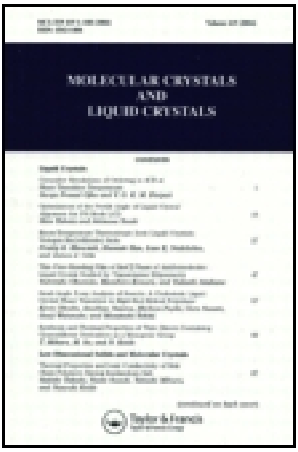

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The Relationship between the Physical Properties of the Alignment Layer and the Quality of SSFLC Cells

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The Relationship between the Physical Properties of the Alignment Layer and the Quality of SSFLC Cells

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Data for the quality of alignment for 130 different polymers tested as alignment layers for surface stabilised ferroelectric liquid crystal displays (SSFLCs) are given. The thermal, mechanical and electrical properties of the polymers are correlated with their ability to give good, bistable alignment in SSFLCs.

Keywords: ferroelectrics, alignment layer

1. INTRODUCTION

The discovery of the ferroelectric smectic C phase (SmC*)[1] and invention of the surface stabilised ferroelectric liquid crystal display (SSFLC)[2] has opened the possibility for extremely fast and bistable displays and optical elements. The fast switching and 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 that has been difficult to achieve, and seems to depend as much on the surface of the cells as on the ferroelectric smectic fluid. The interaction between the polymeric alignment material and the liquid crystal is a complicated one. It is found favourable to use liquid crystals with the phase sequence Isotropic—Nematic (Cholesteric)—Smectic A—Smectic C* and a very long pitch near the Nematic—smectic A phase transition.[3] The cells are filled in the isotropic state and cooled down to the smectic phase. The final alignment of the SSFLC will thus depend on the interaction between the surface and the three different liquid crystalline phases. The nematic phase is aligned parallel to the rubbing direction of the polymeric surfaces. This seems mostly to be an effect of the ordering of the polymeric chains in the alignment layer and less on the physical deformation of the layer.[4] Although the physical deformation of the surface will modify the alignment obtained, sometimes for better, sometimes for the worse.[5] The smectic layers are formed at the nematic—smectic A transition. It is 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.[6] This could be a result of a distribution of pretilt in the nematic phase and thus a variation in layer orientation in the smectic A phase.[7] Recently it has also been found that the pretilt of the molecules changes at the nematic smectic A transition for several different classes of alignment layers.[5] Finally at the smectic A—smectic C* transition the molecules will tilt, while the integrity of the layers is maintained. 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 smectic C* phase is largely favoured and bistability can not be obtained. Due to the chevron structure[8] in the smectic C phase several so called zig-zig defects often do occur. Even in the cases where bistability occur the angle between the director of the two different states is almost universally found to be far less than twice the smectic C tilt.

There has been a number of studies considering different properties of the polymeric alignment layers and how they affect the texture and bistability of SSFLCs. Workers in the field have considered the degree of crystallinity,[6,9–12] the crystal structure,[13] the polarity of the polymer,[14] the surface tension,[15,16] the conductivity of the polymer,[17–19] the dielectric constant[18,19] and Mark-Houwink coefficient,[20] surface anchoring,[21] and chemical structure[22] as well as the layer thickness.[14,17–19] However in most cases only one or maybe two factors have been considered, in addition most of the early work relied on rather subjective evaluations of the SSFLCs. In this work we consider most of what we believe could be relevant properties of the polymers to evaluate the relative importance of the different factors.

For practical SSFLC displays four parameters are of major importance; that is, first the defect density and hence the transmission of the dark state, secondly the cone angle between the two relaxed (no field) states, the third factor is the time taken to switch the cell into one of the stable states and finally the stability of the director orientation towards small disturbing fields. The first two together determine the contrast of the device. These two factors can be treated independently. The dark state contrast can be minimised by the proper mechanical and thermal treatment of the polymer alignment layer. Given the darkness of the dark state the contrast will be determined by the cone angle, with 45 degrees as the optimum cone angle. Control of the cone angle and the relationship between cone angle and properties of the alignment layer is a non-trivial problem. In this work we will try to find relationships between properties of the alignment layers and cone angles of the SSFLC cells.

The time to switch a display element to one of it's stable states is of major importance for the practical use of displays. This time will depend both on the viscosity and spontaneous polarisation of the fluid, the cell construction and the drive scheme used. This problem will not be considered in this study. In multiplexed displays pulses too small for a complete switching of the display will always be present. Although they do not cause complete switching these pulses will often cause an oscillation of the smectic C director around some mean value. This oscillation gives a small time variation of the transmission and most importantly an increase in dark state transmission with a resulting lowering of the contrast. The

TABLE I

Polymers for alignment of FLC

Polymer		Cone[a]	Reference
Polyalkyl			
Polyethylen	PE	bist	48
High density Polyethylene	HDPE	16.2	
Polyethylen	PE	f.c.	14
Low density Polyethylene	LDPE	0	
Polyvinylidenfluoride	PVDF	f.c.[b]	
Polytetrafluoroethylene	PTFE	Good[c]	49
Polypropylene (isotactic)	PP	Homeotrop	49
Poly-1-butene	P-1B	Homeotrop	49
Polyvinyls			
Polyvinylchloride	PVC	Poor	50
Polyvinylacetat	PVAc	Poor	50
Polyvinylalcohol	PVA	20	53
	PVA	21	14
	PVA	25.5	15
	PVA	14	21
	PVA	38[e]	21
	PVA	35[e]	53
American Liquid Xtal SA72	SA72	bist	51
Crosslinked PVA	xPVA	Poor[d]	52
Polyvinylmetylketone	VMK	Poor	48
Polyvinyl cinnamate	VCi	Poor	48
Polystyrene	PS	Poor	6
Polyacrylonitrile	PAN	16.4	
Polyamides			
Nylon 6	PA6	22	15
	PA6	20	14
Nylon 6/6	PA6/6	16.1	
Nylon 6/9	PA6/9	bist	48
Nylon 7/6	PA7/6	0	
Nylon 8/6	PA8/6	bist	49
Nylon 11	PA11	19.5	
Nylon 12	PA12	7.1	
Nylon 2T	PA2T	(22)	9
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)	9
Nylon 9T	PA9T	(3)	9
Nylon 10T	PA10T	(32)	9
Nylon 3, 5, 6T	PA356T	0	
Polyamid resin		1	
DuPont Elvamide 8064	8064	bist	60
Hitachi Kasai HL-1100	HL1100	Poor[d]	52
Hitachi Kasai HL-1100	HL1100	18	59
	HL1100	16.1	36

TABLE I (*continued*)

Polymer		Cone[a]	Reference
Nylon 6T/PHT copolymer		0	
Polyimides			
3,3′,4,4′diphenyl tetracarboxylic anhydride + 1,4-diaminophenyl	DPAP	16	53
3,3′,4,4′diphenyl tetracarboxylic anhydride + 4,4′-diaminodiphenyl	DPDP	Good	54
3,3′,4,4′diphenyl tetracarboxylic anhydride + 4,4′-diaminoterphenyl	DPTP	Good	54
3,3′,4,4′diphenyl tetracarboxylic anhydride + 1,3-diaminophenyl	DPoP	Good	54
3,3′,4,4′diphenyl tetracarboxylic anhydride + 4,4′-diaminodiphenyl-methane	DPDM	Good	54
3,3′,4,4′diphenyl tetracarboxylic anhydride + 4,4′-di(*m*-amino-phenoxyl)diphenyl ether	DPDE	Good	55
3,3′,4,4′diphenyl tetracarboxylic anhydride + 4,4′-diaminodiphenyl-ether	DPDE	Good	54
Pyromellitic anhydride + 1,4-diaminobenzene	Pϕ	14.8	
Pyromellitic anhydride + 4,4′-diaminodiphenyl	Pϕϕ	Good	54
Pyromellitic anhydride + 4,4′-diaminoterphenyl	Pϕϕϕ	Good	54
Pyromellitic anhydride + benzidine	PB	Good	54
Pyromellitic anhydride + 1,2-diaminoetan	P2	15.7	10
Pyromellitic anhydride + 1,3-diaminopropan	P3	2.7	10
Pyromellitic anhydride + 1,4-diaminobutan	P4	14.8	10
Pyromellitic anhydride + 1,5-diaminopentan	P5	3.3	10
Pyromellitic anhydride + 1,6-diaminohexane	P6	16.6	10
Pyromellitic anhydride + 1,7-diaminoheptane	P7	2.1	10
Pyromellitic anhydride + 1,8-diaminooctane	P8	14.3	10
Pyromellitic anhydride + 1,9-diaminononane	P9	3.1	10
Pyromellitic anhydride + 1,10-diaminodecane	P10	12.9	10
Pyromellitic anhydride + 1,6-diaminocyclohexane	P6c	37.0[c]	53
Benzophenone-3,3′,4,4′tetracarboxylic anhydride + 1,2-diaminoetane	B2	15.0	10
Benzophenone-3,3′,4,4′tetracarboxylic anhydride + 1,3-diaminopropane	B3	14.7	10
Benzophenone-3,3′,4,4′tetracarboxylic anhydride + 1,4-diaminobutane	B4	14.5	10
Benzophenone-3,3′,4,4′tetracarboxylic anhydride + 1,5-diaminopentane	B5	14.8	10

