

Extended summary

The cybotactic nematic phase of bent-core liquid crystals: study of a new state of matter with unconventional properties

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Abstract. Bent-core mesogens (BCMs) are non-linear liquid crystals (LCs) with a folded rigid central unit and lateral fluid alkyl chains. They represent a novel class of LCs exhibiting substantially different physical properties than traditional linear (calamitic) materials and for this reason they are attracting ever growing interest in the recent years. In particular, BCMs pose one of the most intriguing challenges of the LC science: the discovery of the elusive biaxial nematic (NB) and ferroelectric nematic phases (NF), theoretically predicted many years ago but never experimentally confirmed so far. The N phase of BCMs constitutes a new type of mesophase, namely a cybotactic nematic phase (N_{cvb}), composed of nanometre-size clusters of bent-core molecules exhibiting a relatively high degree of internal order (orientational as well as translational) imposed by closely packing of the BCM nonlinear shape. The peculiarity of such supramolecular organization accounts for the unique properties of this phase of matter. An extended study of the nematic phase of a variety of BCMs (including low molecular-weight and polymeric mesogens) by means of complementary techniques such as synchrotron X-ray diffraction (XRD), electro-optical characterization and repolarization current measurements, have confirmed the cybotactic nature of the N phase of these materials and suggest an apparent correlation between ferroelectricity and nematic biaxiality. The effects of applied magnetic



and electric fields on the mesomorphic behaviour of BCMs have also been analyzed in-depth, showing for the first time how external fields of modest intensity may strongly affect the phase diagram of these materials.

Keywords. Bent-core mesogens, biaxial nematic, cybotactic nematic phase, ferroelectric nematic phase, liquid crystals.

1 Problem statement and objectives

The first report of a liquid crystal (LC) phase in non-linear molecules dates back to 1929 [1], but it was only recently that bent-core mesogens (BCMs) have become the subject of great scientific interest. In particular, since the seminal work of Naori et al. [2], many studies have pointed out the rich variety of mesophases and odd effects which are proper for this class of compounds: they have attracted significant attention because of the spontaneous polar (and biaxial) order shown by their smectic (Sm) phases, exhibiting ferro-, ferri- or antiferroelectric properties. Indeed, while in calamitic LCs, polar order is always associated to chirality, typical BCMs are achiral molecules composed of a bent central unit and two rod-like segments having flexible alkyl chains at their ends. These molecules usually possess a transverse dipole moment, and show a strong tendency to form closely packed layers, which explains their odd behavior.

Nowadays, growing attention is being focused on the odd properties of the nematic (N) phase of BCMs. In fact, the peculiar properties of BCMs make them the most promising candidates for the achievement of the biaxial nematic (N_B) and the ferroelectric nematic (N_F) phases, both theoretically predicted several years ago [3], but have been experimentally quite elusive. The quest for these new phases is also motivated by their technological potential: whereas in conventional (uniaxial) nematics, the electro-optic response is due to the field-induced reorientation of the molecular director \mathbf{n} (the average orientation of the long molecular axes), in a N_B phase, a much faster response to electric fields can be envisaged by rotation of the secondary director **m** (the average orientation of the short molecular axes). Actually, a NF phase would be even more interesting from this point of view, essentially because: (i) polar LC phases typically exhibit faster response times than apolar LC phases with comparable viscosity, due to the linear coupling between the electric field and the macroscopic polarization vector; (ii) in polar phases, both the switching and the restoring dynamics can be driven by an electric field, without relying on the (usually slower) elastic relaxation torques [4]. Finally, as ferroelectric phases are non-centrosymmetric, they typically show significant second-order non-linear optical properties [5].

The claims of these properties soon fueled an intense scientific debate; the main controversial points concerned: (i) the correct interpretation of experimental data, in particular a characteristic *four-spot pattern* often observed in small-angle X-ray diffraction (XRD) measurements performed on aligned BCMs [6]; (ii) the fact that the observed *macroscopic* biaxiality might actually be induced in a *microscopically* (locally) biaxial sample by external effects, for example, surface interactions or magnetic/electric fields[7]. Eventually, a careful analysis of the experimental data led to the development of a molecular model of the BCMs' N phase, the cybotactic nematic (N_{cyb}) model, originally proposed in 2002 [8] and now widely embraced by the scientific community. According to this model, the N phase of BCMs is characterized by very short range positional and orientational order correlation fluctuations (*cybotactic clusters*). These clusters exhibit Sm-like positional order. If no external effects align the clusters, the transverse, mesoscale orientational order is uncorrelated over macroscopic length scales and the N_{cyb} phase generally appears to be macroscopically uniaxial.

