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A weak surface memory effect in liquid crystal cells with rubbed polyimide layers

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For the first time we have observed a surface memory effect in liquid crystal cells where both surfaces consist of rubbed polymers. In this case the azimuthal orientation of the optical axis in the cell is unchanged, while the polar orientation of the optical axis in the cell changes. This change is brought about by imposing changes in the in-plane order of the molecules at the surface.

1. Introduction

That an isotropic glass surface could be rendered anisotropic by contact with a liquid crystal was discovered by Friedel in 1922 [1]. Six decades later, Clark [2] discovered the same effect on unrubbed polymer surfaces, and introduced the term surface memory effect or SME. He concluded that the unrubbed polymer surfaces have a random planar surface condition, but exposing the surface to a smectic A or G phase creates an anisotropic surface. On subsequent reheating, this anisotropic surface will then orient the bulk of the nematic material, and domains of different orientation are seen.

The SME was further investigated by Ouchi *et al.* [3, 4], by second harmonic generation. They concluded that the liquid crystal molecules are anchored at the surface with a rather weak azimuthal anisotropy. The SME shows that not only does the solid polymer surface influence the liquid crystal in contact with it, but the liquid crystal might also influence the solid surface. So far the SME has only been seen in cells with unrubbed polymer layers. In these cases, there are no preferred azimuthal directions and the changes in director orientation are easily noticed. The SME of previous workers in this field has therefore always been observed microscopically. We have used cells with rubbed polyimide layers, and here the change in director orientation is only a change in the polar orientation. This surface memory effect cannot by seen under the microscope, but can still be clearly demonstrated. For the first time, the SME has been observed in liquid crystal cells with rubbed alignment layers. As part of an on-going effort to understand the surface alignment mechanism of nematic liquid crystals on rubbed polymer surfaces, the series of *n*-alkyl-nitro-esters, shown in figure 1, was investigated using 10 per cent solutions in the liquid crystal mixture ZLI 1602, with the polyimide s-BPDA-6. The ethyl and undecyl homologues gave solutions which were supersaturated and crystallized before measurements of the pretilt angles could be made. The cells were heated back to give the nematic phase and were then completely uniform. No traces of the previous crystallites could be observed visually. However, attempts to measure the pretilt angles showed large and random variations across the cells. This was so surprising that it was decided to investigate the effect further.

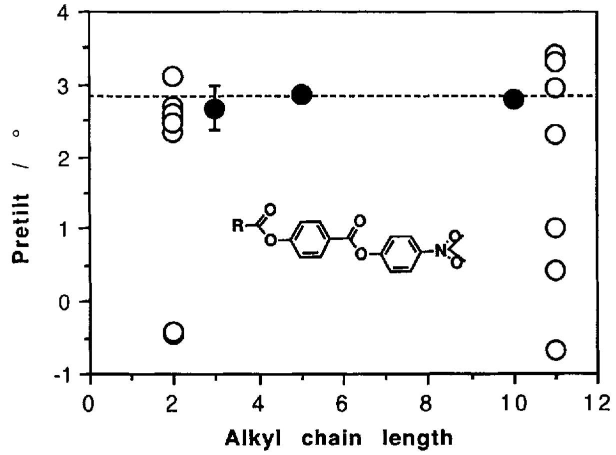

Figure 1. Pretilt angles found for different members of the nitro-ester series as 10 per cent solutions in ZLI-1602 on the polyimide *s*-BPDA-6 (a condensation product of biphenyl-3,3′,4,4′-tetracarboxylic acid and 1,6-diaminohexane). The ethyl and undecyl compounds crystallized before measurements were made and were reheated to give the nematic phase. Even though the cells were completely uniform under the microscope and very good curves for the transmission versus angle of incidence could be obtained, there is a large variation in the pretilt angles across the cells. The insert shows the structure of the nitro-esters.

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2. Experimental

The pretilt angles were measured by the crystal rotation method. Cells ($120\,\mu$m thick) with antiparallel rubbing directions were used. The cells were rotated between a pair of crossed polarizers. The rotation was controlled by a stepping motor in steps of 0·2°, and the transmission of the light from a helium–neon laser was recorded as a function of the angle of incidence. Both the stepping motor and the photo-detector were interfaced to a PC. The motor position and transmission value were both recorded and curves of transmission versus angle of incidence drawn by the computer. This allows us to find the 'symmetry point' and thus the pretilt angle [5].

3. Results

In figure 1, the results for individual measuring points for the ethyl and undecyl homologues (open circles) are shown, together with the average values for the propyl, pentyl and decyl homologues (filled circles). The measured spots are typically a cm apart, while the laser beam covers a few tenths of a mm. The standard deviations for the uncrystallized samples are 0·1–0·3° (two cells with three measuring points each), showing that our sample preparation [6] procedure gives very reproducible values. For the pentyl and decyl compounds, the error bars are less than the diameter of the circle giving the measured value. This is also the typical standard deviation found for a large number of samples [6]. For the crystallized samples the standard deviation is about 1·5°. Thus, we conclude that the pretilt angles show a real, but random variation across the samples that had crystallized.

