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Odd-even effects in the alignment of ferroelectric liquid crystals

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Nine different poly-*n*-alkylterphthalamides have been synthesized, and their properties as alignment layers for chiral smectic C liquid crystals have been determined. Poly-*n*-hexylterphthalamide is found to be particularly well suited for one of the room temperature mixtures used in this study. The contrast between relaxed states shows an odd-even effect that can probably be explained by the crystal form of the different polymers. The tilt angle found between the relaxed states depends only on the polymer used, not on the inherent tilt of the chiral smectic C phases.

1. Introduction

After the invention by Clark and Lagerwall of the surface stabilized ferroelectric liquid crystal display (SSFLC) [1] there has been much interest in finding a method of obtaining the surface stabilized structure over large areas. Several methods have been suggested for work on the laboratory scale; shearing the cell [2], crystal growth from spacer edges [3], magnetic fields [4], electric fields [5], evaporation of silicon monoxide [6] and temperature gradients [7]. In order to be used in a production process the orientation method should be fast, reliable and simple. After any accidental heating above the smectic C* range the cell should also preferably regain the same properties without complicated cooling procedures. Most work has therefore concentrated on the use of polymers for aligning FLCs [8-19]. It has also been shown that the orientation of a ferroelectric smectic C* is easier with the phase sequence isotropic-cholesteric-smectic A-smectic C* and an infinite (or very long) pitch in the cholesteric phase [20]. Other properties are, however, still strongly dependent on the surface treatment.

Many widely different surfaces have been tested. There are several possible effects involved in the surface orientation of smectics: surface tension [13], geometrical considerations [21], surface polarities [13] or epitaxy [9, 12], to name a few. However, because of the large number of possible effects involved, it has been difficult to ascertain the relative importance of the different effects. In this work we want to make as small a difference as possible between the polymers studied, so it was natural therefore to study a homologous series of alkyl compounds. Our choice was a series of polyamides. Many different polyamides have been shown to give good alignment for ferroelectric liquid crystals [9-12, 14, 15]. To avoid the problem of two different chains in the molecule, poly-*n*-alkylterphthalamides were chosen. Polyhexamethylene-terphthalamide has been shown previously to give good results [8, 9]; this polymer and other homologues are easily made and purified.

2. Experimental

2.1. Synthesis

1,2-Diamino-ethane, 1,3-diamino-propane, 1,4-diamino-butane, 1,5-diamino-pentane, 1,7-diamino-heptane, 1,8-diamino-octane, 1,9-diamino-nonane and

1,10-diamino-decane (from E. Merck) and 1,6-diamino-hexane and terphthaloyl chloride (from Aldrich) were used without further purification.

Terphthaloyl chloride (10 mmol) was dissolved in 100 ml of chloroform. The diamine (10 mmol) was dissolved in 100 ml of water and 2 g of sodium hydroxide was added. The water solution was poured carefully on top of the chloroform solution and the desired polyamide formed at the liquid-liquid interface. The polymer was drawn out of solution with a glass rod. The crude product was washed repeatedly with methanol and dried under vacuum. For the polymers with five (Nylon 5T), six (Nylon 6T) or seven (Nylon 7T) carbon atoms in the alkyl chain the melting points showed good agreement with the literature values [22]. For the shorter diamines (Nylon 2T, Nylon 3T and Nylon 4T) the melting points were above the range of our melting point microscope). The properties of the different polyamides are given in table 1.

Table 1. Poly(polymethylene-terphthalamides) and their melting points.

Name	Alkyl chain	Melting point/°C	
		Present work	[22]
Nylon 2T	C ₂ H ₄		455
Nylon 3T	C ₃ H ₆		400
Nylon 4T	C ₄ H ₈		436
Nylon 5T	C ₅ H ₁₀	336 to > 355	355
Nylon 6T	C ₆ H ₁₂	> 355	375
Nylon 7T	C ₇ H ₁₄	340-345	340
Nylon 8T	C ₈ H ₁₆	324-338	
Nylon 9T	C ₉ H ₁₈	298-320	
Nylon 10T	C ₁₀ H ₂₀	323-331	

Nylon 5T, 6T, 8T and 9T start to show some decomposition at 280-285°C; Nylon 7T at 265°C.