Our experimental work focused on the XRD studies and electro-optical characterization of a family of BCMs compounds that exhibit the four-spot XRD pattern. Although XRD data can neither exclude nor confirm spontaneous macroscopic biaxiality, our analysis



clearly points towards the cybotactic model of the N phase for this class of BCMs. The clusters, which are intrinsically biaxial (and possibly polar), exist over the whole N range and explain most of the extraordinary effects observed in BCMs, such as giant-flexoelectricity, unusual rheological properties, large flow birefringence. In particular, we describe how an electric field can align the polar cybotactic clusters and induce a ferroelectric response.

2 Research planning and activities

We performed XRD measurements on several oxadiazole-based BCMs. XRD measurements have been carried out at the BM16, BM26 and ID02 beamlines of the *European Synchroton Radiation Facility* (ESRF) in Grenoble, France. The experimental parameters were: beam wavelength $\lambda = 0.980$ Å and sample-detector distance l = 1.0 m at BM16; $\lambda = 0.827$ Å and l = 1.5 m at BM26; $\lambda = 0.995$ Å and l = 1.5 m at ID02. Samples were placed either in capillaries or in glass cells (Figure 1). The cells (20 µm thick) consisted of two glass plates separated by 20 µm spacers and coated with a conductive indium tin oxide (ITO) layer; a thin SiO_x deposition on the internal cell surfaces provided planar alignment. These cells were used to apply a low frequency (500 Hz) ac electric field **E**, parallel to the X-ray beam, across the conducting plates. Both types of samples were mounted in a temperature-controlled hot stage (precision ± 0.1 °C, accuracy ± 0.5 °C), allowing a static magnetic field (**B** \approx 1 T, measured in air) to be applied perpendicularly to the incident X-ray beam and parallel to the surface anchoring direction.



Figure 1. Experimental set-up: \mathbf{r} is the alignment direction induced by the cell surface.

XRD is a well-established technique to investigate molecular order of LC phases. When the molecular director **n** of a conventional (calamitic) nematic is aligned, e.g. by application of a magnetic field, the typical XRD pattern is like that shown in Figure 2(a): the q-vector of the two wide-angle crescents, orthogonal to **n**, is related to the molecular diameter D ($q_0 \approx 2\pi/D$), whereas the q-vector of the two small-angle diffuse features, parallel to **n**, is related to the molecular length L ($q_0 \approx 2\pi/L$). The radial width of the two pairs of signals is inversely proportional to the positional correlation length in the direction orthogonal and



parallel to **n**, respectively. In contrast, the XRD pattern of ODBP mesogens is significantly different [Figure 2(b)]: the two wide-angle signals, similar to those observed in calamitic nematics, are accompanied by a distinctive small angle four-spot pattern. It was the observation of the latter that first originated the claim of biaxiality in the N phase of BCMs.



Figure 2. XRD diffraction pattern and molecular arrangement in the N phase of calamitic LCs (a) and bent-core LCs (b).

Small-angle XRD measurements allow a straightforward determination of the BCM phase transition temperatures in aligned samples: a diffuse diffraction ring identifies the isotropic (I) phase; the four-spot pattern discussed above characterizes the N_{cvb} phase and sharp diffraction peaks are the signature of a Sm phase. If the sample is not aligned, the four-spot pattern becomes a circle very similar to the diffuse ring in the isotropic phase, so that it is difficult, or even impossible, to distinguish the clearing point. When studying planar cells, we first tried to get alignment just by surface rubbing; although the alignment quality was not particularly good, probably because of the degradation of the polyimide layer at the high working temperatures, we could still infer both the I-N_{cyb} and N_{cyb}-SmC transitions in a temperature scan starting from the isotropic melt. Subsequently, we repeated the measurements with the alignment reinforced by a magnetic field parallel to the rubbing direction. While the transition temperatures found with the former set of measurements were in agreement with differential scanning calorimetry (DSC) and polarization microscopy values, the results in the presence of the field showed an unexpectedly large shift of both the I-N_{cybC} and N_{cybC}-SmC phase transitions temperatures, as discussed in the next section.

