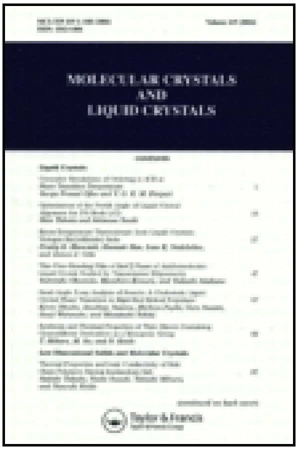

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Torsional Anchoring of 5CB and 5PCH on Various Substrates†

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Using two different methods the surface free energy anisotropies have been determined of both pentyl cyanobiphenyl (5CB) and the corresponding cyclohexane compound (5PCH) on various surfaces. Comparison of the experimental data shows that the use of Freedericksz transition does not yield reliable values. A different method, proposed by the authors and which consists of the determination of the optical birefringence at high electric fields, is shown to yield more consistent results. The experimental values obtained with this method range from 2.5 10^{-5} J/m^2 for 5CB on SiO_x to 10^{-4} J/m^2 for 5CB or 5PCH on polyimide.

INTRODUCTION

The anisotropy of the surface free energy has been determined mainly using the dependence of the Freedericksz threshold on the anchoring strength. The formalism used in the interpretation of such data relies on the surface free energy (anchoring energy) term as defined by Rapini and Papoular[1] i.e.

$$W(\theta) = \frac{1}{2} C \sin^2(\theta - \theta_o), \qquad (1)$$

where θ is the tilt angle induced by an external distortion, θ_o is the original tilt angle at the surface, and C is the relevant anisotropy of the surface free energy.

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Dubois-Violette and de Gennes[2,3] describe theoretically Freedericksz transitions in terms of an extrapolation length which depends on the strength of the anchoring. Later on Motooka et al.[4,5] and Naemura[6] made further analyses of such transitions. More recently Mada[7,8] and Yang[9] presented theoretical contributions on this topic. From these papers it appears that the Freedericksz threshold is rather insensitive to changes in the anchoring energy and moreover its accurate determination is a tedious procedure. In this paper another method is used to determine anchoring energies. This method is based on the fact that, far above the Freedericksz threshold, planar aligned samples still show a residual birefringence due to the presence of transition layers between the wall and the homeotropic bulk of the liquid crystal. The observation of the transition layers is based on the same idea as used to determine excess surface order.[10] This is because in both experiments a minor optical anisotropy is made experimentally accessible by observing it against an (optically) isotropic bulk. Yang[11] describes similar experiments using a magnetic field to align the liquid crystal against the surface anchoring. In the present work an electric field is used instead of a magnetic field and the measurements are carried out at two temperatures for each sample.

The results from both Freedericksz transition and the high-field experiments are presented and discussed below.

THEORETICAL

The torque balance for a bulk liquid crystal can be written as

$$k_{11}\,(1 + k\sin^2\theta)\,\frac{d^2\theta}{dz^2} + k_{11}\,k\sin\theta\cos\theta\left(\frac{d\theta}{dz}\right)^2 + \epsilon_o\Delta\epsilon E^2\sin\theta\cos\theta = 0, \qquad (2)$$

where θ is the tilt angle of the director with respect to the XY plane and $k = (k_{33} - k_{11})/k_{11}$.

Integration of eq. (2) for $0 < z < d/2$ using as a boundary condition $\theta(d/2) = \theta_m$ and $(d\theta/dz)_{d/2} = 0$ leads to the following expression for the minimum free energy of the system:

$$\xi^2(1 + k\sin^2\theta)\left(\frac{d\theta}{dz}\right)^2 + \sin^2\theta - \sin^2\theta_m = 0, \qquad (3)$$

with

$$\xi = (k_{11}/\epsilon_0\Delta\epsilon E^2)^{1/2}.$$

For a surface free energy of the form of eq. (1) the torque balance at the surface becomes:

$$\xi_1^2(1 + k\sin^2\theta_o)\frac{d\theta_o}{dz} + \sin\theta_o\cos\theta_o = 0, \tag{4}$$

where θ_o is the original tilt angle $\theta(z = 0)$ at the surface and $\xi_1 = k_{11}/C$, a correlation length related to the surface torques. Application of eq. (3) at the surface yields:

$$\xi^2(1 + k\sin^2\theta_o)\left(\frac{d\theta_o}{dz}\right)^2 + \sin^2\theta_o - \sin^2\theta_m = 0 \tag{5}$$

