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The effect of thermal treatment of the alignment layer on the electro-optical response of SSFLCs

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Annealing the polyimide alignment layer affected the IR spectra of the alignment layer and correspondingly the electro-optic effect of surface stabilized ferroelectric liquid crystal displays. It was found that with proper annealing a smectic C* liquid crystal with a spontaneous polarization as high as 30 nC/cm^2 can show good stability towards disturbing pulses. The optimum annealing conditions consisted of a rather narrow temperature band. A model where amorphous regions in an otherwise crystalline polymer act as islands of instability is proposed.

1. Introduction

The surface stabilized ferroelectric liquid crystal display (SSFLC) [1] gives the possibility of fast switching electro-optic elements and flat panel displays with a high information content. In addition to the fast switching, the bistability possible with the SSFLC is an attractive feature, and opens the possibility for an extremely high number of lines with multiplex drive. A good surface orientation and bistability has been difficult to achieve, and much work has been performed to find suitable polymers for surface alignment of SSFLCs, and the best treatment of these polymers. We have previously studied the effect of altering the alkyl chain length in polyimides [2, 3] and polyamides [4], the effect of changes in the aromatic core in polyimides [2, 3], the effect of polymer chain length [2] and the effect of varying the linkage group between the aromatic core and the alkyl chain [5]. In all cases it was found that polymers which are highly crystalline perform better than their less crystalline homologues. However only the bistability under no applied external field was studied. In a multiplexed display on the other hand there will always be small pulses present which might lead to partial or full switching. A useful polymer for surface alignment of SSFLCs should thus not only give bistability when no field is applied, but also retain the bistability when disturbing pulses are present. It has recently been suggested that even small variations in the degree of crystallinity can result in large changes in the stability towards applied pulses [6]. Nylon 6/6 was quenched or annealed to obtain samples of low and high crystallinity. The crystallinity of the samples were determined experimentally, and it was found that a few per cent changes in the degree of crystallinity lead to large differences in the stability of the bistable states in the cells.

A well-known method for increasing the crystallinity of a substance is annealing. As the temperature increases the mobility of molecules also increases. Formation of nuclei for crystallization is thermodynamically favoured at low temperature. Varying the temperature will therefore cause variations in the degree of crystallinity of a

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sample. In this study we have systematically varied the annealing temperature for a given polyimide to vary the degree of crystallinity of the alignment layer. We used a newly developed polyimide that is particularly well suited for the surface alignment of SSFLCs.

2. Experimental

The pre-imidized polyester-imide based on trimelittic acid and aliphatic diols was dissolved in *N*-methylpyrolidone. The final solution contained approximately 3 per cent solids. The polyimide solution was sprayed on clean ITO coated glass plates, or KBr windows for use in the IR spectrophotometer. The solvents were driven off at 200°C for 2 hours.

The glass plates were rubbed lightly with a velvet coated rubbing wheel and the plates mounted together with parallel rubbing directions. 2 μm polymeric ball spacers were used. A number of cells were then annealed at different temperatures for 1 hour, or left unannealed. We annealed the cells after rubbing and mounting as we believe the rubbing can change the degree of crystallinity of the samples. Several cells were annealed at 140, 170, 200, 225, 230, 235, 240, 265 and 300°C. After annealing the cells were vacuum filled with ZLI 3774 from E. Merck in the isotropic state, at approximately 110°C. The phase sequence of ZLI 3374 is I–86°C–N*–76°C–S_A–62°C–S_C^*– < – 30°C–C, with a pitch of 80 μm close to the smectic A–nematic transition. At +20°C the pitch is 4 μm, the dielectric anisotropy is −2·0, rotational viscosity 381 mPa s, the tilt angle is 25·5° and the spontaneous polarization is 28·9 nC cm^{-2} [7]. The resulting cells were 1·7 ± 0·1 μm thick.

All cells were inspected under a polarizing microscope before the electro-optical measurements to ensure that they had a virgin texture. The cells were also inspected again under the microscope after the electro-optical measurements to make sure that the virgin texture had not been disrupted by the electrical pulses. At this time the cells that showed bistability were usually uniformly in one state.

The switching speed and contrast were measured with the cell under investigation placed between a pair of crossed polarizers. The signal generator was a Wavetek model 191 A, giving a 1 kHz, 24 V peak-to-peak square wave. The light source was a tungsten lamp and a Si-PIN detector from United Detector Technologies, fitted with a photometric filter, was used for measuring the transmission through the cell. A Model 101 A amplifier from United Detector Technologies amplified the signal before it was fed to a Kikusui DSS 6522 storage oscilloscope and a voltmeter.

In this study the transmission of the cells was determined both by reading from a storage oscilloscope which gave the time variations and with an voltmeter which gave the time average. They were calibrated to ensure that comparable results were obtained with the two instruments.