TABLE I (*continued*)

Polymer		Cone^a	Reference
Benzophenone-3,3′,4,4′tetracarboxylic anhydride + 1,6-diaminohexane	B6	14.8	10
Benzophenone-3,3′,4,4′tetracarboxylic anhydride + 1,7-diaminoheptane	B7	13.2	10
Benzophenone-3,3′,4,4′tetracarboxylic anhydride + 1,8-diaminooctane	B8	9.8	10
Benzophenone-3,3′,4,4′tetracarboxylic anhydride + 1,9-diaminononane	B9	15.8	10
Benzophenone-3,3′,4,4′tetracarboxylic anhydride + 1,10-diaminodecane	B10	10.7	10
Benzophenone-3,3′,4,4′tetracarboxylic anhydride + 1,4-diamino benzene	Bϕ	0	10
Benzophenone-3,3′,4,4′tetracarboxylic anhydride + 1,8-diamino adamantane	BA	36^c	53
Naphthalen-1,4,5,8,-tetracarboxylic anhydride + 1,2-diaminoetane	N2	13.6	10
Naphthalene-1,4,5,8-tetracarboxylic anhydride + 1,3-diaminopropane	N3	6.5	10
Naphthalen-1,4,5,8,-tetracarboxylic anhydride + 1,4-diaminobutane	N4	14.4	10
Naphthalene-1,4,5,8-tetracarboxylic anhydride + 1,5-diaminopentane	N5	7.6	10
Naphthalen-1,4,5,8,-tetracarboxylic anhydride + 1,6-diaminohexane	N6	17.6	10
Naphthalene-1,4,5,8-tetracarboxylic anhydride + 1,7-diaminoheptane	N7	7.0	10
Naphthalen-1,4,5,8,-tetracarboxylic anhydride + 1,8-diaminooctane	N8	14.3	10
Naphthalene-1,4,5,8-tetracarboxylic anhydride + 1,9-diaminononane	N9	9.4	10
Naphthalen-1,4,5,8,-tetracarboxylic anhydride + 1,10-diaminodecane	N10	10.6	10
Naphthalen-1,4,5,8-tetracarboxylic anhydride + 1,4-diaminobenzene	Nϕ	6.5	
cis,cis,cis,cis-1,2,3,4-cyclopentane tetracarboxylic anhydride + 1,2-diaminoetane	C2	f.c	11
cis,cis,cis,cis-1,2,3,4-cyclopentane tetracarboxylic anhydride + 1,3-diaminopropane	C3	0	11
cis,cis,cis,cis-1,2,3,4-cyclopentane tetracarboxylic anhydride + 1,4-diaminobutane	C4	f.c	11
cis,cis,cis,cis-1,2,3,4-cyclopentane tetracarboxylic anhydride + 1,5-diaminopentane	C5	17.9	11
cis,cis,cis,cis-1,2,3,4-cyclopentane tetracarboxylic anhydride + 1,6-diaminohexane	C6	f.c	11
cis,cis,cis,cis-1,2,3,4-cyclopentane tetracarboxylic anhydride + 1,7-diaminoeheptane	C7	14.9	11
cis,cis,cis,cis-1,2,3,4-cyclopentane tetracarboxylic anhydride + 1,8-diaminooctane	C8	12.0	11
cis,cis,cis,cis-1,2,3,4-cyclopentane tetracarboxylic anhydride + 1,9-diaminononane	C9	16.7	11
cis,cis,cis,cis-1,2,3,4-cyclopentane tetracarboxylic anhydride + 1,10-diaminodecane	C10	16.2	

TABLE I (*continued*)

Polymer		Cone[a]	Reference
cis,cis,cis,cis-1,2,3,4-cyclopentane tetracarboxylic anhydride + 1,4-diaminobenzene	Cϕ	24.8	
cis,cis,cis,cis-1,2,3,4-cyclopentane tetracarboxylic anhydride + 4,4′-diaminodiphenylmethane	CPM	bist	56
2,2-bis(4-(4aminophenoxyphenyl))-propane + 3,5,6 – tricarboxy-2-carboxymethylnorbornane – 2:3, 5:6-dianhydrido	CNPPP	36[c]	53
Diaminophenylether + 2,3,5-tri – carboxycyclopentylaceticacid	CPAPE	37[c]	53
2,2-bis(4-(4aminophenoxyphenyl))-propane + 1,2,3,4-cyclobutane-tetracarboxylic anhydride	CBPPP	38[c]	53
1,4-diaminocyclohexane + 1,2,3,4-cyclobutane-tetracarboxylic anhydride	CBCH	37[c]	53
4,4′-diaminophenylether + 1:2, 5:7-bicyclo(4:8)octane – tetracarboxylic anhydride	BCOPE	39[c]	53
American Liquid Xtal SA74	SA74	bist	51
Amoco AI-10	AI10	f.c	
Ciba-Geigy XU285	XU285	0	
DuPont PI 2545	2545	Poor	50
Hitatchi PIQ	PIQ	13.6	36
Japan Synthetic Rubber JIB-1	JIB	0	
M&T Chemicals 2065	2065	f.c	
M&T Chemicals 5000	5000	f.c	
Merck ZLI-2650	2650	0	
Nagase LP-54	LP54	bist	57
Nitto JR-100	JR100	0	
Sumitomo Bakelite CRC-6070X	CRC	25.0	
Toray Semicofine SP-510	SP510	bist	51
Toray Semicofine SP-710	SP710	0	
Toray Semicofine SP-711	SP711	0	
Toray Semicofine SP-910	SP910	16.1	
Nissan Chemical RN305	RN305	bist	18
Hitachi Kasei LQ-1800	LQ	good	58
Hitachi Kasei PIX-1400	PIX	good	58
Polyesters			
Poly(butyleneterephthalate)	PBT	24.7	
Poly(ethyleneterphthalate)	PET	bist	48
Poly(hexyleneterphthalate)	PHT	18.5	
American Liquid Xtal SA73	SA73	bist	51
Polycaprolactone	PCA	f.c	
Poly(ethylene succinate)	PES	f.c	
Polymethacrylates			
Polymethyl methacrylate	PMMA	Poor	6
Poly(cyclohexylmethacrylate)	PCMA	Poor	48
Poly(benzylmethacrylate)	PBMA	Poor	48

TABLE I (*continued*)

Polymer		Cone[a]	Reference
Miscellaneous			
Poly(acetal)	PAC	Poor	48
Polybrene	PB	Poor	48
Polycarbonate	PC	Poor	6
Poly-para-xylene	PPX	bist	51
Poly-phenylquinoxaline	PPQ	f.c	14
Polyformaldehyd	POM	Poor	6
Polydiisopropyl fumarate	IPF	20.7	36
Polydicyclohexyl fumarate	CHF	bist	20
Poly(1-trimethylsilyl-1-propyne)	TSP	bist	20
Poly(isopropyl-1,1,2,2-tetrahydroperfluorodecyl fumarate)	HFF	bist	20

[a] Cone angles are given in degrees except for: bist, bistable cell, but cone angle is not determined. f.c, focal conical texture. Good, polymers reported to give good alignment without any specification of bistability. Poor, polymers reported to give poor results in SSFLCs, either poor alignment or lack of bistability. 0, degree cone angles are used for cells with good alignment, but without bistability. Values in parenthesis are preliminary values.

[b] Drawn films are reported to be good (40).

[c] Due to the insolubility of PTFE it has not been possible to make good cells, the cells are however bistable over smaller areas.

[d] One surface of each gives good cells.

[e] Subjected to low frequency, high voltage before measurement.

degree of crystallinity seems to play an important role when it comes to control this effect,[12,23] but it will not be considered in this study.

2. EXPERIMENTAL

Our experimental procedure for determining the cone angle between the relaxed states have been described in detail earlier.[9–11,23] Some values found in the literature are included for completeness. All cells are 1.5–2.5 microns thick.

