5] the nematic-isotropic transition could not be observed below the decomposition temperature (350 °C).

From Eqs. (2) and (3), one can deduce a qualitative picture of the molecular structure in the uniaxial and biaxial polar nematic phases, which are shown in Fig. 3(a) and 3(b), respectively. In the uniaxial phase [Fig. 3(a)] the molecular plane is parallel to the optical axis and turns around it. The molecular polarization lies within the molecular plane, at an angle Ψ with the optical axis, given by $\tan \Psi = -V/U$. For $V=0$, the molecular polarization is parallel to the optical axis, whereas it is normal to it for $U=0$. Due to the continuous rotations the molecules acquire the effective $C_{\infty v}$ symmetry identical to to the macroscopic symmetry of the phase [18]. In the biaxial phase [Fig. 3(b)], the rotation of the molecular plane around the optical axis is anisotropic and becomes frozen at low temperature, so that the effective molecular symmetry is also C_S. Moreover, the angle between the rotation axis and the polarization varies during the rotation process. Such picture is consistent with the SHG profiles obtained for the biaxial and unixial phases in the HBA-HNA and HBA–HNA–m-HBA polymer systems [1,3].

A number of physical properties of the polar biaxial and uniaxial phases can be determined by considering the coupling of the order parameters $\vec{U}$ and $\vec{V}$ to the optical second-rank traceless tensor Q, where Q represents either the conventional nematic order parameter or the anisotropic part $\varepsilon_{ij}-(1/3)(\mathrm{Tr}\,\varepsilon)\delta_{ij}$ of the dielectric tensor ε. The coupling invariant, linear in the components Q_{ij} of Q, allowed by the O(3) symmetry are $I_4=\Sigma_{i,j}U_iU_jQ_{ij}$, $I_5=\Sigma_{i,j}V_iV_jQ_{ij}$, and $I_6=\Sigma_{i,j}U_iV_jQ_{ij}$, with $(i,j)\in(x,y,z)$. It yields the Landau free-energy,

$$F_2(I_1,I_2,...,I_6,Q_{ij})=F_1(I_1,I_2,I_3)+e_1I_4+e_2I_5$$

$$+e_3I_6+f\sum_{i,j} Q_{ij}Q_{ij},$$

which provides by minimization the general form of the optical tensor components,

$$Q_{ij}=\frac{1}{2f}\left\{-e_1\left(U_iU_j-\frac{1}{3}U^2\delta_{ij}\right)-e_2\left(V_iV_j-\frac{1}{3}V^2\delta_{ij}\right)\right.$$
$$\left.-e_3\left[\frac{1}{2}(U_iV_j+U_jV_i)-\frac{1}{3}\vec{U}\cdot\vec{V}\delta_{ij}\right]\right\}. \tag{5}$$

Since there are three Goldstone order-parameter components which can be fixed arbitrarily, $\vec{U}$ can be oriented along the z axis [$\vec{U}=(0,0,U)$], and $\vec{V}$ can be taken in the x-z plane [$\vec{V}=(V\sin\Phi,0,V\cos\Phi)$] without loss of generality. Accordingly, one has in the biaxial phase: $Q_{12}=Q_{23}=0$ and $Q_{13}=(1/3f)(e_3U-e_2V\cos\Phi)\sin\Phi$. One eigenvector of Q is normal to the mirror plane (x,y), whereas the two remaining eigenvectors are parallel to this plane but in directions neither parallel to $\vec{U}$ nor to $\vec{V}$. In the uniaxial phase one gets $Q_{13}=Q_{12}=Q_{23}=0$, and $Q_{11}=Q_{22}=-2Q_{33}=-2(e_1U^2+e_2V^2\pm e_3UV)$. In this phase, the single optical axis is parallel to $\vec{U}$ and $\vec{V}$. Using the current formalism describing nematic phases [6,14,15], one takes: $\mathrm{Tr}\,Q^2=r^2$, and $\mathrm{Det}\,Q=(2/9)r^3\cos3\theta$. $B=r^3\sin3\theta$ defines the optical biaxial coefficient. Equation (5) shows that B vanishes in the uniaxial phase (for $\theta=n\pi/3$) as

