Symmetry of the aligning polymer and the cone angles in surface stabilized ferroelectric liquid crystal displays

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Symmetry of the aligning polymer and the cone angles in surface stabilized ferroelectric liquid crystal displays

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Data of the cone angles found with 80 different polymers tested as alignment layers for surface stabilized ferroelectric liquid crystal displays are given. The structural properties of the polymers are correlated with their ability to give good, bistable alignment in such liquid crystal displays. The symmetry of the monomers and crystal surfaces are found to be of major importance, with polymers containing an ester group usually giving the best results.

1. Introduction

The invention of the surface stabilized ferroelectric liquid crystal display [1] has opened the possibility for extremely fast and bistable liquid crystal displays and optical elements. The bistability is a quality that has been difficult to achieve, and seems to depend as much on the surface of the cells as on the ferroelectric smectic phase.

The cells are usually filled in the isotropic state and cooled to the smectic phase. The final alignment within the cell will depend, therefore, on the interaction between the surface and the nematic, smectic A and smectic C liquid-crystalline phases. The molecules in the nematic phase are aligned parallel to the rubbing direction of the polymeric surfaces. This seems mostly to be an effect of the ordering of the polymer chains in the alignment layer and less on the physical deformation of the layer [2]. The smectic layers are formed at the nematic–smectic A transition. It is generally believed that the molecules move as little as possible during this phase transition and that their long axes keep the same orientation relative to the rubbing direction. The smectic layers will thus form perpendicular to the rubbing direction. However, many polymers that give very well ordered nematic liquid crystals do not give well ordered smectic A layers [3]. Finally at the chiral smectic C–smectic A transition the molecules will tilt within the layers while the integrity of the layers is kept. At this transition a few complications can appear even if the smectic A is well aligned. Often one of the two tilt directions in the chiral smectic C phase is largely favoured and bistability cannot be obtained. Due to the chevron structure [4] in the smectic C phase several so called zig-zag defects often appear. Even in the case where bistability is achieved, the angle between the director in the two different states is almost universally found to be far less than twice the smectic C tilt angle.

There have been a number of studies which considered the different properties of the polymeric alignment layers and how they affect the texture and bistability of surface

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stabilized ferroelectric liquid crystals. Workers in the field have considered the degree of crystallinity [3, 5–9], the crystal structure [9, 10], the polarity of the polymer [9, 11], the surface tension [9, 12, 13], the conductivity of the polymer [9, 14–16], the dielectric constant [9, 15, 16] and the Mark–Houwink coefficient [9, 17] as well as the layer thickness [11, 14–16]. Although it is known that alignment layers with polymers that can form monoclinic or triclinic crystals will give bistable liquid crystal cells [9, 10], it is not known which properties of these two crystal classes that set them apart from the other five crystal classes or amorphous polymers which will not give bistable operations in such cells.

For practical ferroelectric liquid crystal displays four parameters are of major importance. The first is the defect density and hence the transmission of the dark state. The second is the cone angle between the two relaxed (no field) states. The third factor is the stability of the director orientation towards small disturbing fields. Finally the time taken to switch the cell into one of the stable states is the fourth parameter. The two first factors together determine the contrast of the device under memory conditions. These two factors can be treated independently. The dark state transmission can be minimized by the proper mechanical and thermal treatment of the polymer alignment layer. Given the darkness of the dark state, the contrast and brightness will be determined by the cone angle, with 45° as the optimum cone angle. Most alignment layers seem to give cone angles of about 14–16°, or one third of the optimum value. This leads to only about 25 per cent transmission relative to parallel polarizers and a rather dull display. A few polymers give higher values. It has been our long term goal to find how the physical and structural differences between these different polymers can account for their different behaviour as alignment layers. We limit this work to the cases where there are no additional stabilizing forces such as AC or DC electric fields, or a (quasi) bookshelf geometry created by applying similar forces during the manufacture of the device.

2. Experimental

Our cell preparation has been described elsewhere [6, 18]. The polymers were spray coated onto the glass/ITO surface by an airbrush gun. The polymers were rubbed with a low rubbing pressure to avoid scratches and other induced defects in the surface. If necessary the cells were annealed after assembly to increase the degree of crystallinity of the surface. All of the cells used in this study are 1.7 ± 0.1 μm thick. The cells were filled with either ZLI-3774 or ZLI-3775, two similar room temperature mixtures which gave nearly identical results for the polymers where both were tested. Most polymers were also tested with at least one more room temperature ferroelectric mixture. There were no significant difference between the different mixtures tested [18]. Experimental errors are $\pm 1.5°$ for the polyimides and $\pm 2°$ for the other polymers unless stated otherwise.