Data for polymers, except polyimides, are taken mostly from *Properties of Polymers* by D. W. van Krevelen[24] or from the references given in Table II. Data for commercial polyimides are taken from the manufacturer's data sheets, while physical data for most other polyimides stem from *Polyimides* edited by K. L. Mittal.[25]

3. RESULTS

3.1 Thermal Properties of the Polymer

3.1.1 Melting point. During the rubbing of the polymer layer the polymer is heated and possibly melts,[26] the polymer chains are also organised more parallel as can be seen from an induced birefringence in the polymer layer.[6,24] As we believe

TABLE II

Polymers grouped according to crystal structure and their quality as alignment layers for SSFLC's

Polymer	Quality[a]	Reference[b]
TRICLINIC		
Polytetrafluoroethylene	bist[c]	61
Nylon 6/6	16.1	61
Nylon 8/6[d]	bist	
Nylon 11	19.1	61
Naphthalen-1,4,5,8,-tetracarboxylic anhydride + 1,2-diaminoetane[d]	13.6	62
Naphthalen-1,4,5,8,-tetracarboxylic anhydride + 1,4-diaminobutane[d]	14.4	62
Naphthalen-1,4,5,8,-tetracarboxylic anhydride + 1,6-diaminohexane[d]	17.6	62
Naphthalen-1,4,5,8,-tetracarboxylic anhydride + 1,8-diaminooctane[d]	14.3	62
Naphthalen-1,4,5,8,-tetracarboxylic anhydride + 1,10-diaminodecane	10.6	62
Poly(butyleneterephthalate)	24.7	68
Poly(ethyleneterphthalate)	bist	61
Poly(hexyleneterphthalate)	18.5	64
MONOCLINIC		
High density Polyethylene[e]	16.2	61
Polypropylene (isotactic)	homeotrop	61
Polyvinylalcohol	20	61
American Liquid Xtal SA72	bist	61
Nylon 6	22	61
Nylon12	(7.1)	63
Nylon 2T[d]	(22)	63
Nylon 4T[d]	15.2	63
Nylon 6T[f]	16.7	63
Nylon 8T[d]	(15)	63
Nylon 10T[d]	(32)	63
Pyromellitic anhydride + 1,2-diaminoetan[d]	15.7	65
Pyromellitic anhydride + 1,4-diaminobutan[d]	14.8	65
Pyromellitic anhydride + 1,6-diaminohexane[d]	16.6	65
Pyromellitic anhydride + 1,8-diaminooctane	14.3	65
Pyromellitic anhydride + 1,10-diaminodecane	12.9	65
Poly-para-xylene	bist	66
Poly(oxyethylene)	[j]	61
ORTHORHOMBIC		
Polyvinylchloride	poor	61
Polyvinylidenfluoride	f.c	61
Polycaprolactone	f.c	61
Poly(ethylene succinate)	f.c	61
Polymethyl methacrylate[g]	poor	61
Polycarbonate	poor	61
Merck ZLI-2650	0	67
TETRAGONAL		
Poly(acetal)	poor	61

TABLE II (*continued*)

Polymer	Quality[a]	Reference[b]
TRIGONAL		
Polystyrene	poor	61
Poly(1-butene) (isotactic)	homeotrop	61
Polyformaldehyd[e]	poor	61
HEXAGONAL		
Polyvinylmethylketone	poor	61
CUBIC		
No examples found.		

[a] "2" and "3" of Reference 7 are classified as poor, "1" as bist "Average" of Reference 3 is classified as poor, while "Very good" is classified as bist.

[b] Giving crystal data.

[c] Due to the insolubility of PTFE it has not been possible to make good cells, the cells are however bistable over smaller areas.

[d] Based on the regularity of crystal structure found in most series of homologes.

[e] Also have an orthorhombic modification.

[f] Based on mixed crystal studies.

[g] Pseudoorthorhombic.

[h] Also have a tetragonal modification.

[j] Due to the low melting point of poly(oxyethylene) (66°C) it has not been possible to make cells with FLC mixtures. Low temperature smectic A mixtures like S3 from BDH. Limited does however show good alignment on Poly(oxyethylene) cast from chloroform.

in an epitaxial growth mechanism for the alignment of ferroelectric liquid crystals on polymers[6] the optimum conditions would be one where the polymer is heated to increase mobility of the chains and then stretched by the mechanical action of the rubbing material, but without actually melting, which could again cause a fluid like disorganisation. To check this mechanism, the cone angle found for different polymeric alignment materials were plotted versus the melting point of the polymer.

In all figures we divide the polymers into three different classes: 1) Those with a monoclinic or triclinic crystal structure, marked with open symbols. 2) Polymers with other crystal structures and amorphous polymers shown as filled symbols. 3) Those where data on the crystallinity and crystal structure is unavailable (cross hatched symbols).

The results are shown in Figure 1, where the cone angles are plotted as a function of the melting points of the polymers. There are two clear groups, those with monoclinic or triclinic crystal structures giving bistability and those with other crystal structures that don't. Some of the unknowns give good results some give poor. Looking only at those giving bistability we find no relationship between the melting point and the cone angle.

Figure 2 is a similar plot for the glass transition temperature of the polymers and does not reveal any correlation either.

3.1.2 Melting enthalphy. The heat capacity of the polymers is small. Consequently little energy is required to heat them to their melting points. At the melting point a large amount of energy must be added to actually melt the polymer. As the mobility of the chain is largest and thus stretching easiest just below the melting

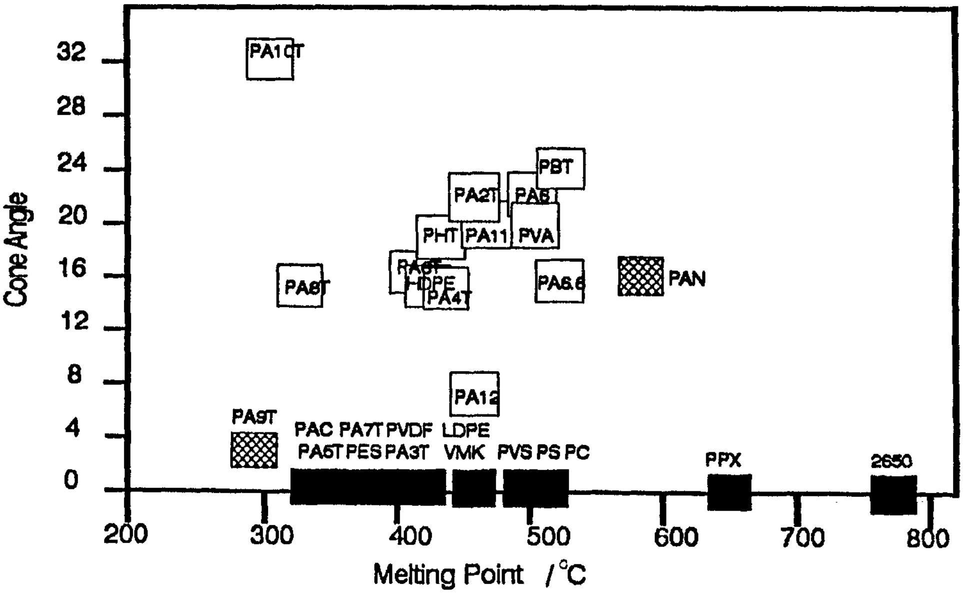

FIGURE 1 Relationship between cone angle found and the melting point of the polymer. □ Polymers with monoclinic or triclinic crystal structure. ■ Polymers with other crystal structures or amorphous polymers. ▨ Polymers where data on crystallinity or crystal structure is not available.