When checking the bistability the cells were short circuited. For cells that showed good bistability the cone angle was determined as described elsewhere [2]. 1 kHz square signals of different amplitudes were then applied across the cell and the transmission variations with the amplitude recorded. This was done first in the dark memory state and then in the bright memory state. The dark memory state grew lighter the larger the amplitude of the applied AC field, and the bright state grew darker the larger the amplitude. At a certain voltage the transmission of the two states became identical. Whether an originally dark state would revert to a dark or bright state when this voltage was removed was completely random.

The KBr windows were rubbed with the same type of velvet, but by hand as they were too thick to fit in our rubbing machine. IR spectra were recorded with a Perkin–Elmer 225 Recording Spectrometer with gold grid polarizers in the spectral range 3500 to 500 cm^{-1}.

3. Results

3.1. *IR spectra*

After rubbing, the absorption bands of the polyimide showed a small polarization. Most bands in the spectra seemed, however, to be composed of several overlapping absorptions. Annealing up to 170°C for an hour did not seem to influence the spectra much although there seems to be a weak loss of birefringence. After annealing above this temperature some weak shoulders grew weaker or disappeared completely from the spectra. The three peaks at 1675, 1545 and 1405 cm^{-1} also decreased in intensity in the unpolarized spectra while the band at 1405 cm^{-1} shows an increased polarization as the annealing temperature increased. In our opinion this shows that one or more conformers disappears or becomes less abundant. There are also small increases in the birefringence of some of the bands in the spectra, but whether these changes are due to an increased order of the band or the disappearance of some differently polarized and partly overlapping bands is impossible to tell. The spectra obtained after annealing the polyimide to different temperatures are shown in figure 1. After heating above 235 to 250°C the dichroic ratio of the absorption bands decreases again. All in all the changes in the spectra are small.

We interpret the slight simplification of the spectra and the increase in the dichroic ratio as signs of a crystal growth from the oriented seeds in the rubbed surface of the polyimide. As the temperature becomes too high the polymer melts and there is a loss of orientation. Due to the overlap among different vibrational bands we have not been able to assign crystal bands and amorphous bands and so a calculation of the degree of crystallinity is not possible.

If the polyimide exists in a fully stretched conformation the imide band at 1777 cm^{-1} is expected to have a negative dichroism, in fact this and all other bands show a weak positive dichroism. This could be expected if the polymer exists as a helical coil.

3.2. *Textures*

The unannealed cells showed a texture with domains and quite a few zig-zag defects. The zig-zag lines typically formed long narrow bands; figure 2 shows an example.

Annealing the cells at 140°C removed most of the zig-zag defects. After this heat treatment the zig-zag defects were much more evenly distributed in the cells and usually formed small closed loops, much like elongated droplets. In some cases the hairpin part of the defect wall was inverted thus giving more or less diamond shaped zig-zag defects [8]. The large difference in area between the inside and outside of the zig-zag defects clearly indicated that the two different chevron structures were now of different energy. There were no obvious correlations between the position of neighbouring zig-zag defects, figure 3 shows a fairly typical example.

Annealing at 170, 200, 225, or 230°C gave practically identical textures to annealing at 140°C, though the number of zig-zag defects seems to decrease a little. The results for 170 and 230°C are shown in figures 4 and 5, respectively. When annealing

