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Electric Field Induced Walls in a Nematic

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Optical microscopic observations have been carried out on the static and dynamic characteristics of the walls induced by electric fields in homogeneously aligned samples of butyl p-(p-ethoxyphenoxycarbonyl) phenyl carbonate ($\Delta\epsilon > 0$). The study reveals that: (a) k_{33}/k_{22} is slightly temperature dependent over most of the nematic range, but varies steeply near the clearing point, (b) the wall-thickness varies as $(V^2\text{-}V_c^2)^{-1}$, V_c being the Freedericksz critical voltage, (c) the angular deviation of the director across the wall conforms to the tanh law derived for magnetic field-induced walls, (d) k_{11} varies between *ca.* 1.36 and 0.34 μdynes in the mesomorphic temperature range and (e) closed domains spontaneously collapse at a constant rate at a given temperature, and this rate increases linearly with temperature.

At higher voltages, the focal line due to the walls shows a complex structure hitherto unreported.

1. INTRODUCTION

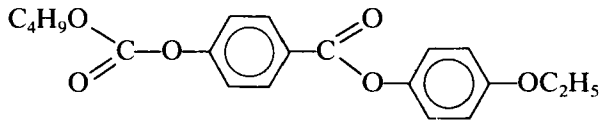
It is well-known that the onset of Freedericksz transition[1] in a nematic liquid crystal which is contained between two glass plates, oriented either homogeneously or homeotropically and acted upon by a field along the normal to the optical axis is marked by a slight tilt of the liquid crystal director towards the direction of the field; the tilt takes place in the mid-region of the sample, in the plane of the director and the field; it can be positive or negative, since both are energetically equivalent. Between contiguous regions where the tilts are opposite, there occurs a transition region extending over a distance large compared to molecular length. This boundary region has been termed a wall.[2,3] Theoretical analysis of the static and dynamic behaviour of such walls due to magnetic fields has been carried out by Brochard.[4] Leger[3,5] has verified the theoretical predictions by optical microscopic

studies of the walls in MBBA due to magnetic fields. The quantitative aspects of these studies pertain mainly to homeotropic geometry. Chuvyrov[6] has reported certain properties of 'cylindrical domains' caused by electric fields in homogeneously oriented samples of some of the p-n-alkoxybenzoic acids (for which the dielectric anisotropy, $\Delta\epsilon$, is positive). Chuvyrov has tried to interpret the behaviour of the domains on the basis of swarm theory.

We have carried out a detailed study of the walls induced by electric fields in a homogeneously aligned nematic liquid crystal with $\Delta\epsilon > 0$ in an attempt to compare the behaviour of the walls induced by electric and magnetic fields. The similarities and dissimilarities between the two cases will be presented and discussed.

2. EXPERIMENTAL

A reagent grade sample of butyl p-(p-ethoxyphenoxycarbonyl) phenyl carbonate (BPC) supplied by Eastman Organic Chemicals was used without further purification. It exhibited an enantiotropic nematic phase between *ca.* 55°C and 85°C. BPC is known to have a positive dielectric anisotropy that, between 55°C and 84°C, varies approximately between 0.21 and 0.06.[7] The static conductivity of BPC was determined by a method which was similar to that used by Bertolotti et al.[8] Essentially, the current-voltage characteristics of the material were studied using the same sample cells as were used for the observation of walls. The conductivity in the mesophase region was of the order of $10^{-8}\ \Omega^{-1}\ cm^{-1}$. The experimental configuration for the study of walls was as follows: The sample was held between tin-oxide-coated glass plates separated by a teflon spacer of thickness 75 μm. The specimen was homogeneously aligned in the field-free state; the alignment was achieved using the rubbing technique. The temperature of the sample which was housed in a hotstage could be maintained at the desired value to within ± 0.1°C. The samples were examined in transmitted light using a Carl Zeiss polarizing microscope. The frequency of the electric field used was 10 kHz, unless otherwise stated. The voltages are rms values.