2.2. Cell construction

Glass plates of thickness 1.1 mm with an indium-tin oxide coating (200 Ω cm⁻²) from Donnelly mirrors were spray coated with a solution of the polymer to be tested in trifluoro acetic acid. The solvent was evaporated at 200°C for 2 h. The plates were buffed lightly with a velvet covered, rotating buffing wheel. Polymeric ball spacers of diameter 2 μm were applied to one of the plates and small dots of U.V. curable glue to mark the outline of the cell on the other plate. The plates were mounted together, with parallel rubbing directions. The glue was cured and the cells were cut to a size of 5 × 5 cm. The cells were then after-sealed leaving a small filling port. They were filled with the room temperature ferroelectric mixtures ZLI-3774 from E. Merck and FELIX-004 from Hoechst, using capillary filling under vacuum. This gives even cells with little or no birefringence colours.

2.3. Measurements

Switching speed and contrasts were measured with the experimental set-up shown schematically in figure 1. The wave generator used was a Wavetek model 191. A square wave of 30 V peak-to-peak was used, the frequency being varied between 100 Hz and 1.5 kHz. The light source was a tungsten lamp. An Si-PIN detector from United Detector Technologies, with a photometric filter, measured the transmission

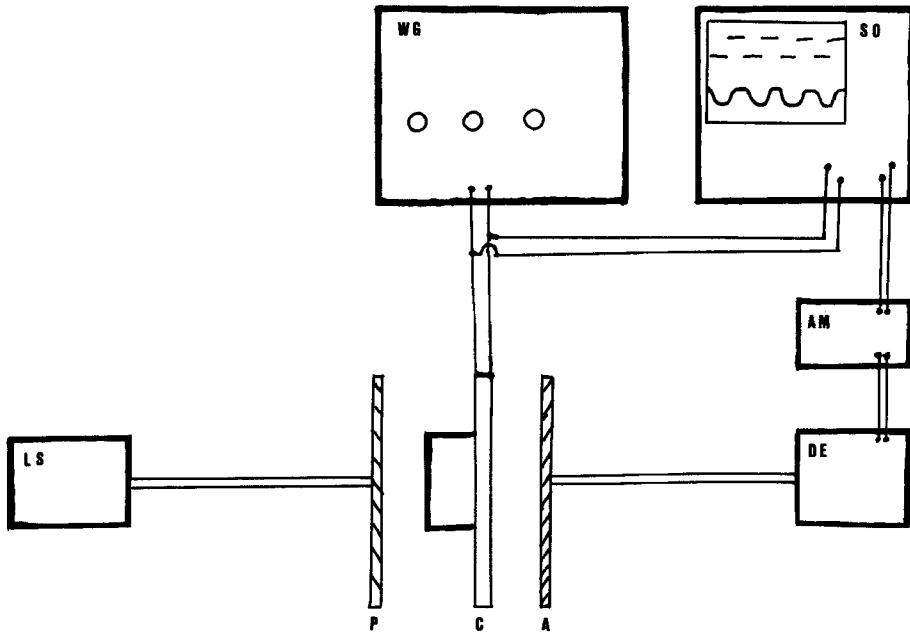


Figure 1. Experimental set-up for the determination of the electro-optic performance of the test cells. LS, White light source; P, polarizer; C, SSFLC-cell; A, Analyser; DE, detector; AM, amplifier; SO, storage oscilloscope, WG, wave generator.

