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Dielectric study of the liquid crystalline dimer α,ω-bis(4′-cyanobiphenyl-4-yloxy)decane

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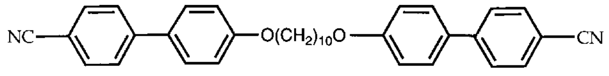
The dielectric properties of a nematogenic dimer α,ω-bis(4′-cyanobiphenyl-4-yloxy)decane in the nematic and isotropic phases have been investigated in the frequency range between 100 Hz and 13 MHz. It was found that the compound is characterized by a positive dielectric anisotropy. The dielectric constant in the nematic phase is lower than that in the isotropic phase, which suggests variation in the conformational distribution of the dimer after the phase transition. Only one relaxation process, both in the nematic and isotropic phases, has been observed in the frequency range used: the relaxation frequency has been found to take values between 2 and 4 MHz, depending on the temperature.

1. Introduction

In recent years, compounds formed with a rigid mesogen–flexible spacer–rigid mesogen sequence have attracted considerable attention by research workers. Such compounds are called liquid crystalline dimers or twins. In many papers, twins comprising two calamitic units connected via their terminal chains have been reported [1–10]. This class of mesogens is very interesting because they may act as model compounds for semi-flexible main chain and side group liquid crystalline polymers. They are also simple model systems which allow us to investigate the effect of the structure of the flexible spacer on the formation of the liquid crystalline phases. Moreover, liquid crystalline dimers possess quite different properties in comparison with conventional low molecular mass mesogens.

It is well known that dielectric studies of liquid crystalline materials are a valuable source of information on molecular arrangement, molecular dynamics and specific intermolecular interactions both in the mesomorphic and isotropic phases. Therefore the dielectric properties of many liquid crystal materials have been investigated both experimentally [11] and theoretically [12–15]. However, despite the fairly extensive literature available on the permittivity of low molecular mass liquid crystal materials and liquid crystalline polymers, there are only few reports relating to dielectric measurements on liquid crystalline dimers [7, 10].

In this work we have studied the temperature and frequency dependence of the dielectric constant for α,ω-bis(4′-cyanobiphenyl-4-yloxy)decane (1) in order to obtain more information about the dielectric behaviour of liquid crystalline materials taking a position between monomers and polymers.



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2. Experimental

The liquid crystalline dimer α,ω-bis(4′-cyanobiphenyl-4-yloxy)decane (BCBOD) was synthesized by the procedure described in [1], i.e. by alkylation of 4′-cyano-4-hydroxybiphenyl with 1,10-dibromodecane (acetone, K_2CO_3). The product was purified by column chromatography (SiO_2, $CHCl_3$); the structure was confirmed by IR and NMR spectroscopy.

The examination of the mesophase type was carried out by polarizing optical microscopy—Leitz Orthoplan equipped with a Mettler hot stage FP82. The observations confirmed a mesophase texture attributable to the nematic phase. Additionally, the DSC scans obtained using a Perkin-Elmer DSC-2 Differential Scanning Calorimeter showed that the value of the clearing point

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was in agreement with that in the literature [1]. The nematic–isotropic phase transition occurred at 182°C, and the melting point at 163°C; recrystallization occurred on cooling at variable temperatures dependent on cooling rate. At 5°C min^{-1} this value was 129°C.

For the dielectric measurements, a Hewlett-Packard 4192A self-balancing bridge controlled by a computer was used. The measurements were carried out in the frequency range from 100 Hz to 13 MHz at different temperatures both for the nematic and isotropic phases. The capacitor used in the dielectric experiments was constructed of two gold-coated glass plates separated by 36 µm spacers. The active area of the capacitor was 78 mm^2. The capacitor was filled with the test substance simply by placing it on one hot electrode and then squeezing it with the other one. Before starting the measurement of the frequency characteristics, the capacitor containing the dimer was heated to 200°C and cooled down to stabilize the thickness of the spacers. A magnetic field of about 1 T was used in order to orient the dimer molecules homeotropically with respect to the electrodes.

The imaginary part of the electric permittivity was fitted with Cole–Cole functions [16] in combination with the loss function describing the conductivity at low frequencies.