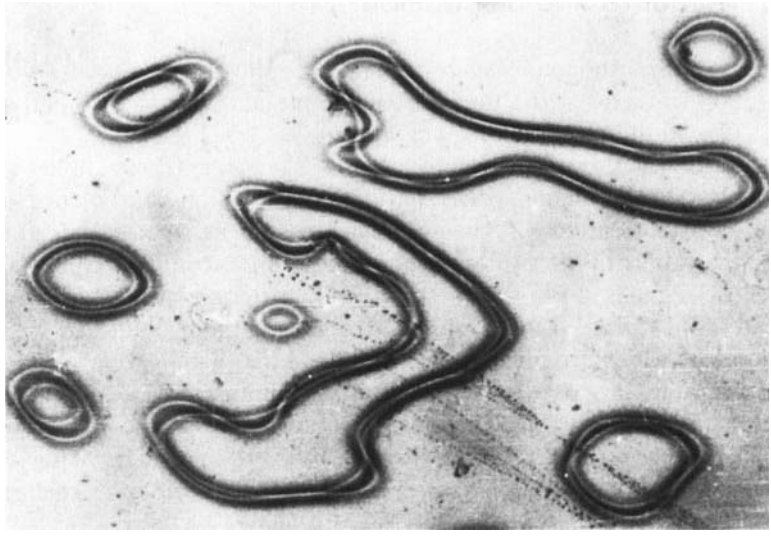
3. RESULTS AND DISCUSSION

We use an orthogonal xyz-coordinate reference system with x along the optical axis of the undistorted sample and z along the perpendicular to the plane of the sample.

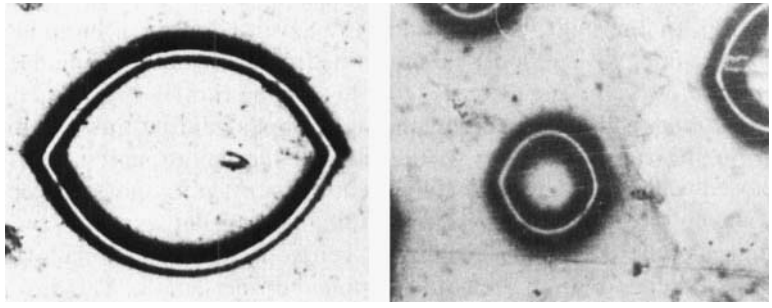
In the low frequency regime (below 2.5 kHz), BPC exhibits zig-zag Williams domains, coherent domain oscillations, turbulence and normal reorientation.[9] The frequency region between *ca.* 2.5 kHz and 5 kHz is the transition region between the conduction and dielectric regimes. In this region, the Williams domains appearing at a threshold voltage transform themselves at elevated voltages into loop domains which are much more extended along y than along x. Generally speaking, as the frequency is gradually increased above 2.5 kHz, the tendency towards normal reorientation increases, and above 5 kHz only normal reorientation is observed. A similar behaviour has also been observed by Chuvyrov with p-n-octyloxybenzoic acid (see Figure 1, ref. 6).

In the dielectric regime (above 5 kHz), on application of a sufficiently high voltage (> 12 V), BPC shows both closed and open walls. They are readily seen in ordinary white light due to their focusing action for the light vibrating along x. Several walls can be induced in the sample by suddenly changing the frequency of the applied field from a low value (i.e. 100 Hz) to a high value (i.e. 10 kHz), keeping the voltage sufficiently large; the walls appear during the transition from the turbulent state to the normal reorientational state. The closed walls spontaneously collapse and, eventually, only some open walls endure; the closed walls are initially irregular in shape, but in time assume a regular equilibrium geometry. The geometry of the walls is dependent on the voltage applied to the sample. This feature appears to be peculiar to electric field-induced walls, since it has not been reported for the magnetic case.[4,5] The equilibrium form, as in the magnetic case, is elliptical only at lower voltages (up to about 16 V, at 10 kHz), but at higher voltages (i.e. 20 V) it becomes angular along x at the extrimities and extended along y. The general tendency of the closed domains is to become angular and shortened along x and bulged along y as the voltage is increased or the frequency is decreased. As a result, near the clearing point, on application of about 25 V, we observe the principal axis, a, along x becoming smaller than the principal axis, b, along y. All these aspects are illustrated in Figures 1 (a)-(c).

We have measured the values of a/b at various temperatures for 16 V and 25 V. The measurements have been made on the equilibrium



(a)



(b) ⟷ 100 μm (c)

FIGURE 1 (a) Double-exposure photograph (interval 10 s) showing the tendency of irregular loops to become elliptical with passage of time (73°C, 16 V, 10 kHz). (b) Closed domain with angular extrimities along the horizontal (58°C, 25 V, 10 kHz). (c) Closed domain, more elongated along the vertical than along horizontal (81°C, 25 V, 10 kHz).

figures for which a/b and $\Delta a/\Delta b$ did not vary significantly during the collapse of the domains. Several domains have been considered at each temperature. Figure 2 shows a plot of average $(a/b)^2$ versus temperature. The significance of $(a/b)^2$ at the higher voltage is not clear, but the values of $(a/b)^2$ at 16 V may be taken to represent the