$$B=\frac{1}{16f\sqrt{2}}C(\eta)[E+C(\eta)]^{1/2}, \tag{6}$$

where the symmetry breaking quantity $\eta=UV\sin\Phi$ varies in the uniaxial phase as $(T-T_C)^{1/2}$. $C(\eta)=(e_3^2-4e_1e_2)\eta^2$, and $E=e_1I_4+e_2I_5+e_3I_6$. Equation (6) shows that B varies linearly with $(T-T_C)$ in the vicinity of T_C. This behavior distinguishes the polar biaxial nematic phase from standard biaxial nematic phases, in which the biaxial coefficient varies as $(T-T_C)^{1/2}$ [14,15]. In the same way, the r parameter characterizing the deviation from isotropy varies as $(T-T_i)$ in the polar uniaxial nematic phase, where T_i is the critical isotropic-uniaxial nematic transition temperature. This is also at variance with the standard uniaxial nematic case in which one finds in the vicinity of the first-order isotropic-uniaxial nematic transition a $(T-T_i)^{1/2}$ temperature dependence for r [14,15].

The specific critical behavior at the transitions to polar uniaxial and biaxial nematic phases may provide an explanation for the absence of electric field induced switching reported by Watanabe *et al.* [1], which was attributed by these authors to the high viscosity of the systems. Within our approach, the response of polar nematic phases to an applied electric field $\vec{E}$, is strongly influenced by the presence of the Goldstone variables. At low field intensity, the polarization in the uniaxial phase must align with the field, whereas in the biaxial phase the mirror plane must adapt its orientation so as
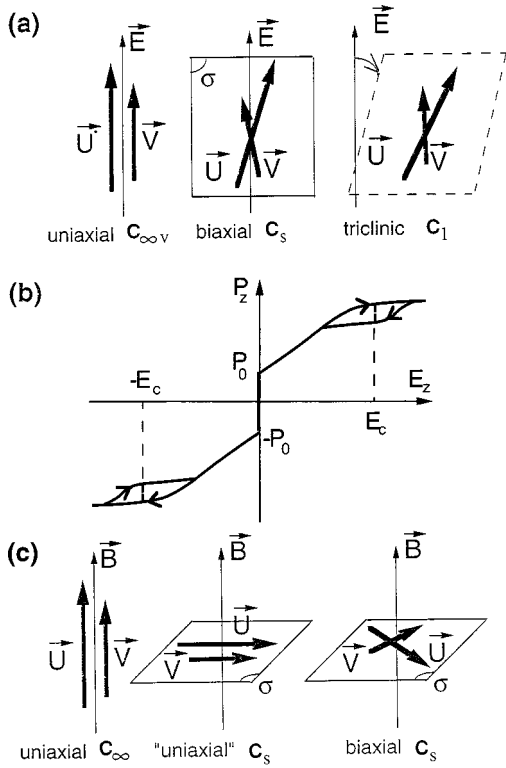
FIG. 4. (a) Configuration of the vector order parameter $(\vec{U}, \vec{V})$ under applied electric field $\vec{E}$. At low field intensity, the vectors align in the direction of the field in the uniaxial phase and in the biaxial phase they lie within the macroscopic mirror plane σ which is parallel to $\vec{E}$. At higher field intensity, a triclinic phase may be stabilized and the mirror plane disappears. (b) Shape of the equilibrium hysteresis curve in the polar nematic phases. $\vec{E}_z$ is the applied electric field, P_z is the induced polarization, and P_0 its spontaneous value at zero field. At low field intensity the curve is reversible and the polarization jumps from P_0 to $-P_0$ when E_z is reversed. At higher field intensity the triclinic phase may be stabilized across a first-order transition, giving rise to an irreversible hysteresis behavior around the corresponding critical field $\vec{E}_C$. (c) Configuration of the vector order parameter under applied magnetic field B. At low field intensity, in the uniaxial phase the vectors align either in the direction of the field or normal to it. In the former case the phase remains uniaxial but becomes chiral, whereas in the latter case the phase remains achiral but becomes slightly biaxial, since $\vec{U}$ and $\vec{V}$ do not remain parallel. In the biaxial phase the mirror plane σ is normal to B at arbitrary low field intensity.