The cells were inspected under a polarizing microscope before the electro-optic measurements, to ensure that they were in the virgin texture. Even with 1.7 μm thick cells and fluids of low birefringence there was usually a shift between blue and white or between black and yellow when rotating the cell under the microscope. In some cells both shifts could be seen simultaneously. No defect lines could be seen between the blue and black or white and yellow areas. The cells were also inspected again under the microscope after the electro-optic measurements to make sure that the virgin texture has not been disrupted by the electric pulses. At this time the cells that showed bistability were usually uniformly in one state.

To measure the cone angle the cell was placed between a pair of crossed polarizers and switched to one of the two relaxed states. After short circuiting the cell it was rotated between the polarizers and the transmission versus the orientation of the cell was recorded. The axis of rotation coincided with the centre of the light path. The cell was then switched to the other relaxed state without removing it from the rotating stage and the procedure was repeated. To check whether the cell was truly bistable the rotating stage was set to its initial setting after each of the two series of measurements. If one of these readings differed from the original the cell was not regarded as bistable. The phase difference between the two sin squared curves is the cone angle between the two relaxed states [19]. In nearly all of the cases the experimental points were within one degree from the ideal sin curve. The two sine squared curves have the same amplitudes and show the same minimum transmission.

Values for most of the polyimides have been reported earlier [6, 7], some literature values for a few polymers are also included where we find that the cell treatment is comparable with ours and so the cone angles found can be compared.

3. Results

3.1. *Polyalkyls and substituted polyalkyls*

In this class we group polymers with only carbon atoms in their backbone, for example the polyalkyls, polyvinyls, as well as the polyfumarate ester of the table. In this class there are some interesting pairs that clearly show the importance of the crystallinity of the polymer, and the importance of which crystal class they belong to. High and low density polyethylene show how the crystalline member of the pair gives good results while the amorphous member gives poor results. The pair high density polyethylene and polyvinylidene difluoride are both crystalline. The fluorine and hydrogen atoms are of similar size as substituents, thus the effect of the substituent size should be small. For high density polyethylene (HDPE) the orthorhombic form is stable under normal conditions, but after stretching the monoclinic form is the more stable [20]. For polyvinylidene fluoride (PVDF) the monoclinic form is the most stable, but after stretching six times at room temperature the orthorhombic form becomes preferred [21]. The induced birefringence of rubbed polymers [3] clearly shows that stretching has taken place during the mechnical treatment of the polymers. We assume, therefore, that both polymers will be in metastable modifications in thin, rubbed layers; that is monoclinic HDPE and orthorhombic PVDF. The HDPE gives good results while the PVDF gives poor results. The necessity of triclinic or monoclinic polymers as alignment layers for bistable surface stabilized liquid crystal cells has been documented earlier [9, 10]. The triclinic polytetrafluoroethylene (PTFE) also gives bistable areas, but it has not been possible to determine the cone angle, as there is no correlation between the directors over different small patches. We take this as evidence of good bistability over each crystallite of PTFE, but that the rubbing procedure is not adequate to orient all of the crystallites in the same direction for this polymer, which has an extremely low coefficient of friction and high melting point.

Chlorine atoms and methyl groups are of the same size, nevertheless polypropylene gives homeotropic orientation while polyvinylchloride gives planar orientation without bistability. Polypropylene normally gives monoclinic crystals, but cooling well-oriented samples gives hexagonal crystals [22]. Standard polyvinylchloride shows syndiotactic sequences and may develop 10–20 per cent crystallinity; the crystals are orthorhombic [20].

Polymers for alignment of ferroelectric liquid crystals.

Polymer	Cone angle†	Reference
Polyalkyl		
High density Polyethylene HDPE	16·2°	
Low density Polyethylene LDPE	0	
Polyvinylidenefluoride PVDF	f.c.	
Polypropylene (isotactic) PP	Homeotropic	
Poly-1-butene	Homeotropic	
Polyvinyls		
Polyvinylalcohol PVA	21°	11
PVA	25·5°	12
Polyacrylonitrile PAN	16·4°	
Polyamides		
Nylon 6 PA6	22°	12
PA6	20°	11
Nylon 6:6 PA6:6	16·1°	
Nylon 7:6 PA7:6	0	
Nylon 11 PA11	19·5°	
Nylon 12 PA12	7·1°	
Nylon 2T PA2T	22±4°	5
Nylon 3T PA3T	f.c.	
Nylon 4T PA4T	15·2°	
Nylon 5T PA5T	f.c.	
Nylon 6T PA6T	16·7°	
Nylon 7T PA7T	f.c.	
Nylon 8T PA8T	15±4°	5
Nylon 9T PA9T	3±2°	5
Nylon 10T PA10T	32±4°	5
Nylon 3,5,6T	0	
Polyamid resin	1°	
Hitachi Kasai HL-1100	16·1°	17
Nylon 6T/PHT copolymer	0	
Polyimides		
Pyromellitic anhydride and 1,4-diaminobenzene	14·8°	
Pyromellitic anhydride and 1,2-diaminoethane P2	15·7°	6
Pyromellitic anhydride and 1,3-diaminopropane P3	2·7°	6
Pyromellitic anhydride and 1,4-diaminobutane P4	14·8°	6
Pyromellitic anhydride and 1,5-diaminopentane P5	3·3°	6
Pyromellitic anhydride and 1,6-diaminohexane P6	16·6°	6
Pyromellitic anhydride and 1,7-diaminoheptane P7	2·1°	6
Pyromellitic anhydride and 1,8-diaminooctane P8	14·3°	6
Pyromellitic anhydride and 1,9-diaminononane P9	3·1°	6