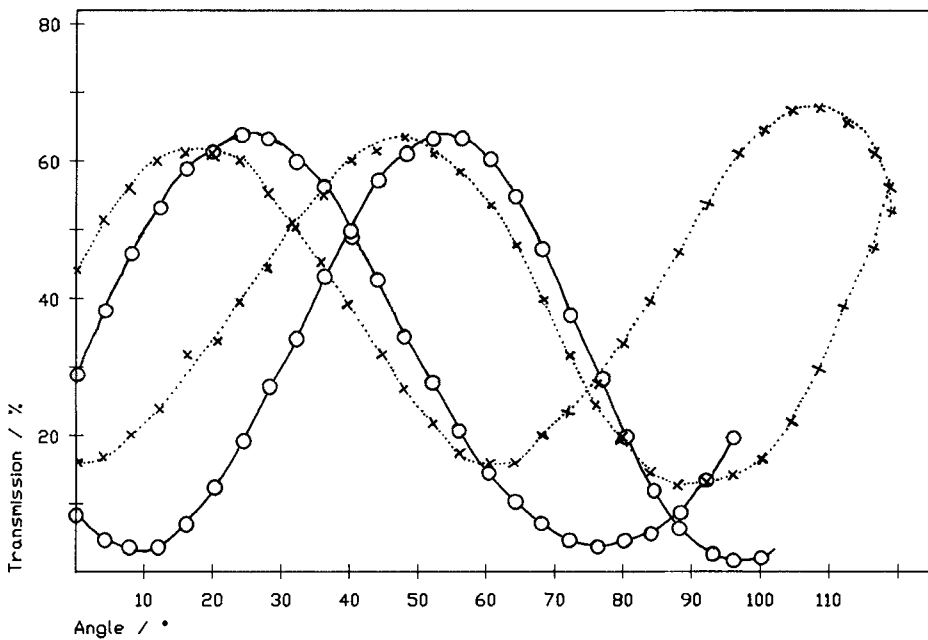


Figure 2. Typical traces for the transmission versus turning angle of the cells. The transmission is measured relative to crossed (0 per cent) and parallel (100 per cent) polarizers.

of the cell. A Model 101A amplifier from United Detector Technologies amplified the signal before it was displayed on a Kikusui DSS 6522 storage oscilloscope. The tilt angle between the two memory states was determined by short circuiting the cell and rotating it between crossed polarizers. The cell was then switched to the other orientation and short circuited again, before rotating once more between the same crossed polarizers. The phase shift between the two transmission curves was twice the tilt angle [23]. The maximum contrast between the relaxed states was found from the same two curves at the angle where the ratio between the two transmissions was greatest. Typical traces are shown in Figure 2. Uncertainties in the measurements are mostly due to small areas that seem to relax very quickly to one particular orientation, as the cells are rotated a small deviation from the ideal sine curves are therefore found. Contrasts between driven states and switching times were measured with the same experimental set-up and the cell turned for maximum contrast between the two states. As long as the cells were able to switch fully on and off, the switching times found were independent of the drive frequency.

3. Results and discussion

The experimental results for ZLI-3774 are summarized in table 2, and the discussion will concentrate mostly on the results for this material. In two cases the contrast between the driven states are found to be slightly lower than the contrast between the driven states, but this difference is well within the experimental error. With a very low transmission in the dark states even a small absolute error in the determination of the transmission will give a large error in the contrast. A lower contrast between the relaxed states than between the driven states is, of course, expected since an electric field will force the molecules to adopt a structure closer to the ideal bookshelf geometry.

Table 2. Summary of results obtained with ZLI-3774 on the different Nylon xTs.

Polymer	Minimum transmission/ per cent	Contrast		Tilt angle, relaxed states/°	Switching times/ms	
		Relaxed 1	Driven 1		On	Off
Nylon 2T	3.0	33.0	55	9 ± 3	0.12	0.12
Nylon 3T	13.0	2.0	10	6 ± 5	0.12	0.12
Nylon 4T	4.0	12.0	26	6 ± 3	0.11	0.11
Nylon 5T	4.0	2.7	66	5 ± 3	0.12	0.12
Nylon 6T	1.0	96.0	90	16 ± 4	0.12	0.12
Nylon 7T	3.5	4.7	72	4 ± 2	0.12	0.12
Nylon 8T	8.0	12.0	10	10 ± 4	0.09	0.09
Nylon 9T	14.0	3.9	10	15 ± 4	0.09	0.09
Nylon 10T	1.5	16.7	88	15 ± 4	0.11	0.11

