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Bernt O. Myrvold

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Polyimide aligned ferroelectric smectic C liquid crystals

by BERNT O. MYRVOLD
Norsk LCD a.s., Eikhaugen, N-3036 Drammen, Norway

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27 alkyl-aromatic polyimides have been synthesized and tested as alignment layers for surface stabilized ferroelectric liquid crystals with a number of room temperature ferroelectric mixtures. The cone angles are used as a quantitative measure of the bistability obtained in these cells. The effect of the structure of the polyimides on the cone angles obtained and the stability of the alignment is discussed.

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. The bistability is a quality which has been difficult to achieve, and which seems to depend as much on the surface of the cells [2, 3] as on the ferroelectric smectic phase.

Although bistability is an important quality in surface stabilized ferroelectric liquid crystal cells, there has been no agreement on how to quantify this. Previously we have used the contrast between the two relaxed states as a measure of the bistability [2]. This contrast is mostly dependent on two factors. First the minimum transmission in the dark state and secondly the cone angle between the directors in the two relaxed states. The first factor is further dependent on the number of defects in the cell, and varies with the method of polymer application, rubbing pressure and spacer density in the cells. We have found the cone angle to be independent of the method used to apply the polymer and also independent of the rubbing pressure or heat treatment of the polymer. However the reproducibility of the cone angle will depend on the mode of preparation and the more crystalline the sample the better the reproducibility of the values for any given mesophase/polymer combination.

2. Experimental

2.1. *Synthesis and cell preparation*

Several different series of alkyl-polyimides with the required triclinic or monoclinic crystal structure [4, 5] have been synthesized. The tetracarboxylic acid moieties tested so far are benzene-1,2,4,5-tetracarboxylic acid anhydride (pyromellitic anhydride) called the P-series; benzophenone-3,3′,4,4′-tetracarboxylic acid anhydride, the B-series; and naphthalene-1,4,5,8-tetracarboxylic acid anhydride, the N-series. The diamines used were 1,2-diaminoethane, 1,3-diamino-propane, 1,4-diaminobutane . . . 1,10-diamino decane. All of the reagents are commercially available.

The polymers in this study are named by a letter giving the aromatic core followed by a number giving the number of methylene groups in the alkyl chains.

1 : 1 amounts of the diamine and tetracarboxylic acid anhydride were reacted in dimethyl acetamide (DMAc) or dimethyl formamide (DMF) at room temperature in a standard way [6]. Up to 10 per cent excess of the acid does not seem to influence the cone angles or defect densities. The resulting polyamic acid solution was filtered to 0·50 μm through a millipore filter. The viscosity was adjusted to give good quality for printing with a Nissha Angstromer (*c* 7·5 per cent solid content). The glass/ITO plates were prebaked at 100°C for 3 h and then hardbaked at 300°C for 5 h giving a weakly golden brown polyimide layer. N2 to N9 gave polyamic acids that were only sparingly soluble. Instead of printing the glass plates were coated by spraying with a saturated (less than 3 per cent) solution.

2.2. *Measurements*

Our cell construction and experimental set-up for the electrooptic measurements has been described in a previous communication [2]. Each polymer was tested with several different room temperature chiral smectic C mixtures which all gave nearly identical results in accord with our previous results [7], thus only average values for all of the different experimental room temperature mixtures will be used.

To check the stability of the alignment towards electric fields the cell was placed under a polarizing microscope, and connected to a Wavetek 191 function generator. A square wave was used and the amplitude and frequency were varied until the first signs of texture changes were observed. The cell was then reheated above the clearing point of the fluid and cooled to regain the original texture, and a new set of points were recorded. Finally smooth lines separating the different textures were drawn.

3. Results and discussion

The cone angles found for different members of the P-series are shown in figure 1. As can be seen there is a marked odd–even effect, with the polyimides with an even membered alkyl chain being clearly superior. This can easily be explained by the greater crystallinity expected for these members of the series [4, 5]. The necessity for crystalline polymers has been documented [2, 3].