Motooka and Fukuhara[4,5] have shown that combination of eqs. (4) and (5) in the limit $\theta_o = \theta_m = 0$, for planar samples, leads to the following expression for the electric Freedericksz threshold E_c:

$$E_c/E_o = \frac{Cd}{\pi k_{11}}\cot\left(\frac{\pi}{z}\frac{E_c}{E_o}\right), \tag{6}$$

where

$$E_0 = \frac{\pi}{d}(k_{11}/\epsilon_0\Delta\epsilon)^{1/2}$$

and is the Freedericksz threshold for infinitely strong anchoring.

Combination of (4) and (5) under the condition that $\theta_m = \pi/2$, which implies $E >> E_c$, leads to

$$\sin\theta_0 = (L - k)^{-1/2}, \tag{7}$$

with

$$L = (\xi^2/\xi_1^2).$$

This boundary condition can be used in the solution of the bulk equation (3). Rearrangement of (3) leads to

$$\xi \frac{d\theta}{dz} = \left(\frac{\cos^2\theta}{1 + k \sin^2\theta}\right)^{1/2} \tag{8}$$

Substitution of eq. (8) in the expression for the birefringence

$$\delta = \frac{2\pi}{\lambda} \Delta n \int_0^{d/2} \cos^2\theta \, dz \tag{9}$$

leads to

$$\delta = \frac{2\pi}{\lambda} \Delta n \xi \int_{\sin\theta_0}^{1} (1 + k \sin^2\theta)^{1/2} \, d \sin\theta, \tag{10}$$

which in combination with (6), leads to the expression for δ for a sample of thickness d given by:

$$\delta = \frac{2\pi}{\lambda} \Delta n \xi \left\{ (k + 1)^{1/2} - \frac{L^{1/2}}{(L - k)} + \frac{1}{k^{1/2}} Ln \left[\frac{(L - k)^{1/2} (k^{1/2} + (k + 1)^{1/2})}{(k^{1/2} + L^{1/2})} \right] \right\} \tag{11}$$

In this equation the influence of the surface is represented by L in which ξ_1 is the C-dependent correlation length. Eq. (11) has been used to calculate C values from experimental measurements of δ as a function of the applied field, and eq. (6) has been used to determine C-values from the experimentally observed Freedericksz thresholds. Although the above theory is exact for the case of an external magnetic field, it is only an approximation for an electric field as used in our experiments. Calculations with the exact equations have been performed too. No significant differences are observed for $C > 2\ 10^{-5}$ J/m^2.

EXPERIMENTAL

We performed our experiments using samples consisting of 3 × 3 cm^2 glass plates with transparent ITO electrodes covered with an orienting layer and joined to form a cell.

For planar samples these layers were:

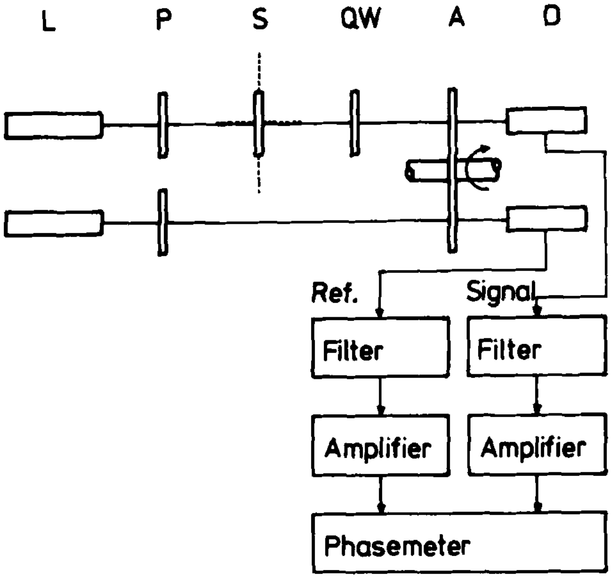
polyparaxylylene,

polyimide (PI 2566, Dupont),

SiO_x evaporated under 60° to the perpendicular.

For hybrid aligned samples one of the surfaces consists of SiO_x which was evaporated isotropically and further modified by esterification with $C_{16}H_{33}OH$, which provided an excellent homeotropic orientation. Sample thicknesses were obtained interferometrically before filling the cells. The liquid crystals used were either 5CB or 5PCH.