3. Results

Figure 1 presents the static electric permittivity ($f = 100$ kHz) for BCBOD as a function of temperature in the nematic and isotropic phases. The measurements of ε_s in the nematic phase were made without the external orienting magnetic field and also for the case when the magnetic field was parallel to the measuring electric field. In both cases a decrease of the dielectric constant with respect to that obtained in the isotropic phase was observed. The dependence of ε_s on the magnetic induction **B** at three different temperatures in the nematic phase is shown in figure 2. It is seen, that with increase in the magnetic field intensity, the dielectric constant increases after crossing the threshold value of **B**, and, practically, at $\mathbf{B} = 0.6$ T reaches saturation.

Figures 3 and 4 demonstrate, respectively, the real and imaginary parts of the electric permittivity as a function of frequency for BCBOD in the isotropic ($T = 192$°C) and nematic ($T = 155$°C, $\mathbf{B} = 0$, $\mathbf{B}\|\mathbf{E}$) phases. The solid lines in figure 4 present the dielectric spectra after elimination of the conductivity contributions (dashed lines). A three-dimensional plot of the dielectric loss versus frequency and temperature for the cases $\mathbf{B} = 0$ and $\mathbf{B}\|\mathbf{E}$ is shown in figure 5, while figures 6 and 7 present the values of the dielectric increment, $\varepsilon_s - \varepsilon_\infty$ and the relaxation time, τ_R as a function of temperature, respectively.

4. Discussion

Each of the mesogenic parts of BCBOD exhibits a considerable dipole moment caused by the presence of the strongly polar terminal –CN group ($\mu_{CN} = 4$ D). The groups –COC ($\mu_{COC} = 1.25$ D) in the spacer also give contributions to the dipole moment. However, for the molecule of BCBOD treated as a whole, the resultant dipole moment should be equal to zero, if one assumes

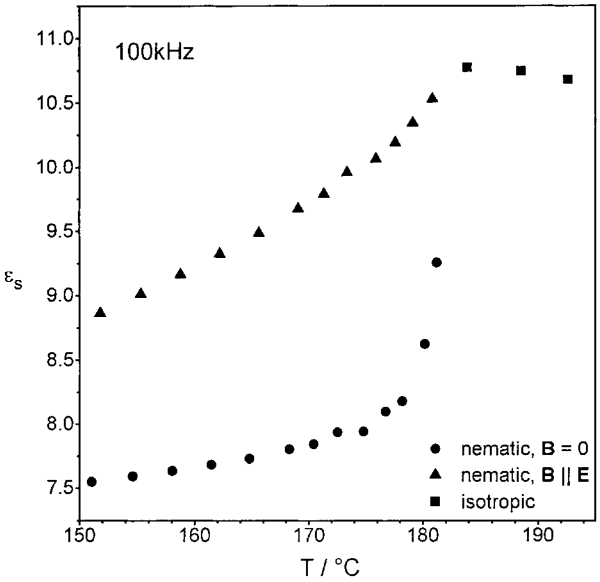

Figure 1. Static electric permittivity as a function of temperature in the nematic and isotropic phases of BCBOD.

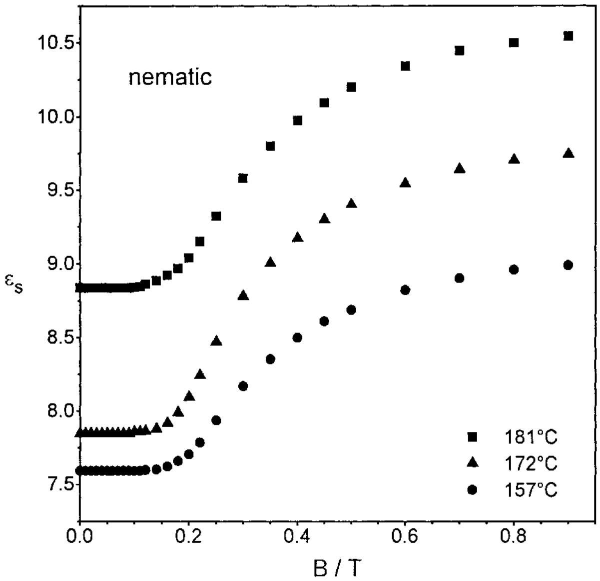

Figure 2. Change of static electric permittivity in the applied magnetic field for BCBOD in the nematic phase.

