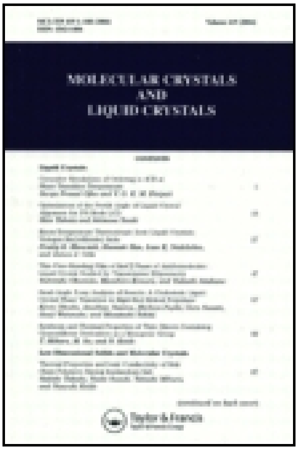

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Relationships Between the Bulk Properties of Nematic Liquid Crystals and their Pretilt Angles

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Version of record first published: 04 Oct 2006.

To cite this article: Bernt O. Myrvold , Katsumi Kondo & Shuichi Oh-hara (1994): The Relationships Between the Bulk Properties of Nematic Liquid Crystals and their Pretilt Angles, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 239:1, 211-228

To link to this article: http://dx.doi.org/10.1080/10587259408047184

Mol. Cryst. Liq. Cryst., 1994, Vol. 239, pp. 211–228
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Printed in the United States of America

The Relationships Between the Bulk Properties of Nematic Liquid Crystals and their Pretilt Angles

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(Received April 9, 1993; in final form May 28, 1993)

Liquid crystal cells with five different polyimide alignment layers have been made for the study of liquid crystals alignment mechanisms. Two of the alignment layers are crystalline and three are amorphous. These cells have been filled with twenty different nematic liquid crystalline materials, and the relationship between the bulk properties and the pretilt angles has been studied. We find that the polarity of the liquid crystal is the best predictor for the pretilt angle. This effect can be explained by assuming that dimeric pairs of liquid crystal molecules are formed in the bulk, but that they are broken up on the crystalline surfaces.

Keywords: pretilt angles, nematic liquid crystals, polyimides, birefringence, dielectric anisotropy, elastic constants, clearing point

1. INTRODUCTION

The surface pretilt found when nematic liquid crystals are aligned on polymer surfaces is a function of both the polymer used and the liquid crystal. We have previously studied the effect of the polymer structure and treatment.[1] The purpose of this work is to investigate the effect of the liquid crystal, in particular the effect the bulk properties of the liquid crystal has on the pretilt angle.

There are two main questions we would like to answer.

1. Is there any simple relationship between the bulk properties of the liquid crystal and the pretilt angle?
2. Will the difference in pretilt between two different fluids on surface A be the same as their difference on surface B? It is of interest to know if one fluid can be used to investigate the effect changes in polymer structure or processing has on the pretilt, or if the surface/liquid crystal interactions are so specific that it is impossible to draw general conclusions.

To answer these questions we have used five different alignment layers giving pretilt angles in the range of 0.5–5.0° and filled the cells with 20 different nematic fluids. The fluids have been chosen to span a wide range of the bulk properties under investigation.

The pretilt angle depends on the interaction between the surface and the liquid crystalline material. The interaction can be divided into geometric, steric, polar and dispersive parts. Unfortunately only the dispersive part is easily calculated.[2] The anisotropic parts of the steric, polar and dispersive forces are only a few percent of the total forces. As the pretilt angle depends on this anisotropy of these forces, it is extremely difficult to calculate the pretilt angle. Even a small error in one of the components will give a large error in the anisotropy and thus in the pretilt angle. To make the situation even worse when the refractive index of the substrate is close to 1.5 theoretical calculations have shown the influence of the dispersive forces are small.[2] We thus have the situation that the only part of the surface interaction that can be calculated with some certainty might be relatively unimportant, as most polymers have refractive indexes in the vicinity of 1.5. Other workers[3] have, however, concluded that dispersive forces are responsible for 75% of the total surface energy.

As we cannot expect to be able to calculate the pretilt angle from first principles, in the foreseeable future, it is of interest to find simpler means of predicting the pretilt angle. There are already some rules of thumb given in the literature.[4-8] The aim of this work is to test the different claims put forward, with a larger number of liquid crystalline materials; and to see whether we can find any relationship between the bulk properties and the magnitude of the surface pretilt. The results for previous investigations are summarized in Table I and II. Table I gives actual data for the pretilt angles, while Table II summarizes the conclusions drawn.

The first study by Becker *et al.*[4] found an increasing pretilt angle with increasing dielectric anisotropy of the liquid crystalline material used, while a later study[5] showed a decreasing pretilt with increasing dielectric anisotropy. When mixing the two liquid crystals ZLI-1132 and ZLI-3086 there was a non linear increase in the pretilt with increasing dielectric anisotropy.[6] The group at GEC states clearly that they found no systematic variation in the pretilt angle with changes in the birefringence of the liquid crystals,[9] although they note that the material with the lowest birefringence also shows the highest pretilt. The group at Asahi Glass[7] on the other hand, finds a nearly linear relationship between the birefringence and the pretilt angle. From the theory put forward by this group[11] the pretilt angle is strongly dependent on the specific conformation of the alignment layer. From this theory we do not expect any relationship between the bulk properties of the liquid crystal material and the pretilt angle.