Freedericksz thresholds were determined for some samples in both a magnetic and an electric field using an optical detection line. The set up used to determine the optical phase shift has been described before[11] and is briefly shown in Figure 1. The electric field applied



Set up for phase shift measurements

FIGURE 1 Set-up for the determination the optical phase shift. P is a polariser, QW a quarterwave plate, A a rotating analyser and D a photo multiplier. The slightly expanded (0.5 cm^2) beam of a He-Ne laser L passes through the samples placed in an oven. The phase shift of the optical signal is detected by a lock-in amplifier. This signal can be plotted on an X-Y recorder either versus temperature or (not shown here) versus the applied electric field. A second He-Ne laser is used to supply the reference signal for the lock-in amplifer.

during the $\delta(E)$ measurements was a 10 kHz square wave whose amplitude can be varied continuously up to 10 V RMS.

RESULTS AND DISCUSSION

Our main results concern planar samples and the results for hybrid samples are discussed later on.

First we have measured electric and magnetic Freedericksz transitions for three samples at two temperatures each. The results are summarized in Table I, in which values of H_0, V_0, and some lower limits for C, calculated using eq. (6) or its magnetic equivalent, have been included. The required material parameters for 5CB have been obtained from the literature: $\Delta\chi$ from Buka and de Jeu,[12] k_{11} from Bunning et. al[13] and $\Delta\epsilon$ from Dunmur et. al.[14] The experimental data and the corresponding C values show that the accuracy with which C can be determined from threshold measurements is rather poor. The variation for the magnetic data is almost random, and the electrically obtained C values can hardly be called consistent. In our opinion, this is due to the inadequacy of the Freedericksz threshold method for determining C values, especially when C exceeds 10^{-5} J/m^2. Under such circumstances the errors in k_{11}, $\Delta\chi$, $\Delta\epsilon$, or the sample thickness d dominate the very small shifts in threshold which are expected theoretically. Fortunately we are now able to refine the approach by studying the field incuded birefringence at $E >> E_c$ as described above. For this technique it is necessary to know accurately the anisotropy of the index of refraction of 5CB and 5PCH at the experimental temperatures. To this aim we have measured curves of δ versus $T_c - T$ for samples of 5CB and 5PCH with an accurately known thickness and between parylene coated surfaces. These are known to give an almost fully planar orientation. An example of such a curve is shown in Figure 2. From this type of curve we have determined the dependence of Δn on $(T_c - T)$, using $\Delta n = \lambda\delta/2\pi d$. This dependence is shown for 5CB and 5PCH together with the known values for 5CB of Karat and Madhusudana[15] in Figure 3. It has also been verified that Δn depends on temperature in the same way as the order parameter S by calculating the quotient $\Delta n/S$ using S values from literature.[12] The quotient is found to be constant down to $T_c - T = 0.2K$. In Figures 4 and 5 the experimental points and theoretical lines from eq. (11) are shown for all planar samples at two temperatures. Relevant material parameters for 5PCH are taken from Schad et al.[16] The values of C corresponding to the drawn curves

TABLE I

Magnetic and electric Freedericksz thresholds for 5CB on planar surfaces.

orientation	d (μm)	T_c-T (K)	H_c (T)	H_o[a] (T)	C (J/m²)	V_c (V)	V_o[a] (V)	C (J/m²)
parylene	21.5	6.2	0.305	0.326	$8\ 10^{-6}$	0.72	0.73	$4\ 10^{-5}$
		2.3	0.298	0.299	—	0.68	0.71	$8\ 10^{-6}$
polyimide	16.2	6.0	0.439	0.440	—	0.72	0.73	$5\ 10^{-5}$
		2.0	0.409	0.396	(b)	0.68	0.71	$1\ 10^{-5}$
SiO_x(60°)	19.0	8.3	0.379	0.387	$3\ 10^{-5}$			
		1.4	0.341	0.326	(b)			
SiO_x(60°)	19.0	6.1				0.69	0.73	$1\ 10^{-5}$
		2.0				0.68	0.71	$1\ 10^{-5}$

(a) $H_0 = \pi/d\ (\mu_o k_{11}/4\pi\Delta\chi)^{1/2}$
$V_0 = \pi\ (k_{11}/\epsilon_o\Delta\epsilon)^{1/2}$
(b) No value of C can be found because $H_c > H_o$

are compiled in Table II. As is clear from (11), C is the only unknown in the whole adaptation process. The fit is good for all samples and the values of C are accurate to within ±10%. Data for two hybrid samples of 5CB which have been plotted in Figure 6(a,b) have also been included in this table. The SiO_x (60°) data agree very well with those for the corresponding planar sample. For parylene a slight discrepancy seems to exist which we cannot explain.