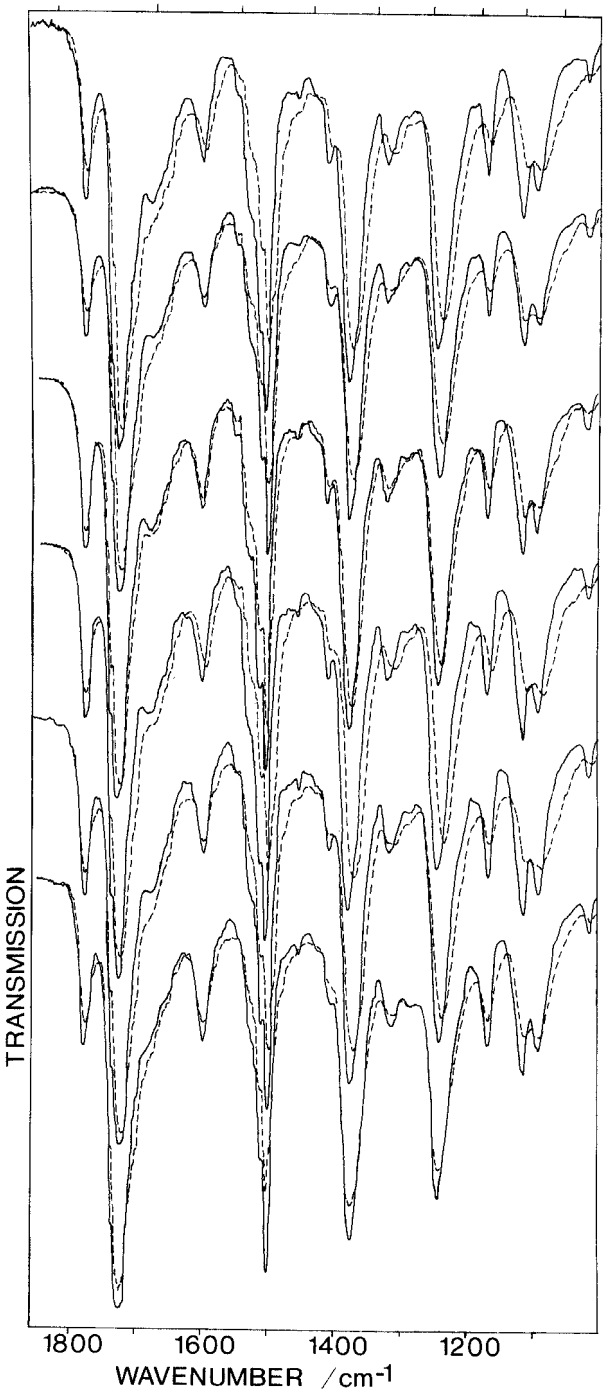

Figure 1. Infrared spectra of the polymer investigated annealed at different temperatures. Top to bottom, unannealed, 140°C, 170°C, 200°C, 225°C, 235°C and 275°C. Full line polarized parallel to the rubbing direction, dashed line polarized perpendicular to the rubbing direction.

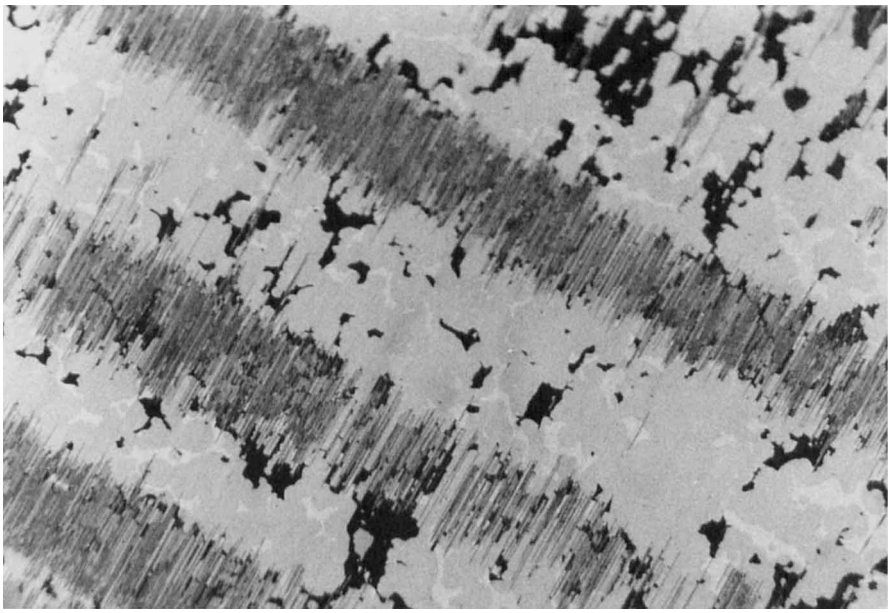

Figure 2. Microphotograph of a cell made with unannealed orientation layers and filled with ZLI 3774.

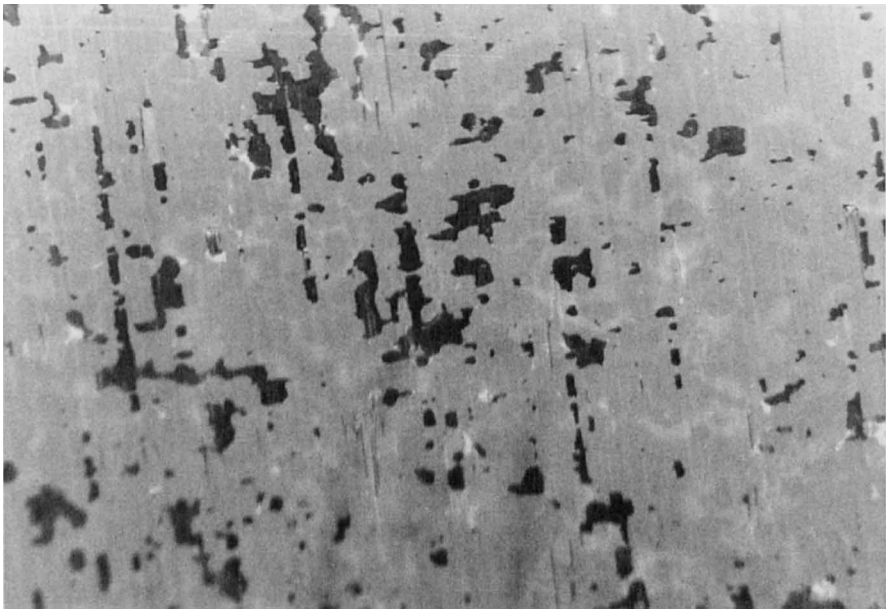

Figure 3. Microphotograph of a cell made with orientation layers annealed at 140°C for 1 hour and filled with ZLI 3774.