For the B-series the results are shown in figure 2. Here the odd–even effect is absent. We believe this is due to a much larger flexibility in the tetra carboxylic acid part of the molecule, and thus a more favourable packing of the polymer chains for crystalline samples are possible both with odd and even number of carbon atoms in the alkyl chain. We have no explanation for the surprisingly low values found for B8, as yet.

Substituting a stiff phenyl ring for the flexible alkyl chain in the B-series, a polyimide which will not induce bistability in our cells is obtained, while the same substitution in the N- or P-series gives good polyimides with cone angles similar to those with even alkyl chains. With this stiff diamine the P- and N-series should still give linear or nearly linear polymer chains, as with those with an even membered alkyl chain. For the benzophenone tetra carboxylic acid *p*-phenylene diamine condensate on the other hand the molecule would be strongly bent, packing in the crystal would therefore be much more difficult.

The results for the N-series are shown in figure 3. The larger naphthalene group is expected to give better crystallinity than the phenyl group. For the polyimides with

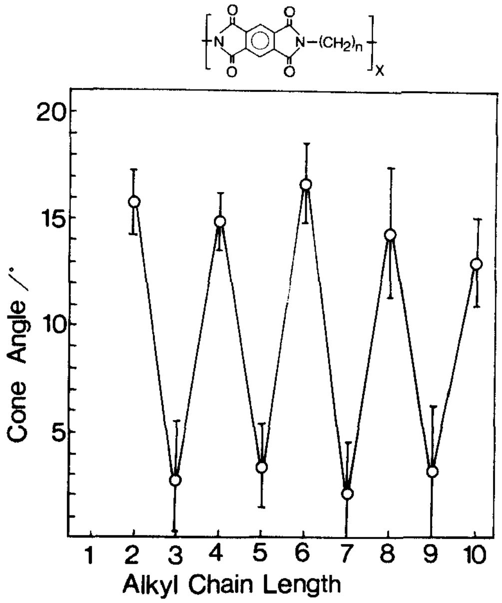

Figure 1. Cone angles found with different members of the P-series as alignment layers.

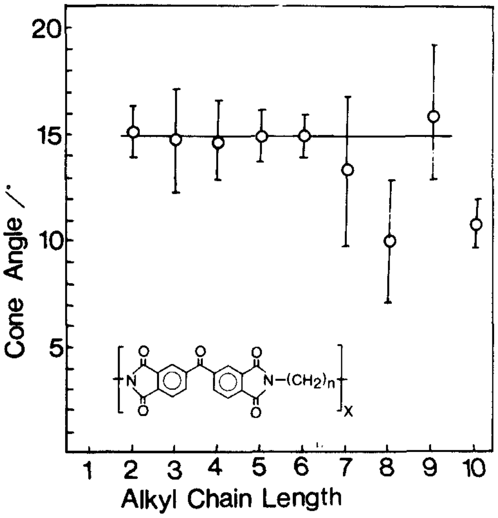

Figure 2. Cone angles found with different members of the B-series as alignment layers.

an even alkyl chain the difference is not evident, but for those with an odd alkyl chain we see larger cone angles in the N-series than in the P-series. So even if there is an odd–even effect, it is weaker in this case than for the P-series. N10 gives a much lower value than expected. This polymer is also peculiar in giving the only polyamic acid which was freely soluble in DMAc among the polymers in the N-series. The smaller than expected angle could therefore be a result of a different polymer chain length. P4 with different excesses of the tetra carboxylic anhydride did not however show any significant variation in the cone angle when tested with ZLI-3774 as shown in the table.