ratio of the bend elastic constant (k_{33}) to the twist elastic constant (k_{22}), because the domains were strictly elliptical at this voltage.[3,5] It follows from Figure 2 that k_{33}/k_{22} varies slightly and nearly linearly over most of the nematic range; it drops rapidly after 82°C as the clearing point is approached. For comparison, we may mention that the value of k_{33}/k_{22} in BPC changes from *ca.* 2.95 at 55°C to *ca.* 2.17 at 82°C. In PAA, k_{33}/k_{22} changes from *ca.* 3.2 at 117°C to *ca.* 2.75 at 132°C[10] and for MBBA it is 2.89 at 23°C.[3] The value of k_{33}/k_{22} is not available for PAA or MBBA close to the clearing temperature. The rapid change of k_{33}/k_{22} in BPC between 82°C and 85°C may be attributed to the rapid weakening of lateral forces between the molecules near the transition to isotropic state. For electric field induced domains in p-n-octyloxybenzoic acid, Chuvyrov[6] reports that $(a/b)^2$ decreases from about 1.77 at 112°C to about 1.05 at 146°C. However, these measurements have been made on the ellipses having 'beaks' as they have been called. It may be that the applied voltage (not mentioned in ref. 6) was too large for $(a/b)^2$ to represent k_{33}/k_{22}, as in the case of BPC at 25 V (Figure 2).

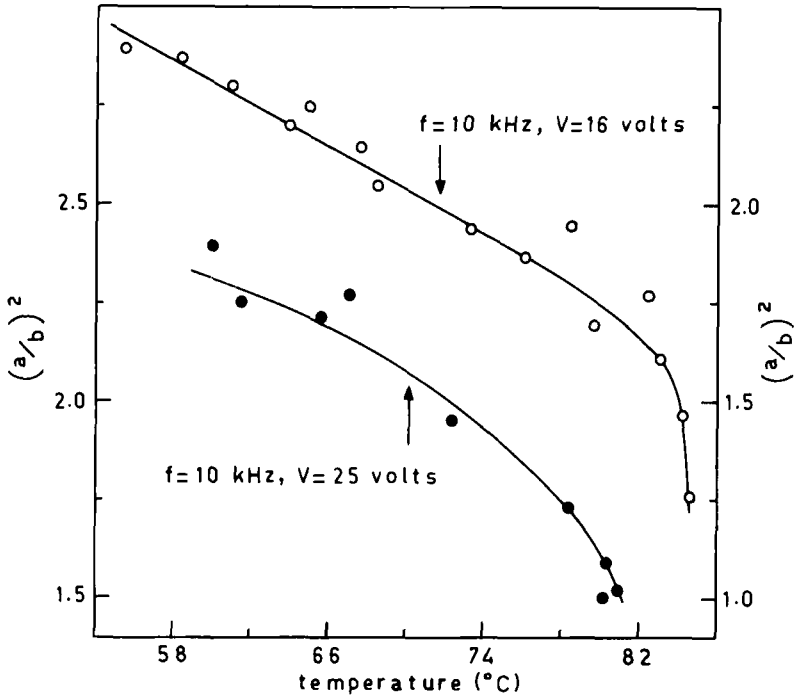


FIGURE 2 Plot of $(a/b)^2$ versus temperature. The ordinates to the left and right apply, respectively, to open and solid circles.

Chuvyrov[6] reports the major axis of the closed domains as lying perpendicular to the original optical axis. This is rather surprising since the twist-bend wall is lower in energy when compared to the splay-bend wall.[2] Hence the major axis is expected to be along x rather than y (as shown in Figure 1). Chuvyrov[6] considers the equilibrium form of the loops as governed by forces of surface tension. Using the equation for the equilibrium shape of crystals derived by Landau,[11] he finds the ellipticity, b/a, to represent $\gamma_{\parallel}/\gamma_{\perp}$ where $\gamma_{\parallel}$ and $\gamma_{\perp}$ are the surface tensions parallel and perpendicular to the director respectively. Interestingly, as shown by Brochard,[4] this conclusion also follows from Frank's expression for the free-energy density of a nematic in a magnetic field provided one assumes $k_{11} = k_{33}$. Therefore, the ellipticity of the loops may be taken as equal to either $\gamma_{\parallel}/\gamma_{\perp}$ or $\sqrt{k_{22}/k_{33}}$. Since k_{33} is generally greater than k_{22}, $\Delta\gamma$ ($= \gamma_{\parallel} - \gamma_{\perp}$) has to be negative. This is also evident since the atomic density is greatest for a plane parallel to the director and least for a plane perpendicular to it.[12] Thus it is difficult to see how Chuvyrov[6] could have observed the major axis of the ellipse as directed along y in a nematic originally aligned along x.