There is a pronounced odd-even effect for the contrast between the relaxed states, with even numbered carbon chains giving better contrast, and Nylon 6T a particularly high contrast. This is shown in figure 3 (a). For the contrast between the driven states this odd-even effect is absent and, even though there are large variations in the contrast, it bears no simple relationship to the number of carbon atoms in the chain.

Defects in the alignment will scatter light and increase the transmission of the dark states, and will lower the transmission of the bright states, with the former being most important in lowering the contrast of the device. The density of defects have been checked visually and determined by the minimum transmission between crossed

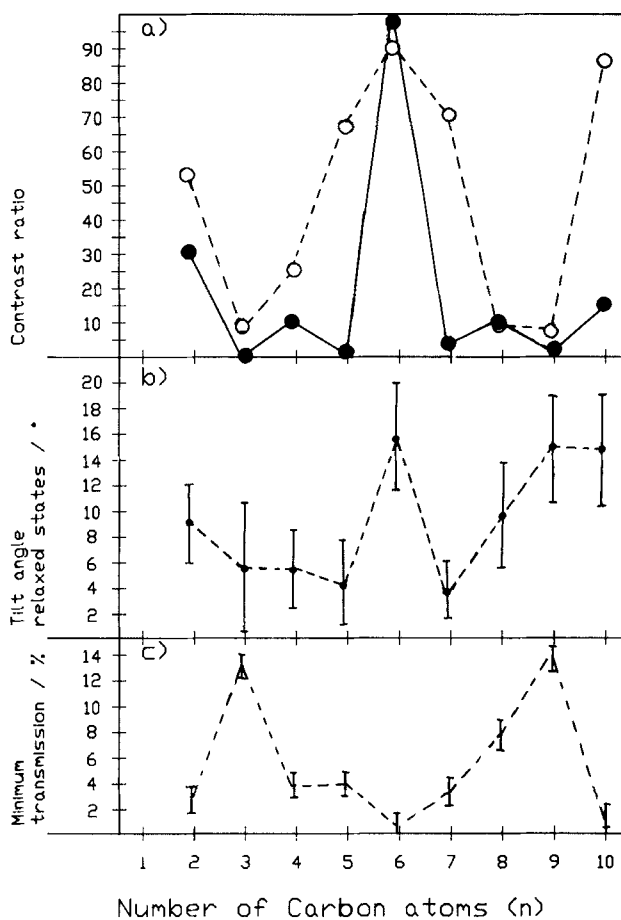


Figure 3. Variation in the electro-optic properties with alkyl chain length. (a) The contrast ratios between (O) driven and (●) relaxed states. (b) The tilt angle between the relaxed states. (c) The minimum transmission, which is a measure of the defect density.

polarizers; being more qualitative, only the latter is reported. However, the results obtained by the two methods are in good agreement, with Nylon 6T clearly the superior polymer, visually. As can be seen from figure 3(c), there is an inverse correlation between the transmission in the dark state and the contrast between the driven states, whereas any correlation between the contrast between the relaxed states and the minimum transmission is far less evident. With an applied field the structure will be close to the ideal bookshelf geometry and the transmission will depend mostly on the number of defects. The difference in transmission between the relaxed states will vary both with the number of defects and with the apparent tilt angle. The apparent tilt angle is usually less than the smectic C* tilt angle found for the bulk material.

The apparent tilt angles for the relaxed states are shown in figure 3(b). The relationship between the tilt angles found and the contrast of the relaxed states is not very good. Nylon 9T and Nylon 10T gave the same tilt angle, but the latter gave a far better contrast, due to the smaller number of defects. Nylon 8T gave a smaller tilt angle than Nylon 9T, but still has a better contrast because of far fewer defects. Within the experimental accuracy the tilt directions were symmetric about the rubbing direction.

