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Epitaxial growth alignment of ferroelectric smectic C phases on rubbed polymers

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Several of the polymers reported for surface alignment of ferroelectric smectic C phases in the literature are tested with a ferroelectric room temperature mixture. The results for this material and the reported findings in the literature are compared to the known crystal structure of the polymers. It is found that polymers with triclinic or monoclinic crystals give good alignment and bistability for the smectic C phase. Other crystal structures or non-crystalline polymers give a poorer performance. The mechanisms for creating a highly crystalline polymer surface are discussed, and the epitaxial growth of smectic phases on the crystalline surface is shown to be in accord with experiment.

1. Introduction

The surface alignment of nematic liquid crystals on rubbed polymers has been an established art for several years. With the invention of the surface stabilized ferroelectric liquid crystal display (SSFLC) [1] there has been a renewed interest in the mechanisms for the surface alignment. Several polymer coatings that work very well for nematics give poor results for the smectic phases. There have been a few systematic studies of the effect of different polymers on the alignment quality of SSFLC cells [2–10]. However, different workers have used a variety of smectic materials, different cell constructions and different cell thicknesses.

There are no established criteria for the evaluation of the quality of smectic cells. The microscopic texture in the smectic A phase [2–4], bistability and uniformity of the chiral smectic C phase [5, 6], and switching speed and contrast in the chiral smectic C phase [7] have been applied as criteria. We have employed three criteria that bear some relevance to the practical use in displays [10]. They are (1) the maximum contrast found between crossed polarizers, (2) the contrast between the relaxed states with the same polarizer orientations as for (1), and (3) the uniformity over an area of 5 cm by 5 cm judged by the naked eye. To check whether a direct comparison of the results obtained with different criteria could be made, we evaluated a few of the polymers previously reported in the literature again, using our three criteria and a standarised cell construction.

The polymers tested previously are given in table 1, together with our results. There seems to be broad agreement between different investigations using a wide variety of smectic materials, as well as several different coating and rubbing techniques. In our opinion this indicates the importance of the polymer used, and so we started to search for systematic differences between the polymers giving good and poor alignment of smectic phases.

The smectic C phase has a monoclinic symmetry [11]. Epitaxial growth has been suggested [4] as one mechanism for the alignment of smectics on polymers. We

Table 1. Polymers tested as alignment layers for ferroelectric liquid crystals. The results obtained for each polymer and the crystal structures show a good correlation.

Polymer	Quality (*a*)	Reference	Crystal form	Reference
Polyalkyl				
Polyethylene	Good	[2]		
High density polyethylene (HDPE)	Good		Monoclinic/Orthorhombic	[13]
Polyethylene	Poor	[6, 8]		
Low density polyethylene (LDPE)	Poor		Amorphous	[13]
Polyvinyls				
Polyvinylacetate (PVAc)	Poor	[6]	Amorphous	[28]
Polyvinylchloride (PVC)	Poor	[6]	Orthorhombic	[13]
Polyvinylalcohol (PVA)	Good	[2, 4, 6, 8, 9]	Monoclinic	[13]
American Liquid Xtal SA72	Good	[3]	Monoclinic	[13]
Crosslinked PVA	Poor (*b*)	[25]	Non-crystalline	
Polyvinylmetylketone	Poor	[2]	Hexagonal	[13]
Polyvinyl cinnamate	Poor	[2]	(*d*)	
Polystyrene	Poor	[4]	Trigonal	[13]
Polyesters				
Poly(butyleneterephthalate) (PBT)	Good	[2]	Triclinic	[17]
Poly(ethyleneterphthalate) (PET)	Good	[2, 4]	Triclinic	[13]
Poly(hexyleneterphthalate) (PHT)	Good		Triclinic	[18]
American Liquid Xtal SA73	Good	[3]		
Polyamides				
Nylon 6	Good	[6, 8, 9]	Monoclinic	[13]
Nylon 6/6	Good	[2, 3, 4, 6]	Triclinic	[13]
Nylon 6/9	Good	[2]	(*e*)	[22]
Nylon 11	Good	[3]	Triclinic	[13]
Nylon 12	Good		Monoclinic	[29]
Nylon 6T	Good	[2]	Monoclinic (*f*)	[21]
Polyamid resin	Poor	[2]	Non-crystalline	
DuPont Elvamide 8064	Good	[26]		
Nylon 6T/PHT copolymer	Poor		(*d*)	