2. EXPERIMENTAL

2.1. Cell Preparation

For this work we have chosen five different polyimide alignment layers based on pyromellitic dianhydride (PMDA) and biphenyl-3,3′,4,4′-tetracarboxylic dianhydride (s-BPDA) combined with the 1,5-diamino pentane (-5), 1,6-diamino hexane (-6) or 1,7-diamino heptane (-7). The names of the polyimides in this study are

TABLE I

A summary of previous investigations of how the pretilt varies with the liquid crystalline material

Nematic fluid	Aligning Polymer	Pretilt	Ref.
ZLI-1085	AI-1130-L	0.65	4
ZLI-1957/5	AI-1130-L	1.10	4
ZLI-1132	AI-1130-L	1.40	4
ROTN-605	AI-1130-L	1.45	4
ROTN-403	AI-1130-L	1.60	4
E7	Nolimid 32	3.6	9
E63	Nolimid 32	3.8	9
ZLI-1844	Nolimid 32	3.7	9
ZLI-1132	Nolimid 32	4.2	9
ZLI-2787	Nolimid 32	3.4	9
ZLI-1695	Nolimid 32	4.3	9
HLR 3040	Nolimid 32	3.3	9
I eutectic (BDH)	Nolimid 32	3.2	9
ZLI-4246-000	SE-4110	6.4	5
ZLI-2293	SE-4110	6.3	5
89-557	SE-4110	6.2	5
ZLI-4245-000	SE-4110	5.7	5
ZLI-4389	SE-4110	5.5	5
ZLI-1132	A	3.5	10
ZLI-1565	A	2.6	10
ZLI-2293	A	2.5	10
ZLI-3086	A	1.5	10
ZLI-4338	A	3.4	10
ZLI-4540	A	3.3	10
ZLI-4792	A	2.1	10
MLC-2001	A	2.4	10
ZLI-1132	SE-150	4.2	6
ZLI-1132/ZLI-3086 (9:1)	SE-150	4.1	6
ZLI-1132/ZLI-3086 (4:1)	SE-150	4.3	6
ZLI-1132/ZLI-3086 (1:1)	SE-150	4.2	6
ZLI-1132/ZLI-3086 (1:4)	SE-150	4.0	6
ZLI-1132/ZLI-3086 (1:9)	SE-150	3.7	6
ZLI-3086	SE-150	3.4	6
ZLI-3086/PCH-3 (1:1)	SE-150	4.4	6
ZLI-3086/PCH-4 (1:1)	SE-150	4.2	6
ZLI-3086/PCH-5 (1:1)	SE-150	4.4	6
ZLI-3086/PCH-7 (1:1)	SE-150	4.2	6
ZLI-3086/Cyanobiphenyl (3:1)	SE-150	4.6	6
ZLI-3086/PDX (3:1)	SE-150	4.6	6
ZLI-3086/Pyrimidines(3:1)	SE-150	4.3	6
ZLI-3086/PCH(3:1)	SE-150	4.1	6
ZLI-3086/PECH(3:1)	SE-150	4.0	6
ZLI-3086/Fluorinated CH esters (3:1)		3.9	6
ZLI-3086/Fluorinated pyrimidines (3:1)		3.9	6
ZLI-3086/Dialkylpyrimidines (3:1)		3.9	6
ZLI-3086/Terminally fluorinated pyrimidine (3:1)		3.6	6
ZLI-3086/Alkoxy-alkyl-phenyl-cyclohexane (3:1)		3.5	6
ZLI-3086/Dialkyl-tolan (3:1)	SE-150	3.3	6
ZLI-1132	B	7.7	8
ZLI-1565	B	5.7	8
ZLI-2293	B	6.2	8
ZLI-4338	B	8.8	8
ZLI-4540	B	5.7	8
ZLI-4792	B	3.3	8
MLC-2001	B	4.5	8

A and B are the authors designation of the polyimides, complete structures are not given.

TABLE II

Relationships between bulk properties of the liquid crystals and the pretilt angle in the nematic phase

Bulk property	Pretilt angle change on increase of bulk property	Number of fluids	Number of polymers	Ref.
Diel. anisotropy	Increase	5	1	4
Diel. anisotropy	Decrease	5	1	5
Diel. anisotropy	Increase	7	1	6
Birefringence	None	8	1	9
Birefringence	Increase	5	1	7
Diel.constant perpendicullar	Increase	7	1	8

given by the abbreviation for the dianhydride followed by the number indicating the alkylene chain length. The five polyamic acids were all synthesized by adding a slurry of the dianhydride in *N*-methyl pyrrolidone (NMP) to a solution of the diamine in NMP at room temperature.