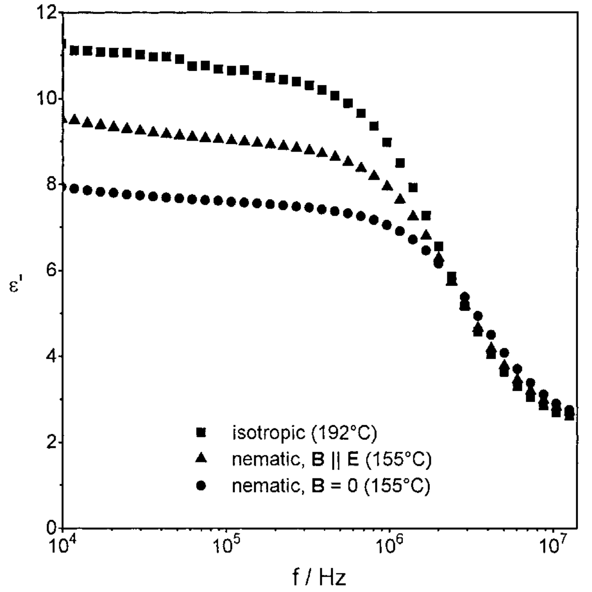

Figure 3. Real part of the electric permittivity as a function of frequency for BCBOD in the nematic and isotropic phases.

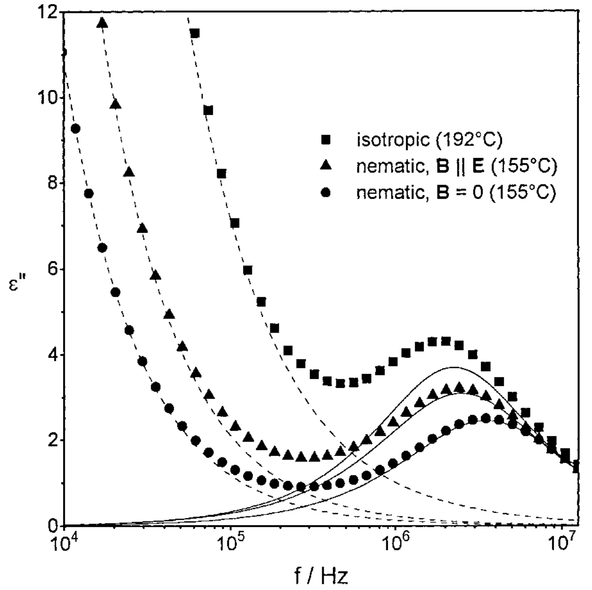

Figure 4. Imaginary part of the electric permittivity as a function of frequency for BCBOD in the nematic and isotropic phases (solid lines—dielectric absorption; dashed lines—conductivity contribution).