Between 2 V and 3 V the theoretical curve starts to deviate from the experimental data. As derived above the theory is applicable for the case where $\theta_m = \pi/2$ and both halves of the cell can be considered separately. The voltage for which this occurs can be easily observed in twisted samples where decoupling means the end of the rotation of the polarisation of an incident light beam. In general full decoupling seems to require 3–4 V and hence it is quite acceptable that our theory no longer works below 3 V. The deviation does occur to a much smaller extent for hybrid samples. Comparison of the data in

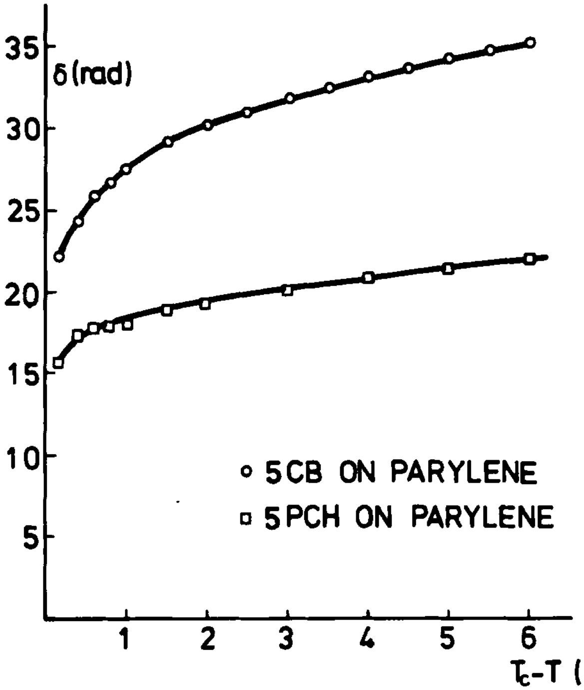


FIGURE 2 Phase shift δ as a function of $T_c - T$ for 5CB and 5PCH between parylene orienting layers at $E = 0$ V.

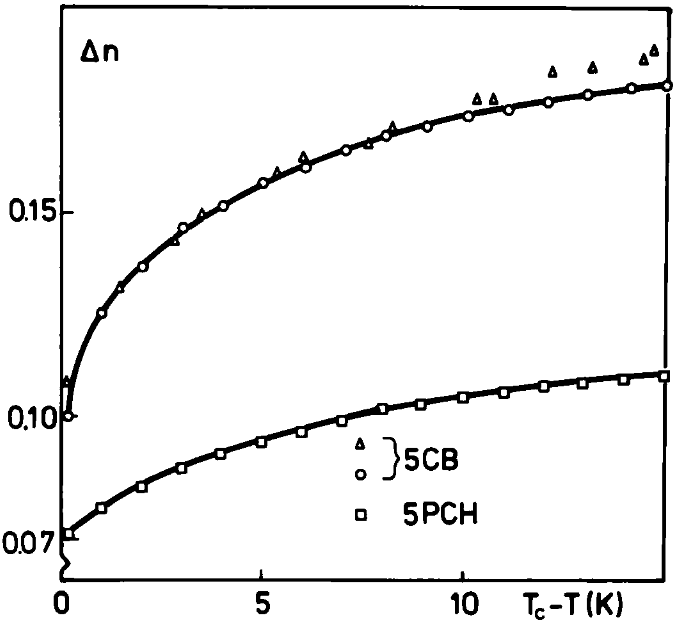


FIGURE 3 Δn versus $T_c - T$ for 5CB and 5PCH. The measurements indicated with a triangle have been taken from ref. 15.