By adjusting the position of the liquid crystal cell with a micrometer screw, we tried to measure spots 0·1 mm apart. The variation of the observed pretilt between neighbouring spots could then in principle give us the size of the domains. We obtained poor resolution in this experiment. We believe there are two reasons for this. Firstly, the domains are probably about the same size as the diameter of the laser beam, for example, a few hundred microns. The crystallites we saw during crystallization were 0·1–1·0 mm across, and we would expect the domains to be of the same size. Secondly, this method of determining the size of the domains is probably too slow. One single measurement takes about 20 min. During a complete scan, there was therefore a large relaxation back towards the equilibrium situation. When we plotted the observed pretilt versus position for the undecyl homologue, we obtained a line that started quite randomly, but after a millimetre or so (corresponding to 3 h of measurement) reached the equilibrium value.

We have recently proposed [7, 8] that the surface pretilt can be expressed as $\beta_{\text{obs}} = [(d^*/d)\alpha + (\beta_0 - \alpha]a_1$, where β_{obs} is the observed pretilt angle of the director of the nematic phase, d is the thickness of the cell, d^* is the thickness of the surface layer in this cell, β_0 is the angle between the optical axis of the molecules and the surface, α is the angle between the optical and mechanical axes of the molecule, and a_1 is the in-plane order of the mesogens at the surface, as introduced by Barmentlo *et al.* [9]. This gives the preference for the molecules to lie along the rubbing direction, as opposed to against the rubbing direction. We note here that β_{obs} is a collective property, the pretilt angle of the director of the nematic phase, which is related to the symmetry of the nematic phase. β_0 is a molecular property, the pretilt angle of the optical axis of individual molecules. d^* is the thickness of the layer where the symmetry of the nematic phase is broken. We have measured this layer and the thinner layers of the base mixture employed to be 0·1–1·0 μm thick [10]. For the $120\,\mu$m thick cells used in this study, $d^* \ll d$, we can ignore the effect of the surface layer and simplify to $\beta_{\text{obs}} = (\beta_0 - \alpha)a_1$.

For an unrubbed surface, as used in previous investigations of the SME, there is no preferred azimuthal direction at the surface. When the bulk of the more ordered smectic phases imposes an external direction, there is then no azimuthal force acting on the molecules after heating back into the nematic phase. The domains created in the smectic phases can thus be clearly seen under the microscope. For the rubbed polyimide surface, there is a strong tendency for the mesogens to align along the direction of the ordered polyimide chains. The bulk forces are strong enough to prevent this when the samples crystallize. After reheating to the nematic phase, the mesogens do, however, want to align parallel to the rubbing direction again. This is achieved by the shortest possible azimuthal movements. This means that the in-plane order a_1 now varies across the surface. Thus we observe this as the variations in pretilt angles across the surface. The proposed sequence of events is illustrated in figure 2. We rule out a variation in β_0 as the main source of the observed pretilt for two reasons. Firstly, this cannot explain negative values. A negative value would imply that the mesogens are penetrating into the surface. Secondly, SHG measurements [9] show that the polar anchoring of the molecules is fairly strong, and so β_0 changes little due to external influences. There is the possibility that the crystallization of the liquid crystal will give concentration gradients and thus changes in the refractive indices. As the pretilt angles are related to the symmetry point (θ_{sym}) of the transmission versus angle of incidence curve and the refractive indexes by $\beta_{\text{obs}} = -\theta_{\text{sym}}/(n_e + n_o)$ [5], a variation in the refractive indexes will also give a variation of the observed pretilt angle. For both the ethyl and undecyl compounds, we found points with a negative pretilt, indicating that the optical axis of the liquid crystal is tilting against the rubbing direction. No physically meaningful values for the refractive indices can give this result. We thus