Once the cybotactic nature of the N phase was established, we performed repolarization current measurements to check for the presence of a ferroelectric-like response. Measurements were performed on a cell planar alignment assured by a thin SiO_x film. In contrast to aligning polymer coatings, SiO_x deposition was found to prevent parasitic current responses to applied electric fields, for example, those due to free charge adsorption/desorption processes. A low-frequency (f = 1 Hz) triangular voltage waveform was applied across the cell, and the generated current was measured on a high precision resistor connected in series with the sample and the voltage generator. Figure 3 shows representative examples of



Immacolata Fausta Placentino The cybotactic nematic phase of bent-core liquid crystals: study of a new state of matter with unconventional properties

the response curve, measured at T = 248 °C and T = 216 °C with a peak-to-peak driving voltage $V_{pp} = 60$ V, corresponding to an electric field amplitude of 1 V μ m⁻¹. Two peaks, indicate by arrows, one per half cycle of the input wave voltage, clearly emerge (with opposite sign) from the linear ohmic background generated by the ionic flow, delayed with respect to the zero-crossing point of the voltage waveform. These peaks are consistent with a ferroelectric-like switching, generated by the reversal of a macroscopic electric polarization *P* having a lifetime longer than the half-period of the voltage waveform.



Figure 3. Repolarization current response in the N_{cyb} phase measured upon application of a triangular wave voltage (f = 1 Hz, $V_{pp} = 60$ V, black dotted line). In the inset, the same measurement performed in the isotropic phase (green solid line) with $V_{pp} = 70$ V.

3 Analysis and discussion of main results

As example, a representative selection of the SAXS patterns collected in the N phase of a bent-core mesogen (ODBP-Ph-OC₁₂H₂₅) in the heating cycle up to the isotropic phase is shown in Figures 4 with the molecular structure of the compound.



Figure 4. Molecular structure and SAXS diffraction patterns of ODBP-Ph- $OC_{12}H_{25}$ at different temperatures



The main experimental findings by small-angle XRD data can be summarized as follows: (1) the four-spot pattern is presented over the whole N range for the long alkyl chain compounds and persists over its greatest part for the short chain compounds;

(2) the occurrence of the four-spot pattern does not depend on the particular mesophase underlying the N phase, that could be crystalline (Cr) or SmC;

(3) the four-spot patterns shows a clear evolution with increasing temperature, with the split angle β , the angle between q_0 and the magnetic field, decreasing on approaching the I phase in all the samples;

(4) the *d*-spacing, corresponding to the maxima of the four spots in the reciprocal space q_0 ($d = 2\pi/q_0$), increases on approaching the clearing point. However, its value is always considerably less than the expected molecular length *L*;

(5) the full width at half maximum of the spots measured along cuts parallel (horizontal) and orthogonal (vertical) to \mathbf{n} , $\Delta q_{\parallel,l}$, increases slightly with temperature;

(6) when measurements are performed on a planar cell and an electric field \mathbf{E} is applied parallel to the incident X-ray beam and orthogonally to the initial direction of \mathbf{n} (imposed by the surface treatment), one observes the change of the four spot pattern into an isotropic ring when \mathbf{E} exceeds a threshold value.

The model we propose is based on the existence of cybotactic groups (or *clusters*) in the N phase (N_{cyb}) of BCMs in agreement with the observations in 2002 [9] and the theory developed by Vanakaras and Photinos[7]. According to this picture, the BCM N_{cyb} phase consists of nanosized biaxial clusters with very short-range Sm order (usually a skewed SmC order). While the BCM principal director **n** can be aligned by a magnetic field or surface anchoring, the normal **k** to the Sm planes can take any orientation on a cone of semi-aperture β around **n** [see the scheme in Figure 2(b)]. Experimentally, both β and d are found to depend on the temperature.