Table I with those in Table II makes it clear that only the order of magnitude is similar. As mentioned, the threshold data are inconsistent and cannot be understood in a general framework. The high-field data in Table II, however, show a consistent picture where the anchoring on polyimide is somewhat stronger than that on parylene, but both have larger C values than SiO_x (60°). The values obtained

TABLE II

C values from birefringence measurements at high electric fields

	Homogeneous		Homogeneous		Hybrid	
	5CB		5PCH		5CB	
orienting layer	T_c-T (K)	C (J/m^2)	T_c-T (K)	C (J/m^2)	T_c-T (K)	C (J/m^2)
parylene	1.7	4 10^{-5}	2.4	7 10^{-5}	2.0	8 10^{-5}
	6.3	4 10^{-5}	6.4	8 10^{-5}	6.2	8 10^{-5}
polyimide	2.0	7 10^{-5}	2.0	7 10^{-5}		
	6.0	10 10^{-5}	6.0	10 10^{-5}		
SiO_x(60°)	1.9	2 10^{-5}	2.4	5 10^{-5}	2.4	2.5 10^{-5}
	5.9	3 10^{-5}	6.4	5 10^{-5}	6.2	2.5 10^{-5}

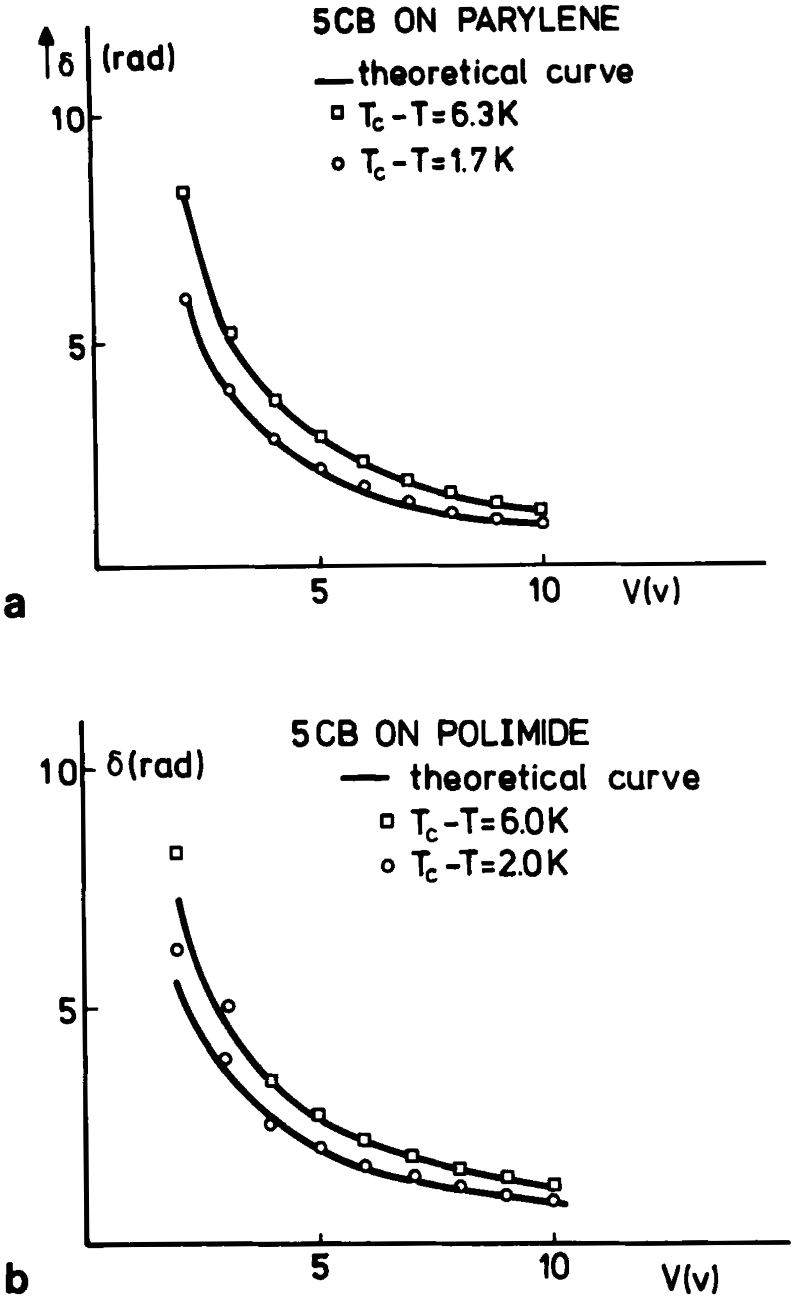


FIGURE 4 δ versus V for (a) 5CB on parylene, (b) polyimide, and (c) $SiO_x(60°)$.