to be parallel to $\vec{E}$ [Fig. 4(a)]. Therefore, considering a homogeneous domain of the polar uniaxial phase where the polarization is directed along $+\vec{e}_z$, application of an electric field $E\vec{e}_z$ increases slightly the nematic polarization. When the sense of the electric field is reversed ($-E\vec{e}_z$), the polarization remains oriented along the z axis but corresponds to an unstable state, and not to a metastable state as in solid ferroelectrics, since there is no energy barrier preventing the switching of the polarization. This is due, on the one hand, to the isotropic symmetry of the parent liquid state with respect to which the polarization can rotate as a whole without changing the internal free energy of the system and, on the

other hand, to the existence of the nonenergetic Goldstone variables which make possible such rotation. As a consequence, the polarization is in a mechanically unstable equilibrium state as long as no transverse component of the electric field is applied to the system. The absence of polarization switching may therefore result from the fact that for beginning the switching process, a thermodynamic fluctuation has to generate a macroscopic transverse polarization during a time scale $\tau = \nu (p|\vec{E}|)^{-1}$, where p is the molecular polarization and ν the rotational viscosity. Since τ is much larger then the molecular rotation time, such fluctuation is very unlikely, and the system persists in its mechanically unstable state. At a high threshold field $\vec{E}_C$ the biaxial phase can undergo a first-order transition into the uniaxial state. The metastability of both states around the corresponding threshold fields $\pm\vec{E}_C$ yields a double hysteresis loop, in addition to the reversible switching jump at $\vec{E}=0$ [Fig. 4(b)]. At still higher field intensities, nonlinear couplings may stabilize a polar nematic phase of symmetry C_1, in which the field is not parallel to the $(\vec{U}, \vec{V})$ plane.

The magnetic field action on the polar biaxial and uniaxial nematic phases is different due to its axial symmetry. At low field intensity in the biaxial phase, the mirror plane orientates perpendicularly to the field, i.e., the magnetic field enforces the biaxiality of the phase, which keeps its C_S symmetry. On the contrary, application of a magnetic field lowers the symmetry of the uniaxial phase to C_∞ if the polarization is along the field direction, or to the biaxial symmetry C_S, if $\vec{U}$ and $\vec{V}$ are normal to the field [Fig. 4(c)].

In Refs. [1,2] the dependence of the SHG intensity as a function of the degree of polymerization was measured using samples of increasing molecular weight. The SHG signal vanishes below a critical degree of polymerization. It indicates that below a critical length of the polymer molecules, the biaxial nematic state become nonpolar. Such behavior was predicted theoretically by Terentjev *et al.* [19] and Lee and Lee [20] for uniaxial polar nematic phase of liquid crystalline polymers. The two studies differ in their approaches, but both find that the polar ordering should appear beyond a given dipole strength of the rigid polymer chains. In our approach, the onset of a nonpolar nematic state, below a biaxial or uniaxial polar state, reflects the vanishing of the $\vec{U}$ and $\vec{V}$ vectors: the second-rank Q tensor becomes the symmetry breaking order parameter at the observed critical degree of polymerization. In a more general way the sequence of isotropic liquid-polar nematic-centrosymmetric nematic phase transitions requires to take into account two primary (critical) order parameters: Q and $\vec{U}$ ($\vec{V}$ becoming a secondary noncritical order parameter, since it cannot break the symmetry further than Q and $\vec{U}$ alone). The free energy F_3 associated with the preceding sequence of phases depends on six invariant monomials: I_1, I_4, $I_7 = \mathrm{Tr}\, Q^2$, $I_8 = \mathrm{Det}\, Q$,