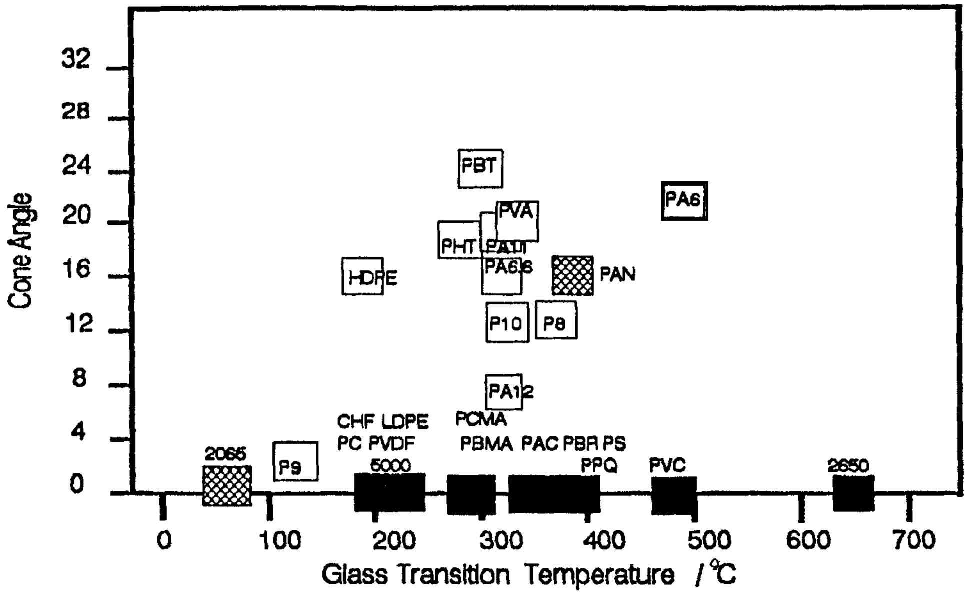

FIGURE 2 Relationship between glass transition temperature and cone angle. Symbols as for Figure 1.

point it is advantageous to keep them at this temperature. Rubbing is, however, a very crude method of adding energy and little control can be obtained. If the polymer has a high melting enthalphy the chances of accidently heating it into the liquid state is, however, smaller. In cases where the melting enthalpy has not been determined experimentally it is possible to calculate this with good accuracy from the melting point of the polymer and the melting entropy which is additive in group contribution.[24] In Figure 3 the cone angle *vs.* enthalpy of melting is plotted.

As can be seen there is a positive correlation between the melting enthalpy and the cone angle, although the variation is large. A more accurate calculation would be to take into account the heat capacity and melting point of the polymers as well and calculate the total energy needed to melt the polymers as $C_p(T_m - T_{room}) + \Delta H$. The heat capacities of the polymers are small and do not vary much either. The correction to ΔH will be of the order 0.1–0.3 *kJ*/mol, and does not influence the conclusion.

The coefficient of friction will also be different for different polymers and this will complicate the picture even more as low friction will mean less effective heat generation. Low friction will also lead to less effective stretching of the polymers chains. For poly-tetrafluoroethylene (Teflon) if is very difficult to get SSFLC cells well aligned over large areas, instead the director will change from one part of the cell to another. This is probably a result of the crystalites not being aligned parallel over the whole surface. Small areas under the microscope will show good bistability.

3.2 Mechanical Properties

3.2.1 Shear modulus. During buffing, the thin polymer film is caught between two broad planes, one stationary (the substrate) and the other moving (the fiber

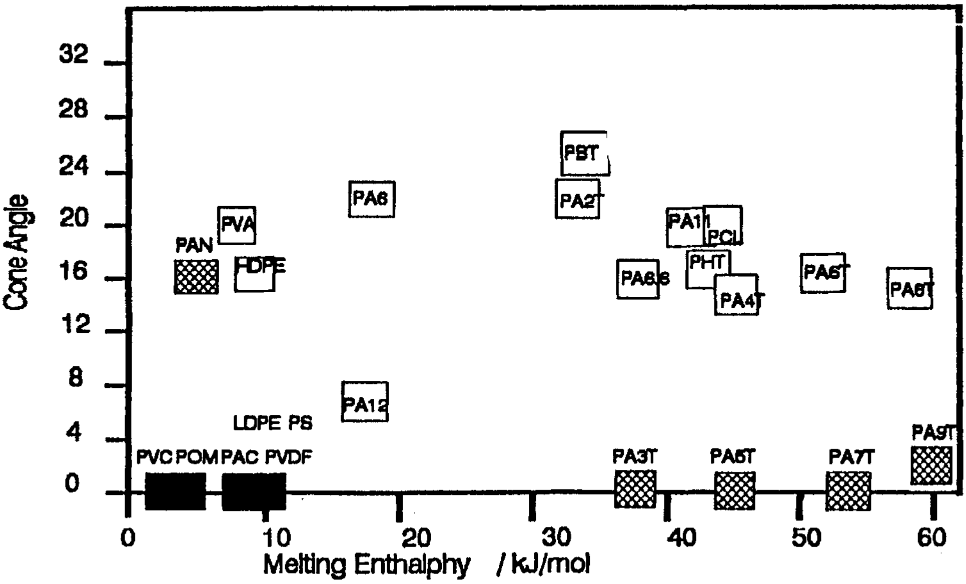

FIGURE 3 Relationship between cone angle and melting enthalpy of the polymers. Symbols as for Figure 1.

contact area). The polymer will thus experience a shearing force and, possibly a permanent shearing deformation. This permant deformation has been shown by the birefringence of rubbed polymers[6] and dichroism of infrared absorption bands.[23] The shear modulus is defined as the ratio between the deformation and the applied force. The lower the shear modulus the larger the deformation for a given force. It could thus possibly be a relationship between the shear modulus of the polymer alignment layer and the alignment quality in SSFLCs. For crystalline polymers an empirical relationship has been found between the shear modulus, G and the melting point.[24]

$$G = (T_m - 298)\ 10^7\ N/m^2 \qquad (1)$$

As was seen in Figure 1 there was no correlation between the melting point and the cone angle, hence there is no correlation between the shear modulus and the cone angle, either. Direct determinations of the shear modulus are relatively few, but in all cases the modulus is within 10% of that calculated from Equation 1.

3.2.2 Tensile strength. The group at Bell Lab regarded the polymer layer as sheared between two plates.[6] The rubbing material is usually some form of cloth and the contact between the rubbing material and the polymer thus will not be even over the whole surface. Instead, the different fibers in the rubbing cloth will catch different parts of the polymer surface. The tensile strength is the ratio betwen the applied force and the elongation of a fiber of unit cross section. The tensile strength will depend on the processing of the polymer material, and a range of values are found for each polymer.[27,28] In Figure 4 a value in the middle of the

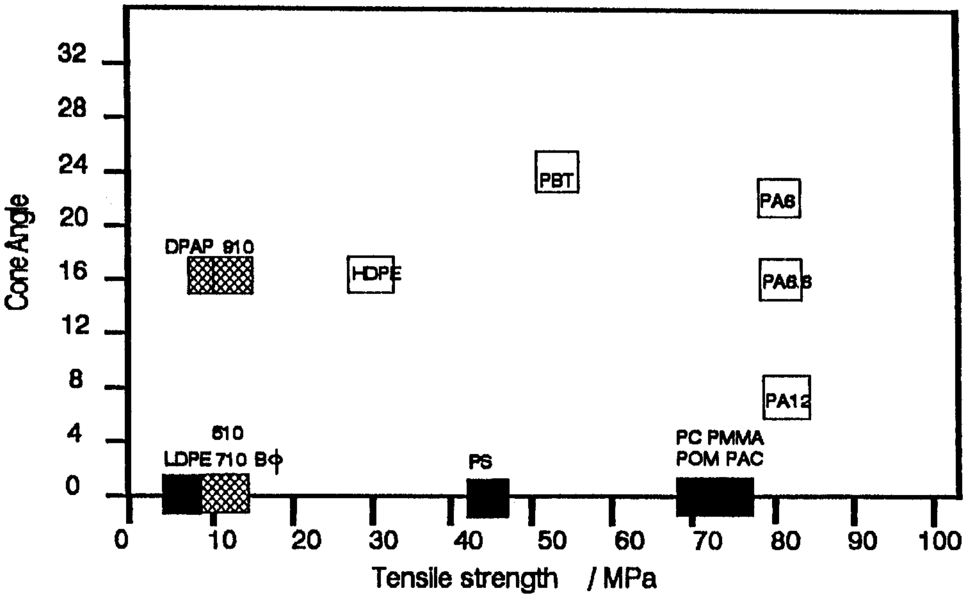

FIGURE 4 Relationship between the tensile strength of the polymers and the cone angle. Symbols as for Figure 1.

range of the tensile strengths found for the different polymers is used. There is no evidence for any correspondence between the mechanical property of the polymers and the cone angle or quality of the SSFLC cells.

3.2.3 Mark-Houwink coefficient. The Mark-Houwink coefficient is defined by the equation

$$[\eta] = KM^{\alpha} \tag{2}$$

where $[\eta]$ is the limiting viscosity, M is the molecular weight (or average molecular weight) of the polymer K is a constant and α is the Mark-Houwink coefficient. It has been suggested that a Mark-Houwink coefficient of more than 0.85, preferably more than 0.95 is a prerequisite for good alignment and bistability in SSFLCs.[20] It might be a little surprising to use the Mark-Houwink coefficient which describes dilute polymer solutions as a guideline for the properties of the solid polymer layers that are found in liquid crystal cells. The rationale behind this is as follows. A coefficient above 0.85 means that the polymer has a rigid and rod-like main chain. If the polymer has bulky side chains the free rotation of the main chain is hindered and the polymer effectively becomes rod shaped. If the polymer molecules are rod-like in dilute solutions they will also be so in the solid state.