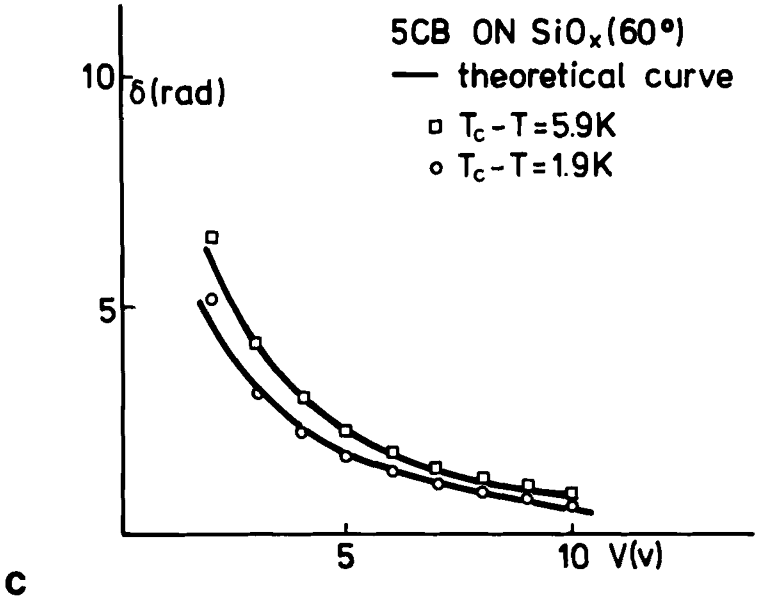


FIGURE 4 (*Continued*)

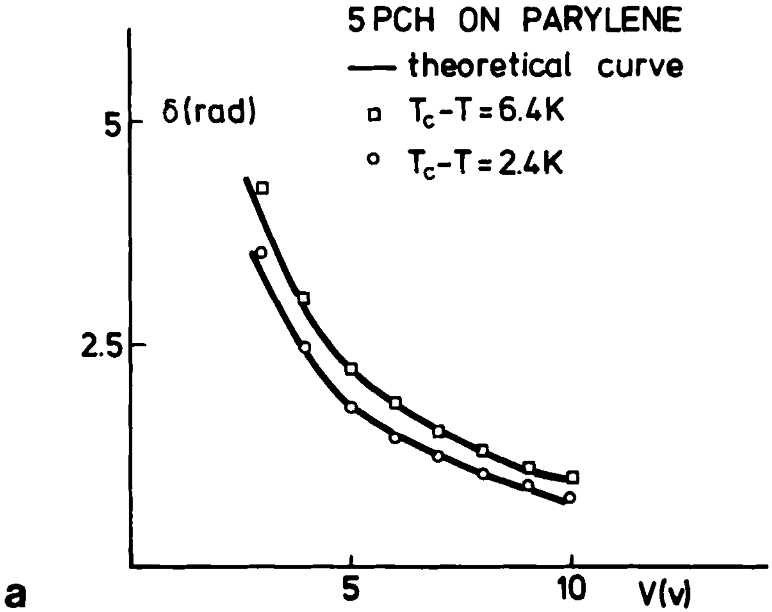


FIGURE 5 δ versus V for (a) 5PCH on parylene, (b) polyimide and (c) SiO_x(60°).