Table *(continued)*.

Polymer	Cone angle†	Reference
Pyromellitic anhydride and		
1,10-diaminodecane P10	12·9°	6
Benzophenone-3,3′,4,4′-tetracarboxylic		
anhydride and 1,2-diaminoethane B2	15·0°	6
Benzophenone-3,3′,4,4′-tetracarboxylic		
anhydride and 1,3-diaminopropane B3	14·7°	6
Benzophenone-3,3′,4,4′-tetracarboxylic		
anhydride and 1,4-diaminobutane B4	14·5°	6
Benzophenone-3,3′,4,4′-tetracarboxylic		
anhydride and 1,5-diaminopentane B5	14·8°	6
Benzophenone-3,3′,4,4′-tetracarboxylic		
anhydride and 1,6-diaminohexane B6	14·8°	6
Benzophenone-3,3′,4,4′-tetracarboxylic		
anhydride and 1,7-diaminoheptane B7	13·2°	6
Benzophenone-3,3′,4,4′-tetracarboxylic		
anhydride and 1,8-diaminooctane B8	9·8°	6
Benzophenone-3,3′,4,4′-tetracarboxylic		
anhydride and 1,9-diaminononane B9	15·8°	6
Benzophenone-3,3′,4,4′-tetracarboxylic		
anhydride and 1,10-diaminodecane B10	10·7°	6
Benzophenone-3,3′,4,4′-tetracarboxylic		
anhydride and 1,4-diaminobenzene	0	6
Naphthalene-1,4,5,8,-tetracarboxylic		
anhydride and 1,2-diaminoethane N2	13·6°	6
Naphthalene-1,4,5,8,-tetracarboxylic		
anhydride and 1,3-diaminopropane N3	6·5°	6
Naphthalene-1,4,5,8,-tetracarboxylic		
anhydride and1,4-diaminobutane N4	14·4°	6
Naphthalene-1,4,5,8,-tetracarboxylic		
anhydride and 1,5-diaminopentane N5	7·6°	6
Naphthalene-1,4,5,8,-tetracarboxylic		
anhydride and 1,6-diaminohexane N6	17·6°	6
Naphthalene-1,4,5,8,-tetracarboxylic		
anhydride and 1,7-diaminoheptane N7	7·0°	6
Naphthalene-1,4,5,8,-tetracarboxylic		
anhydride and 1,8-diaminooctane N8	14·3°	6
Naphthalene-1,4,5,8,-tetracarboxylic		
anhydride and 1,9-diaminononane N9	9·4°	6
Naphthalene-1,4,5,8,-tetracarboxylic		
anhydride and 1,10-diaminodecane N10	10·6°	6
Naphthalene-1,4,5,8,-tetracarboxylic		
anhydride and 1,4-diaminobenzene	6·5°	
cis,cis,cis,cis-1,2,3,4,-cyclopentane		
tetracarboxylic anhydride		
and 1,2-diaminoethane C2	f.c.	7
cis,cis,cis,cis-1,2,3,4,-cyclopentane		
tetracarboxylic anhydride		
and 1,3-diaminopropane C3	0	7
cis,cis,cis,cis-1,2,3,4,-cyclopentane		
tetracarboxylic anhydride		
and 1,4-diaminobutane C4	f.c.	7
cis,cis,cis,cis-1,2,3,4,-cyclopentane		
tetracarboxylic anhydride		
and 1,5-diaminopentane C5	17·9°	7

Table (*continued*).