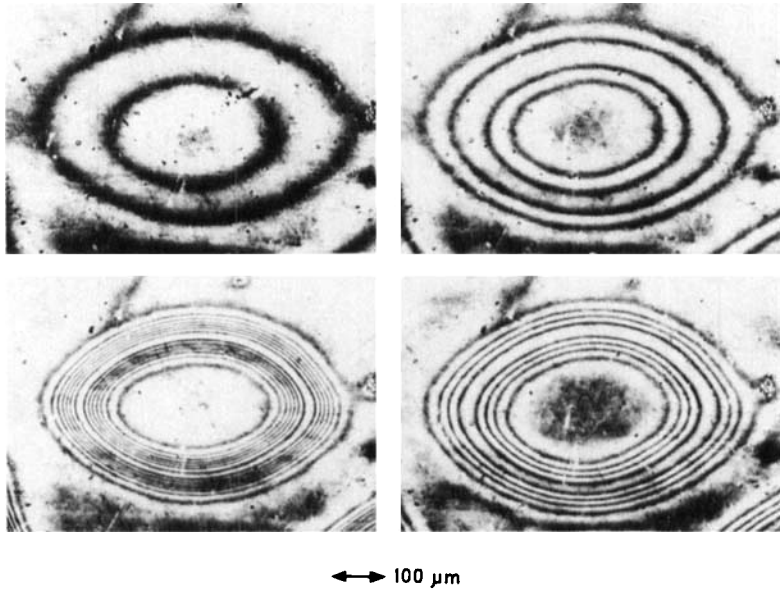


FIGURE 3 Interferograms of an elliptical wall obtained with mercury green light and specimen aligned at 45° between crossed polarizers. The voltages are 9, 9.5, 10.6 and 12.2 V, for the photographs in clock-wise order from top-left. 10 kHz, 65°C.

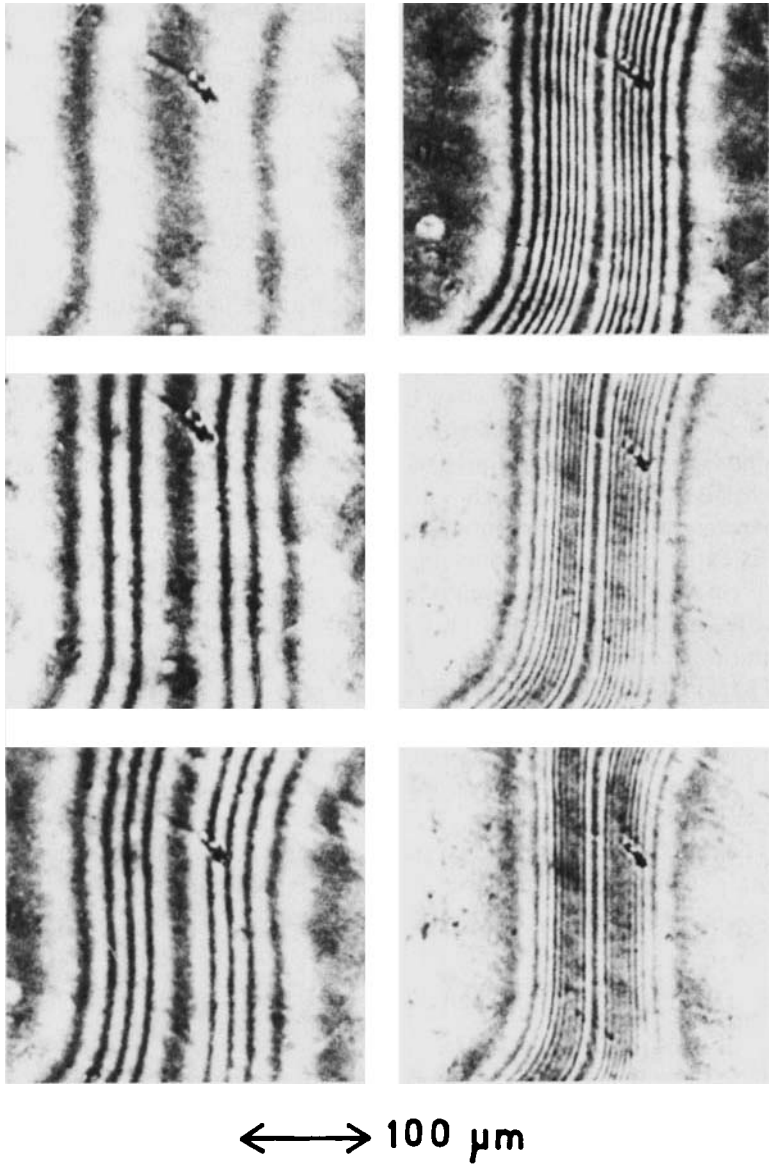


FIGURE 4 Interferograms of an open splay-bend wall obtained with mercury green light and specimen in the 45°-position. The voltages from top to bottom are: (left) 9.9, 10.8 and 11.5 V, and (right) 13.1, 14.2 and 15 V. 10 kHz, 65°C.