The resulting polyamic acids were spin coated on to clean ITO-covered glass plates. The polyamic acids based on s-BPDA were cured at 250°C for one-half hour while those based on PMDA were cured at 300°C for 2 hours. The resulting polyimide films were rubbed, and a pair of glass plates mounted together with anti-parallel rubbing directions, using 120 micron thick mylar spacers. The resulting as-cast films are crystalline for those polyimides with an even number of methylene groups, and amorphous for those with an odd number of methylene groups. The determination of the crystallinity for the s-BPDA-derivatives by SEM and X-ray scattering has been described earlier.[11]

The resulting cells were vacuum filled with the liquid crystalline material. The liquid crystalline fluids used are listed in Table III, together with their relevant physical parameters. ZLI and MJ refer to liquid crystalline mixtures from E. Merck, RO-TN to mixtures from L. Hoffmann LaRoche and E to mixtures from BDH Ltd. (now part of E. Merck). All physical data for these fluids are taken from the manufacturers data sheets. The eight last fluids in the table were only filled in cells with the two alignment layers that gave the highest pretilt among the crystalline (s-BPDA-6) and amorphous (PMDA-7) polyimides.

2.2. Measurements

Pretilt angles have been determined by the crystal rotation method in an automated optical bench. Our experimental set-up has been described in detail earlier.[1] The measurements were all performed at room temperature (22 ± 1°C). For the relationship between the symmetry point of the transmission versus rotation curves and the pretilt angles we used the simplified equations[12]:

$$\sin 2\beta = \frac{-2 \sin\Phi_{\mathrm{sym}}}{(n_o + n_e)\sqrt{1 - (\sin\Phi_{\mathrm{sym}}/n_o}} \tag{1}$$

TABLE III

Liquid crystalline mixtures used and their relevant bulk properties

Mixture	Clearing point ℃	Dielectric anisotropy	Birefringence	Elastic ratios		Composition *
				$\frac{k_{33}}{k_{11}}$	$\frac{k_{33}}{k_{22}}$	
ZLI-684	60	11	0.21			CB
ZLI-1557	61	4.2	0.1147	1.21	2.3	PCH/BCH
ZLI-1602	59	-0.59	0.10			
ZLI-1646	61	6.5	0.0800			PCH/BCH/ esters
ZLI-1701	61	4.4	0.1062			PCH/BCH
ZLI-1800-000	60	6.4	0.0773	1.63	2.7	PCH/CCH
ZLI-1800-100	61	2.9	0.0705			PCH/CCH
ZLI-3700-000	105	11.5	0.1010	1.26	2.5	
ZLI-3497-000	106	23.0	0.1366	1.41	2.7	
RO-TN-103	81	25.6	0.223			esters
RO-TN-200	65	18.3	0.276			SCH
RO-TN-619	60	5.8	0.123	0.98	2.1	

ZLI-1081	65	0	0.16			esters
ZLI-1237	58	11.2	0.14			PCH
ZLI-1275	80	-0.8	0.10			PCH
ZLI-3102	86	8.4	0.123	1.27	2.8	
ZLI-3276-000	89	11.0	0.104	1.42	2.8	
ZLI-3276-100	89	4.6	0.099	1.27	2.8	
ZLI-3783	91	3.4	0.100			
MJ62738	87	9.2	0.1383			

* BCH = cyanobiphenyl cyclohexane, CB = cyanobiphenyl,
CCH = alkylcyclohexyl-cyanocyclohexane, PCH = cyanophenyl-alkylcyclohexane
SCH = Schiffs bases

where β is the pretilt angle measured for thick samples, Φ_{sym} is the symmetry angle found for the transmission *versus* angle of incidence curves, while n_o and n_e are the ordinary and extraordinary refractive indexes of the liquid crystal.

In this study all the pretilt angles encountered are less than 5°. The pretilt angles are thus, overestimated by a maximum of 0.15°—this is less than one standard deviation in our experimental values. No corrections have thus been made.

3. RESULTS

3.1. Pretilt Angles as a Function of Clearing Point

Table IV summarizes the pretilt angles found with different combinations of nematic fluids and alignment layers.

Figure 1 shows the pretilt angles found as a function of the clearing point (nematic to isotropic transition) of the materials under investigation. The alignment layers in Figure 1 are s-BPDA-6 and PMDA-7. The other three alignment layers show

TABLE IV

The pretilt angle found on the different alignment layers, with standard deviations in parentheses