However, the molecular length $L = d/\cos\beta$ remains virtually constant over the whole N range, with a value in good agreement with structural estimations. This indicates the evolution of the cybotactic cluster organization from the more common skewed SmC-type positional order (N_{cybC}) to a Smectic A(SmA)-type order (N_{cybA}) [10]. Within this model, the split of the small angle diffraction pattern is an effect of the tilt of the molecules with respect to the normal to the Sm planes, rather than a consequence of the BCM form factor.

Analytically, this implies the need to model the cluster short-range fluctuations by means of a SmC-like structure factor averaged over all possible directions of the Sm layer normal **k**, which leads to [11]:

$$S(q) \propto \left\{ 1 + \xi_{\parallel}^{2} \left(q_{\parallel} \pm q_{0\parallel} \right)^{2} \right\}^{2} + 2\xi_{\perp}^{2} \left[1 + \xi_{\parallel}^{2} \left(q_{\parallel} \pm q_{0\parallel} \right)^{2} \right] \left(q_{\perp}^{2} q_{0\perp}^{2} \right)^{2} + \xi_{\perp}^{4} \left(q_{\perp}^{2} - q_{0\perp}^{2} \right)^{2} \right\},$$
(1)

It is important to notice that this equation reproduces the split of SAXS pattern, but is not able to fit the fine details of the lineshape of the scattered signal over a large q-range, which requires a more refined model including the effects of the form factor (after identification of a more accurate model of the bent-core molecule), of the orientational distribution function of the clusters and of the molecules within each cluster, and finally of a possible non-exponential decay of the correlation function leading to a slightly modified Lorentzian lineshape for $\mathbf{S}(q)$. Whatever the exact lineshape of the peaks, it remains true that the peak full width at half maximum Δq is inversely proportional to the correlation length. Therefore, by assuming $\xi_{||, \mathcal{I}}=2/\Delta q_{||, \mathcal{I}}$ [12], we can calculate the correlation lengths at different temperatures. The temperature dependence exhibits a reduction of the correla-



tion lengths on approaching the clearing point, more pronounced for long chain compounds (probably related to the flexible nature of the terminal alkyl chains). In general, our results show that $\xi_{||}$ and ξ_{\perp} are of the order of the molecular length and a few intermolecular distances, respectively, indicating very short-ranged correlations over the entire N range.

Looking at the two-dimensional (T, E) phase diagram of the bent-core mesogen ODBP-Ph-OC₁₂H₂₅ over the entire N temperature range in Figure 5 delineated by the thermotropic phase sequences measured at different *E*-field intensities, it is clear that a shift of the phase transition temperatures should also allow the observation of field-induced phase transitions. This is the mesogen for which the above-mentioned extraordinary magnetic field effect was first demonstrated [13] and also one of the two BCMs originally reported to exhibit biaxiality in the N phase [14].



Figure 5. Two dimensional (T, E) phase diagram of bent-core mesogen ODBP-Ph-OC₁₂H₂₅. Square symbols represent the experimental phase transition temperatures. The error bars take into account the uncertainty due to electrical heating. Phase boundaries are drawn as guides for the eye. Vertical dashed lines a, b, and c represent three isothermal paths.

The highest applied voltage amplitude was $V = \pm 175$ V (i.e. root mean square voltage $V_{\rm rms} = 123.7$ V), corresponding to a maximum field amplitude across the 50 µm cell of $E = \pm 3.5$ V µm⁻¹ ($E_{\rm rms} = 2.47$ V µm⁻¹). By setting $E_0 = 2.47/4$ V µm⁻¹ = 0.62 V µm⁻¹, we chose to perform the measurements at the following discrete set of $E_{\rm rms}$ field values: 0, E_0 , $2E_0$, $3E_0$ and $4E_0$. Measurements were carried out in consecutive cooling cycles from the isotropic melt, one for each set field value starting from $E_{\rm rms} = 0$; at the end of each cycle, the sample was always annealed above its clearing point in the *E*-field. To exclude any role of possible thermal degradation of the sample, a control cooling cycle with $E_{\rm rms} = 0$ was performed at the end of all reported measurements. The control experiment showed full recovery of the initial, zero *E*-field, phase transition diagram.