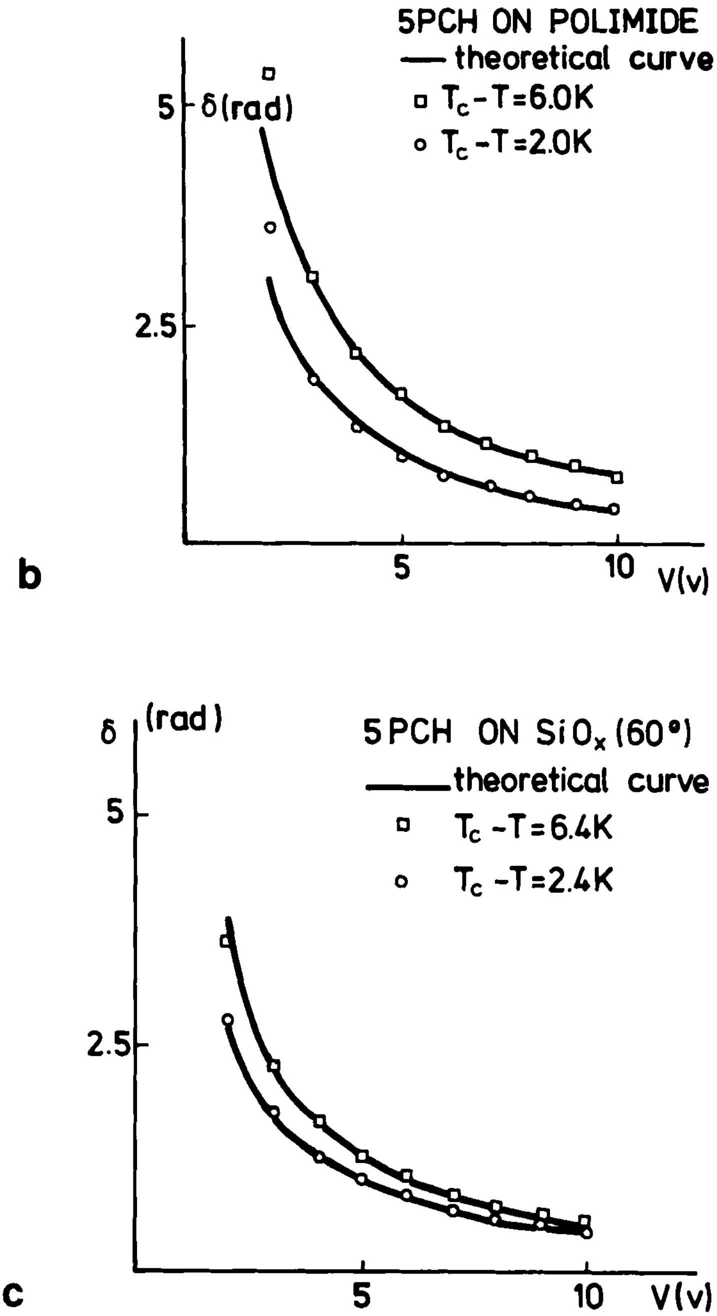


FIGURE 5 (*Continued*)