It seems that the odd-even effect observed for the contrast between the relaxed states is an artifact, and neither of the two underlying causes shows any odd-even effect. Other properties like switching times and contrast, between driven states do not show odd-even effects, either. The odd-even effect is also absent in some other series of polymers which we have studied for both ZLI-3774 and other smectic mixtures, but present in other [25].

Table 3. Summary of results obtained with FELIX-004 on the different Nylon *x*Ts.

Polymer	Minimum transmission/ per cent	Contrast		Tilt angle, relaxed states/°	Switching times/ms	
		Relaxed 1	Driven 1		On	Off
Nylon 2T	7.6	2.1	6	13 ± 2	0.16	0.16
Nylon 3T	4.8	2.0	4	8 ± 2	0.07	0.07
Nylon 4T	—	—	—	—	—	—
Nylon 5T	11.0	1.0	1.3	N.A.	—	—
Nylon 6T	8.5	2.0	6	12 ± 3	0.20	0.16
Nylon 7T	16.0	1.1	2	3 ± 1	0.20	0.20
Nylon 8T	14.0	1.4	4	5 ± 2	0.20	0.20
Nylon 9T	11.0	1.3	2	12 ± 5†	0.20	0.20
Nylon 10T	21.0	1.9	20	17 ± 4	0.20	0.20

† Determined by visual inspection.

The results for FELIX-004, given in table 3, show much lower contrasts both for driven and relaxed states, this is mostly due to the higher number of defects in the alignment, as indicated by rather high minimum transmission. As we can see, the odd-even effect is not evident for this ferroelectric mixture. For Nylon 9T the cell relaxed to one state in about 10 s, thus the tilt angle could not be found using the slow method of turning the cell between a pair of crossed polarizers. Judging the angle between two domains visually, a tilt angle of 12° was found.

To obtain a good contrast between the relaxed states it is also important that the effective angle between the two states be as close to 45° as possible. Most ferroelectric fluids are made with an inherent tilt angle of approximately half this value; it is usually found that the tilt between the two relaxed states in an SSFLC cell is much smaller than this [24]. For ZLI-3774 and FELIX-004 the inherent tilt angles are 25.5° and 33°, respectively, at 20°. Despite this 30 per cent difference in inherent tilt angles for the two fluids, there are no significant differences between the tilt found for the relaxed states, as can be clearly seen from figure 4. From these experiments it seems that the polymer surface plays a major role in determining the tilt between the relaxed states, and thus also the possible contrast in the bistable operation of an SSFLC device.

Crystal structures of the different poly-*n*-alkylterphthalamides are not known, except for Nylon 6T which gives mixed crystals of high crystallinity with Nylon 6/6. The crystallinity increases slightly with increasing amounts of Nylon 6T. This compound is probably triclinic, therefore. For a similar series of polyimides [26] and polyesters [27] it is found that members with an even number of carbon atoms are highly crystalline with the same crystal structure, whereas those with an odd number of carbon atoms are amorphous [26] or have a different crystal structure [27]. For the low molecular alkylidibenzamides which have been studied as model compounds for the Nylon *x*Ts, the ethyl- and pentylidibenzamides have orthorhombic crystal structures, whereas all the others are monoclinic [28].