The phase transitions were determined from the evolution of the XRD pattern with slowly changing temperature (in steps of 1 K), after allowing the sample to equilibrate at



each set point. Under these conditions the system was in thermodynamic equilibrium, thus obviating any supercooling artifacts.

Different colours represent distinct mesophases on the horizontal transition lines, and the two continuous curves interpolating the SmC–N and N–I transition temperatures are the phase boundaries. What is immediately apparent is that on increasing the *E*-field intensity, there is a continuous shift toward lower temperatures of both the SmC–N and N–I phase transitions. This shift becomes remarkable above $E_{\rm rms} \approx 2E_0$.

All the measurements (at varying temperature under a selected *E*-field value) were carried out with the cell sample subjected to a static magnetic field B = 1 T parallel to the rubbing direction. The reason for this was the relatively poor alignment of the director **n** in the cell by the rubbed polyimide layer at high experimental temperatures. The role of the applied magnetic field was twofold: (i) to provide enough of a strong planar alignment of the LC to make it possible to discriminate the XRD pattern of the axially oriented N phase from that of the isotropic fluid: (ii) to prevent the sample from possible electro-convection instabilities triggered by the applied *E*-field. The magnetic field effect on the thermotropic behavior of ODBP-Ph-OC₁₂H₂₅ was previously characterized [13]. In particular, it was found that a *B*-field of 1 T shifts the zero-field phase transition temperatures upwards by 4 K for both the SmC–N and N–I transitions. Accordingly, under our experimental conditions, the phase transition map used as the reference for the effects of an applied *E*-field is the following: SmC-197 °C–N-208 °C–I,14 which was confirmed by an isothermal scan from the isotropic melt at B = 1 T and $E_{\rm rms} = 0$.

The largest shifts (measured at $E_{\rm rms} = 4E_0$) are 4 K and 11 K for the SmC–N and N–I transitions, respectively, and represent unexpectedly high values. Opposite to what is observed with the *B*-field, the sign of these *E*-field induced shifts, $\Delta T = T(E) - T(0)$, is negative, which raises the question whether this might be somehow connected to the negative value of the dielectric anisotropy of the material (measured under our experimental conditions of temperature and frequency) [15]; the diamagnetic anisotropy is positive (e.g., n aligns along the *B*-field). In addition, another important field effect is manifested in the phase diagram when the field intensity exceeds $E_{\rm rms} \approx E_0$: the zero-field skewed layered (SmC-like) cybotactic N phase, N_{cybC}, is transformed into a cybotactic N phase, N_{cybA}, having a normal (i.e. orthogonal) layered SmA-like structure.

A quantitative analysis of the N–I phase transition temperatures reveals extraordinarily high absolute values of $\Delta T_{\text{N-I}}$ compared with those measured in conventional linear (calamitic) LCs. In order to place these results into context, we first make a comparison with conventional LCs having a positive dielectric anisotropy, as such mesogens have been more extensively studied. In that case, the LdG approach predicts a quadratic dependence of $\Delta T_{\text{N-I}}$ on the applied *E*-field strength [16,17]:

$$\Delta T_{N-I}(E) = \frac{1}{3} T_0 \frac{S \Delta \varepsilon_M}{Q \rho} E^2, \qquad (2)$$

where T_0 is the zero-field N–I transition temperature, S is the scalar order parameter, $\Delta \varepsilon_M$ is the saturated anisotropy of the absolute dielectric permittivity in the N phase, Q is the latent heat of transition per unit mass, and ρ is the mass density. Eqn (2) was experimentally confirmed in nematics with a high positive dielectric anisotropy ($\Delta \varepsilon / \varepsilon_0 \approx 10$) under *E*-fields up to a maximum of 16 V µm⁻¹, corresponding to a maximum observed shift $\Delta T_{N-I} = 1$ K [16]. If, for the sake of a superficial comparison, we extend eqn (1) to our experimental conditions, i.e. $T_0 = 481$ K, Q = 0.9 kJ mol⁻¹ = 1084 J kg⁻¹, 36 $\rho \approx 2.4 * 103$ kg m⁻³, $\Delta \varepsilon / \varepsilon_0 =$



