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Surface-induced pretransitional order in the isotropic phase near the isotropic–nematic phase transition

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We have studied the formation of a nematic layer in the isotropic phase of members of the homologous series of alkylcyanobiphenyl liquid crystals (*n*CB, $n = 5$–12) near a polyamide-coated glass surface. From the temperature dependence near the isotropic–nematic transition of the standard ellipsometric quantity Δ, which is directly related to the residual birefringence, the wetting behaviour of the nematic layer was investigated using a high precision rotating analyser ellipsometer. In contrast to the results of Chen *et al.*, who observed a wetting transition for *n*CB-DMOAP-glass systems, our results indicate that for the *n*CB-polyamide-glass configurations the wetting is always partial.

1. Introduction

The behaviour of liquid crystals close to solid interfaces is of special importance with regard to applications in display technology. Various physico-chemical surface treatments can induce specific structures near the substrate in the diverse mesophases. The orienting properties are then due to anisotropic forces exerted by the substrate. For example, it is well known that polymer-coated surfaces can induce nematic ordering near the surface, while the bulk liquid crystal is still in the isotropic phase. Birefringence measurements [1, 2] and experiments using evanescent-wave ellipsometry [3, 4] showed a strong increase in this induced pretransitional order in the isotropic phase when approaching the isotropic–nematic transition temperature T_c. Theoretical discussions [5–7] predict partial or complete wetting of the isotropic phase by a nematic film, depending on the relative strength of the intermolecular and the molecule–surface interactions. We report on a systematic study of the surface-induced pretransitional order in the isotropic phase of members of the homologous series of alkylcyanobiphenyl liquid crystals (*n*CB, $n = 5$–12), in contact with a polyamide coated glass surface, using a transmission ellipsometric technique [8]. The results are analysed using a theory [5, 7] based on the Landau–de Gennes approach [9] for the isotropic–nematic transition.

2. Experimental

The experiments were performed using sample cells obtained from Linkam Scientific Instruments (UK). They consist of two polymer-treated glass plates (1 cm^2), with glass fibre spacers scattered within the cell to ensure constant gap thickness (typical 5 µm or 7·5 µm). The alignment layer is formed of rubbed polyamide, a treatment which is known to induce *planar* alignment. We checked the quality of this alignment in the nematic phase (for the homologues 5CB to 9CB), by investigating the transmission of linearly polarized light, which is transformed to elliptically polarized light, because of the birefringence of the sample. A straightforward calculation (via the Jones-matrix formulation) shows that the variation of the ellipticity angle ε of the transmitted light with the angle α between the polarization of the incident light and the director is given by:

$$\varepsilon = \arctan \times \left(\frac{\cos^2(\chi_M) - \sin(2\alpha - 2\chi_M)\sin(2\alpha)\sin^2(\delta/2)}{\cos^2(\chi_m) - \sin(2\alpha - 2\chi_m)\sin(2\alpha)\sin^2(\delta/2)}\right)^{1/2} \qquad (1)$$

where δ is the phase difference between the ordinary and extraordinary waves and

$$\chi_M = \frac{1}{2}\arctan\left(\frac{\sin(4\alpha)\sin^2(\delta/2)}{1 - 2\sin^2(2\alpha)\sin^2(\delta/2)}\right), \quad \chi_m = 90^\circ + \chi_m.$$

Results at various temperatures in the nematic phase for the different samples are shown in figure 1 and the agreement with the theoretical curves of equation (1) indicate an alignment of excellent quality. The cells were filled by capillary forces under reduced pressure and then placed in a two stage oven, allowing temperature control within 0·002 K. The liquid crystals were obtained

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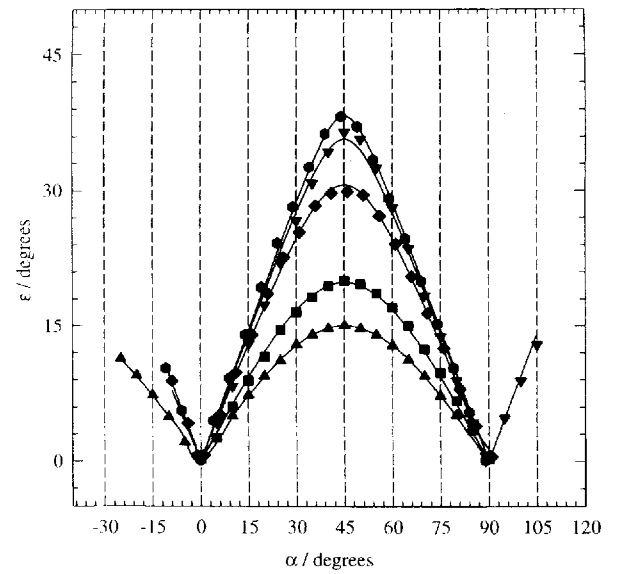

Figure 1. Ellipticity angle ε of the transmitted light as a function of the angle α between the polarization of the incident light and the director. Solid lines are theoretical fits, according to equation (1); 5CB at 34·5°C (■), 6CB at 28·0°C (▲), 7CB at 37·0°C (●), 8CB at 36·0°C (▼), 9CB at 49·0°C (◆).

from Merck Ltd (UK). For 5CB to 9CB we studied the induced ordering in the isotropic phase near the isotropic–nematic transition; for 10CB, 11CB and 12CB, which have no nematic phase, we investigated the isotropic–smectic A transition.