Polyimides				
American Liquid Xtal SA75	Good	[3]		
Amoco AI-10	Poor	[10]		
Ciba-Geigy XU285	Poor	[10]		
DuPont PI 2545	Poor	[6]		
Hitatchi PIQ	Poor	[3, 7, 9, 10]		
Hitachi Kasai HL-1100	Poor (*b*)	[25]		
Japan Synthetic Rubber JIB-1	Poor	[10]		
M&T Chemicals 2065	Poor	[10]		
M&T Chemicals 5000	Poor	[10]		
Merck ZLI-2650	Poor	[10]		
Nitto JR-100	Poor	[10]		
Sumitomo Bakelite CRC-6070X	Good	[10]		
Toray Semicofine SP-510	Good	[3]		
Toray Semicofine SP-710	Poor	[10]		
Toray Semicofine SP-711	Poor	[10]		
Toray Semicofine SP-910	Poor	[10]		
Rhone Poulenc Noliimide 32	Good	[8]		
3,3′,4,4′Diphenyl tetracarboxylic anhydride + 1,4-diaminophenyl	Good	[7] (*c*)		
3,3′,4,4′Diphenyl tetracarboxylic anhydride + 4,4′-diaminodiphenyl	Good	[7]		
3,3′,4,4′Diphenyl tetracarboxylic anhydride + 4,4′-diaminoterphenyl	Good	[7]		
3,3′,4,4′Diphenyl tetracarboxylic anhydride + 1,3-diaminophenyl	Good	[7]		
3,3′,4,4′Diphenyl tetracarboxylic anhydride + 4,4′-diaminodiphenylmethane	Good	[7]		
Pyromellitic anhydride + 1,4-diaminophenyl	Good	[7]	(*e*)	[27]
Pyromellitic anhydride + 4,4′-diaminodiphenyl	Good	[7]	(*e*)	[27]
Pyromellitic anhydride + 4,4′-diaminoterphenyl	Good	[7]		
3,3′,4,4′Diphenyl tetracarboxylic anhydride + 4,4′-di(*m*-amino-phenoxy)diphenyl ether	Good	[38]		

Table 1 (*continued*).

Polymer	Quality (*a*)	Reference	Crystal form	Reference
Polymethacrylates				
Polymethyl methacrylate	Poor	[4]	Pseudo-orthorhombic	[13]
Poly(cyclohexylmethacrylate)	Poor	[2]	Amorphous	[24]
Poly(benzylmethacrylate)	Poor	[2]	Amorphous	[24]
Miscellaneous				
Poly(acetal)	Poor	[2]	Tetragonal	[13]
Polybrene	Poor	[2]	Amorphous	[30]
Polycarbonate	Poor	[4]	Orthorhombic	[13]
Polyformaldehyd	Poor	[4]	Trigonal/orthorhombic	[13]
Poly-para-xylene	Good	[3]	Monoclinic	[31]
Poly-phenylquinoxaline	Poor	[8]		

(*a*) '2' and '3' of [3] are classified as poor, '1' as good. 'Average' of [6] is classified as poor, while 'very good' is classified as good.
(*b*) One surface of each is good.
(*c*) [7] does not report the bistability obtained with these polyimides.
(*d*) Probably amorphous.
(*e*) Highly crystalline, but crystal form not given.
(*f*) Based on mixed crystal studies.

therefore looked at the crystal structures of the polymers; these are also given in table 1. As can be seen, there is a strong correlation between the crystal structure and the quality obtained for the cells.

The rubbing process strongly influences the polymeric surface. The polymers are heated by frictional forces [12] and mechanically stretched [4]. This gives a birefringent surface. The parallel polymer chains obtained are a prerequisite for crystallization of the polymer. Annealing polymers will increase the degree of crystallization. In addition there will be mechanical distortions of the surface topology. For practical applications, cells with differently treated surfaces or inorganic alignment layers might be of interest, but they have not been included in this study.