The Mark-Houwink coefficient will depend on both polymer and solvent, and has only been experimentally determined for a relatively small number of polymer solvent combinations.[24] It is possible to calculate the coefficient from additive properties of the polymers and the solubility parameters of the solvents.[24]

The results are plotted in Figure 5. As can be seen, polymers over the whole

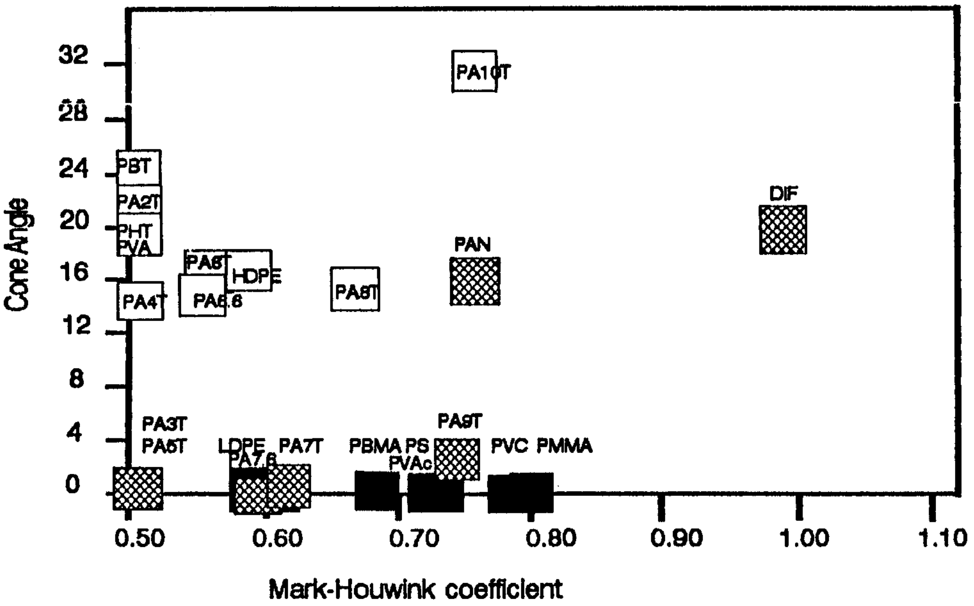

FIGURE 5 Relationship between the Mark-Houwink coefficient for the polymer and the cone angle found. Symbols as in Figure 1.

range of Mark-Houwink coefficients give alignment layers that show good bistability, as long as they have a monoclinic or triclinic crystal structure. Examples of poor alignment are not found for polymers with a coefficient above 0.85. Three polymers have Mark-Houwink coefficients above 0.85 and give bistable cells,[20] but the cone angle is not given. We conclude that a Mark-Houwink coefficient of more than 0.85 might be a sufficient condition for bistable operation of SSFLCs, but it is not a necessary condition. It is however difficult to see the application of this rule for polyimides as they are usually applied in the form of polyamic acids, and become much more rigid as the imide rings are closed upon further processing.

A recent work[29] also shows that polyfumarates will give an extremely thin layer when spin coated, and postulates an intimate relationship between the thin film processibility by spin coating and the rigidity or the thermodynamic main-chain folding of macromolecules. Part of the effect of a large Mark-Houwink coefficient might thus be explained by an extremely thin alignment layer. See 3.3.1 for further discussion of this effect.

3.3 Electrical Properties of the Polymer

Ions will wander in electric fields. This will occur both during switching, when a large external field is applied across the SSFLC structure and in the relaxed state when the spontaneous polarisation of the ferroelectric smectic C phase creates its own electric field. The electrical behaviour of an SSFLC device is much more complicated than for a twisted nematic device. This warrants a close look at the electric and dielectric properties of the alignment layer.

3.3.1 Dielectric constant. The dielectric constant of the polymer alignment layer has been explicitly taken into account when the switching mechanism of the cell is described.[18,19] No attempts have been made to relate this to the cone angle. As can be seen from Figure 6 we find no correlation either.

3.3.2 Resistivity. Yang and co-workers[17,30,31] considered the depolarisation field in SSFLC cells and found that thin or conductive alignment layers are required for good bistability. It has also been found experimentally that doping the polyimide RN305 with the charge transfer complex tetramethyltetrathia-fulvalene-octadecyl-tetracyano-quinodimethane (TMTTF-ODTCNQ) improves the bistability of the corresponding cells.[18,32] Most other charge transfer complexes, however, will not give the same improvement of bistability.[32] It has also been concluded that a conductive orientation layer will reduce the internal field and hence the effect of ions in the cell.[19] A conductive—or very thin—orientation layer is in all cases found to an advantage in addressing the cell. In Figure 7 the cone angles found in different cells are plotted as a function of the resistivity of the polymers used. No correlation can be found. But even if the difference in resistivity between the different polymers is of the order of 10^{12} only two of the polymers tested here are conducting (PVA and PVDF, both with $R = 10^7\ \Omega m$) and below the limit calculated for perfect bistability. The resistivity of the TMTTF-ODTCNQ doped polyimide is 100–10000 less than for PVA.[18] Recent work gives a cone angle of 35–38 degrees for PVA after the cell has been subjected to electrical pulses.[21,53] A low resistivity

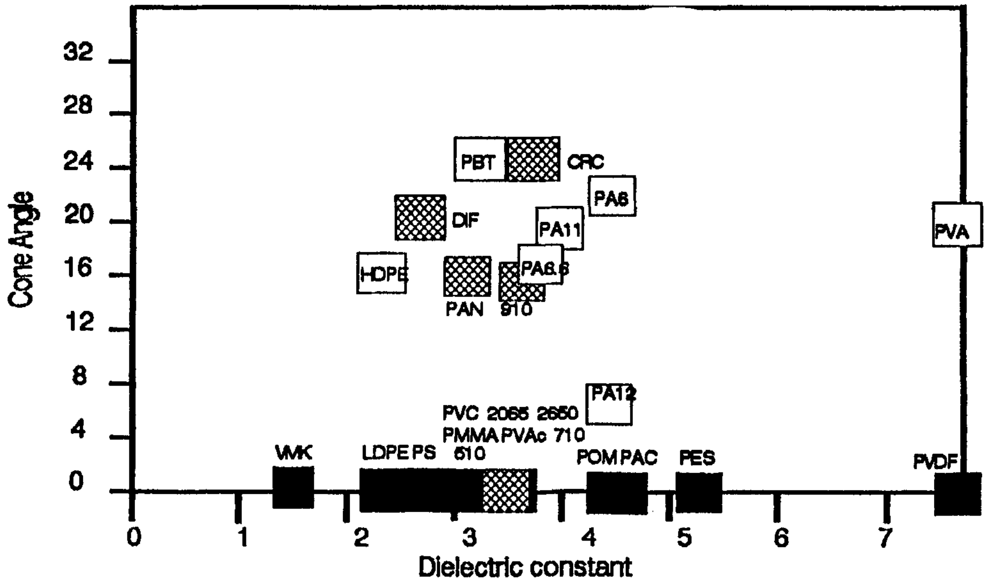

FIGURE 6 Relationship between the dielectric constant of the polymer and the cone angle. Symbols as in Figure 1.

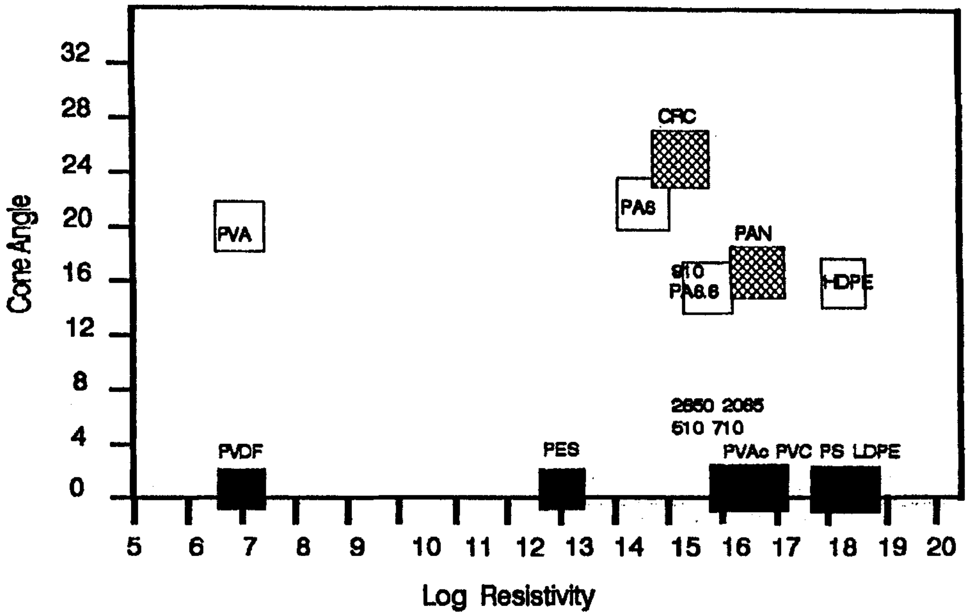

FIGURE 7 Relationship between the resistivity of the polymers and the cone angle. Symbols are the same as in Figure 1.

of the alignment layer improves the switchability of the SSFLC cell, but there is no evidence for an increased cone angle between the relaxed states.