Mixture	Crystalline polyimide		Amorphous polyimide		
	s-BPDA-6 deg.	PMDA-6 deg.	PMDA-7 deg.	PMDA-5 deg.	s-BPDA-5 deg.
ZLI-684	4.52 (.88)	1.64 (.10)	2.39 (.24)	0.75 (.12)	0.10 (.17)
ZLI-1557	3.42 (.20)	1.20 (.10)	2.43 (.13)	0.80 (.28)	0.36 (.20)
ZLI-1602	2.68 (.41)	1.23 (.12)	1.52 (.24)	0.38 (.23)	0.58 (.40)
ZLI-1646	2.94 (.10)	0.94 (.10)	2.36 (.10)	1.23 (.20)	0.44 (.11)
ZLI-1701	3.55 (.20)	1.61 (.30)	2.26 (.16)	1.03 (.11)	0.28 (.20)
ZLI-1800-000	3.51 (.55)	0.86 (.10)	2.36 (.11)	1.01 (.34)	0.60 (.14)
ZLI-1800-100	3.14 (.37)	1.11 (.31)	2.47 (.13)	1.82 (.20)	0.56 (.18)
ZLI-3700-000	4.26 (.36)	1.54 (.20)	3.12 (.30)	1.56 (.51)	0.77 (.16)
ZLI-3497-000	3.78 (.31)	1.12 (.18)	2.90 (.65)	0.67 (.27)	0.51 (.11)
RO-TN-103	3.98 (.10)	2.33 (.44)	2.43 (.38)	0.73 (.18)	0.76 (.10)
RO-TN-200	4.19 (.68)	0.92 (.26)	1.75 (.26)	0.59 (.29)	0.45 (.29)
RO-TN-619	3.80 (.34)	1.10 (.25)	2.97 (.10)	1.40 (.45)	0.78 (.10)
ZLI-1081	2.91 (.12)		1.50 (.28)		
ZLI-1237	3.81 (.12)		2.64 (.58)		
ZLI-1275	2.73 (.16)		1.51 (.39)		
ZLI-3102	2.62 (.29)		2.19 (.34)		
ZLI-3276-000	3.13 (.28)		2.45 (.18)		
ZLI-3276-100	3.39 (.19)		2.29 (.10)		
ZLI-3783	3.24 (.27)		2.38 (.13)		
MJ62738	3.17 (.17)		2.92 (.51)		

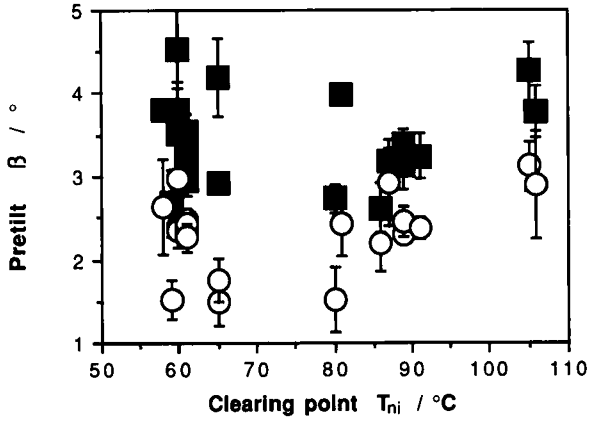

FIGURE 1 The pretilt angle as a function of the clearing point of the liquid crystalline mixtures used. Filled squares for the crystalline s-BPDA-6 and open circles for the amorphous PMDA-7.

similar behaviour and for brevity they are not shown. As can be seen the pretilt angle is independent of the clearing point. The order parameter of the liquid crystal can be found to a good approximation[13] by $S = (1 - T/T_{ni})^{0.18}$. As there is no correlation between the transition temperature and the pretilt angle, we can also conclude that there is no correlation between the order parameter and the pretilt angle.

3.2. Pretilt Angles as a Function of the Elastic Ratios

To obtain the steep electro-optical response required for supertwisted nematic displays it is necessary to adjust the elastic ratios to within narrow limits. To obtain the gradual response needed for grey scale in TFT-driven or other twisted nematic displays it is also necessary to adjust the elastic ratios. It is thus of interest whether these adjustments have any adverse effects on the pretilt angle, which also must be controlled tightly in supertwist displays. Figures 2 and 3 clearly show that there is no influence on the pretilt angle by changing the elastic ratios. For clarity only the high tilt, crystalline s-BPDA-6 and the low tilt, amorphous PMDA-5 are shown. The other three polyimides also give pretilt angles independent of the elastic ratios and the values fall between the two sets shown here.

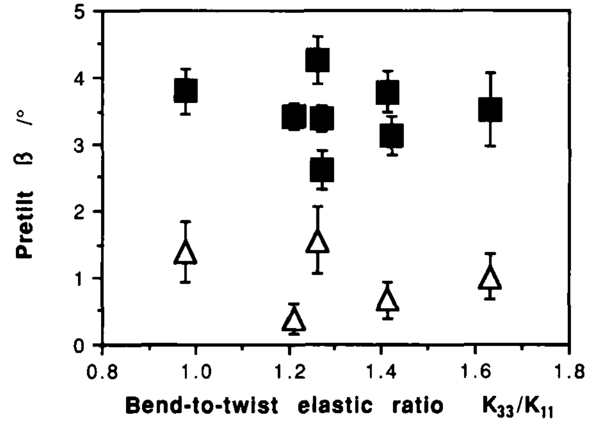

FIGURE 2 The pretilt angle as a function of the bend-to-twist elastic ratio for five different alignment layers. Filled squares for the crystalline s-BPDA-6, and open triangles for the amorphous PMDA-5.