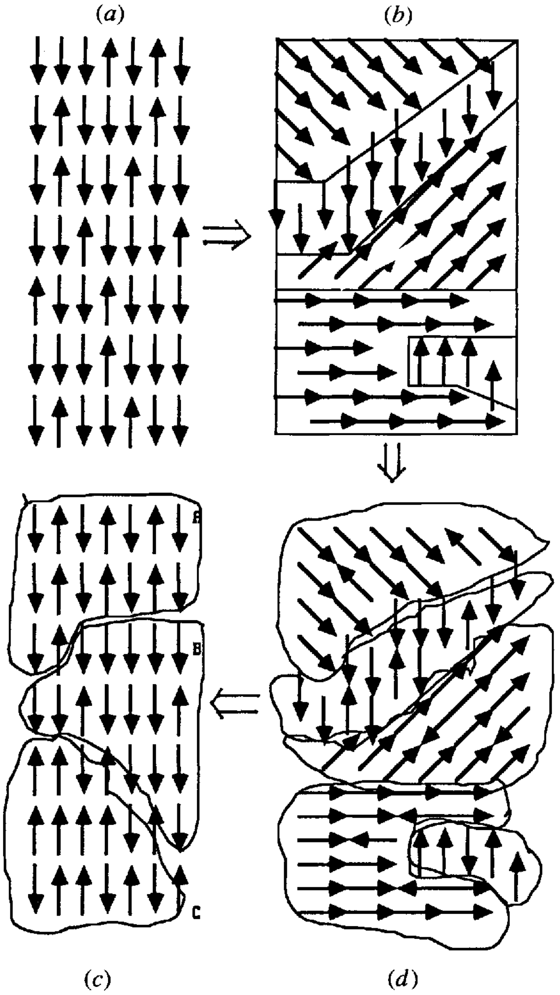

Figure 2. A proposed model for the surface memory effect on unrubbed and rubbed polymers. An initially homogeneous domain (*a*) is forced into a multi-domain structure by bulk forces in the nematic or crystalline phase (*b*). Subsequent heating to the nematic phase gives nematic multi-domains on the unrubbed surface (*c*). On the rubbed surface, the molecules reorient back to the initial direction, but their in-plane order is changed, thus giving varying pretilt angles across the cell (*d*). The mesogens are drawn as arrows to indicate their polar orientation at the surface.

conclude that the observed changes in the bulk pretilt angles are real.

The SME forces the molecules at the surface into a non-equilibrium situation. There should thus be a tendency to restore the equilibrium. Ouchi *et al.* [3,4], obtained a non-equilibrium situation on unrubbed polyimide by magnetic alignment and studied how the magnetically aligned samples returned back to random alignment as a function of temperature. We did a similar experiment. The cells showing a random distribution in bulk pretilt were heated at a given temperature for a period of time. The cells were cooled down to room temperature and the bulk pretilt angle determined again over a number of spots before the heating was continued. Figure 3 shows the development of the standard deviation of the pretilt as a function of accumulated heating time. The samples that never crystallized, for example, the propyl, pentyl and decyl homologues, all had a standard deviation of less than 0·3° for the pretilt angle. In 95 per cent of the cases that we have studied, the standard deviation has been less than 0·3° [6]. We thus chose a standard deviation of less than 0·3° as the point where the cells were in equilibrium.

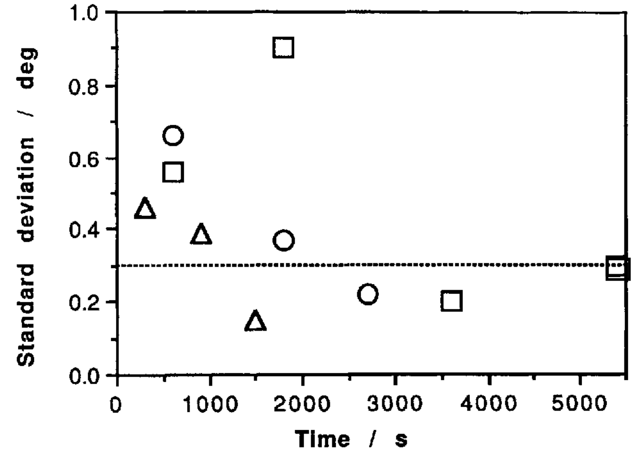

Figure 3. The change of the observed bulk pretilt angle as a function of accumulated heating time for previously crystallized samples of 10 per cent of the ethylhomologue of the nitro-ester in ZLI-1602. Triangles are for heating at 120°C, circles at 100°C, and squares at 80°C.

In figure 4, the time to reach equilibrium is plotted as a function of temperature for the ethyl compound. We see that this time shows a logarithmic dependence on the inverse temperature, indicating an Arrhenius type behaviour. The calculated barrier to the reorientation is 24·0 kJ mol^{-1}.

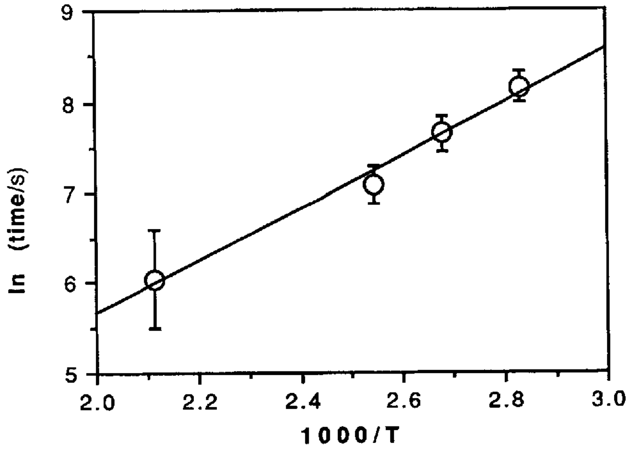

Figure 4. The time for previously crystallized samples of 10 per cent of the ethyl-nitro-ester in ZLI-1602 to reach a uniform pretilt angle as a function of temperature.