3.3.3 Polarity. By looking at different surfaces, it was empirically found that polar polymers gave cells with good bistability, while non-polar gave poor alignment quality.[14] As the ferroelectric smectic C phase contains permant dipoles which can, and almost certainly do, interact with the surface, a relationship between the polarity of the surface and the quality of alignment will also be reasonable to expect. Direct evidence for polar interactions with the surface have been found in the case of an isotropic ITO on glass surface.[32]

When the dielectric constant and refractive index of a polymer is known, the dipole moment can be found by Debye's equation:[24]

$$\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right]\frac{M}{\delta} = \frac{4}{9}\pi N_A \frac{\mu^2}{kT} \tag{3}$$

If either the dielectric constant or the refractive index, or both, is lacking, a good estimate of the dipole moments can be found via additive group contributions.[24]

Values for the dipole moments of different polymers and the corresponding cone angles are shown in Figure 8. As can be seen there is no correlation. The original correspondence was based on five polymers where the two poor ones were amorphous and two of the three good polymers had monoclinic crystal structure. The structure of the last one has not been determined.

3.3.4 Surface tension. Surface tension has been considered extensively in

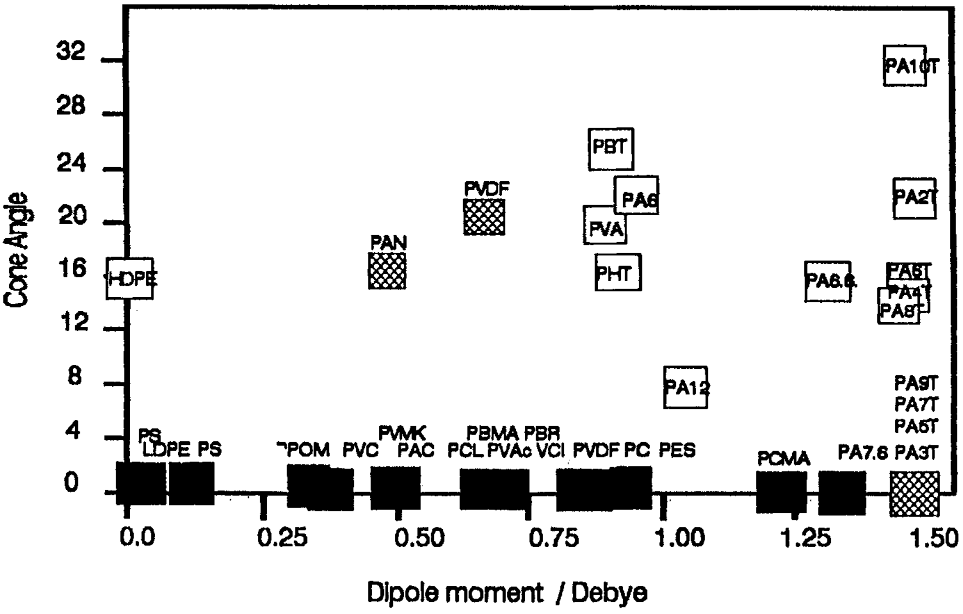

FIGURE 8 Relationship between the dipole moment of the polymer and the cone angle. Symbols as for Figure 1.

alignment of nematic liquid crystals,[34] and also for smectic *C*.[15,16,20] A low surface tension has been found to be advantageous for ferroelectric smectic *C* mixtures.[20]

The surface tension of solid polymers can be obtained by extrapolation from the melt or from the contact angle between the solid and different liquids. The two methods show good agreement. Extensive tables of surface tensions of different polymers are available.[24] It is also possible to calculate the values for the surface tensions of polymers via the Parachor and molecular volume.[24] The results are shown in Figure 9. A weak negative correlation between the surface tension and the cone angle is found.

The Friedel-Creagh-Kmetz rule[35] states that

$$\gamma_s < \gamma_{lc} \text{ gives homeotropic alignment}$$

$$\gamma_s > \gamma_{lc} \text{ gives parallel alignment}$$

for nematic liquid crystals, where γ_s and γ_{lc} are the surface tensions of the surface and liquid crystal respectively. A surface tension of the polymer that is too low could thus create problems with homeotropic alignment. However the only two polymers we have found that give homeotropic alignment of smectic *C* are polypropen and poly-1-butene. They also gave homeotropic alignment of the higher temperature nematic phase. These two polymers have intermediate values for the surface tension. Teflon has been reported to give homeotropic alignment for some nematic liquid crystals and planar for others. For the smectic *C* mixtures tested it gave planar alignment. Other groups have also found this simple rule of limited use when working with ferroelectric mixtures.[15]

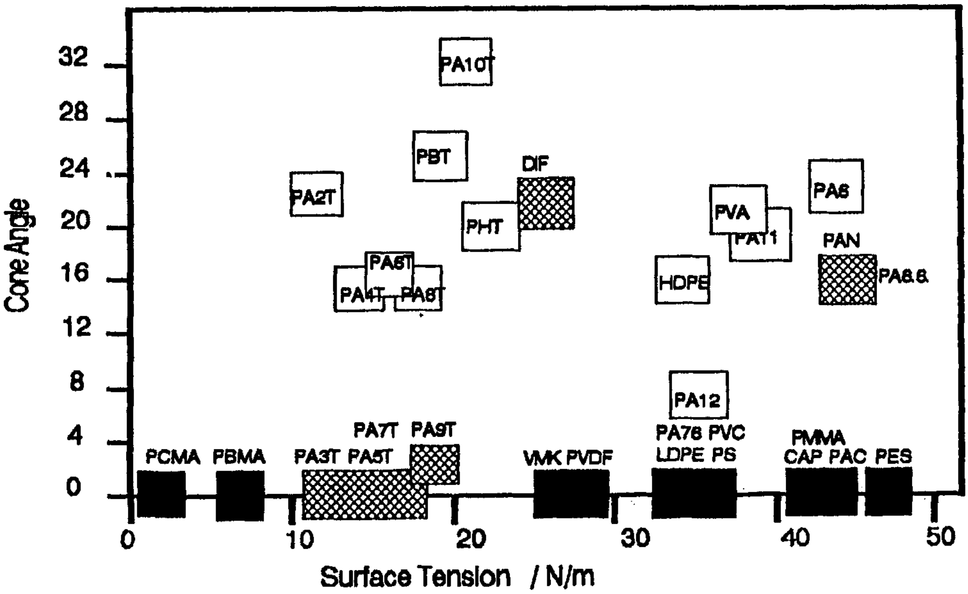

FIGURE 9 Relationship between the surface tension and the cone angle. Symbols are the same as in Figure 1.

The surface tension can be split into a dispersive and a hydrogen bonding part. Both components have been measured for a few polymers.[15,24] The permanent dipoles of the ferroelectric smectic phase will possibly interact with dipoles in the surface, the density of surface dipoles can be found from the polar part of the surface tension. Figures 10 and 11 show the correlation between the cone angle and the dispersive or hydrogen bonding part of the surface tension, respectively. Due to the small number of polymers where both are known no firm conclusions can be made. When two different treatments are used for the two surfaces of an SSFLC cells the polarity difference between the two surfaces ($\Delta\nu^p$) should be as small as possible. $\Delta\nu^p$ should be less than 10 dynes/cm for bistability and close to zero for real black and white memory states.[15] The same has also been found theoretically where zero polarity difference is required for uniform bistable states.[16] As long as the polarity difference between the cell walls is close to zero, which is the case with identically treated cell walls, the surface tension or components of the surface tension do not seem to influence the alignment quality.

An interesting relationship between the cone angle of the relaxed states and the influence of AC-stabilisation fields, can be seen in Reference 36. The higher the cone angle the lower the AC field required to saturate the cone. It seems that a weak surface interaction between the surface and FLC-mixture is essential for high cone angles. On the other hand should a correlation based on only three polymers not be given too much weight.