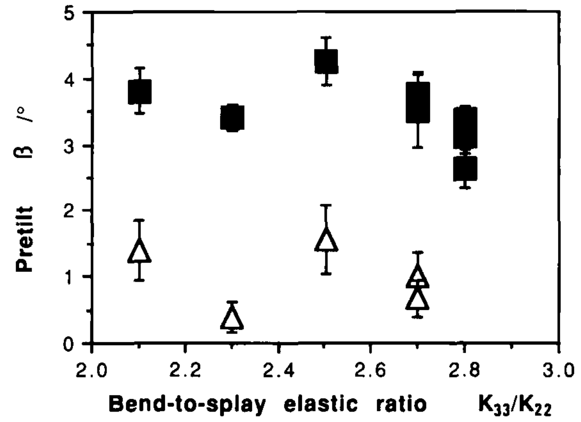

FIGURE 3 The pretilt angle as a function of the bend-to-splay elastic ratio for five different alignment layers. Legend as for Figure 2.

3.3. Pretilt Angles as a Function of the Birefringence

In Figure 4 we have plotted the pretilt angles as a function of the birefringence of the nematic materials with positive dielectric anisotropy. For s-BPDA-6 and PMDA-6 there is clearly an increase in the pretilt angle with increasing birefringence. For PMDA-7 and PMDA-5 there is equally clearly a decrease, while s-BPDA-5 gives so low a pretilt that it is more difficult to see a clear trend.

There are exceptions to these trends. Materials with a negative dielectric anisotropy give lower pretilts than expected from just a comparison of the bulk properties. This will be elaborated further upon in the next section.

3.4. Pretilt Angles as a Function of the Dielectric Anisotropy

It has been found that the pretilt angle increases with increasing dielectric anisotropy when the polyamide-imide AI-1130-L was used as alignment layer,[4] while a decrease with increasing dielectric anisotropy was found on the polyimide SE-4110.[5] When

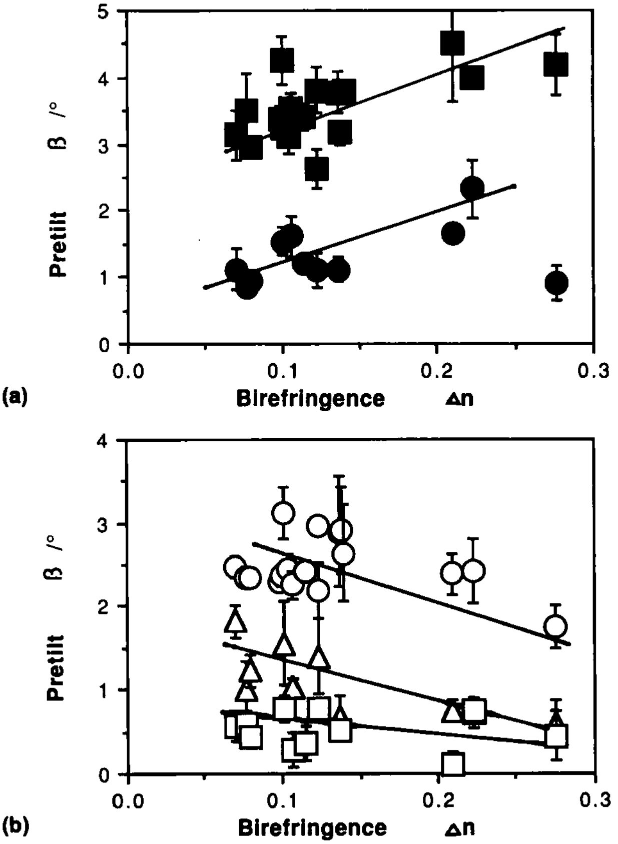

FIGURE 4 The pretilt angle as a function of the birefringence of fluids with positive dielectric anisotropy. (a) With crystalline alignment layers, squares s-BPDA-6, circles PMDA-6. (b) With amorphous alignment layers, circles PMDA-7, squares s-BPDA-5, triangles PMDA-5. The lines are guides to the eye only.

the two commercial mixtures ZLI-1132 and ZLI-3086 were mixed, a non linear increase in the pretilt angle with increasing dielectric anisotropy was found.[6]

Our results are shown in Figures 5. For the two crystalline polyimides s-BPDA-6 and PMDA-6 there is clearly an increase in the pretilt angle with increasing dielectric anisotropy.

On the amorphous polyimide PMDA-7 there is no clear trend, and the pretilt seems to be independent of the dielectric anisotropy. For the closely related PMDA-5 and s-BPDA-5 there is a small decrease in the pretilt with increasing dielectric anisotropy of the nematic materials. We also note that the fluids with negative dielectric anisotropy fall 0.5–1° below what we would expect from the correlation found from the fluids with positive dielectric anisotropy on PMDA-7 and PMDA-5.