2. Experimental

2.1. *Cell construction*

ITO coated glass was cleaned and spray coated with the desired polymer in an appropriate solvent. The solvents were evaporated, and the polymers cured when necessary. The plates were buffed gently with a rotating velvet coated wheel. One plate was sprayed with 2 μm polymeric spacers. On the other plate small droplets of u.v.-curable glue were applied to mark the outline of the cells (approximately 5 cm by 5 cm). The two plates were mounted together with the rubbing directions parallel. After curing the glue, the cells were cut to the desired size and then sealed. The cells were placed on a hot stage and vacuum filled with the fluids in the isotropic state. No precautions were taken to cool the cells slowly after filling.

The results reported are for ZLI-3654, a ferroelectric mixture from E. Merck with the following phase sequence: C < -30°C S_C^* 62°C S_A 76°C N* 86°C I. The pitch in the nematic and smectic C phases are 60 and 5 μm respectively. Most of the surfaces were also tested with CS-1015, a mixture from the Chisso Corporation with the phase sequence C -17°C S_C^* 57°C S_A 68°C N* 78°C I, and a pitch of 3 μm in the smectic C phase. No data are given for the pitch in the nematic phase.

2.2. *Measurements*

Contrast in the activated and relaxed states was measured with the cells between crossed polarizers (Nitto NP-QE 10-39). The cells were rotated between the polarizers to give the best possible contrast during switching. A 100 Hz 30 V peak-to-peak square wave was used; the wave generator was a Wavetek model 191. The cells were measured in transmission using a tungsten lamp and a Si-PIN detector from United Detector Technologies equipped with a photometric filter. The signals were amplified (United Detector Technologies Model 101A) and fed to a Kikusui DSS6522 storage oscilloscope. Contrasts between the relaxed states were obtained 30 s after short circuiting the cell. For ZLI-3654 these values were stable for several minutes afterwards. The uniformity of the cells was judged by the naked eye, with the cells between crossed polarizers on a light table. The density of defects was also determined through a polarizing microscope.

The results found for ZLI-3654 on different surfaces are given in table 2, together with a short designation 'good' or 'poor'. They are also listed in table 1 as 'good' or 'poor'. Our results are in very good agreement with the results obtained by previous workers in the field.

The mechanical stability of the smectic alignment is of great concern in practical applications. The alignment layers tested here gave stable orientation during our handling, but tests to find the limits of mechanical stability are not performed.

Table 2. Different performance parameters obtained with the ferroelectric smectic C material ZLI-3654 from E. Merck on different alignment layers.

Polymer	Contrast		Density of zig-zag lines	Cell eveness	Quality
	Driven	Relaxed			
High density polyethylene	12·0	2·0	Low	Excellent	Good
Low density polyethylene	3·3	1·1	High	Poor	Poor
Polybutylene-terphthalate	6·7	7·5	Low	Good	Good
Polyhexylene-terphthalate	6·0	5·0	Low	Average	Good
Nylon 6/6	28·0	2·3	Low	Good	Good
Nylon 11	9·0	5·7	Average	Average	Good
Nylon 12	8·0	2·8	Very high	Good	Good
Nylon 6T	8·0	5·0	Low	Good	Good
Polyamide resin	3·0	1·0	Very high	Good	Poor
Nylon 6T/PHT copolymer	19·0	1·0	Very high	Average	Poor

3. Discussion

3.1. *The polyethylene case*

Polyethylene is one of the few polymers giving different results for different workers [2, 6, 8]. We tested both high density polyethylene (HDPE) and low density polyethylene (LDPE). LDPE showed approximately ten times as many zig-zag defects as HDPE, and furthermore the director varied over the cells so that it was impossible to obtain complete extinction over the whole area of 25 cm^2 at the same time. With LDPE there was no bistability while HDPE gave a contrast of 1 : 2 between the relaxed states. In the driven state an LDPE cell showed lower contrast than an HDPE cell, mostly due to a higher transmission in the dark state. Microphotographs of the alignment obtained on HDPE and LDPE are shown in figures 1 and 2, respectively. The different results can easily be explained by the different structure of the two forms. The low density polyethylene is made by free radical polymerization and contains numerous five or six carbon side-chains. This will cause poorer packing and a greatly reduced tendency to form crystals. High density polyethylene is obtained by catalytic polymerisation, and contains long unbranched chains; this shows very good crystallinity. Polyethylene also has two different crystal forms. The orthorhombic is the stable form normally obtained. The monoclinic form is obtained by mechanical distortion of the orthorhombic [13]. The rubbing process would be expected therefore to induce a transition from the orthorhombic to the monoclinic crystal form.