at 235°C some of the cells started to show an increased number of defects. Mostly in the shape of zig-zag defects with rather long and narrowly spaced zigs and zags; this is shown in figure 6. Increasing the temperature to 240°C led to further deterioration of the texture with many of these long narrow zig-zag defects. After 1 hour

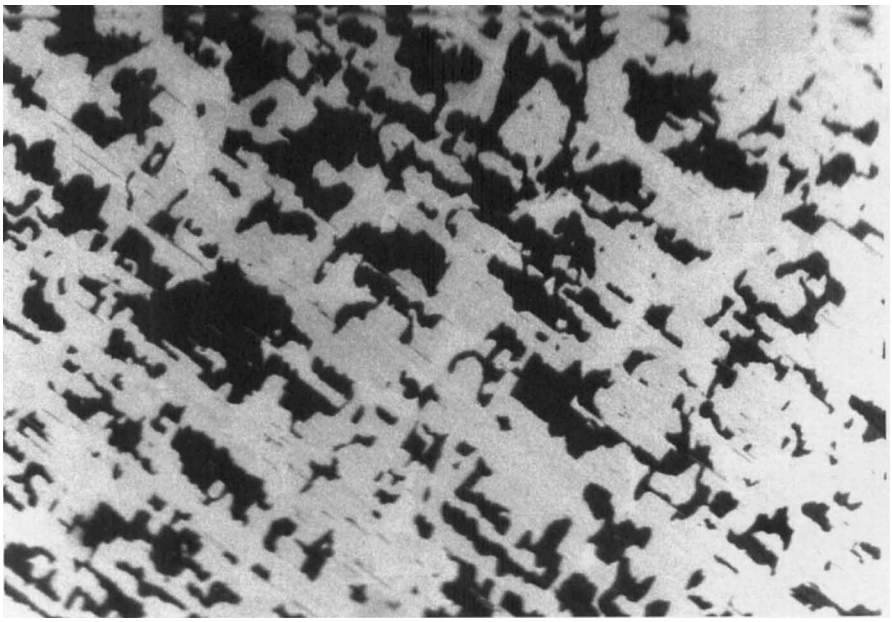

Figure 4. Microphotograph of a cell with orientation layers annealed at 170°C for 1 hour and filled with ZLI 3774.

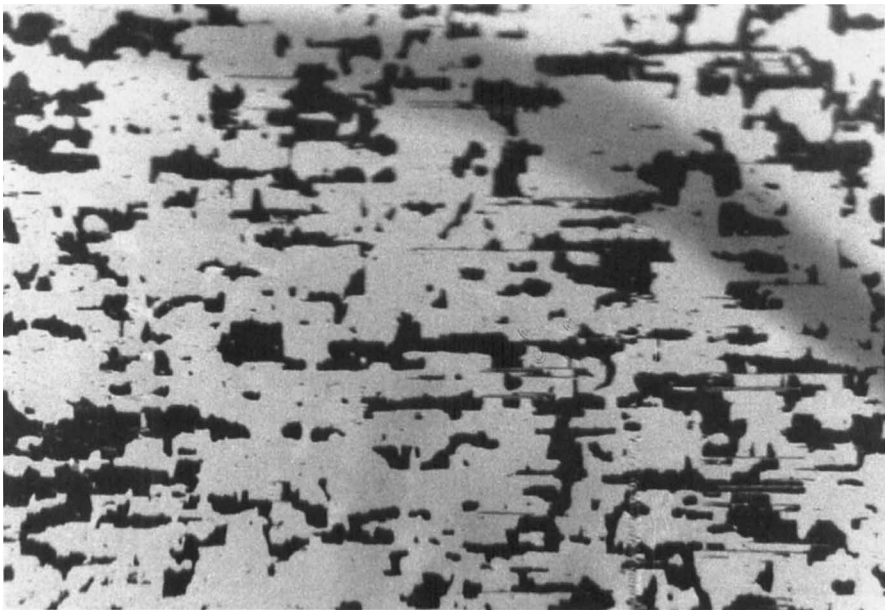

Figure 5. Microphotograph of a cell made with orientation layers annealed at 230°C for 1 hour and filled with ZLI 3774.

at 265°C it was barely possible to find small, good domains among the dominating defect lines. Although most of the defects still seemed to be zig-zag defects they are no longer all parallel, but varied in direction from one part of the cell to another; figure 7 shows a typical example of this texture.