For the crystalline surfaces we find an increase in pretilt angles with increasing dielectric anisotropy. For the amorphous surfaces we find that the pretilt angle is independent of the dielectric anisotropy. However, as we will show, also for the amorphous polyimides there is a very weak increase in the pretilt with increasing dielectric anisotropy, if the birefringence is held constant.

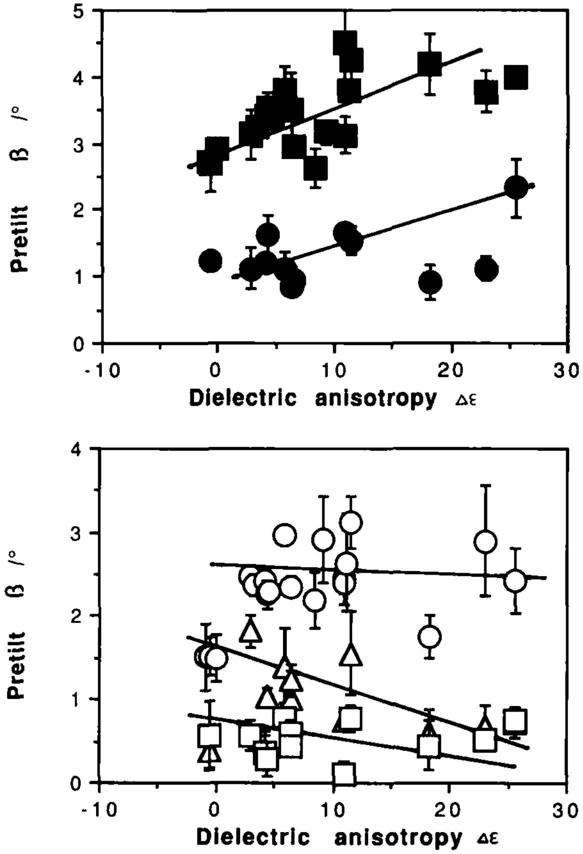

FIGURE 5 The pretilt angle as a function of the dielectric anisotropy. (a) With crystalline alignment layers. (b) With amorphous alignment layers. Legend as for Figure 4.

Figure 6 shows that birefringence and dielectric anisotropy are closely related properties for the fluids we have investigated. Both dielectric constants and refractive indexes are bulk properties of the materials and related to the more fundamental polarizability of the molecules and the order parameter. The dielectric anisotropy is normally measured at 1 kHz, while the birefringence is given at visible frequencies. As the pretilt angles on crystalline surfaces show the same dependence on both, it is not clear which is the most important factor. In Figures 7 and 8 we attempted to separate the effects of the two different properties.

When the birefringence is held constant as in Figure 7, the pretilt for the fluids with positive dielectric anisotropy shows an increase of the observed pretilt with increasing dielectric anisotropy. In other words, the data shown in Figure 7 reverse the trends found for PMDA-7 in Figure 5B.

For the liquid crystals with negative dielectric anisotropy there is a 0.5 to 1 degree lowering of the pretilt angle, compared to what is expected from the trend. Due

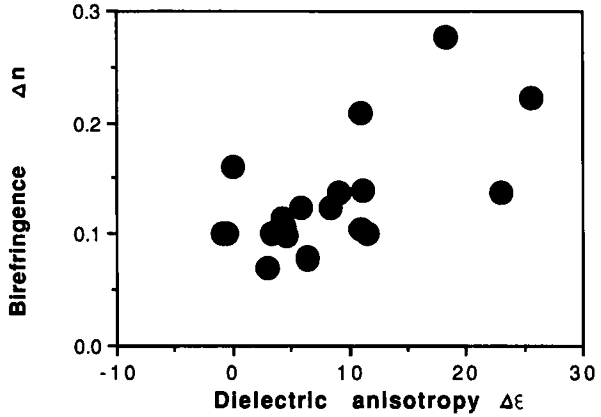

FIGURE 6 The correlation between the dielectric anisotropy and the birefringence for the liquid crystalline materials used in this study.

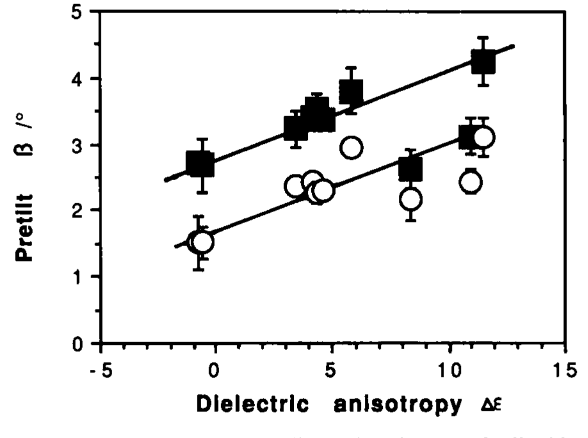

FIGURE 7 The pretilt angle as a function of the dielectric anisotropy for liquid crystals with constant birefringence (0.11 ± 0.013). Legend as for Figure 4.