By changing the rubbing density, Uchida and co-workers changed the surface anchoring.[21] Lower surface anchoring gave higher cone angles after a low frequency, high voltage field was applied to the cell, but did not influence the value found before the field was applied. No relationship between the polymer structure

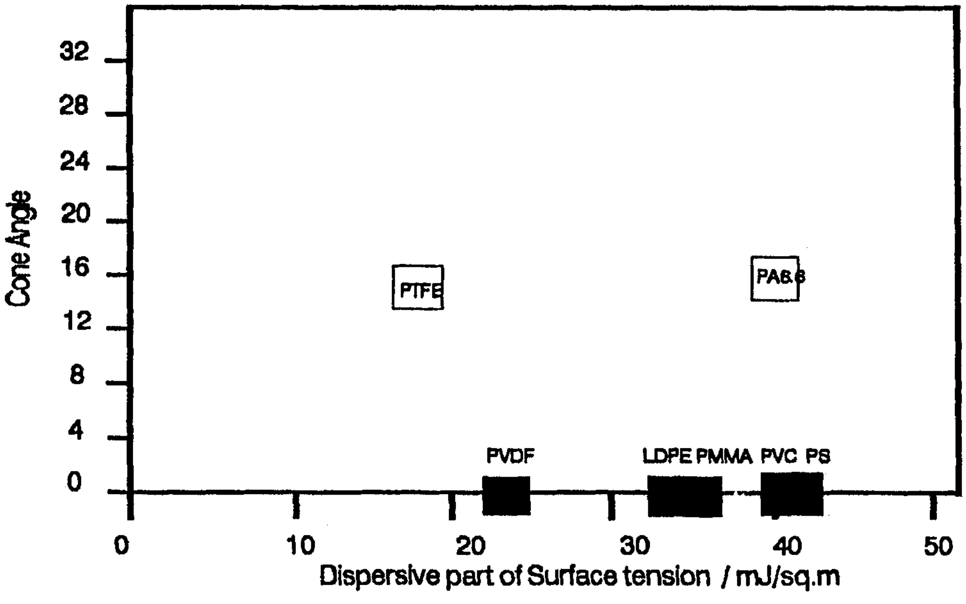

FIGURE 10 Relationship between the dispersive part of the surface tension and the cone angle. Symbols as in Figure 1.

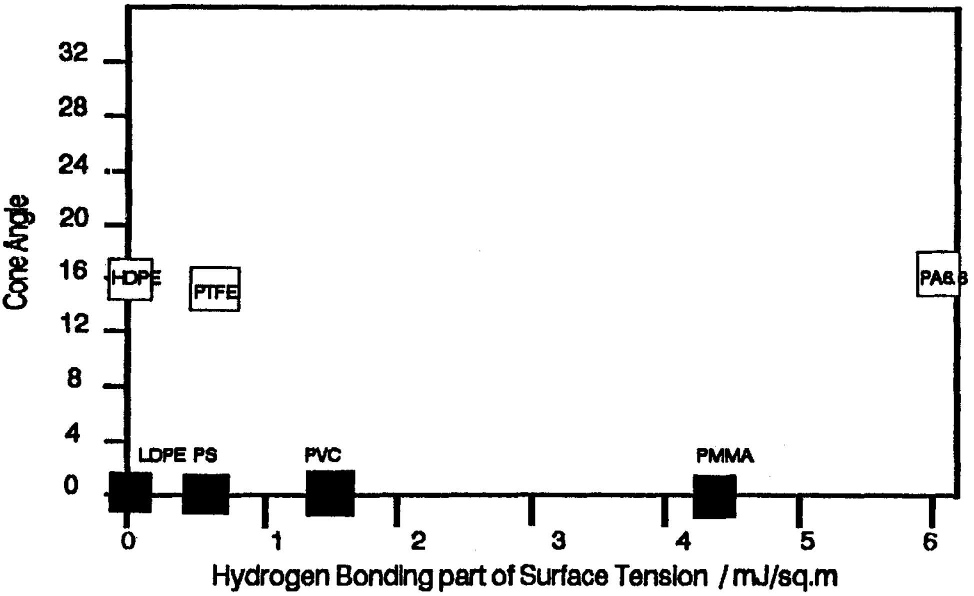

FIGURE 11 Relationship between the hydrogen bonding part of the surface tension and the cone angle. The symbols are the same as in Figure 1.

and the surface anchoring is given. Rubbing density will however be influenced by the friction between the rubbing roll and the polymer surface.

3.4 Crystal Structure

3.4.1 Crystallographic class. Based on the limited number of substances tested as alignment layers for SSFLC up until 1987 we proposed that a monoclinic or triclinic crystal structure was necessary for bistable operation of an SSFLC cell.[13] No explanation was given for this emperical finding. In all Figures in this work a distinction is made between polymers belonging to these two classes and the rest, and the assumption seems to hold. In Table II the polymers with known crystal structures are grouped according to the crystallographic class where they belong. Except for the branched polypropen, which give homeotropic alignment, all polymers of monoclinic or triclinic structure give bistable SSFLC structures while polymers belonging to other crystallographic classes invariable give poorer results, either focal conical textures or monostable cells.

3.4.2 Degree of crystallinity. The crystal structure of the polymer clearly affects the bistability of the SSFLC cells. While the highly crystalline high density polyethylene gives well oriented, bistable cells, the amorphous low density polyethylene gives alignment with many defects and no bistability.[13] The degree of crystallinity of the polyamides[12] or polyimides[23] has also been shown to strongly influence the stability of alignment towards disturbing electrical pulses.

The degree of crystallinity of a sample gives the ratio of crystalline to amorpheous polymer. The degree of crystallinity can be determined from specific volumes, specific heat, specific enthalpy or specific enthalpy of fusion. It can also be determined by x-ray scattering, NMR spectroscopy or IR spectroscopy. The degree of crystallinity found will vary slightly due to the experimental method used to determine it. The physical treatment of the polymer will however have a much greater impact on the crystallinity. Annealing time and temperature, cooling rate, and molecular orientation have a profound impact on the degree of crystallinity. The heating and uniaxial stretching of the polymer during rubbing will most likely cause a high degree of crystallinity.

In a simple model where crystalline areas support bistability and amorphous areas are monostable, it is easy to show that the cone angle measured over larger areas will depend on the degree of crystallinity as this figure will be a weighted average over crystalline and amorphous areas, with the degree of crystallinity as the weighting factor. The difference in cone angles between different polymers could thus be a result of varying degrees of crystallinity. In Figure 12 the maximum degree of crystallinity reported for polymers[24,37–40] together with the cone angle is shown. We believe this will give comparable figures as the polymer treatment is nearly the same in all cases, and expected to give a high degree of crystallinity. There is however evidence that annealing a rubbed polyimide sheet will further increase the degree of crystallinity.[23]

From the Figure there is no obvious correlation between degree of crystallinity and cone angle.

3.4.4 Epitaxial growth. Some work regarding the epitaxial growth of paraffin ($C_{28}H_{58}$) on different polymers has been performed. The length of the paraffin molecule is approximately that of an smectogen and thus a comparison of the results could be of interest. Paraffin showed epitaxial growth on polypropylene

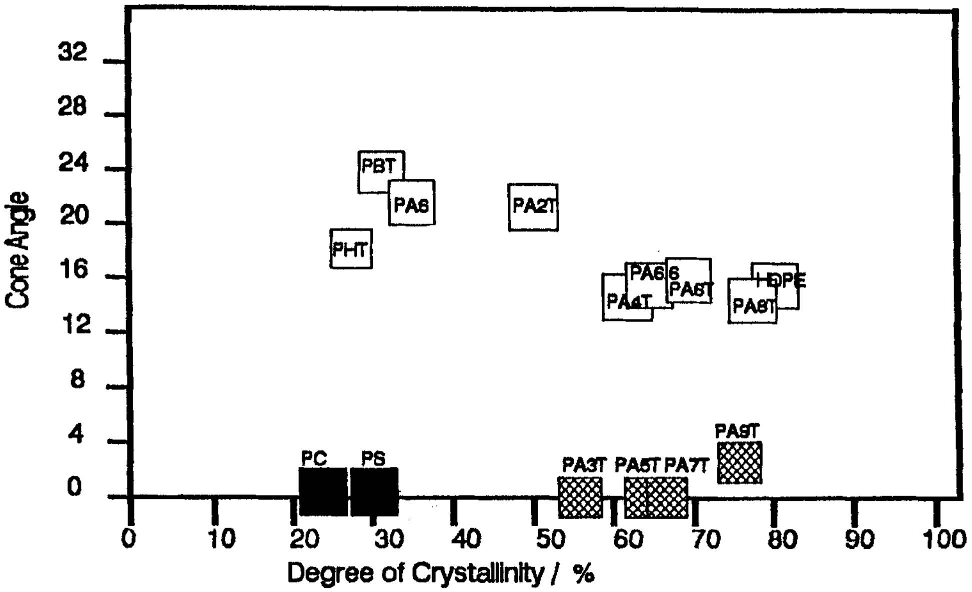

FIGURE 12 Relationship between the degree of crystallinity and the cone angle. Symbols as for Figure 1.

and poly-1-butene, but not on polystyrene.[41] The authors conclude that "lattice matching is not the only controlling parameter for epitaxial growth. But from experiments . . . one may conclude that least two-dimensional order is necessary for epitaxial growth."