Polymer	Cone angle†	Reference
cis,cis,cis,cis-1,2,3,4,-cyclopentane tetracarboxylic anhydride and 1,6-diaminohexane C6	f.c.	7
cis,cis,cis,cis-1,2,3,4,-cyclopentane tetracarboxylic anhydride and 1,7-diaminoheptane C7	14·9°	7
cis,cis,cis,cis-1,2,3,4,-cyclopentane tetracarboxylic anhydride and 1,8-diaminooctane C8	12·0°	7
cis,cis,cis,cis-1,2,3,4,-cyclopentane tetracarboxylic anhydride and 1,9-diaminononane C9	16·7°	7
cis,cis,cis,cis-1,2,3,4,-cyclopentane tetracarboxylic anhydride and 1,10-diaminodecane C10	16·2°	
cis,cis,cis,cis-1,2,3,4,-cyclopentane tetracarboxylic anhydride and 1,4-diaminobenzene	24·8°	
Amoco AI-10	f.c.	
Ciba-Geigy XU285	0	
Hitatchi PIQ	13·6°	17
Japan Synthetic Rubber JIB-1	0	
M and T Chemicals 2065	f.c.	
M and T Chemicals 5000	f.c.	
Merck ZLI-2650	0	
Nitto JR-100	0	
Sumitomo Bakelite CRC-6070X	25·0°	
Toray Semicofine SP-710	0	
Toray Semicofine SP-711	0	
Toray Semicofine SP-910	16·1°	
Polyesters		
Poly(butyleneterephthalate) PBT	24·7°	
Poly(hexyleneterphthalate) PHT	18·5°	
Polycaprolactone	f.c.	
Poly(ethylene succinate)	f.c.	
Polydiisopropyl fumarate	20·7°	17
Miscellaneous		
Polyphenylquinosaline PPQ	f.c.	11

† Cone angles are given except for focal conical (f.c.) texture.
Experimental errors are ±1·5° for the polyimides and ±2° for other polymers unless stated otherwise.

All examples of polymers with large substituents (five or more atoms) on every other carbon in the chain give poor results [3], while the polyfumarate esters [17] with bulky substituents on all atoms in the backbone give good results. The bulky substituents force the backbone to adopt a helix structure thus making the macromolecule rigid and rod-like [17]; this will make crystal packing easier. Most of the polyvinyls [3] and polymethacrylates [3] on the other hand are atactic polymers and crystal packing will be difficult.

3.2. *Polyamides*

One of the first known examples of a good alignment layer for surface stabilized ferroelectric liquid crystals was nylon 6:9 [23]. Most of the polyamides have monoclinic or triclinic crystal structures and so give good results. Although polymorphism is widespread among the polyamides all modifications normally have the same crystal structure [20]. Nylon 6:6 gives a fairly average cone angle of 16·1°, while Nylon 7:6 does not give bistable cells. Nylon 8:6 is also found to give good results, but the cone angle has not been determined. The apparent odd–even effect is probably due to differences in crystal structure. The alkyl-aromatic polyamides also show an odd–even effect [5]; all of these are highly crystalline and the difference must again be explained by different crystal structures.

3.3. *Polyesters*

The alkyl polyesters give focal conic textures while their alkyl-aromatic counterparts give good bistable cells, in all cases with higher than average cone angles. These differences can again be explained by differences in the crystal structure [9]. The polyfumarates would normally not be classified as polyesters as the ester linkage is in the side group. The only polyfumarate with the cone angle determined is, however, also found to give a very high cone angle [17]. Another indication of the importance of the ester group is found in the polyimide CRC-6070X, which is based on trimellitic acid and so is more properly classified as a polyester-imide. This polymer also gives one of the highest cone angles found among the polyimides.

3.4. *Polyimides*

Polyimides are widely used as alignment materials in the liquid crystal display industry. By the right combination of diamine and tetracarboxylic groups the physical properties of polyimides can, to a large extent, be tailored to meet the requirements of curing temperature, adhesion to glass, dielectric constant and chemical resistance. The polyimides have also been the subject of several studies [6, 7, 24–27] as alignment layers for ferroelectric liquid crystals, and more than half of the polymers in the table are polyimides.

For alkyl-aromatic polyimides with a flexible tetracarboxylic acid moiety it has been found that both polyimides with an even number of carbon atoms in the alkyl chain and polyimides with an odd number of carbon atoms give good results. For polyimides with a rigid tetracarboxylic acid group and the C_{chain}–N bonds collinear only those with an even number of carbon atoms in the alkyl chain give good results [6]. For the cyclopentane tetracarboxylic acid based polyimides the C_{chain}–N bonds are not collinear, here the alkyl chains with an odd number of methylene groups give the best results [7]. This can be explained with a simple picture where the alkyl chains exist in their most elongated conformation. For an odd number of carbon atoms the alkyl chains will be bent and there are difficulties in achieving good packing of the polymer chains with bent alkyl groups and linear aromatic groups. On the other hand an even number of carbon atoms will give linear alkyl groups, and the packing together with linear aromatic groups seems easy [7]. Substituting a rigid benzene ring for the alkyl chain in the pyromellitic, naphthalene tetracarboxylic acid or benzophenone tetracarboxylic acid based polyimides confirms this simple picture. When a 1,4-diamino benzene is introduced in the cyclopentyl tetracarboxylic acid based polyimide a strongly bent structure is expected, which according to this simple picture should give poor results. What is found, however, is an exceptionally large cone angle of 24·8°.