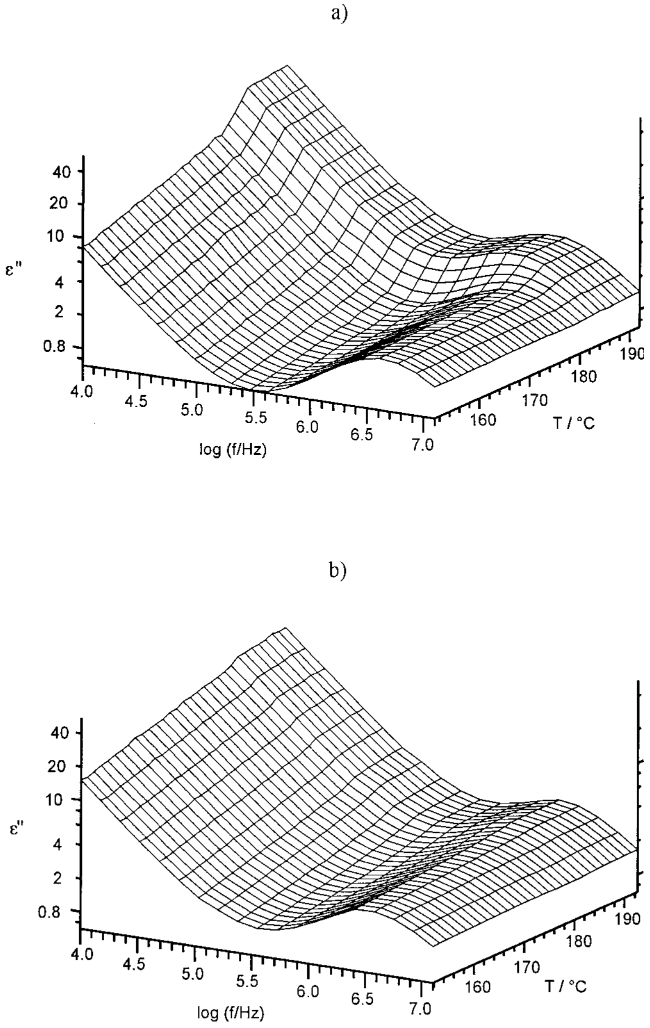

Figure 5. Three-demensional plot of ε'' versus frequency and temperature without the magnetic field (*a*) and for **E**|| **B** (*b*) for BCBOD.

a planar *trans*-conformation of the oxyalkane spacer. Then, the mesogenic units of the dimer with an even number of methylene groups adopt a mutually parallel arrangement [17, 18] and their dipole moments are reduced. In such a case the dielectric constant should be equal to $\varepsilon_\infty \approx n^2$ ($n \approx 1.6$ for typical liquid crystalline materials). Meanwhile, from the results presented in figure 1, it is seen that the dielectric constant in the isotropic phase for BCBOD is about 10.7 (depending on temperature), which corresponds, on a rough estimation, to the effective dipole moment $\mu \approx 6$ D. This value is in good agreement with $\mu \approx 6.76$ D obtained previously, on the basis of dielectric measurements for BCBOD dissolved in 1,4-dioxane, by Furuya *et al.* [7]. They explained this result by suggesting that the flexible spacer $-O(CH_2)_{10}O-$ carrying the mesogenic groups assumes a random-coil conformation in solution. It is also reasonable to assume that for pure BCBOD in the neat isotropic phase, the spacer is allowed to take up a variety of possible conformations which then determine that the relative orientation of the mesogenic rigid cores is not parallel, leading to the large value of ε_S. When this mesogenic compound is brought into the nematic phase, ε_S decreases, which means that the dimer molecules adopt a more extended form. However, the system must still be treated as a multicomponent nematogenic

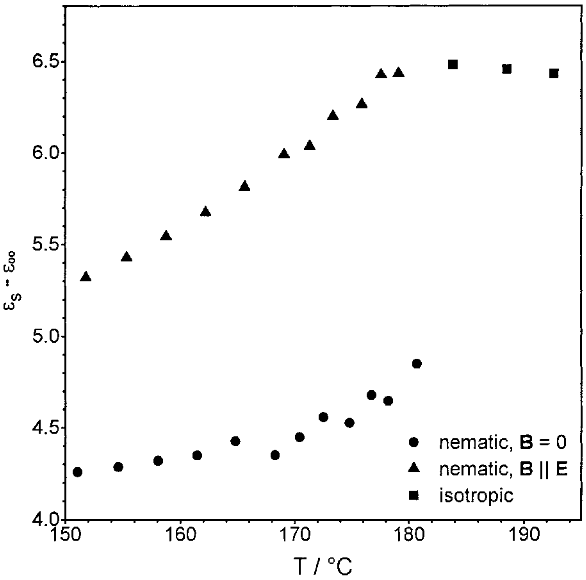

Figure 6. Dielectric strength versus temperature for BCBOD in the nematic and isotropic phases.

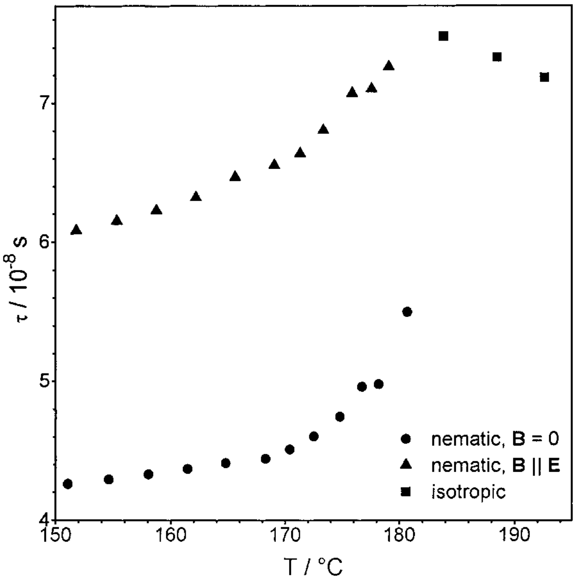

Figure 7. Relaxation time versus temperature for BCBOD in the nematic and isotropic phases.

mixture composed of various conformers, except those strictly incompatible with the nematic arrangement.