Stretching of polyethylene sheets has been studied in some detail [14, 15]; it is shown that spherulites are pulled apart and new crystalline regions with well-ordered lamellar crystallites are formed. It has also been shown that for acridine dissolved in polyethylene, microcrystals of acridine will grow epitaxially on the (1 1 0) slip planes of polyethylene crystallites [15]. The epitaxial growth of smectic phases on polymers has been suggested as a general mechanism for orienting ferroelectric smectic C phases [4].

3.2. *Polyvinyls*

We have not been able to find crystal data for polyvinylcinnamate, but we expect this, like most atactic polymers, to be amorphous. There are thus three non-crystalline polymers among the polyvinyls and, as reported previously [4], non-crystalline polymers give poor alignment for ferroelectric liquid crystals. All the other polymers are crystalline, but they still give widely different results.

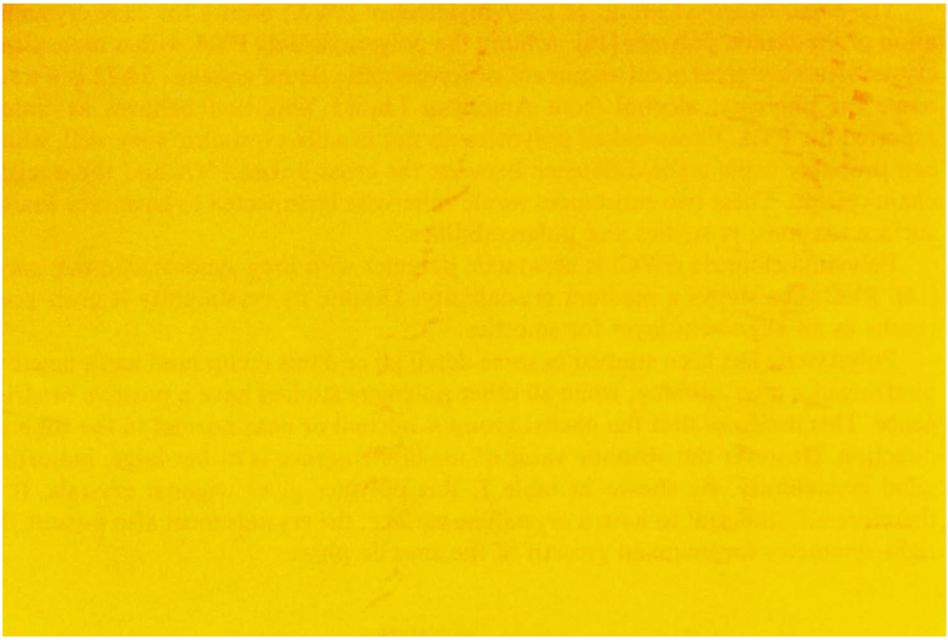

Figure 1. ZLI-3654 aligned on high density polyethylene, seen between crossed polarizers. The area of the photograph is 3·6 mm by 2·4 mm and the thickness of the sample is 2·5 μm.