Below 15 V, the walls in BPC are indistinct in white light due to their low focusing power. But by using monochromatic light and placing the sample between crossed polarizers such that its director is oriented at 45° to the transmission axes of the polarizers, interference fringes can be seen in the region of walls down to about 9 V. Some typical interferograms of closed as well as open walls are reproduced in Figures 3 and 4. The order of the fringes, unlike for homeotropic geometry, decreases from the centre of the wall outwards. The distance, d, between the central bright (or dark) fringe to the next bright (or dark) fringe is a measure of the wall-thickness.[3,5] A plot of d vs voltage (V) shows the nature of divergence of the wall-thickness with decreasing voltage (Figure 5). As shown in the inset of Figure 5, d^{-1} varies as $(V^2\text{-}V_c^2)$ for both splay-bend and twist-bend walls; V_c, the Freedericksz critical voltage, is about 8.5 V. It has been found by Leger[5] that, for the magnetic field induced splay-bend walls in MBBA, d^{-1} is proportional to $(H^2\text{-}H_c^2)^{\frac{1}{2}}$. The reason for not observing a similar variation of d with field-strength in our electric field experiments is possibly the high electrical conductivity (10^{-8} $\Omega^{-1}\,\text{cm}^{-1}$) of BPC. High ionic conductance however would not affect the magnetic field to any great extent. Therefore, magnetic field experiments on BPC may be expected to show a variation of d^{-1} as $(H^2\text{-}H_c^2)^{\frac{1}{2}}$. Likewise, electric field experiments on MBBA (for which the conductivity in the mesophase region is of the order of 10^{-11} Ω^{-1} cm^{-1}) or any other material of low conductivity may show a variation of d^{-1} as $(V^2\text{-}V_c^2)^{\frac{1}{2}}$. We propose to carry out experiments to verify these predictions.

The Freedericksz threshold voltage, V_c, for a homogeneously aligned sample has been shown to be given, in the CGS system, by

$$V_c = 2\pi^{\frac{3}{2}} \sqrt{\frac{k_{11}}{\Delta\epsilon}}$$

where k_{11} is the splay modulus.[13] Using the values of $\Delta\epsilon$ for BPC at different temperatures as determined by de Jeu and Lathouwers,[7] we have approximately deduced the dependence of k_{11} on temperature (Figure 6); k_{11} ranges between 1.36 and 0.34 μdynes in the mesophase region.

For magnetic field induced walls, Brochard[4] has derived expressions for the mean tilt angle, θ_M, of the molecules as a function of the distance, x, from the core of the wall. The equation for the splay-

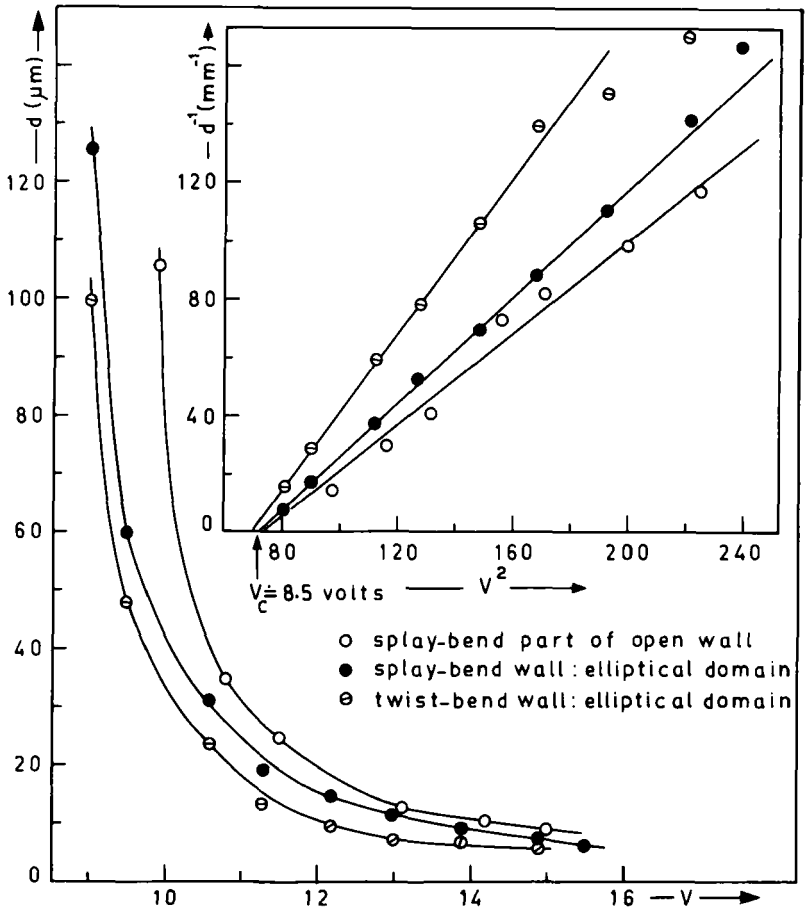


FIGURE 5 Plot of the distance, d, between the central bright (or dark) fringe and the next bright (or dark) fringe versus the applied voltage V. The inset shows that $1/d$ varies as $(V^2\text{-}V_c^2)$.