 $S\Delta\varepsilon_{\rm M}/\varepsilon_0 \cong 16.5$ [15], and use the absolute value of the dielectric anisotropy, we find that a field $E = 10 \text{ V } \mu\text{m}^{-1}$ would be needed to get a shift $|\Delta T_{\rm N-I}| = 1 \text{ K}$. However, in the N phase with negative $\Delta\varepsilon$, the director tends to be perpendicular to the field direction (z axis), and the field quenches director fluctuations deviating from the *xy* plane (i.e. the plane orthogonal to *E*). Thus, the field induces, in general, biaxial ordering and, accordingly, in the LdG approach the free energy density *F* must be expanded in powers of the tensor order parameter $Q_{\alpha\beta}$ involving two scalar order parameters

$$F = -\frac{\varepsilon_0}{2}\Delta\varepsilon_{\alpha}E_{\alpha}E_{\beta}Q_{\alpha\beta} + \frac{1}{2}A'TrQ^2 + \frac{1}{3}B'TrQ^3 + \frac{1}{4}C'Tr(Q^2)^2, \qquad (3)$$

where Q is the tensor order parameter, $A' = a'(T - T^*)$, B', C' are the Landau coefficients, and T^* the lowest supercooling limit of the isotropic phase. The tensor order parameter is defined as

$$Q_{\alpha\beta} = \begin{pmatrix} -(x+y)/2 & 0 & 0\\ 0 & -(x+y)/2 & 0\\ 0 & 0 & x \end{pmatrix},$$
(4)

where x = 2/3S, and y is the biaxial order parameter which distinguishes between the two directions orthogonal to the director.

The symmetry breaking induced by the field turns the N–I phase transitions into a biaxial nematic-paranematic transition, N_B-N_U , with a transition temperature, T_{NP} , dependent on the field intensity [17]. The calculated phase diagram using this model is shown in Fig. 17 of ref. 17, where a tricritical point is apparent that corresponds to a critical field above which the first order N_B-N_U transition becomes second order. The dependence of T_{NP} on E can be expressed analytically only when the transition is second order. At such high fields, $\Delta T_{\rm NP}(E) = T_{\rm NP}(E) - T_{\rm NI}$ (where $T_{\rm NI}$ is the field-free N–I transition temperature) is found to depend both on E as well as E^2 [18]. However, at lower fields, the first order transition temperature can only be calculated numerically and $\Delta T_{\rm NP}(E)$ has a nearly quadratic dependence on E. According to these considerations, the N-I phase transition detected in our experiments should theoretically refer to the NB-NU⁻ transition predicted by the LdG model of conventional nematics. In this respect, we should consider the Nu⁻ paranematic phase to be an essentially isotropic phase with negligibly small orientational order of the long molecular axes normal to the field direction and a random distribution of the of azimuthal angles of the molecules in the plane perpendicular to the field. Therefore, in the geometry of our experiment (X-ray beam parallel to E), the resulting diffraction pattern is practically indistinguishable from that of the isotropic phase.

Very few experimental papers dealing with the effects of *E*-fields on N LCs with negative dielectric anisotropy exist in the literature. One noteworthy example relevant to our findings is ref. [19], reporting an experimental high *E*-field phase diagram of a N LC with a large negative dielectric anisotropy. In that paper, a maximum shift $\Delta T_{\rm NP}$ of 0.3 K is measured with an *E*-field as high as 17 V μ m⁻¹ and, differing from the prediction of the LdG theory, $\Delta T_{\rm NP}$ is found to vary linearly with the field. While our results are in qualitative agreement with the reported linear dependence on *E* (at least for higher fields), two major differences are apparent: (i) the sign of $\Delta T_{\rm NI}$ is opposite, i.e. we measure a reduction of the transition temperature with increasing field instead of the increase predicted by theory and



confirmed by experiment; (ii) the absolute value of the $\Delta T_{\rm NI}$ shift exhibited by our BCM is much larger than that found in conventional LCs having comparable dielectric anisotropy [19].