The anisotropic boundary layer was investigated using a high precision rotating analyser ellipsometer (figure 2) in transmission mode. In earlier ellipsometric experiments [3, 4] on homeotropic aligned samples, a (reflection) evanescent-wave technique was used to measure Δ as a function of the angle of incidence θ near the critical angle θ_c, because this method is very sensitive to the optical properties of the interfacial region. However, for the planar aligned samples we were studying, the most obvious set-up is one with the incident laser light perpendicular to the optical axis of the sample (and hence $\theta = 90°$), because in this configuration the measured phase difference and the accuracy of the results are maximal. In addition this technique is interesting because of its simplicity for performing the experiments and analysing the data. The dynamic photometric ellipsometer consists of a 3 mW He–Ne Laser and a polarizing prism in the transmitter unit, and a polarizing prism connected to a stepper motor in the receiver unit. Used in transmission mode the ratio of the complex transmission coefficients t_p and t_s, associated with light polarized parallel (p) and perpendicular (s) to the plane of incidence, is determined by Fourier analysis of the modulated detector signal. Using the standard ellipsometric quantities Ψ and Δ, this ratio is expressed as:

$$\frac{t_p}{t_s} = \tan \Psi \exp i\Delta.$$

The intrinsic measuring accuracy of the ellipsometer is $4{\cdot}10^{-5}$ rad and $7{\cdot}10^{-5}$ rad for Ψ and Δ, respectively. Temperature control, driving of the stepper motor and monitoring the detector signal were controlled by two linked computers (figure 3).

The samples which show a nematic mesophase (5CB to 9CB) were oriented in the nematic phase with the optical axis parallel to the plane of incidence. The polarization of the incident beam was then oriented at an angle of 45° to the optical axis, so that the ellipticity angle of the transmitted light was maximal. In this situation, the phase difference Δ between p- and s-waves, equals the phase difference δ between the ordinary and the extraordinary wave, which can be expressed as:

$$\delta = \frac{2\pi}{\lambda} \int_0^h \Delta n(z) \mathrm{d}z$$

where λ is the wavelength of the He–Ne laser light, $\Delta n = n_e - n_o$ is the difference between the indices of refraction for the ordinary and extraordinary wave, h is the thickness of the birefringent layer and z extends into the bulk of the liquid crystal.

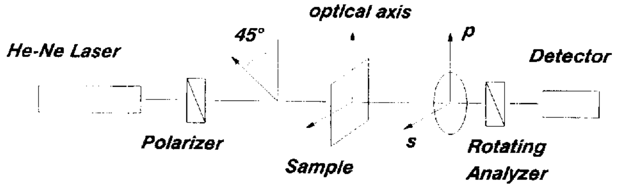

Figure 2. Optical path of the Rotating Analyser Ellipsometer.

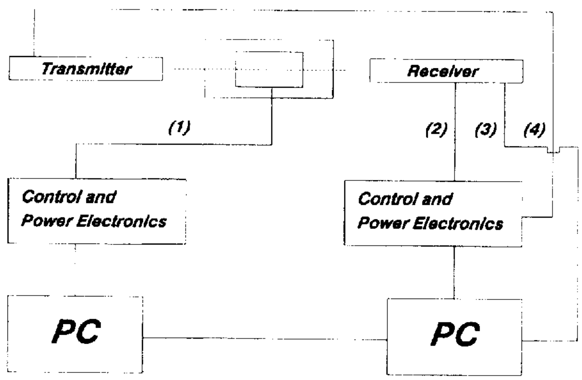

Figure 3. Block diagram of the overall experimental set-up; temperature control of the sample (1), driving of the stepper motor (2), detector signal (3).