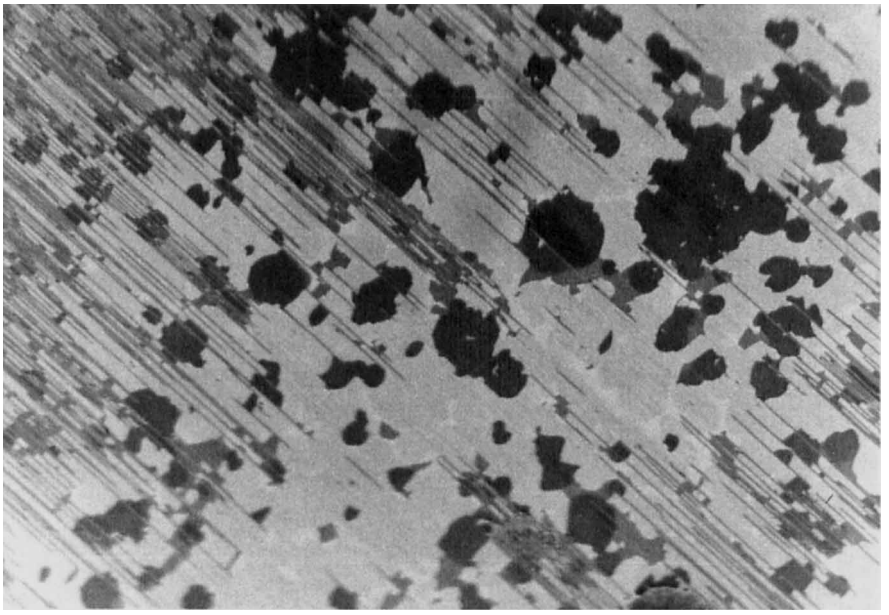

Figure 6. Microphotograph of a cell made with orientation layers annealed at 235°C for 1 hour and filled with ZLI 3774.

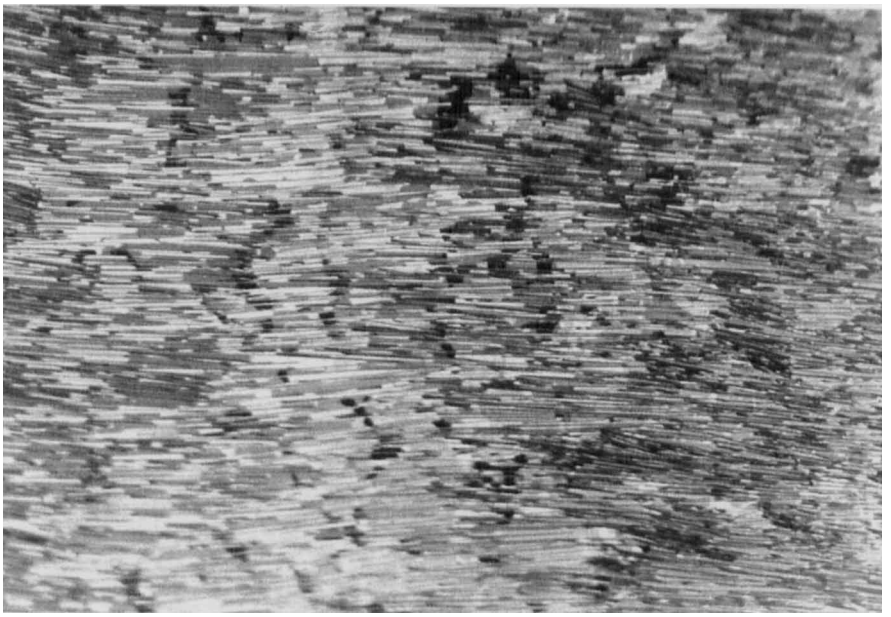

Figure 7. Microphotograph of a cell made with orientation layers annealed at 265°C for 1 hour and filled with ZLI 3774.

Final annealing at 300°C is shown in figure 8. There were small areas with domains looking very much like the texture shown in the preceding photograph, but most of the cell is in a focal conic-like texture. In a thin cell like this it seemed to be difficult for the typical focal texture to appear and we have called this