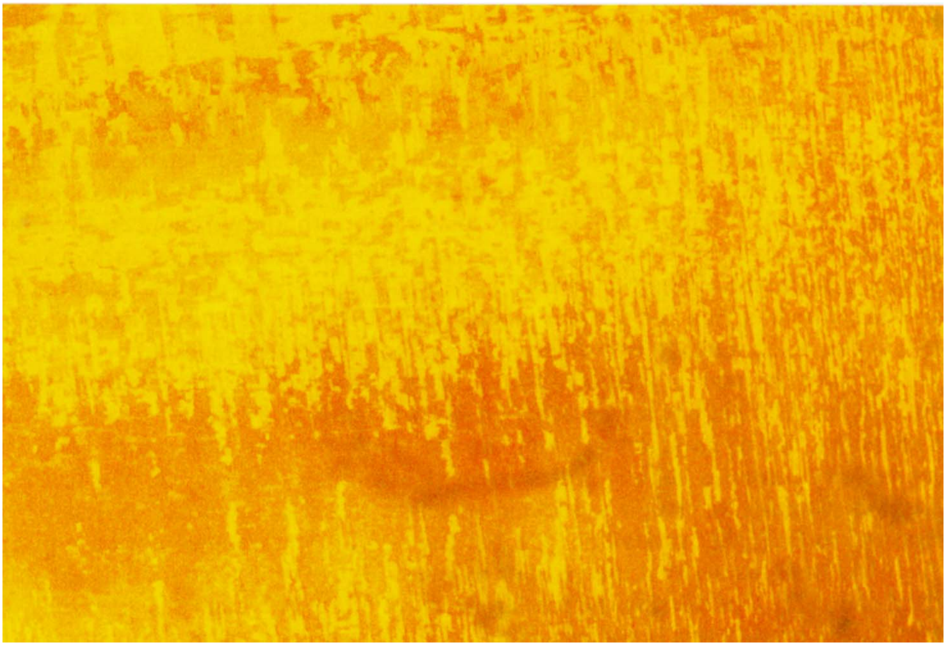

Figure 2. ZLI-3654 aligned on low density polyethylene, seen between crossed polarizers. The area of the photograph is 3.6 mm by 2.4 mm and the thickness of the sample is 2·7 μm.

The small hydroxyl group of polyvinylalcohol (PVA) allows for easy crystallisation of the atactic polymer [16]. Among the polyvinyls only PVA with a monoclinic crystal structure gives good alignment of ferroelectric liquid crystals. SA72 is a trade name for polyvinyl alcohol from American Liquid Xtal, and behaves as widely reported for PVA. Cross-linked polymers do not usually crystallize very well, which can probably explain the difference between the cross-linked PVA and the straight chain version. These two substances would otherwise be expected to have very similar surface tensions, polarities and polarizabilities.

Polyvinyl chloride (PVC) is an atactic polymer with long syndiotactic sequences [16]. PVC thus shows a medium crystallinity. Despite its crystallinity it gives poor results as an alignment layer for smectics.

Polystyrene has been studied in some detail [4] and this compound has a negative birefringence after rubbing, while all other polymers studied have a positive birefringence. This indicates that the phenyl group is normal or near normal to the rubbing direction. However the absolute value of the birefringence is rather large, indicating good crystallinity. As shown in table 1, this polymer gives trigonal crystals. It is therefore not sufficient to have a crystalline surface; the crystals must also possess the right symmetry for epitaxial growth of the smectic phase.

3.3. *Polyesters*

All three polyesters of known structure have triclinic crystals [13, 17, 18]. We found no significant difference between the terphthalates with four and six carbon chains. Epitaxial growth from polyethylene terphthalate (PET) spacer edges has been shown to produce good alignment if cut along the drawing direction of the PET film. If the spacer is cut perpendicular to the drawing direction then the alignment obtained is poor [19]. For PET it has been found that the long axis of the fibrils obtained on drawing and the molecular long axis made an angle of 5°. The same is expected for all polymers of triclinic symmetry [20].

3.4. *Polyamides*

Different nylons are known to be good alignment layers for ferroelectric liquid crystals, and Nylon 6 or Nylon 6/6 are the two most widely used surface materials. Among the nylons built from ω-amino acids those with an odd number of carbon atoms (7, 9, 11) give triclinic crystals while those with an even number of carbon atoms (4, 6, 8, 10) give monoclinic crystals [13]. Nylons formed from diamines and diacids give either triclinic (6/6 and 6/10) or monoclinic (7/7) crystal structures. In some cases nylons can be obtained in two different forms, but in all cases reported both modifications have the same crystal structure. The crystal structure of hexylenterphthalamide (Nylon 6T) has not been studied on its own, but Nylon 6T gives mixed crystals with Nylon 6/6 of good crystallinity for the whole concentration range [21]. The crystallinity increases slightly with increased amounts of Nylon 6T. We feel it is justified therefore to assign a triclinic structure to this compound. Nylon 6/9 is reported to be highly crystalline [22], but the crystal structure has not been given.