3. Results and discussion

For each sample the (I–N, S_A) bulk transition temperature T_c was identified within 0·05°C through the sudden increase in the intensity of unpolarized scattered light. The measured values for T_c are listed in the table. A temperature scan was done in the range $T_c + 1{\cdot}5$°C down to T_c. The scanning rate had no influence on the results. Typical runs are shown in figure 4 for 5CB to 8CB. The data for Δ show a significant increase in the birefringence on approaching T_c, indicating the formation of a nematic boundary layer. It can be shown [10] that:

$$\delta = \delta_0 \int_0^h S(z)\mathrm{d}z$$

where $S(z)$ is the order parameter profile in the nematic layer (z-axis perpendicular to the surface). Tarczon and Miyano [5] derived an analytical expression of $S(z)$ based on the Landau–de Gennes expansion of the free energy. This leads to:

$$\delta = \delta_0 \xi_0 \left(\frac{2aT^*}{c}\right)^{1/2} \ln\left(\frac{P(T,S_0) + \frac{1}{2}c^{1/2}S_0}{P(T,S_0) - \frac{1}{2}c^{1/2}S_0}\right) \qquad (2)$$

where

$$P(T,S_0) = \left[\frac{1}{2}a(T-T_c) + \frac{1}{4}c(S_0 - S_c)^2\right]^{1/2} + \left[\frac{1}{2}a(T-T_c) + \frac{1}{4}cS_c^2\right]^{1/2}$$

with $S_0 = S(z=0)$, the order parameter at the wall, $S_c = S(T_c)$, the order parameter at the clearing temperature and T^*, a, c are the Landau expansion parameters; ξ_0 is the Landau correlation length. Depending on the ratio of S_0 and S_c, the residual birefringence shows a divergence or remains finite: if $S_0/S_c > 1$, the optical phase shift diverges logarithmically at T_c (complete wetting), but if $S_0/S_c < 1$, the signal approaches a finite value (partial wetting).

Measured values for the transition temperature T_c and S_0 values obtained with equation (2).

nCB	T_c/°C	S_c [12]	S_0	S_c/S_0
5CB	35·04	0·27	0·25	0·91
6CB	29·03	0·25	0·23	0·92
7CB	42·55	0·27	0·24	0·90
8CB	40·43	0·29	0·27	0·93
9CB	50·00	0·29	0·19	0·63
10CB	51·16	0·54	—	—
11CB	57·28	0·50	—	—
12CB	58·39	0·61	—	—

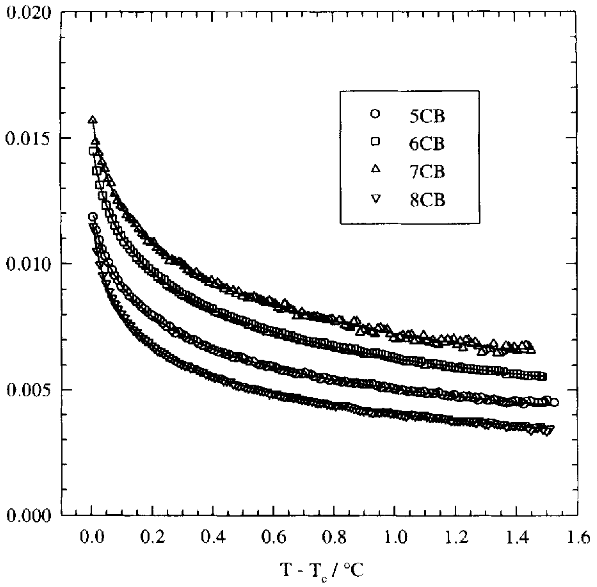

Figure 4. The phase difference $\Delta(T)$ in the isotropic phase for 5CB, 6CB, 7CB and 8CB. Solid lines are theoretical fits, using equation (1).

From figure 4 it is clear that for 5CB to 8CB the pretransitional behaviour looks similar and that the birefringence approaches a finite value. Using known values for δ_0 [11] and the Landau parameters [12] for the different compounds, the experimental data have been fitted to equation (1) via a least squares fitting procedure, providing a numerical value for S_0 (see the table). Besides S_0, two variables were taken as adjustable parameters in the fits. Firstly, the results showed a small (temperature independent) background, probably due to some birefringence of the cell and the aligning polymer. This background birefringence was found to depend on the relative position of the laser beam with respect to the sample cell and was taken as an adjustable parameter in the fits, but as can be readily seen from figure 4, this had no influence on the temperature dependence of the residual birefringence. The resulting value for this background was around 10^{-3} rad. Secondly, the quality of the fits was improved by taking the Landau correlation length ξ_0 as a free parameter in the fits. For 6CB and 7CB we found a value of 5 Å, which agrees with literature values [2]; for 5CB and 8CB the correlation length is only 3 Å. Furthermore, S_0 can in general not be assumed to be independent of T over the temperature range being studied here. Sheng [7] calculated the variation of S_0 with T, depending on the Landau expansion parameters and a temperature independent parameter characterizing the substrate potential. However, the quality of our fits could not be improved by including such a variation of the order parameter at the wall. This is not surprising, because the increase in birefringence on approaching T_c

is, although significant, relatively small, indicating a small value for the surface potential and hence a (negligible) small increase in S_0 with decreasing temperature. We found S_0 to have a value between 0·23 and 0·27 for the different samples, resulting in a ratio $S_0/S_c = 0{\cdot}92 \pm 0{\cdot}02$, which is characteristic for partial wetting and an indication that this partial wetting is independent of the compound in the homologous series.