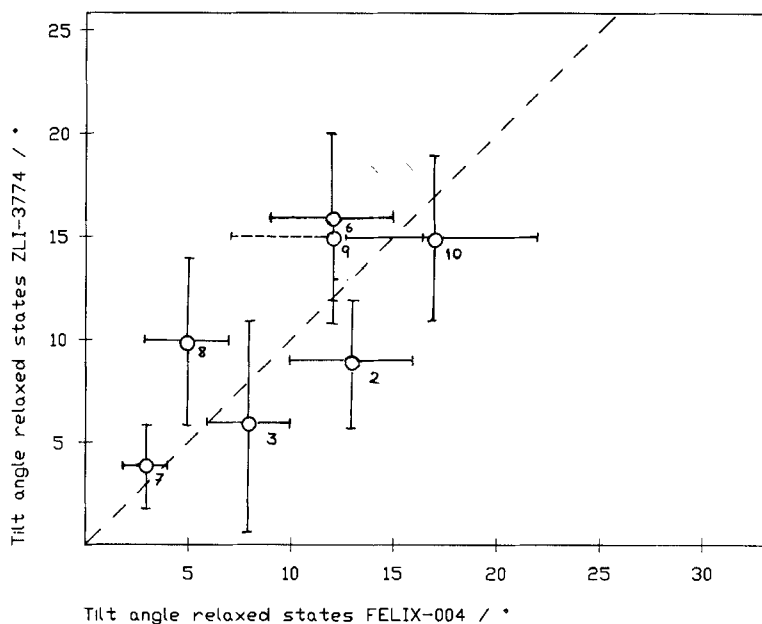


Figure 4. Comparison of the tilt angle between the relaxed states found for FELIX-004 and ZLI-3774 on seven of the different Nylon xTs studied. '2' refers to Nylon 2T, '3' to Nylon 3T, etc. Despite a 30 per cent difference in the smectic C tilt angles for the two materials, the tilt angles between the relaxed states are the same.

Table 4. Comparison of the tilt angles found for ZLI-3774 and FELIX-004 on the different Nylon xTs.

Polymer	Tilt angle, relaxed states/°	
	ZLI-3774	FELIX-004
Nylon 2T	9 ± 3	13 ± 3
Nylon 3T	6 ± 5	8 ± 2
Nylon 4T	6 ± 3	N.A.
Nylon 5T	5 ± 3	N.A.
Nylon 6T	16 ± 4	12 ± 3
Nylon 7T	4 ± 2	3 ± 1
Nylon 8T	10 ± 4	5 ± 2
Nylon 9T	15 ± 4	12 ± 5†
Nylon 10T	15 ± 4	17 ± 5

† Determined by visual inspection.

The natural tilt of ZLI-3774 is 25.5° whereas that of FELIX-004 is 33°.

We have shown previously that triclinic or monoclinic crystal structures in the aligning polymer are a prerequisite for good alignment and bistable operation of SSFLC devices [9]. The relatively good performances of all the even numbered members of the Nylon xT series should be no surprise, therefore. For members with an odd number of carbon atoms there is clearly no single source of their poorer performance. Whether this is due to different crystal structures among these polymers or to other reasons is still an open question.

The surfaces of the Nylon x Ts have a microdomain structure composed of crystalline and amorphous regions [29]. If the smectic C* phase (or the smectic A phase) grows epitaxially we should expect a less perfect surface to give a less perfect orientation of the smectic phase. Thus, the higher the crystallinity of the surface is, the better the quality of the alignment, and the lower the minimum transmission of the cell. We have not been able to determine the degree of crystallinity of these thin rubbed films on glass. Data for the crystallinity of bulk samples of Nylon 2T, Nylon 6T and Nylon 10T [30] show a good correlation with the minimum transmission, and hence with the density of defects. Other and more complete data for the crystallinity [29, 31] do not show such a good correlation. Values from different sources also disagree. The preparation and purity of the samples and the conditions under which they were annealed will influence the crystallinity to a large degree. At present it is not possible to draw any definite conclusions about the role of the degree of crystallinity.

4. Conclusions

For the room temperature smectic C* mixture ZLI-3774 the density of defects and apparent tilt angle between relaxed states combine to give a pseudo odd-even effect, but none of the underlying properties shows an odd-even effect. On Nylon 6T the combination of a very low number of defects and a high smectic tilt gives an extremely good contrast between the relaxed states. It is also found that the apparent tilt angle between the relaxed states are strongly dependent on the orienting surface used, whereas the inherent tilt angle of the smectic C* phase plays only a minor role.

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