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4. Discussion

To describe the surface stabilized ferroelectric liquid crystal cell we use the conventional coordinate system, shown in figure 1, where the z axis is normal to the cell walls, and is the direction of light progration under normal viewing. The x axis is the rubbing direction of the cells and gives the normal to the smectic layers, while the y axis is the intersection between the smectic layers and the electrode planes. For simplicity we refer to smectic layers in the discussion, but it should be remembered that this is a periodicity in the density of the smectic liquid crystal and not a discrete entity.

At the transition from the smectic A to the smectic C phase the molecules tilt within the layers. If we do not assume any large changes in the conformation of the molecules this implies a larger amplitude of the density function as we move along the x axis. A larger amplitude implies a system of higher energy. The liquid crystal usually resists this by a bending of the layers to form a chevron structure [4]. For many surface treatments which give well-ordered smectic A phases the angle between the layer and the surface normal will be exactly the same as the smectic C tilt angle and the cell shows no bistability. For other surfaces the bending of the layers will be less, and the cells show bistability, albeit with a cone angle less than the smectic C tilt angle. In a cell without bistability the spontaneous polarization will point along the y axis, while the ideal bookshelf structure will have the spontaneous polarization pointing along the z axis. As most surface stabilized cells show bistability with cone angles less than twice the smectic C tilt angle, the spontaneous polarization will make some intermediate angle in the yz plane. For cells with dipoles pointing out of or along the surface the situation will now be even more complicated. As the layers bend to form a chevron the spontaneous polarization will be more and more misaligned with respect to the surface dipoles, and so the energy increases. The final structure in the cell will then be the result of a fine balance between the energy due to the periodic density variation of the smectic C phase, the energy required to bend the layers to form the chevron structure, and the energy due
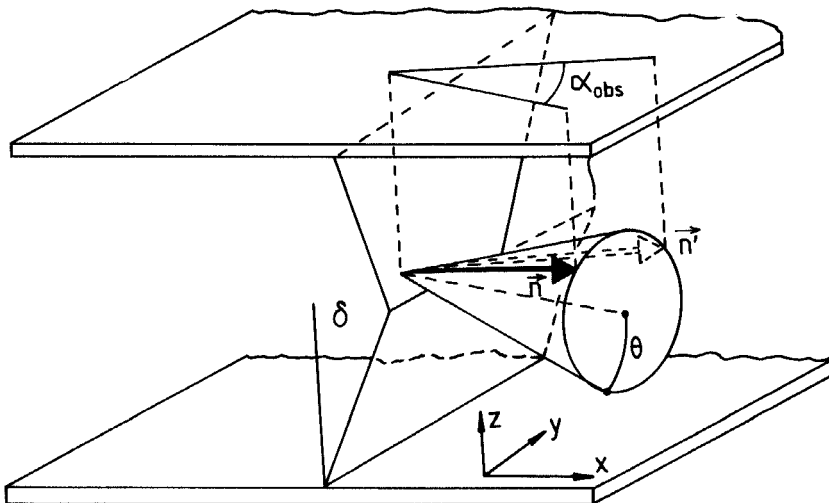

Figure 1. Coordinate system used to describe the ferroelectric liquid crystal structure. Light passes through the cell in the z direction. The x axis is the rubbing direction in the cell. δ is the layer tilt angle and θ the chiral smectic C tilt angle. α_{obs} is the observed angle between the two relaxed states.

to misalignment of the spontaneous polarization and the surface dipoles, and any other forces responsible for the alignment of the liquid crystals.

Recent work has shown that the average director moves parallel to the surface during switching from one of the stable orientations to the other in chevron cells. In the bookshelf geometry the director moves along the cone formed by the smectic C tilt. In quasi bookshelf geometries the director shows intermediate behaviour. This is interpreted as a reorientation of the layers during the switching while the molecules themselves stay parallel to the surface [28]. The potential energy shows two shallow minima for the two stable states. The group at Philips Laboratories have shown that under low fields the chevron structure straightens up to a banana shape, but that the layer tilt angle at the surface is relatively constant [29]. They do not give any reason for the constant layer tilt at the surface. We wish to note that a relatively rigid coupling between the surface and the molecules, giving two possible fixed stable orientations relative to the rubbing direction, and thus a fixed cone angle, could explain their result. Annealing the alignment layer to increase the crystallinity has recently been shown to lower the pretilt angles for nematics [30]. This can be interpreted as an argument for stronger coupling between the aligning surface and the molecules in the liquid-crystalline phases.