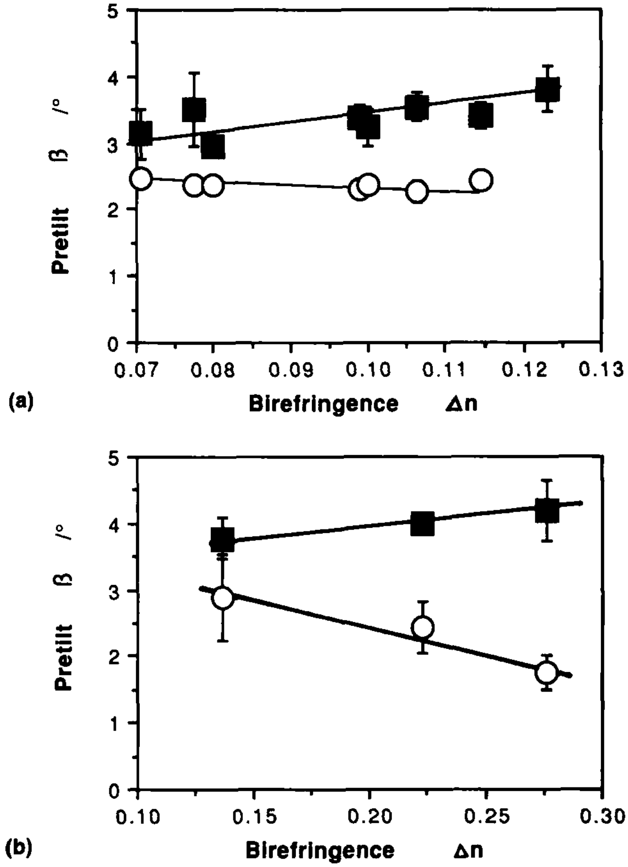

FIGURE 8 The pretilt angle as a function of the birefringence for liquid crystals with constant dielectric anisotropy. (a) A dielectric anisotropy of 4.5 ± 2. (b) A dielectric anisotropy of 21 ± 5. Legend as for figure 4.

to the large differences in structures between nematic liquid crystals with positive and negative dielectric anisotropy, it is often convenient to divide liquid crystals into two groups based on the sign of the dielectric anisotropy.[14] In mixtures there is, however, a possibility of continuous changes in the bulk properties. For our discussion it seems to be useful to keep this distinction between materials of positive and negative dielectric anisotropy, as the materials clearly divide themselves into two groups also as far as the pretilt angle is concerned.

Figure 8 shows the situation when the dielectric anisotropy is held constant and the birefringence is varied. The situations for a dielectric anisotropy of 4.5 ± 2 and 21 ± 5 are shown. In this case there is a divergence, with the crystalline alignment layer s-BPDA-6 giving an increased pretilt with increased birefringence, while the amorphous alignment layer PMDA-7 gives a slightly decreasing pretilt with increasing birefringence. The results are summarized in Table V.

The results shown in Figures 4 to 8, and summarized in Table V show that on the amorphous polyimides we have two different trends. When the dielectric anisotropy is held constant, there is a decrease of the pretilt with increasing bire-

TABLE V

A summary of the correlations between the pretilt and birefringence and dielectric anisotropy found in this work

Polyimide		Changes in pretilt on increasing			
		Biref.	Biref. at constant diel. anisotropy	Diel. anisotropy	**Diel. anisotropy at constant biref.**
Crystalline	**s-BPDA-6**	+	+	+	(+)
	PMDA-6	+	n.a	+	(+)
Amorp.	**PMDA-7**	-	-	(-)	(+)
	PMDA-5	-	n.a.	-	(+)
	s-BPDA-5	(-)	n.a.	0	(+)

+ positive correlation , (+) weak positive correlation, 0 no correlation
- negative correlation, (-) weak negative correlation, n.a. not available.

fringence. If the birefringence is held constant, there is a weak increase in the pretilt with increasing dielectric anisotropy. On the other hand, changing either of them without taking precautions to hold the other constant, we find a decrease in pretilt in both cases. As Figure 6 shows, the birefringence and dielectric anisotropy are well correlated.

For the crystalline alignment layers both increased dielectric anisotropy and increased birefringence will give an increase in the pretilt angle. As birefringence and dielectric anisotropy are related properties, we thus get a clear trend on the crystalline alignment layers. We observe a positive correlation with either property. However, this excludes the possibility of determining which of the two is the more important for determining the pretilt angle.

For the amorphous alignment layers the situation is more complex. The pretilt angles show a negative correlation with the birefringence, while there is a weak positive correlation with the dielectric anisotropy. An increase in one of the two properties will usually also give an increase in the other. The net effect on the pretilt is thus not easy to predict, but Figure 5 suggests that it will be small.