If there is no magnetic field applied to the sample, surface interactions make the molecules align mostly planar (not necessarily homogeneously) to the electrodes. Because the layer of BCBOD in our experiment is relatively thin ($d = 36\,\mu$m), we are able to assume, that the dielectric constant measured for $\mathbf{B} = 0$ corresponds approximately to $\varepsilon_\perp$. In the magnetic field the mesogenic parts of the dimer molecules proceed to align parallel to **B** because of the presence of the aromatic rings. It had been found by NMR measurements that the order parameter $\langle P_2 \rangle$ of BCBOD at T_{NI} is equal to 0.5 [2]. However, Tsvetkov *et al.* [18] estimated the order parameter from birefringence measurements (the orientation was achieved by rubbing the glass plates in the desired direction) and obtained values of $\langle P_2 \rangle$ between 0.52 and 0.66 at temperatures varying from 10 to 63°C below T_{NI}. This leads to the conclusion that the BCBOD molecules are able to attain a very high degree of long range orientational order. Therefore, the dielectric constant measured in the case of $\mathbf{B} \| \mathbf{E}$ can be interpreted as $\varepsilon_\|$. From the results presented in figures 1 and 2, it is seen that after applying the magnetic field the dielectric constant rises, which means that the dielectric anisotropy $\Delta\varepsilon$ is positive. This seems to be a very unexpected result, keeping in mind the molecular structure of BCBOD: at first sight one would assume that with increase in the orientational order, the resultant dipole moment should decrease and lead to diminishing values of ε_s as well. However, Tsvetkov *et al.* [18] also found a positive $\Delta\varepsilon$ for BCBOD from measurements of the threshold voltage of the homologous series of α,ω-bis(4′-cyanobiphenyl-4-yloxy)alkanes. They also ascertained that for both even and odd members of the series, increase in the carbon atom numbers leads, on average, to an increase in the $\Delta\varepsilon$ value, while $\langle P_2 \rangle$ remains almost constant. This indicates that the intramolecular orientational-polar order [18], which determines the dielectric properties of liquid crystalline dimers, can be very different from the long range intermolecular orientational order and depends on the spacer length. Since for BCBOD molecules the oxyalkane chain is relatively long, it is possible to suggest, that the time necessary for their orientation in the magnetic field is longer than the time required for the chain conformation changes, which signifies that the assumption of kinetic flexibility [19] should be taken into account. This means that the dimeric molecules rotate in the magnetic field, but their behaviour is determined by their kinetically flexible chains, i.e. the kinetic units oriented in the field are not the molecules as a whole, but their mesogenic parts. A similar effect had been previously observed for some main chain polymers [20, 21]. The kinetic flexibility of the long spacer causes the mutual correlation in the orientation of the polar mesogenic units of the BCBOD molecule to be relatively weak and gives a dipole moment value $\mu \neq 0$ with $\mu_\| > \mu_\perp$.

In the dielectric spectrum of BCBOD only one relaxation band with a maximum at the frequency of 2–4 MHz, depending on the temperature, is observed (figures 3 and 4). Similarly, Dunmur *et al.* [22] found no relaxation in the frequency region below 10^6 MHz for even members of the α,ω-bis(4′-cyanobiphenyl-4-yloxy)-alkane series. However, Hohmuth *et al.* [10] have reported two relaxation processes for dimeric liquid crystalline siloxanes: a low frequency relaxation process at a few kHz (observed only in the isotropic phase and the liquid crystalline phase as it formed) and a second relaxation process appearing only in the smectic phase. One cannot, of course, exclude the possibility that a relaxation for BCBOD occurs at frequencies lower than 10 kHz, but then ε_s in the nematic state should be greater than it is, which seems not to be very probable.