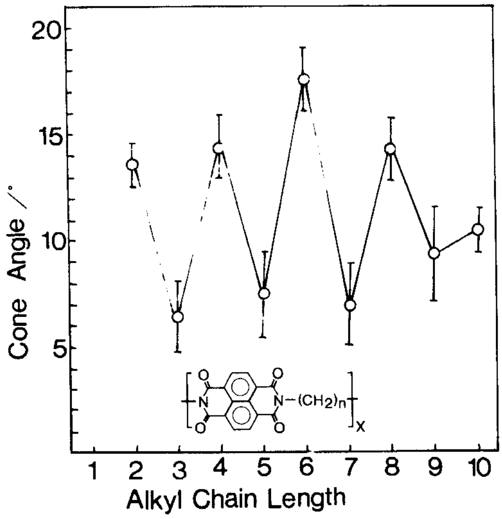

Figure 3. Cone angles found with different members of the N-series as alignment layers.

Variations on cone angles as a function of amine : acid ratio for ZLI-3774 in cells prepared with P4.

Amine/acid ratio	Cone angle ZLI-3774/°
0·99998	15·7 +/− 1·1
0·9822	15·7 +/− 2·0
0·9501	17·6 +/− 2·7
0·9060	16·7 +/− 2·5

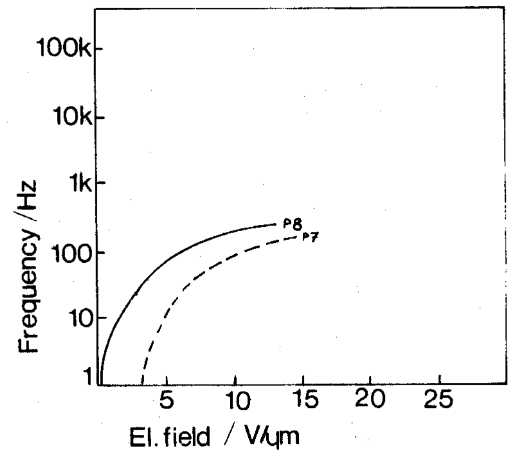

Figure 4. Voltage frequency lines separating the original texture from the roof texture for ZLI-3774 in cells with P7 and P8 as alignment layers.

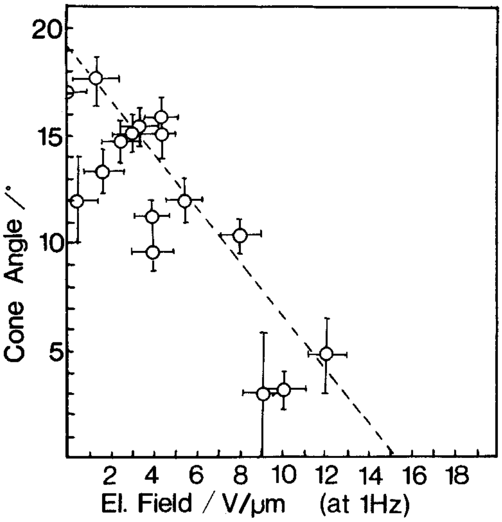

Figure 5. The relationship between the cone angle found and minimum voltage for disrupting the original texture of the cells at 1 Hz. The results shown are for ZLI-3774.

For the P- and B-series we also looked at the electrically induced changes of texture when the cells are subject to square waves with different amplitude and frequency. An example is shown in figure 4. A strong correlation was found between the cone angle observed and the ease with which the structure broke up. In figure 5 the cone angle found is plotted as a function of the minimum voltage needed to disrupt the structure at 1 Hz, for the room temperature mixture ZLI-3774 from E. Merck. It has been suggested that the textural changes are due to a straightening of the tilted smectic layers (chevron structure) when they are subject to an electric field. A large cone angle corresponds to relatively upright smectic layers and so a smaller alteration of the layers is needed before the texture changes.

4. Conclusions

It has been shown that the structure of the polymer alignment layer strongly influences the cone angle found between the relaxed states in an SSFLC cell. Highly crystalline polymers give a larger cone angle than their less crystalline homologues. For alkyl-aromatic polyimides with a stiff aromatic core this leads to a marked odd–even effect. For more flexible aromatic cores this odd–even effect is absent.

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