We also investigate the mesomorphic behavior of a LC polymer based on a bent-core monomer founding that the low tendency of this polymeric material to crystallize makes it possible to supercool the N_{cyb} phase down to room temperature (RT), paving the way for a glassy phase in which the polar order is frozen at RT. We performed repolarization current measurements to check for the presence of a ferroelectric-like response: these measuremets underline two peaks, one per half cycle of the input wave voltage, that clearly emerge (with opposite sign) from the linear ohmic background generated by the ionic flow, delayed with respect to the zero-crossing point of the voltage waveform. These peaks are consistent with a ferroelectric-like switching, generated by the reversal of a macroscopic electric polarization P having a lifetime longer than the half-period of the voltage waveform [20]. A similar behavior was observed with V_{pp} voltages as low as 30 V, that is, with E = 0.5 V μ m-1. Although in principle the observed peaks could originate from undesired effects such as sample impurities or surface effects, the observation that the peaks disappear in the isotropic phase provides strong evidence against such spurious contributions. Accordingly, by integrating the current peak and dividing by twice the electrode area we estimated the intensity of the polarization to be $P = 0.49 \pm 0.04 \ \mu C \ cm^2$ at T = 216 °C and $P = 0.85 \pm$ 0.07 μ C cm⁻² at T = 248 °C. These values are about one order of magnitude larger than those measured in the N_{cyb} phase of the compound and other oxadiazole-based low molecular weight BCMs ($P \le 0.10 \ \mu C \ cm^{-2}$ upon application of an electric field of a few V μm^{-1} ¹) [21,22], as well as in the polar Sm phases of different bent-core LC polymers (0.10-0.50 μ C cm⁻²) [23,24,25,26]. However, these latter compounds either did not exhibit any switching response [24,25] or instead required a significantly larger field ($\geq 10 \text{ V} \mu \text{m}^{-1}$) to reverse the polarization direction [23,26].

4 Conclusion

Several studies have shown how the nonlinear shape of BCMs leads to a N phase which is drastically different from the classical N phase of calamitic liquid crystals. A careful analysis of XRD data, in agreement with other recent theoretical and experimental works, clearly point to a cluster N phase, namely, a N_{cyb} phase, characterized by short range correlation fluctuations of positional (layered) and orientational (biaxial) order. In contrast to calamitic nematics, BCM cybotaxis is not a pretransition phenomenon. Rather, it should be considered as a new type of masophase, characteristic of BCMs throughout their entire N range, even when no underlying Sm phase occurs. This microscopic structure explains many unconventional macroscopic properties observed in BCM nematics. In particular, it can explain the extraordinary sensitivity of these materials to magnetic and electric fields, which leads to unexpectedly large modifications of the phase diagram in presence of relatively low external fields.

An extraordinary field-induced shift of the N–I phase transition is found, which has neither any experimental counterpart in conventional calamitic LCs, nor can be explained in terms of the presently available theories. We believe that this effect is strictly connected to the enhanced sensitivity of the N phase of BCMs to external fields which follows from the cybotactic nature of the phase. The phase diagram points out the existence of exotic phase transitions driven by either the *E*-field or temperature along specific paths in the (T, E)



space. In particular, the field-induced transition from the N_{CybC} to the N_{CybA} phase (at constant *T*) represents a breakthrough in the interpretation of previous XRD experimental results, results that have generated conflicting interpretations over recent years [16,22].

Beyond its fundamental relevance, the exceptional sensitivity of this state of matter is important from a practical point of view: when working with BCMs, external fields cannot be regarded as a mere tool to control the alignment of the molecular director(s), but their effect on the thermodynamic properties of the materials must always be considered in the framework of a two-dimensional, field strength-temperature phase diagram.

Finally, we provide the first experimental evidence of a ferroelectric-like switching response in the N_{cyb} phase of an LC polymer based on a bent-core monomer that is strongly supported by the comparative repolarization current measurements in the nematic and isotropic phases. The enhanced polarization of this compound is to be attributed to the polymeric nature of the material, that is, to the effects of intrachain bonds that strengthen the dipolar orientational correlation among the cybotactic clusters. Once definitely confirmed, the large polarization value and the relatively low switching field of this material (due to the rather fluid nature of the N phase compared to the more solid-like Sm phases) would open new perspectives for innovative applications in the fields of polymeric ferroelectric devices.

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