The polyimides based on the *cis,cis,cis,cis*-tetracarboxy-cyclopentane is strongly bent and thus the symmetry of the monomeric units is low. The condensation product of 1,4-diaminobenzene and *cis,cis,cis,cis*-tetracarboxy-cyclopentane correspondingly gives a very high cone angle. CRC-6070X based on trimellitic anhydride has both a low symmetry and an ester group; this polymer gives cone angles among the highest reported so far. Figure 2 shows how the two highly symmetrical polyimides give fairly standard cone angles of 15° or less, while the two unsymmetrical examples both give cone angles of 25°. Recently it has been shown that dyes containing ester groups will reduce the spontaneous polarization of ferroelectric mixtures much more than other dyes [31]. This can be taken as further evidence for the strong interaction between the polarization of the ferroelectric liquid crystal and any esters present.

Of all the different properties of the bulk polymer suggested as responsible for the bistable operation of ferroelectric liquid crystals [9] only the polarity of the polymer is a polar vector property. It seems reasonable, therefore, that monomeric units where dipoles are not forbidden for symmetry reasons could give better results, for example, higher cone angles. On the other hand it is also clear that this is not the only determining factor, as most polymers that give bistable operation of the device give cone angles of 14–16°, regardless of the structures of the monomeric units in the polymers. The pretilt at the surface and epitaxial growth are two other factors besides the dipole moment that show polar vector properties. Both of these effects depend on the properties of both the substrate and the liquid crystal. We have not found any relationship between the pretilt on polymer surfaces and the magnitude of the cone angles [9, 30]. Epitaxial growth is, however, a likely candidate [3]; being monoclinic the smectic C phase itself has rather low symmetry.

Other polyimides based on aliphatic tetracarboxylic acids will mostly show the same low symmetry as the *cis,cis,cis,cis*-cyclopentane tetracarboxylic acid based polyimides. Several of these are found to give high cone angles [32], but due to different cell treatment a direct comparison is not possible.

Figure 3 compares some different polymers which can all be regarded as having a four carbon alkyl chain and different groups in between. We see that the non-polar polyethylene (HDPE) gives approximately the same cone angles as the polyimide (P4)
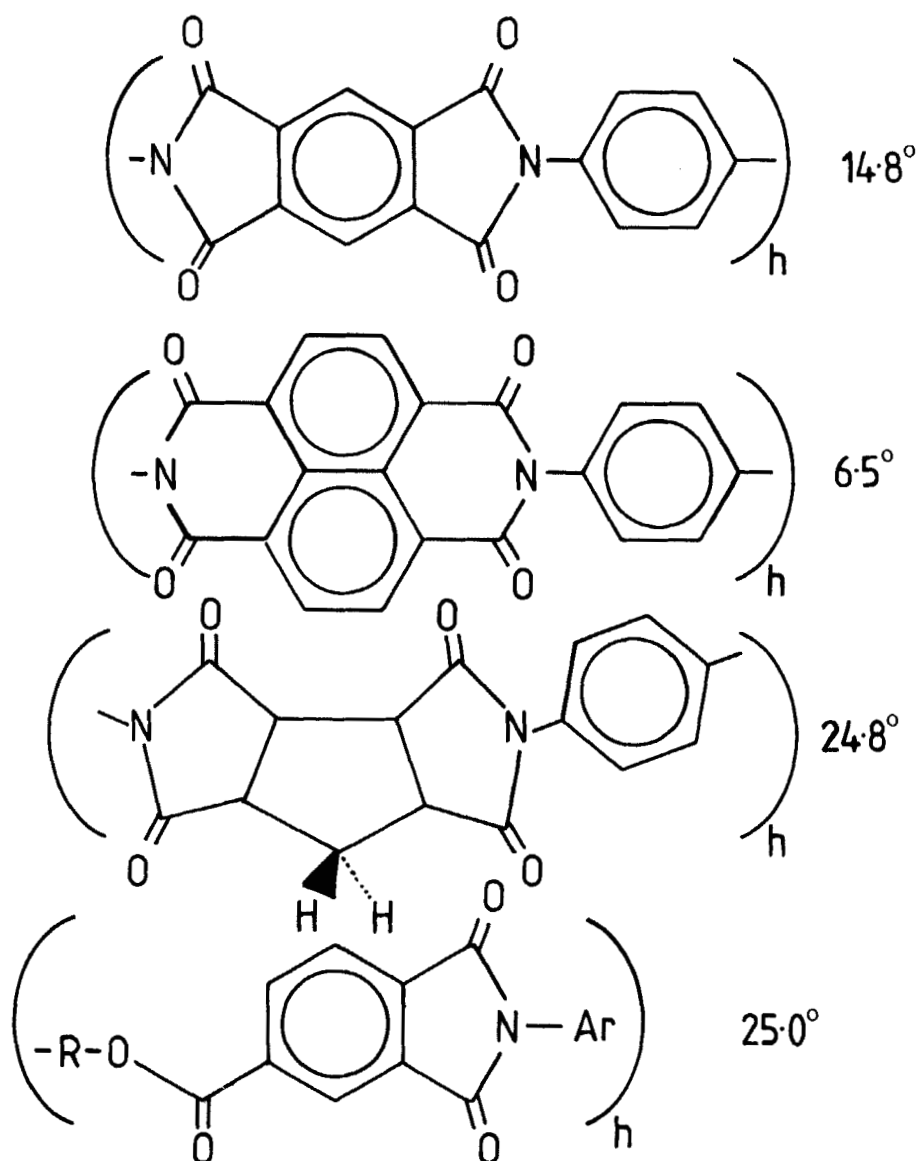
Figure 2. Structures and cone angles of four polyimides. The highly symmetrical pyromellitic acid and naphthalene tetracarboxylic acid based polyimides give low to average cone angles, while the unsymmetrical polyimides based on cyclopentane tetracarboxylic acid or trimellitic acid give high cone angles.