The undecyl compound never recrystallized after the first heating, and consequently no barrier was obtained. The samples showed a uniform pretilt after heating to 50°C for 1 h. This indicates that the barrier is lower than for the ethyl compound.

The barrier found in this study is 25–30 times higher than the barrier found previously on an unrubbed polyimide [3,4]. The previous studies looked at the transition from uniform to disordered, while we looked at the transition from disordered to uniform. The definitions of both order and disorder are of course somewhat arbitrary, but we do not feel that this can explain the large discrepancy. Relaxing our criterion for uniformity to a standard deviation of 0·4° or sharpening it to 0·2° will only change the barrier by about $1{\cdot}5\,\mathrm{kJ\,mol^{-1}}$. We thus believe that the rubbing process strongly limits the number of possible orientations of the mesogens at the surface, and increases the barrier between them.

In our model, we can regard the molecules as pointing along the rubbing direction or perpendicular to the rubbing direction, while there is a plane of mirror symmetry along the rubbing direction. If the situation at the surface is in thermal equilibrium, the number of molecules pointing along the rubbing direction and against the rubbing direction will be given by the Boltzmann distribution. This gives us the simple relationship between the population in the different states and the energy difference between the states. Recent investigations by second harmonic generation using the liquid crystal 4-octyl-4′-cyanobiphenyl [11] on the structurally similar polyimide PMDA-6 gives the moments of the in-plane distribution as $a_1 = 0{\cdot}35$, and $a_2 = 0{\cdot}89$. We have $1 - a_2$ molecules perpendicular to the rubbing direction and $1 + a_2$ molecules along the rubbing direction. We can thus find an equilibrium constant $K = (1 - a_2)/(1 + a_2)$. From this we can calculate the energy difference by the Boltzmann equation $\Delta G = -RT \ln K$. Neglecting the few molecules perpendicular to the rubbing direction, we can also define another equilibrium between the number of molecules parallel to the rubbing $(1 + a_1)$ and antiparallel to the rubbing $(1 - a_1)$. Inserting the numbers into the Boltzmann equation, we obtain an energy difference of $1{\cdot}9\,\mathrm{kJ\,mol^{-1}}$ between the states parallel and antiparallel to the rubbing direction, and an energy difference of $7{\cdot}3\,\mathrm{kJ\,mol^{-1}}$ between the states along the rubbing direction and perpendicular to it. The lowest possible barrier for a molecule reorienting from the antiparallel to the parallel orientation would thus be $7{\cdot}3\,\mathrm{kJ\,mol^{-1}}$. This is about 3·5 times lower than we observe. Most of the difference in the barrier height is probably due to differences between the liquid crystals used. Differences in the polyimide structure and rubbing conditions between the two studies will also influence the barrier height.

4. Summary

For the first time we have observed reorientation of the liquid crystal molecules at the surface of cells where both surfaces consists of rubbed polymers. In this case the azimuthal orientation of the optical axis in the cell is unchanged (well-ordered homogeneous orientation), while the polar orientation of the optical axis in the cell changes (varying bulk pretilt angles). This change is brought about by imposing changes in the in-plane order of the molecules at the surface. Like previous workers [2,4], we conclude that the mesogens are relatively fixed at the surface, and that these surface molecules impose the orientation on the bulk of the material in the nematic phase. For the more highly ordered smectic and crystalline phases the bulk forces are strong enough to reorient some of the surface mesogens. For samples with unoriented polymer surfaces, there are no restoring forces and the new direction will be imposed on the bulk in the nematic phase. As shown by Barmentlo *et al.* [9], only a small excess of molecules pointing in one direction is enough to give uniform alignment in that direction. It is thus not necessary that all molecules reorient for the surface memory effect to occur; just a slight excess of molecules pointing in one direction is enough to give a domain showing the same preferred direction. The beautiful and highly noticeable change of colours and textures, due to different director orientations, is caused by only minor changes in the distribution at the interface. For samples with rubbed, and thus oriented, polymer surfaces there are strong restoring forces and the mesogens prefer to lie along the rubbing direction. However, the barrier between the two possible states is high and the in-plane order might be permanently changed. This will change the polar orientation of the director in the bulk and thus the pretilt angle we observe by the crystal rotation method.

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