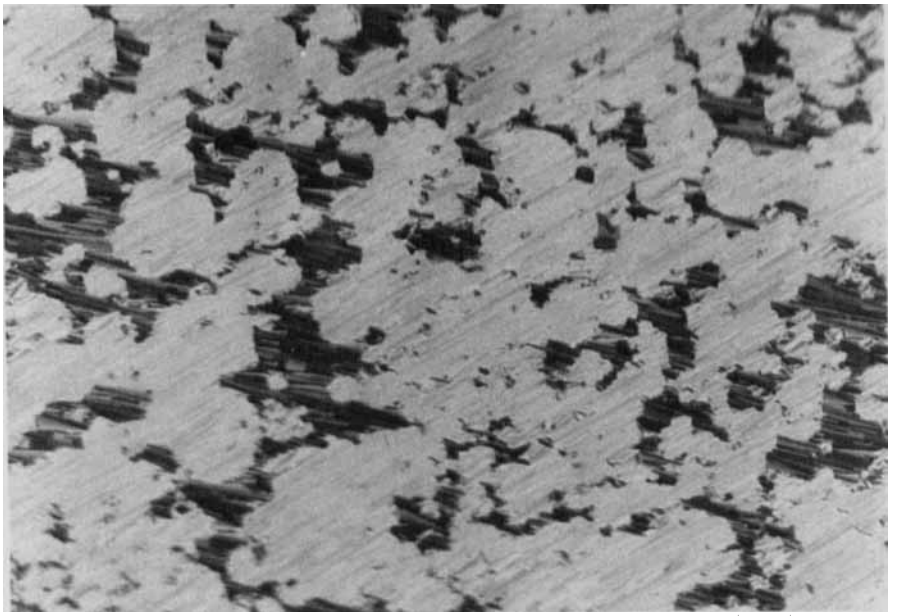

Figure 8. Microphotograph of a cell made with orientation layers annealed at 300°C for 1 hour and filled with ZLI 3774.

the oriented focal conic texture as all the fans point more or less in the same direction.

The structure in the cells have not been determined conclusively. Viewed between crossed polarizers most of the cell showed switching between blue and white colours. This is usually taken as a sign of a twisted director alignment [9]. About one-quarter of the cell showed switching between black and yellow, corresponding to a uniform director alignment [9]. The relative abundance of each director alignment seemed unaffected by the annealing temperature. However, the boat shaped (or hexagonal at higher fields) domains typical of internal disclination loops in twisted cell structures [10] have not been observed during switching. An observed cone angle independent of the tilt angle of the smectic mixture and only dependent on the surface alignment layer [11] is also more consistent with a uniform alignment.

3.3. *Electro-optic behaviour*

In addition to these changes in the texture there were marked changes in the electro-optic behaviour of the cells. At all annealing temperatures we obtained cells which were bistable when short circuited. The minimum transmission of these cells in one of their stable states decreased as the number of defects decreased. As the alignment deteriorated with too high an annealing temperature there was also a catastrophic increase in the minimum transmission. For cells made with alignment layers annealed up to 235°C there were no changes in the rise and fall times (10 to 90 and 90 to 10 per cent transmission respectively), and the rise and fall times were also identical.

To be used in multiplexed cells there should not only be bistability when a cell is short circuited, but, in addition, the two stable states should be stable towards small

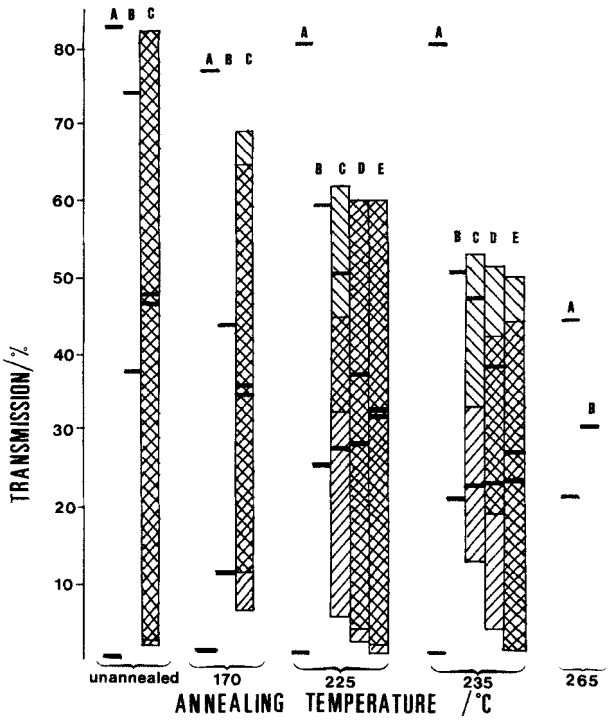

Figure 9. Effect of AC fields on the transmission of cells made with polyimide annealed at different temperatures. A, switching with 1 kHz 24 V peak-to-peak; transmission of the memory states with the same relative polarizer orientation as for A; C, the fluctuations in transmission for B when subjected to 1 kHz 4 V peak-to-peak; D, as C with 6 V peak-to-peak; E, as C with 8 V peak-to-peak.

pulses, e.g. small compared to pulses used for switching the cell. Figure 9 summarizes the effect of applying small AC fields to the cells annealed at different temperatures. A shows the maximum and minimum transmission of the cells switched by a 24 V peak-to-peak square wave at 1 kHz. The cells have been turned between the pair of crossed polarizers to obtain maximum contrast under the switching condition. As can be seen this is fairly independent of the annealing temperature as long as the cells have the texture with domains. B shows the transmission of the two bistable states, neither in this case is there much variation between the different treatments of the cells. This is also evident from a cone angle of 25 $\pm$ 2°C found in all cases. The orientation of the cells relative to the polarizers is the same as for A. Thus the transmission in this case is higher than when the short circuited cells in the relaxed states are turned to minimize the transmission between crossed polarizers.