The values of the relaxation strength, $\varepsilon_s - \varepsilon_\infty$ and of the relaxation time, τ_R of the process observed for BCBOD (figures 6 and 7) in the nematic phase are lower than in the isotropic phase and diminish with decreasing temperature. However, for the case $\mathbf{B} \| \mathbf{E}$, both these values are different (greater) than for $\mathbf{B} = 0$. These observations are very difficult to explain and could suggest that the relaxation observed for BCBOD in the dielectric spectrum is a result of the overlapping of contributions from several relaxation processes related to various molecular motions (rotational, librational, precessional, etc.) However, the low value of the parameter α occurring in the Cole–Cole equation [16], which characterizes the distribution of the relaxation times, seems to contradict this statement. In order to resolve this problem, further investigations of dimeric liquid crystals with different molecular structures are necessary.

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References

[1] Emsley, J. W., Luckhurst, G. R., Shilstone, G. N., and Sage, I., 1984, *Mol. Cryst. liq. Cryst. Lett.*, **102**, 223.

[2] Emsley, J. W., Luckhurst, G. R., and Shilstone, G. N., 1984, *Mol. Phys.*, **53**, 1023.

[3] Emsley, J. W., Heaton, N. J., Luckhurst, G. R., and Shilstone, G. N., 1988, *Mol. Phys.*, **64**, 377.

[4] Watanabe, J., Komura, H., and Niori, T., 1993, *Liq. Cryst.*, **13**, 455.

[5] Barnes, P. J., Douglass, A. G., Heeks, S. K., and Luckhurst, G. R., 1993, *Liq. Cryst.*, **13**, 603.

[6] Hardouin, F., Richard, H., and Achard, M. F., 1993, *Liq. Cryst.*, **14**, 971.

[7] Furuya, H., Okamoto, S., Abe, A., Petekidis, G., and Fytas, G., 1995, *J. phys. Chem.*, **99**, 6483.

[8] Andersch, J., and Tschierske, C., 1996, *Liq. Cryst.*, **21**, 51.

[9] Rozhanskii, I. L., Tomita, I., and Endo, T., 1996, *Liq. Cryst.*, **21**, 631.

[10] Hohmuth, A., Schiewe, B., Heinemann, S., and Kresse, H., 1997, *Liq. Cryst.*, **22**, 211.

[11] For a summary see: (*a*) de Jeu W. H., 1980, *Physical Properties of Liquid Crystalline Materials* (Gordon and Breach), Chap. 5; (*b*) Blinov, L. M., 1983, *Electro-optical and Magneto-optical Properties of Liquid Crystals* (J. Wiley), pp. 49–68; (*c*) Kresse, H., 1983, *Advances in Liquid Crystals*, Vol. 6, edited by G. H. Brown (Academic Press), pp. 109–172; (*d*) Williams, G., 1994, *The Molecular Dynamics of Liquid Crystals*, edited by G. R. Luckhurst and C. A. Veracini (Kluwer Academic), Chap. 17.

[12] Martin, A. J., Meier, G., and Saupe, A., 1971, *Symp. Faraday Soc.*, **5**, 119.

[13] Nordio, P. L., Rigatti, R., and Segre, U., 1973, *Mol. Phys.*, **25**, 129.

[14] Araki, K., Attard, G. S., Kozak, A., Williams, G., Gray, G. W., Lacey, D., and Nestor, G., 1988, *J. chem. Soc., Faraday Trans. 2*, **84**, 1067.

[15] Kozak, A., and Mościcki, J., 1992, *Liq. Cryst.*, **12**, 377.

[16] Cole, K. S., and Cole, R. H., 1949, *J. chem. Phys.*, **9**, 341.

[17] Ferrarini, A., Luckhurst, G. R., Nordio, P. L., and Roskilly, S. J., 1993, *Chem. Phys. Lett.*, **214**, 409.

[18] Tsvetkov, N. V., Tsvetkov, V. N., Zuev, V. V., and Didenko, S. A., 1995, *Mol. Cryst. liq. Cryst.*, **265**, 487.

[19] Tsvetkov, V. N., Rjumtsev, E. I., and Shtennikova, I. N., 1978, in *Liquid Crystalline Order in Polymers*, edited by A. Blumstein (Academic Press), Chap. 2.

[20] Tsvetkov, V. N., and Frisman, E. V., 1944, *Acta Physicochim. URSS*, **18**, 358.

[21] Champion, J. W., Dessen, R. A., and Meeten, G. H., *Polymer*, **15**, 301.

[22] Dunmur, D. A., La Porta, F., and Luckhurst, G. R., 1997, European Conference on Liquid Crystals, Abstracts, p. 57.