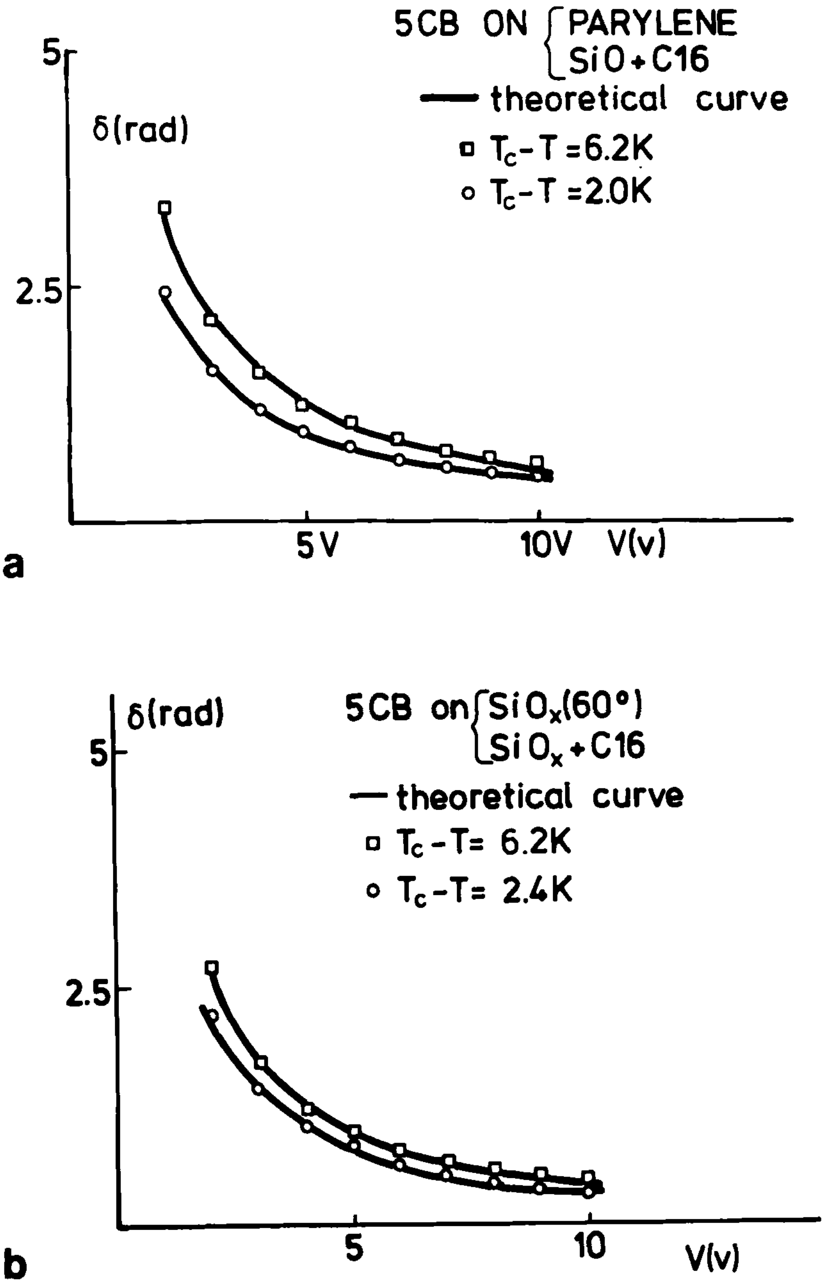


FIGURE 6 δ versus V for 5CB in hybrid samples using (a) parylene or (b) SiO$_x$(60°) as a planar orienting layer.

here are in agreement with those measured using another independent method.[17]

There are no previous measurements of C values for planar samples with which the data from this work or ref(17) can be compared. The only values known relate to homeotropic samples of MBBA oriented on various boundary layers. Those values range from 3–6 10^{-6} J/m^2 to 10^{-5} J/m^2, (refs 10, 18).

CONCLUSION

It has been shown that measurement of the birefringence at high electric fields is a reliable technique to determine anisotropies of surface free energies for various planar orienting surfaces. Extraction of such anisotropies from Freedericksz thresholds yields rather inaccurate results because errors from other sources mask the small shifts in the threshold fields due to the surface interaction. Values are found to be 2.5 10^{-5} J/m^2 for SiO_x(60°), 4–8 10^{-5} J/m^2 for parylene, and 7–10 10^{-5} J/m^2 for polyimide, slightly increasing with decreasing temperature. The magnitudes of the C values for planar layers are higher than those previously found for homeotropic samples (3–6 10^{-6} J/m^2, Naemura;[6] 10^{-5} J/m^2, Yang,[10] and 10^{-5} J/m^2 Mada[18]) but there are no data available for planar samples with which our values can be compared.

References

1. A. Rapini and M. Papoular, *J. Phys.*, **30C4**, 54 (1969).
2. E. Dubois-Violette and P. G. de Gennes, *J. Phys.*, **36**, L255 (1975).
3. E. Dubois-Violette and P. G. de Gennes, *J. Coll. Int. Sci.*, **57**, 403 (1976).
4. T. Motooka, A. Fukuhara and K. Suzuki, *Appl. Phys. Lett.*, **34**, 305 (1979).
5. T. Motooka and A. Fukuhara, *J. Appl. Phys.*, **50**, 3322 (1979).
6. S. Naemura, *Appl. Phys. Lett.*, **33**, 1 (1978).
7. H. Mada, *App. Phys. Lett.*, **39**, 701 (1981).
8. H. Mada, *Mol. Cryst. Liq. Cryst.*, **82**, 53 (1982).
9. K. H. Yang, *Appl. Phys. Lett.*, **43**, 171 (1983).
10. K. H. Yang, *Appl. Phys. Lett.*, **43**, 62 (1983).
11. H. A. van Sprang, *J. Phys.*, **44**, 421 (1983).
12. A. Buka and W. H. de Jeu, *J. Phys.*, **43**, 361 (1982).
13. J. D. Bunning, T. E. Faber and Ph. Sherrell, *J. Phys.*, **42**, 1175 (1981).
14. D. A. Dunmur, M. R. Manterfield, W. H. Miller and J. K. Dunleavy, *Mol. Cryst. Liq. Cryst.*, **45**, 127 (1978).
15. P. P. Karat and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **36**, 51 (1976).
16. H. P. Schad, G. Baur and G. Meier, *J. Chem. Phys.*, **70**, 2770 (1979).
17. H. A. van Sprang and J. A. M. van de Venne, Submitted to *J. Appl. Phys.*
18. H. Mada, *J. Chem. Phys.*, **75**, 372 (1981).