or the polyamide (N4T), while the polyester (PBT) gives much higher cone angles. The single carbon–carbon bond in HDPE has neither more nor less effect than the phenyl ring and two amide groups in N4T or the phenyl ring and two imide groups in P4. The phenyl diester on the other hand gives a large increase in the cone angle. The polyimide contains several strongly polar groups, such as C=O, and C–N. The symmetry of the polyimide group is, however, high, and the different dipoles will cancel out and give no net dipole. In the ester groups the symmetry is lower, thus the dipole moment might be larger. As drawn the PBT has a centre of symmetry, but the two carbonyl groups do not

HDPE $16.2 \pm 2.0°$

P4 $14.8 \pm 1.0°$
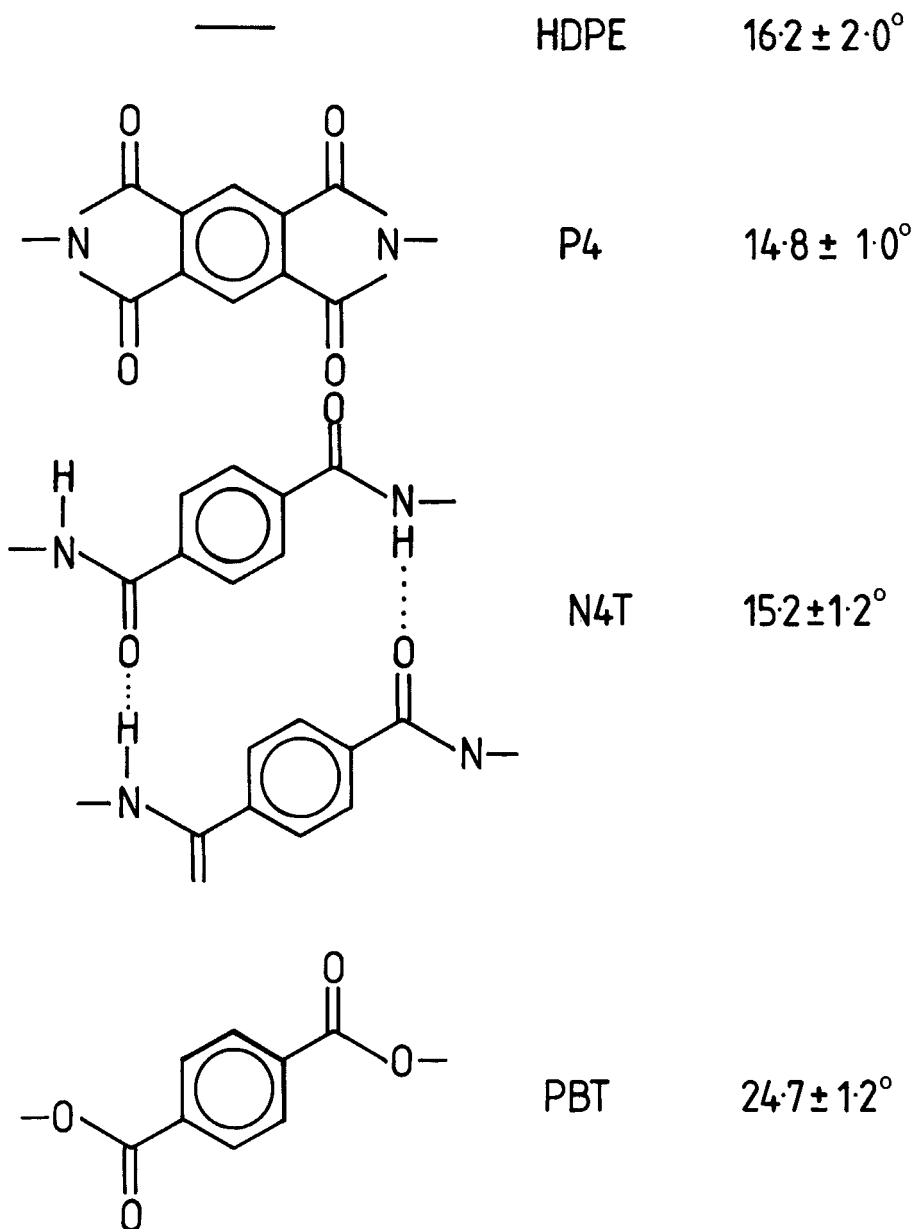
N4T $15.2 \pm 1.2°$

PBT $24.7 \pm 1.2°$

Figure 3. The core of four polymers incorporating an *n*-butyl chain, and the cone angles observed with each of them. HDPE is high density polyethylene, P4 is poly-*n*-butyl-pyromellitic imide, N4T is poly-*n*-butyl-terphthalamide and PBT is poly-*n*-butyl-terphthalate.

necessarily lie in the same plane. In the polyamide the symmetry is comparable to that of the ester. Thus we do not expect cancellation of the dipole from symmetry considerations, but the amide groups are very likely to form hydrogen bonds with neighbouring amide groups and so effectively reduce the net dipoles present. This provides a possible explanation for the difference between polyamides and polyesters.

With a hexyl chain instead of a butyl chain the cone angles show the same trend, with PHT (18·5°) giving a superior cone angle compared with P6 (16·6°) or N6T (16·7°); the latter two both give cone angles comparable to HDPE.

It is clear from the table that those polymers which show the largest cone angles (20–25°) all have monomeric units of low symmetry. This seems to be a necessary condition for the high cone angles. On the other hand it is clearly not a sufficient condition, as the whole series of benzophenone-tetracarboxylic acid based polyimides all give fairly average cone angles of 14–16°. The same holds for the series based on *cis,cis,cis,cis*-cyclopentane-tetracarboxylic acid and diamino-alkyls.

At this stage it should be noted that most polymers do not exist as elongated chains and that the symmetry of the monomeric unit, or one of several monomeric units, is too simplified. But if the monomers are non-polar it is not possible to arrange them in any way that will give polar bulk or surface structures. On the other hand it is still possible to arrange polar units in such a way that the bulk or surface will have no net polarization. As figure 3 shows, the four $C=O$ dipoles in the polyimide cancel out. Different helix