It has been shown that mixtures of nylons will give results as good as the pure compounds [2]. Considering the similar structure of the polymers and the ability to form mixed crystals this is not surprising. In the case of a copolymer between Nylon 6T and polyhexyleneterphthalate (PHT) the resulting alignment was much poorer than for the two single polymers, and bistability was not obtained. We believe this is the result of a mismatch between the two structural units. PHT has a triclinic unit cell and that for Nylon 6T is monoclinic. Crystal packing will be difficult in a random copolymer, and hence the polymer will show very low crystallinity.

Elvamide 8064 is a alcohol soluble polyamide from DuPont. As for PVA, the crosslinked resin of this class of compounds gives a poor performance in aligning smectics.

3.5. *Polyimides*

All but one of the polyimides given by trade names in table 1 are designed for alignment of twisted nematic liquid crystal displays and give good alignment for this purpose. The last one, M&T 2065, also gives good alignment of nematic liquid crystals. Generally these polyimides do not function very well for smectics.

We have shown previously [10] that CRC-6070X, a polyimide with an alkyl chain and just two different monomeric units, gives the best alignment. These are two factors that possibly increase the crystallinity of the polymer. Just two units will make the packing necessary for good crystallinity easier, while flexibility is needed for the fold-back normally seen in crystalline regions of polymers. Most of the other polyimides, where data are available, are made from two or more different diamines and/or two or more different tetracarboxylic acids.

Detailed crystal structures for the different polyimides are not available. But the one with the potential for the highest degree of crystallinity also shows the best alignment properties for ferroelectric liquid crystals.

All the polyimides synthesized by Iwasaki *et al.* [7] show good alignment and contrast, but data for bistabilities are not given. All of these polyimides incorporate only one diamine and one tetracarboxylic acid; the regular structure thus obtained should allow easy crystallisation, and two of them have been shown to be crystalline [27].

Among the polyimides we find the only discrepancy between our results and the literature data. SP-510, SP-710 and SP-711 from Toray all have the same polyimide structure [23]. However the latter two also contain adhesion promoters, which we believe has disrupted the crystal structure.

3.6. *Methacrylates*

Two of the methacrylates are amorphous [24] and give a poor performance. In addition the crystalline polymethylmethacrylate [13] gives poor results. Again we see that not only must the polymeric surface be crystalline, but the crystal structure must also be either monoclinic or triclinic.

3.7. *Miscellaneous*

We have not found any crystal data for poly-phenylquinoxaline, but for all the other polymers in this group it is seen that monoclinic crystal structures lead to good alignment while other structures result in a poor performance. No examples of polymers with triclinic crystals are found among the polymers tested.

3.8. *On the mechanism*

As can readily be seen from table 1, for a wide selection of different polymers those that have monoclinic or triclinic crystal structures give the best SSFLC cells, while polymers having other crystal structures give poor alignment and no bistability. It is worth noticing that monoclinic and triclinic crystals have the lowest number of symmetry elements and most closely resemble the smectic C phase. In our opinion this supports the proposed mechanism of epitaxial growth of smectics on the crystalline polymer surface [4]. The same mechanism has been shown for crystalline substances on polyethylene [15], and also proposed for the alignment of nematics on silicon monoxide surfaces [32], and for smectics from spacer edges [19].

During the rubbing process the top layers of the polymers melt, as is shown by a decrease in the friction coefficient [12]. The molecules are stretched in the rubbing direction which can be seen by the birefringence of the polymer [4]. The birefringence of rubbed samples is much smaller than that of stretched polymers indicating, in our opinion, that only part of the polymers crystallize during the rubbing process. Most of the polymers that show good alignment properties for ferroelectric smectic C phases have relatively low glass transition temperatures, although there are several exceptions. It is generally found to be an advantage to use a low rubbing pressure. The light rubbing pressure will heat the polymers above the glass transition, but not so much that they actually melt. This is a temperature range which is known to be advantageous for annealing polymers [33]. At the same time the polymer chains are stretched parallel by the mechanical forces of rubbing. This is the same relative orientation they must have in a crystal. Light rubbing will be effective therefore in creating a highly crystalline surface upon which the smectic phase can grow.