$$I_9 = \Sigma_{i,j,k} Q_{ij} Q_{jk} U_i U_k,$$

and

$$I_{10} = \Sigma_{i,j,k,l,m} Q_{ij} Q_{jk} Q_{kl} Q_{lm} U_i U_m.$$

Minimization of F_3 with respect to the Q and $\vec{U}$ components yields six possible stable nematic phases below the isotropic liquid, with the symmetries $D_{\infty h}$, $C_{\infty v}$, D_{2h}, C_{2v}, C_S, and C_1. The corresponding phase diagram shows, in particular, a second-order transition between the nonpolar ($D_{\infty h}$) and polar ($C_{\infty v}$) uniaxial nematic phases, while the transition between the biaxial D_{2h} and C_S phases is first order. Accordingly, the nonpolar phase observed below a critical length of the polymers molecules may result from the activation of a different symmetry breaking mechanism, associated with the Q tensor order parameter. The phase should display a uniaxial $D_{\infty h}$ or biaxial D_{2h} symmetry.

Polar nematic phases of thermotropic liquid crystals may have interesting technological applications, but are also of fundamental interest, since they constitute the first example of a true free vector field in condensed matter physics. One may expect for such phases, a rich variety of unusual textures and defects. The remarkable critical behavior of uniaxial and biaxial polar nematic phases, established in the present work, and especially the second-order character of the isotropic→uniaxial polar nematic transition [21], reveals that these phases do not form a banal subclass of nematics. In particular, the two-vector order parameter used in our approach is independent of the current nematic tensor, and is adapted to the low molecular symmetry (C_S) of the polymer subunits. More symmetric molecules would cancel the vector $\vec{V}$ and would forbid the stabilization of a biaxial polar nematic state. A molecular group of lower C_1 symmetry should, on the contrary, require to introduce a third vector order parameter ($\vec{W}$), which would allow stabilization of a uniaxial polar state of triclinic C_1 symmetry.

Although the existence of biaxial and uniaxial polar nematic phases requires further experimental confirmation in other liquid crystal systems, the fact that such phases have been evidenced for the first time in a system displaying the molecular symmetry C_S is not surprising. Our analysis shows that only for the low molecular symmetries C_1 and C_S the coexistence of polarity and biaxiality is permitted as the result of a single (irreducible) symmetry-breaking mechanism. A number of theoretical studies have focused on the possibility of realizing polar uniaxial nematic phases [22–25] because of their potential technological interest. However, polar uniaxial nematics can be predicted using many different theoretical approaches based on dipolar interactions of molecules with cylindrical symmetry, which lead to trivially ordered nematic configurations. The originality of the present study is that the existence of uniaxial and biaxial polar phases is deduced from the sole molecular symmetry, independent of the specific nature of the molecular interactions.

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[16] The second term in brackets corresponds to $\vec{U} \cdot R\vec{e}_x + \vec{V} \cdot R\vec{e}_y$, where $\vec{e}_x \vec{e}_y$ are the unit vectors along x and y. $R(\alpha, \beta. \gamma)$ is the rotation matrix $\vec{i} = R\vec{e}_x$ and $(\vec{j} = R\vec{e}_y, \vec{k} = R\vec{e}_z)$ are the directions in the molecular vector space along the molecular polarization, and in the perpendicular plane, respectively. $\vec{e}_z$ is taken normal to the molecular mirror plane. Note that a $\vec{W} \cdot R\vec{e}_z$ term, where $\vec{W}$ is a third vector order parameter, is forbidden by the C_S molecular symmetry.

[17] Equation (2) neglects the secondary order parameters transforming as higher-rank tensors and corresponding to terms proportional to $D^L_{mm'}(L>1)$.

[18] The effective molecular symmetry depends on the macroscopic symmetry, but these two symmetries do not influence one another in a simple way. For example, in the conventional centrosymmetric uniaxial nematic phase with macroscopic $D_{\infty h}$ symmetry the molecules having the symmetry C_S reach an effective symmetry D_{2h}. The continuous effective symmetry in the polar uniaxial nematic phase results from the absence of the Euler angle α in the corresponding distribution function, as defined by Eq. (2).

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