structures which are usually present will also reduce the net dipole of other structures. Crystalline PBT exists in two monoclinic modifications, each with the apolar C_i point group; this is a structure with a centre of symmetry, and consequently all dipole moments are cancelled within the unit cell [33]. The presence of a dipole in the monomeric unit is no guarantee for the polarity of the bulk or the surface of the polymer, but it is a necessary condition.

The surface of a crystal is not just a truncation of the bulk; we need, therefore, to discuss the symmetry of the surfaces. There are ten possible surface point symmetry groups [34]; they are 1, 2, 3, 4, 6, m, 2mm, 3m, 4mm and 6mm. The symmetry will prevent any dipoles for 2, 3, 4, 6, 2mm, 3m, 4mm and 6mm, and the surfaces with dipoles will thus be restricted to the point groups 1 and m. These will combine with the different lattices to form the two dimensional space groups P1, Pm, Pa and Im. The first of these belong to the triclinic crystallographic system, the last three to the monoclinic. It has been found earlier that these classes are the only two that give bistable operation of the surface stabilized ferroelectric liquid crystal device [9, 10]. The surface symmetry might be the common theme that sets the monoclinic and triclinic polymers apart from the other five crystal classes or amorphous polymers. Unfortunately the structures of the surfaces of the polymers are not well-known, and no surface studies of polymers useful for liquid crystal cells after a realistic surface treatment have been undertaken. There is one more space group belonging to the monoclinic system, namely P2. It is not known which surface the different crystallites will present to the liquid crystal, but according to this argument it could be possible that some polymers with monoclinic crystal structure will not support bistability.

5. Conclusions

Low symmetry monomeric units in the polymeric surface layer seem to play an important role in stabilizing ferroelectric liquid crystals when high cone angles are required. Also the surface point group should be of low low symmetry. Only crystals belonging to the triclinic or monoclinic classes have low enough symmetry to give two energy minima for the orientation of the director relative to the rubbing direction and thus support bistability. Chain folding and helix formation of the polymer chain makes the prediction of the magnitude of the cone angles difficult, but ester groups normally stabilize the highest cone angles. Cone angles up to about 25° can be achieved, resulting in a transmission of 59 per cent which compares favourably with super twist nematics.

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