When a 4 V peak-to-peak square wave at 1 kHz is applied to the two relaxed states the effect is shown by C. In all cases the transmission of the dark states increase and the transmission of the bright states decreases as a field is applied. The average transmission is given by the bars in figure 9. These changes in transmission are due to a ripple effect clearly seen by displaying the detector signal on a storage oscilloscope. The director in the relaxed states fluctuates due to the external field. The fluctuations are indicated by the hatched areas. In some cases the fluctuations are unsymmetric. For the first time a clear effect of the different annealing temperatures

is shown in our cells. Up to an annealing temperature of 170°C the fluctuations caused by a 4 V field are large enough to give the same or very nearly the same transmission for both the bright and the dark relaxed state. It is also purely random which of the two states will be obtained when the field is removed. In other words there is no bistability when subjected to even this relatively low field. At an annealing temperature of 200 to 235°C there is bistability under this condition. Increasing the voltage to 6 V peak-to-peak there is still bistability when the cells have been annealed at 225 to 235°C for 1 hour as indicated by D. With an 8 V field these cells also yield and the bright and dark relaxed states coalesce. Removing the field again it is random which of the two states will be obtained.

Summing up there is bistability found in all cases when the cells are short circuited. The bright and dark relaxed states are stable toward low AC fields. The strength of the field that can be tolerated is, on the other hand, strongly dependent on the annealing which the polymer surface has undergone.

The bistability can be quantified by the expression

$$\frac{T_2 - T_4}{T_1 - T_3} \times 100 = M, \tag{1}$$

where T_1 is the transmission of the bright state under full driving voltage, T_2 is the transmission of the bright state under memory conditions, T_3 and T_4 are the transmissions of the dark states under full drive voltage and memory conditions, respectively. M is then the per cent memory [12]. In figure 10 the per cent memory is shown as a function of the low disturbing field for several different annealing conditions of the polyimide. The memory improves only slightly upon annealing in the case where the cell is short circuited (0 V disturbing field). But as soon as disturbing pulses are applied there is a clear improvement in the cells which have been annealed at temperatures of 200 to 235°C. The improvement is larger at higher annealing temperatures. As mentioned earlier some of the cells annealed at 235°C begin to show a deterioration in alignment they also seem to be without the improved tolerance to disturbing fields.

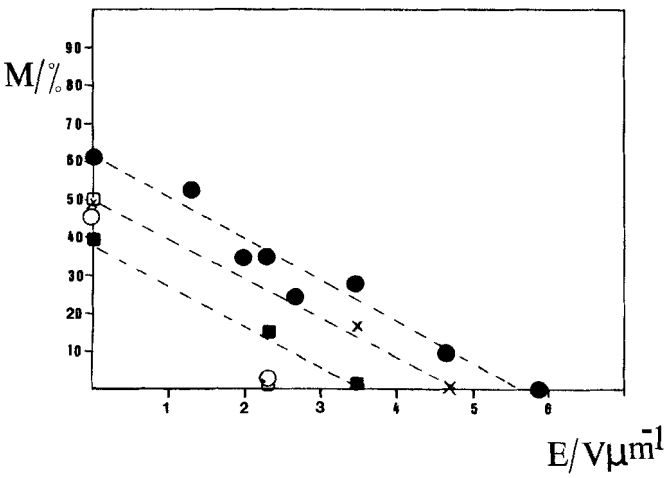

Figure 10. Per cent memory of the cells as a function of the applied disturbing AC field. ●, cell annealed at 235°C; x, annealed at 225°C; ■, annealed at 200°C; □ annealed at 170°C, ○, unannealed.

The effect of the disturbing AC field on the per cent memory appears to be linear in the field strength. By proper annealing of the polyimide it is possible to retain the memory in an SSFLC cell with disturbing pulses as high as one-third of the select pulses, even for ZLI 3774 which has a spontaneous polarization as high as 28·9 nC/cm^2.

4. Discussion

From the IR spectra the polyimide seems to undergo only minor changes when annealed. The effect on the electro-optic characteristics of the cells are, however, dramatic. We would like to consider some possible causes for the improved stability towards disturbing electric fields.