This observed wetting behaviour is in contrast to results of Chen *et al.* [4] who observed a wetting transition for *n*CB compounds in contact with glass surfaces coated with m,m-dimethyl-*n*-octadecyl-3-aminopropyl-trimethoxysilyl chloride (DMOAP) which induces a homeotropic alignment. For 5CB their results indicate partial wetting and for 6CB to 9CB the wetting is complete. They observed in general a more pronounced complete wetting behaviour with increasing *n*. Our results indicate that for the *n*CB-polyamide-glass configurations the wetting is always partial. The change in the liquid crystal–surface interaction, via the changing alkyl chain length, has no influence on the pretransitional behaviour.

For 10CB, 11CB and 12CB, the orientation of the sample in the smectic A phase relative to the polarization of the incident beam was studied in the same way as for the nematics, by searching for the maximum ellipticity angle of the transmitted light. However, changing the polarization angle did not result in a variation of the ellipticity angle like that in figure 1, as expected for well aligned samples. Typical results for the birefringence behaviour of these compounds above T_c are shown in figure 5; they are fundamentally different from those for the nematic samples. It is clear that there is no increase in the birefringence when approaching T_c and this behaviour is independent of the rotation of the sample relative to the polarization of the incident light. It is evident that those effects are related. A possible explanation for this absence of increase in birefringence is the formation of a nematic or smectic layer with a *homeotropic* orientation. We checked this by measuring the transmission at an angle of incidence of 45° instead of normal incidence. Any homeotropic alignment should then result in an increase in birefringence on approaching T_c. However, even in this configuration the measurements did not reveal any systematic pretransitional increase. These results indicate that there is no uniform aligning of the samples. It appears that the polyamide coating on the glass plates is unable to induce a uniform smectic ordering for the samples used.

As can be seen from figures 4 and 5, the temperature dependence of Δ for 9CB is also substantially different from that of the other nematics, resulting in a much lower value for S_0; hence S_0/S_c is only 0·63 (see the table). This small increase in birefringence for 9CB can be related to the relatively small temperature region where 9CB shows the nematic phase; this is only 1·5°C. Although the variation of the ellipticity angle (figure 1) indicated good alignment in the nematic phase, this result suggests that the closeness of the smectic phase influences the pretransitional nematic behaviour.

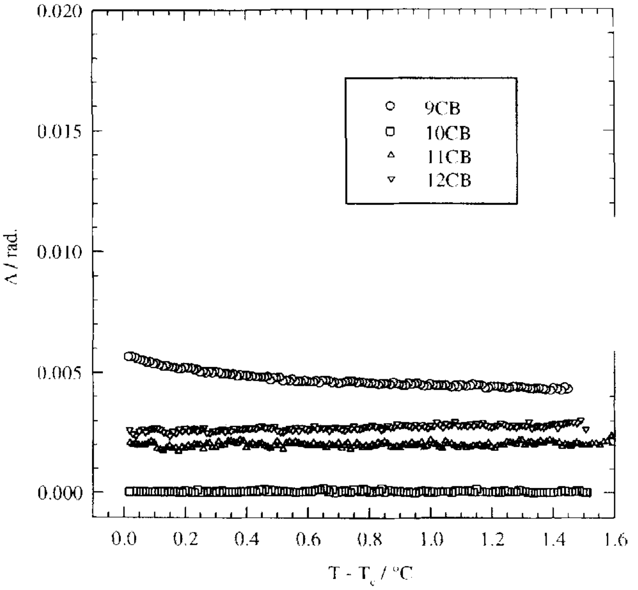

Figure 5. The phase difference $\Delta(T)$ in the isotropic phase for 9CB, 10CB, 11CB and 12CB.

4. Summary and conclusions

In this study we investigated the wetting behaviour of cyanobiphenyl compounds on polyamide-coated glass surfaces. Our results show that for these *n*CB-polyamide-glass configurations, the wetting is always partial. For 5CB to 8CB there is a significant increase in birefringence on approaching the isotropic–nematic transition temperature, but the ratio S_0/S_c is only 0·92 although the aligning ability in the nematic phase appeared to be very good. For 9CB, the pretransitional increase is even less ($S_0/S_c = 0{\cdot}63$). For 10CB, 11CB and 12CB, we studied the isotropic–smectic A transition, but were unable to measure any pretransitional surface order in the isotropic phase of these three compounds. There are several indications that this is caused by smectic phase-related non-uniform alignment.

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