Light rubbing will also cause less grooving of the surface. Grooving has been shown to cause good orientation for the nematic phase [34]. It has been shown for PET [20] and also for certain polyamides [35] and polyimides [36] that the long axis of the polymer chain and the long axis of the fibrils will be at an angle of 5°–10° relative to each other. This is close to the angles usually found between the relaxed states of a chiral smectic C phase. We could speculate that this surface with two preferred directions is necessary for the bistable operation of SSFLC devices. Work on the relationship between the crystallographic angles of the polymers and the apparent tilt angles between the relaxed states of the smectic liquid crystal is in progress.

Different polymers show different degrees of crystallization, and the degree depends strongly on the treatment of the polymer. Annealing and stretching during the rubbing process are expected to produce a high degree of crystallization. Crystalline polymers have been shown to cause epitaxial growth over macroscopical areas [37], it is thus not necessary that the whole surface is crystalline to obtain high quality ferroelectric cells.

It has also been seen that when a cell with only one of the two surfaces rubbed is placed on a hot stage and cooled, the quality of the cell is better when the rubbed surface is on the top [6]. This is due to a slight temperature gradient through the cell. When the smectic phase grows from the well-ordered and highly crystalline surface better results are obtained than when it grows from the unrubbed, less ordered and crystalline surface.

The accepted mechanism for the alignment of ferroelectric fluids with the phase sequence I–N*–S_A–S_C^* consists of three distinct steps. The first is the alignment of the director parallel to the rubbing direction in the nematic phase. The second is the formation of smectic layers at the nematic–smectic A transition. The final step is the tilting of the director at the smectic A–smectic C transition [3]. Alignment of the molecules in the nematic phase is easier with an infinite or very long helical pitch [39]; in particular the pitch at the smectic A–nematic transition should tend towards infinity. This feature is incorporated into most of the newer mixtures and gives cells of good uniformity over large areas. However it does not seem to influence the bistability very much. If one or more of the intermediate phases between isotropic and smectic C are missing two or three of the steps must take place simultaneously. This usually gives poorer performance, although the complete lack of a nematic phase can give better results than one with a short pitch [2]. In addition for the chiral smectic C phase a long helical pitch will make uniform alignment easier, but it will only show a minor influence on the bistability of an SSFLC device [40, 41].

Most workers seem to prefer the occurrence of a smectic A phase during cooling of the cells. This leads to layer formation and tilting within the layers occurring as two separate steps. On the other hand, on a high tilt silicon monoxide surface mixtures without the smectic A phase have been shown to give better results [42] and tilting of the smectic A layers has been given as a source of the zig-zag defects at the smectic C–smectic A transition [43].

The wide agreement between many workers using materials of different chemical composition, pitch, phase sequence, transition temperatures and widths, with regard to bistability and quality, in our opinion indicates the minor influence of the material used on the bistability. However, most of the different surfaces were tested with both ZLI-3654 and CS-1015. In all cases a slightly lower contrast between the memory states were found for CS-1015 than for ZLI-3654. The contrast between the driven states showed a more erratic behaviour with ZLI-3654 being the better in some cases and CS-1015 on other surfaces. On the 'good'–'poor' scale the results were the same for the two fluids. An insignificant exception being HDPE where CS-1015 only showed a 1 : 1·9 contrast, thus falling 5 per cent below our limit for bistability. In addition earlier workers have found only small variations from one ferroelectric material to another [4].

4. Conclusion

Epitaxial growth of smectic liquid crystals on highly crystalline surfaces of polymers is consistent with all known data for the quality of alignment, bistability and contrast in chiral smectic C phases. For the epitaxial growth to occur it is not enough to have a highly crystalline surface, the crystals must also be either monoclinic or triclinic.

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