bend wall in a homogeneously oriented sample is

$$\theta_M = \theta_\infty \tanh \frac{\theta_\infty x}{2\xi}$$

where θ_∞ and ξ denote the mean molecular tilt angle far from the wall and the magnetic coherence length respectively; ξ/θ_∞ represents the coherence length in the plane of the layer. We made use of

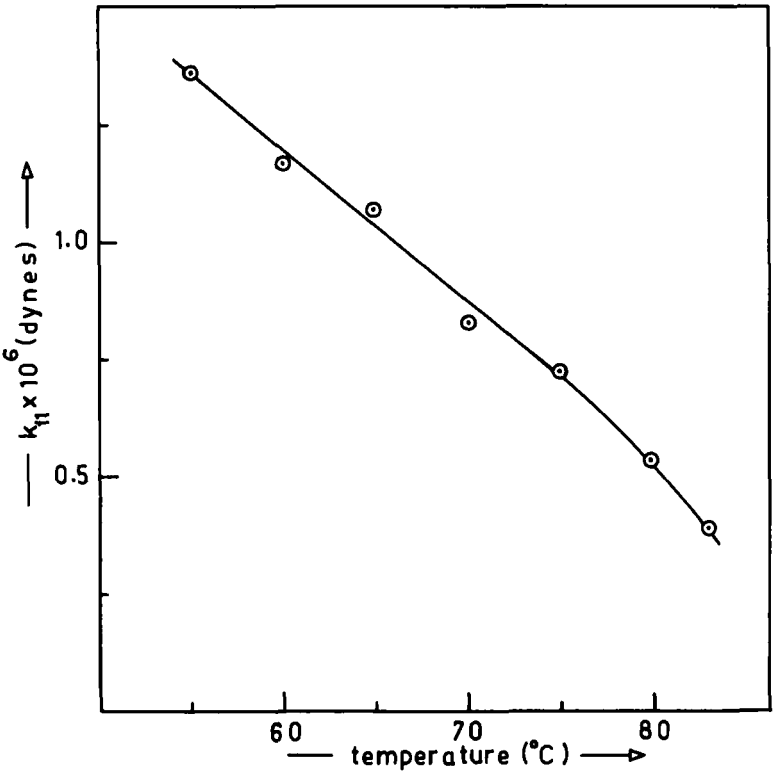


FIGURE 6 Temperature dependence of the splay modulus (k_{11}) for BPC.

birefringence fringes (as shown in Figure 3) to verify that this equation also holds true for electric field induced walls. It may be seen that, under small angle approximation, the value of θ_M^2 changes by a constant quantity in going from one bright (or dark) fringe to the next bright (or dark) fringe. Thus, by assuming the above equation as valid at any three bright-fringe positions, one can deduce the value of $(2\xi/\theta_\infty)$ and then use it to construct a curve of $(\theta_M/\theta_\infty)^2$ as a function of distance x. Figure 7 shows a plot of $(\theta_M/\theta_\infty)^2$ vs x at 13 V. It is seen that the experimental fringe-positions (circles) fall on the theoretical curve (solid line), thus verifying the validity of the tanh law.

Experiments concerning the dynamic behaviour of closed domains are still underway. Preliminary results obtained from measurements of photographs taken at specific time intervals of collapsing domains indicate that the rate of decrease in A, the area of the ellipse, is a

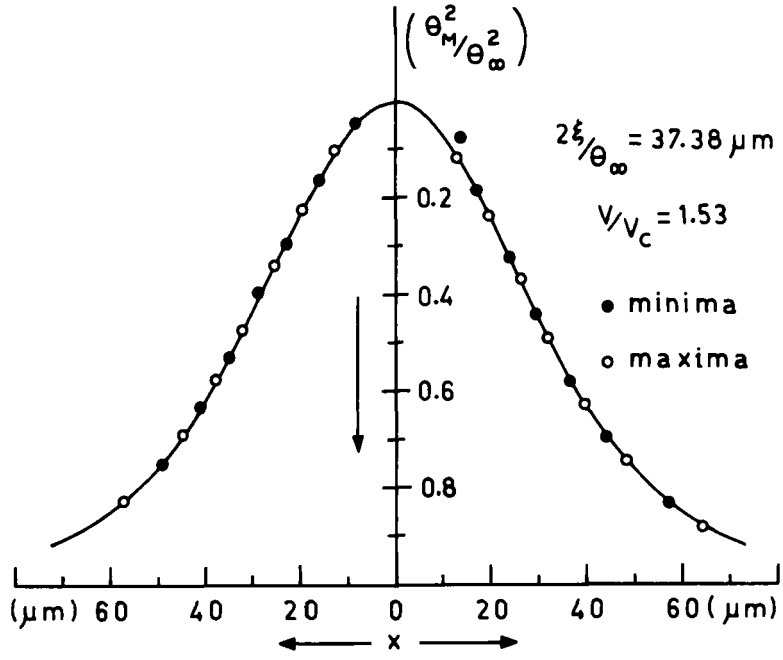


FIGURE 7 Dependence of the square of mean molecular tilt (θ_M^2) on the distance from the centre of the splay-bend wall (x). Data are from the interferogram of an elliptical wall for 65°C, 13 V and 10 kHz. The first, fourth and seventh bright fringe locations were assumed to obey the tanh law.