After further studies of epitaxial growth of HDPE on polypropylene and poly-1-butene the same authors conclude that "perfect matching of identical planes and directions is not observed. Chain configurations and lattice geometries may, however, play a major role in the epitaxial behaviour."[42] When LDPE was used instead of HDPE no specific orientation relationship with the substrate was found.[42] Even in the simple case of alkanes on polyalkyl surfaces it has not been possible to find the exact mechanism responsible for the epitaxial growth. In the case of SSFLCs the situation is much more difficult as hydrogen bonding, dipole-dipole and dipole-induced dipole forces are likely to play a major role betwen the highly polar liquid crystal molecules and most of the polymers listed in Table I.

3.4.5 Pretilt. By using obliquely evaporated silicon monoxide, cells with a large pretilt of the molecules on the surface have been made.[43] These cells show good bistability, few defects and large cone angles. We take known values of the pretilt obtained with different polymers.[26,44–46] For most polymers a range of pretilt values are given depending on the fluid used. A low dielectric anisotropy of the fluid give a low pretilt,[26] as most ferroelectric fluid mixtures have a negative dielectric anisotropy the lower end of the reported pretilt values will probably be best for our comparison. We see from Figure 13 that polymers with low pretilt also give good results. The relationship between the pretilt of the liquid crystal molecules

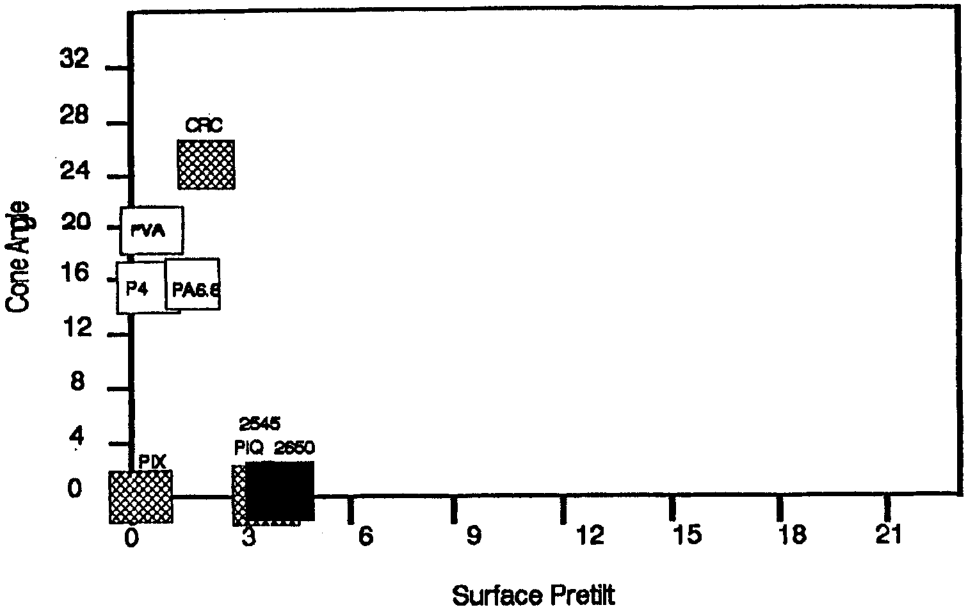

FIGURE 13 Relationship between the surface pretilt and the cone angle. Symbols as in Figure 1.

on the surface and surface structure is probably at least as difficult as the problem this work is addressing.

4. DISCUSSION

It seems that rather few of the bulk properties of the polymer play an important role in the determination of the cone angle between the two relaxed states. The electrical properties are important when it comes to addressing the cells and the ease with which the bistable states can be realised, but does not influence the cone angle once a bistable state appears. It is clear from Table II that only polymers with monoclinic or triclinic crystal structures give the necessary energy barrier between the two stable states of the monoclinic smectic C mixture. Why crystal structures with higher symmetry do not give the same barrier is not known as yet. It should be noted that when a low frequency, high voltage field is applied to the cell a new structure is obtained which might show higher cone angles, but it seems that only the bulk of the material is affected[47] and the surface layers are unchanged.

To realise a high cone angle between the two relaxed states of the virgin texture, three parameters seem to be of importance. The melting enthalpy should be high. This probably results in the polymer being heated close to the melting point, but not above it during rubbing, thus effectively increasing the degree of crystallinity. On the other hand thermal annealing of a polymer does not change the cone angle even though the degree of crystallinity increases. Low surface tension gives the best results. There is no tendency to form homeotropic alignment even with the lowest surface tensions tested. A Mark-Houwink coefficient of more than 0.80 is

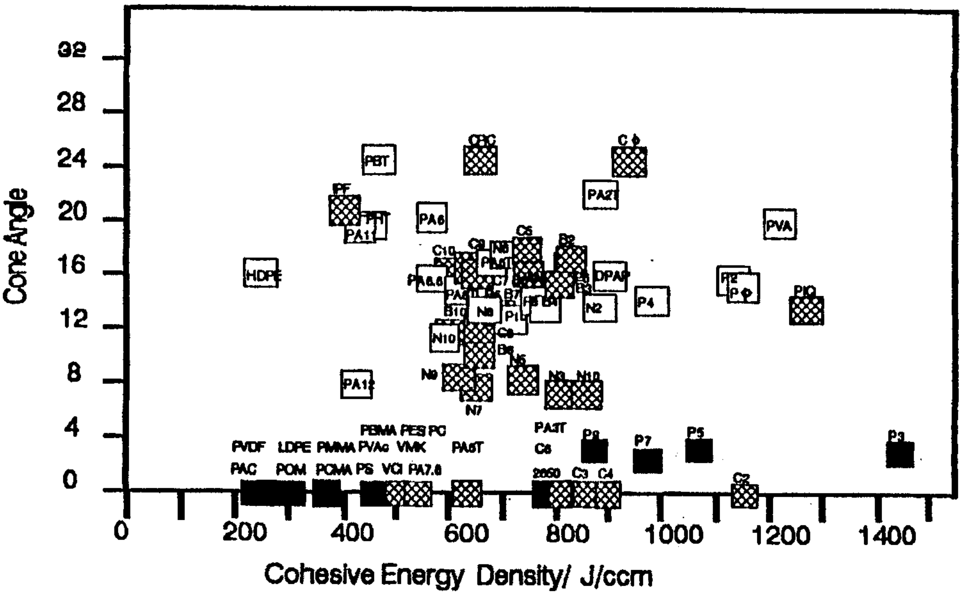

FIGURE 14 Relationship between the cohesive energy density and the cone angle. Symbols are the same as in Figure 1.

an advantage. This indicates that rigid and rodlike polymers give best results. The rigidity of polymers is not easily judged *a priori* as substituents or rigid groups in the molecule might force what seems like a rather flexible backbone into a more or less tightly wound helix and thus greatly increase the rigidity.

The crystal structure, Mark-Houwink coefficient, enthalpy of melting and surface tension all depend strongly on the packing of the polymer chain and the interactions between them. Both the Mark-Houwink coefficient and the surface tension can be related to the cohesive energy of polymers.[24] The cohesive energy of a polymer can easily be calculated from additive group contributions.[24] As the repeating unit of the polymer becomes more complicated the cohesive energy increases. To be better able to compare the polymers we thus prefer the cohesive energy density, $e_{coh} = E_{coh}$/mol-volume. In Figure 14 the cone angle obtained is plotted as a function of the relative cohesive energy. At first glance there seems to be a slight maximum in the range 500–1000 J/cm^3, but as half the polymers tested are found in this range it is not surprising that the few really good ones should also be found here. We thus do not believe this very broad maxima is significant.

5. CONCLUSION

Several parameters have been suggested in the literature as important in realising good, bistable SSFLCs. We have found the crystal structure of the polymer to be of major importance. Monoclinic or triclinic seem to be a prerequisite for bistable operation of SSFLCs. On the other hand we have not been able to find any correlation between the magnitude of the cone angle and the physical properties of the polymers for polymers belonging to these two classes.

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