The polymer used gives approximately 0° pretilt in the nematic phase [13]. As the sample is annealed we see clearly that one of the two possible chevron structures are preferred. In the unannealed sample the areas outside and inside the zig-zag defects are roughly equal as would be expected for a surface with no selective pretilting. After annealing one of the two chevrons dominates indicating that they are no longer of identical energy. This can be taken as evidence for a selective pretilting on the surface [8]. On the other hand heating of polyimides after rubbing is found to decrease any pretilt on the surface [14]. An increased tendency for the molecules to align parallel to the surface has also been suggested as a reason for the increased stability towards electric pulses [6]. The resolution in our tilt measurements have not been good enough to detect any selective pretilting in the nematic phase on annealed surfaces.

Defects in the alignment layers and uneveness in the rubbing will often cause zig-zag defects. The reduction in the number of zig-zag defects can then be taken as a sign of a smoothing of the surface. In SSFLC there will be both bulk switching and surface switching. Both seem to be promoted by defects that act as seeds for the switching [9]. Fewer zig-zag defects are a sign of fewer defects in the alignment of the cell, thus also fewer seeds for switching. With fewer seeds for switching the barrier would be higher and consequently also the stability towards disturbing pulses. It should be noted that most of the zig-zag defects disappear after annealing to 140°C, while an annealing temperature above 200°C is necessary for improvement of the stability of the cell. This might indicate that only major deformations in the alignment layer give rise to zig-zag defects while much smaller seeds are sufficient to initiate back switching under low applied fields.

It has been found that amorphous polymers will not give bistable cells [2, 3, 15], in other words there is no barrier between different memory states. Some crystalline polymers support bistability. It is also possible to grow good domains from the edges of crystalline polymers [16]. Thus a small enough amorphous region in an otherwise crystalline polymer could very well show bistable behaviour. As a disturbing pulse is applied the lack of threshold or energy barrier between the dark and bright states manifests itself. The direction will switch back and forth with the applied field. The two bistable states on the other hand are separated by a first order orientation transition, both having the director **n** parallel to the surface [17]. In many first order phase transition phenomena, e.g. crystallization, it is found that the thermodynamically stable phase will not form spontaneously because the energy for forming the first seeds is too large. In SSFLCs under an applied field the energetically most stable condition is with the spontaneous polarization antiparallel to the external field. However, with low fields the energy for forming the first switched domains are too high and bistability can be found on properly crystalline surfaces.

Stroboscopic micrographs show that after the first switched domains are formed these will grow, rather than new domains forming in bistable cells [9, 18]. As amorphous polymers give no barrier between the two possible states switching will occur easily here. These switched areas will then act as seeds for the switching of the neighbouring areas of crystalline polymers. The initial, high energy of forming small areas of the thermodynamically most stable state have been lowered by the inclusion of amorphous regions in an otherwise crystalline surface. As annealing is known to promote crystallinity, annealed polymers will consequently have fewer and smaller amorphous regions. A more stable structure towards small external fields is expected and this is indeed what we find.

The relatively high barrier on crystalline surfaces than on amorphous could result from a stronger tendency of the director to align parallel to the surface [6]. Consequently there will be a higher barrier for the smectic C director switching from one stable state to the other stable state. During this switching the director moves along the one of constant smectic C tilt and has to leave one stable state parallel to the surface before coming back to the other stable state, also parallel to the surface. Within the accuracy of our experiment we find a symmetric behaviour for all surfaces, for example, the field that will render the dark state unstable will also render the bright state unstable. On the other hand a field that is too small to disrupt the dark state will not disrupt the bright state either. This indicates that the barrier between the two stable states is the same whether it is approached from the dark or the bright side. The identical switching times from dark to bright and bright to dark is consistent with this. In other words the dark and bright states are of equal energy. Also the stable cone angle of $25 \pm 2°$ indicates that the potential well does not change shape during the annealing. We have previously shown the great importance of the alignment layer in determining the cone angle [11].

The rise and fall times of the cells are unaffected by the annealing, showing that the growth rate of switched domains once formed is the same in all cases. The effect of a larger field being necessary for disturbing the cell could be an effect of a larger product of voltage pulsewidth being needed for switching, but this should also give an increase in switching times. Again we are led to the conclusion that the annealing increases the barrier to the formation of small switched domains, but as soon as they are formed their growth rate is unaffected.

5. Conclusion

Annealing the polymer increases the stability of the relaxed states towards disturbing electrical pulses. Good bistability with a P_S of 29 nC/cm^2 has been obtained. The amorphous areas left in the polymer after annealing acts as seeds for the flickering seen when disturbing pulses are applied to the cell. Polymers with a maximum degree of crystallinity should be sought for when considering alignment layers for SSFLCs.

We are grateful to Professor Peter Klaeboe for placing the IR spectrometer at our disposal and to E. Merck, Darmstadt for samples of ZLI 3774.

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