constant at a given temperature and voltage. These rates increase almost linearly with temperature (Figure 8). If the viscosity of the fluid is the only factor deciding the collapse, one would expect a constant rate of decrease (at a given temperature and voltage) of a and b rather than of a^2 and b^2. The significance of our results in relation to material properties still remains to be completely understood.

Earlier workers[3,5,6] report that an increase in the intensity of the magnetic or electric field has no effect on the equilibrium shape of closed walls. Our findings for BPC, however, are that the shape and structure of the walls change at elevated voltages. At moderately high voltages (around 20 V), as mentioned earlier, the ellipse becomes angular along x. At still higher voltages (30 V and above), the focal line due to the wall shows a complex structure: at first, the focal line becomes slightly zig-zag in the twist-bend portion of the wall, along

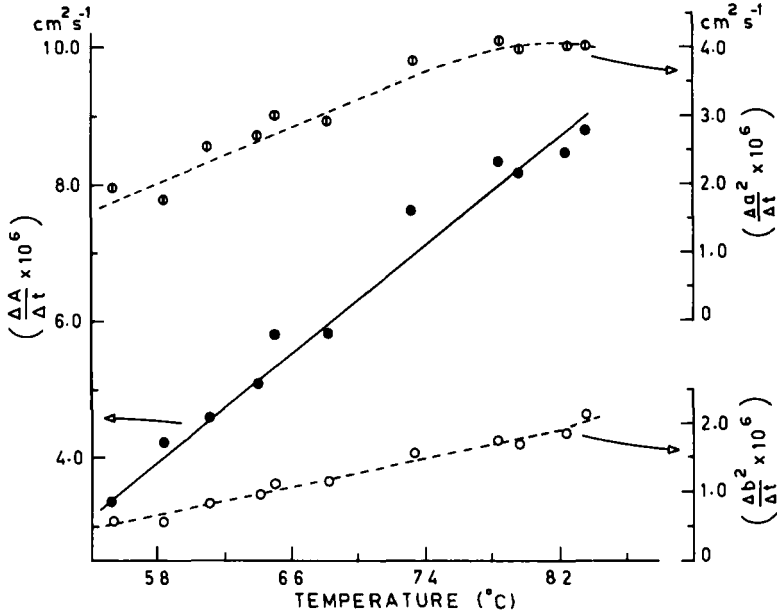


FIGURE 8 Temperature dependence of the rates of decrease in A (area of the elliptical domains), a^2 (a being the semi-major axis) and b^2 (b being the semi-minor axis).

y (Figure 9a); with a further increase in voltage, the zig-zag structure extends on either side and the central component becomes thicker (Figure 9b); eventually, above 50 V, the closed domains rapidly collapse and the open walls degenerate into a pair of disclinations (Figure 9c). At a lower frequency (5 kHz), as the voltage increases, the same features are observed as for 10 kHz, except that the central component of the focal line triplet becomes wavy (Figure 10). An additional interesting feature is that the zig-zag structure of the focal-line shows a reflection symmetry for the upper and lower halves of a closed wall. This same symmetry is also present for two closed domains separated by an open wall (Figure 9a). These facts are related to the sign of inclination of the molecules on either side of a wall. The molecular orientation corresponding to the zig-zag structure itself is not clear; it may be related in some way to the normal reorientation of the molecules occurring at the core of the walls.

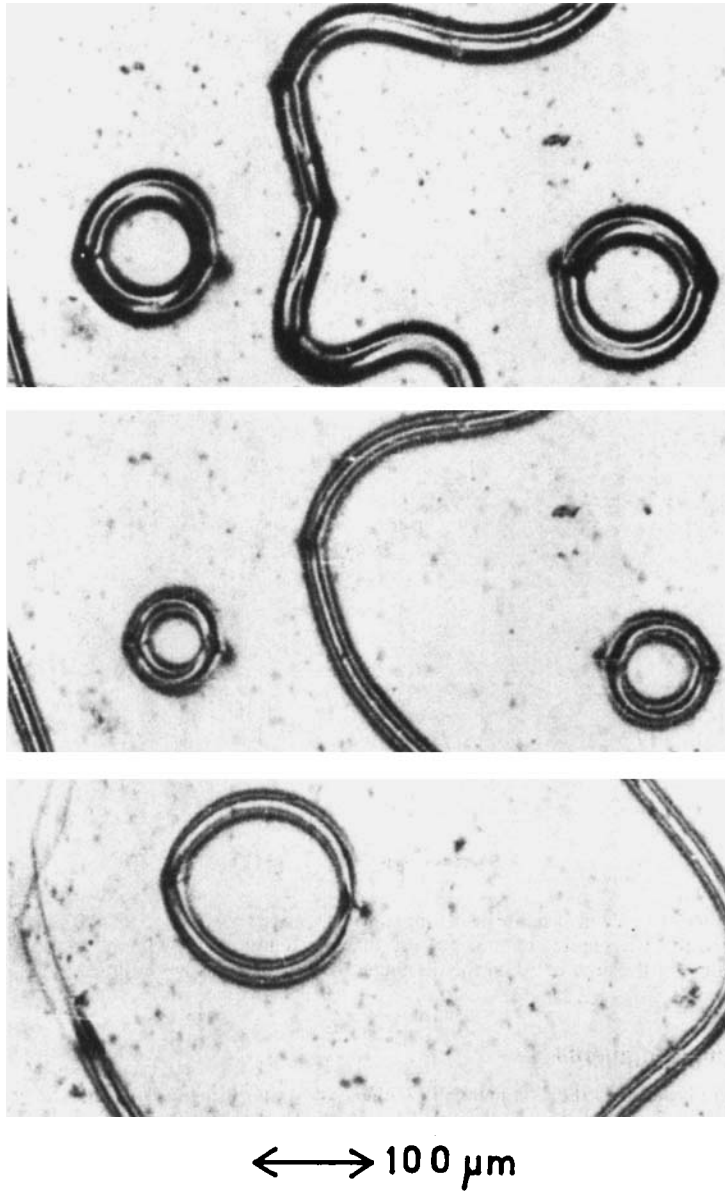


FIGURE 9 Domain walls at higher voltages. Photographs (a) and (b) are of the same region at 37 V and 47 V respectively, showing two closed domains separated by an open wall. Photograph (c), taken at 55 V, shows the degeneration of an open wall (left) into a pair of disclinations. 72.8°C. 10 kHz. Analyser along the director, x.

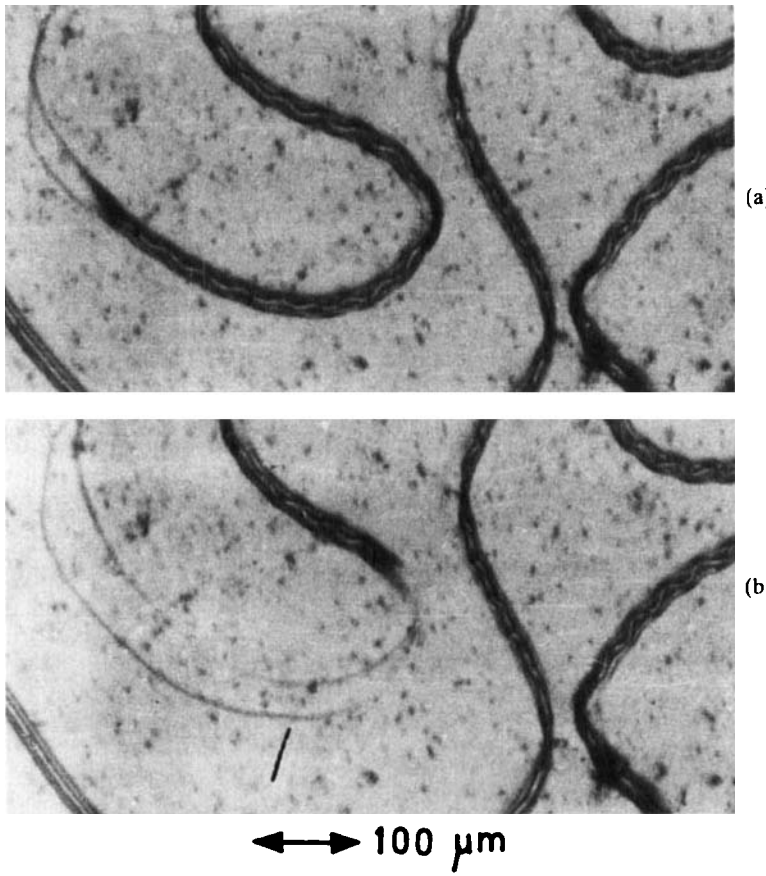


FIGURE 10 Typical textures of domain walls at low frequency (5 kHz) and high voltage (68 V). Figures (a) and (b) are of same region of the sample. Observe the widening of the area between the disclination lines with passage of time.

Acknowledgments

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