It has recently been proposed[8] that the dielectric constant perpendicular to the director is an important parameter in determining the pretilt. For liquid crystals with the same dielectric anisotropy, we do not find any correlation between the dielectric constant perpendicular to the director and the pretilt angle.

3.5. Effects of the Composition

All of the fluids investigated here are commercial mixtures where precise structural data are not available. There are, however, a few comments that can be made. Typical components to achieve negative dielectric anisotropy are shown in Figure 9. In addition to the strong transverse dipoles these compounds also have alkyl chains in both ends of the molecule. The data of Reference 6 (also given in Table I) show that addition of dialkyl compounds typically reduces the pretilt by about 0.5°, e.g. the addition of 25% of alkylcyclohexane-cyanophenyl to ZLI-3086 gives a pretilt of 4.1° while the addition of 25% of alkoxyalkyl phenyl cyclohexane gives

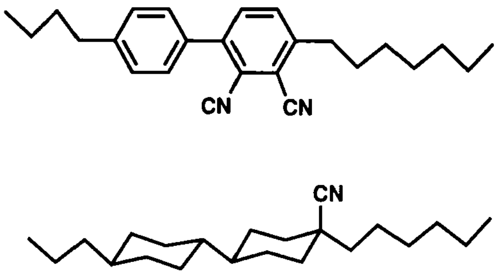

FIGURE 9 Two typical structures for materials with negative dielectric anisotropy.

a pretilt of 3.5, the addition of 25% of pyrimidines gives a pretilt of 4.3°, compared to 3.9° for dialkylpyrimidines.

4. DISCUSSION

4.1. What are We Measuring?

By using an optical method we are measuring the angle between the major optical axis of the uniaxial medium and the projection of this axis on the surface. By our cell construction the bulk value we are measuring will be the same as the value at the surface, if the two surfaces give the same value.

Unfortunately, it is not entirely clear how this optical "long" axis relates to other "long" axes of the molecules. Other long axes have been determined by minimizing the moment of inertia; by minimizing the rotation ellipsoid needed to circumscribe the molecule; or by different spectroscopic techniques looking at particular transitions. Although they are all related to each other, it is not obvious how to transform between the different sets of major axes.

To complicate matter further we are working with mixtures of several different compounds, which all are free to attain several different conformations, all with their own unique axes. It is thus not obvious how the "average" bulk value we measure is related to the situation at the surface.

These considerations are of importance when trying to understand the mechanisms underlying the surface alignment. For practical display use they are luckily less relevant as it is the average optical tensor that matters for the electro-optical switching of the display.

4.2. The Crystalline Surfaces

Nearest neighbour correlations between molecules are always important in condensed matter. For crystalline materials the position shows long range correlation as well. For polymers crystallinity is not as clear cut concept as for low molecular mass solids. There will normally be islands with regular packing over longer distance within a matrix where only short range correlation exists. It is thus more useful to consider degrees of crystallinity for polymers. The degree of crystallinity normally varies between 20 and 80%, although the exact value depends on the method used to determine the crystallinity.

Scanning tunneling microscopy (STM) of liquid crystals on highly crystalline surfaces like graphite or molybdenium disulphide[15] shows that the nematogens are arranged in an orderly fashion on the surface. Recent STM observations of 8CB on a Langmuir-Blodgett monolayer of polyimide have been interpreted to show the same.[16] Most liquid crystals are highly polar substances, and for STM studies almost exclusively the cyanobiphenyl derivatives have been used. In the bulk the cyanobiphenyls normally exist as more or less tightly bound dimeric pairs, with a head to tail organization.[14] On the crystalline surfaces, on the other hand, these pairs always seem to be broken. Even though different organization on the surface can be seen depending on whether smectic or nematic materials have been investigated, the tightly bound dimers have not been observed, yet.[17]

Second harmonic generation is one of the few techniques which directly probe the orientation of the liquid crystal molecules at the surface. It has been concluded that the cyano groups point into the surface for 4,4′-*n*-octyl-cyanobiphenyl on a polyimide surface.[18] The pretilt angle for the optical tensor was found to be 19°, much higher than the pretilt angle from bulk measurements. The same nematogen has been studied later,[19] also in this case with the same pretilt angle. In both cases unspecified commercial polyimides were used. As both investigations gave the same value, the results seem to be fairly universal and we will adopt this value in the following discussion.

We thus suggest that on crystalline, regular surfaces the polar end groups will be attached to the surface. The forces between the liquid crystals and the surface are strong enough to break the symmetry of the nematic phase in the vicinity of the surface. For those liquid crystals that exist as dimeric pairs in the bulk, the dimeric pairs will also be broken up at the surface. We will thus have a situation as shown schematically in Figure 10. The nematogens can be regarded as composed of two parts. One is the alkyl chain which shows small birefringence, and the other is the core which shows much larger birefringence. The optical tensor will be a sum of optical tensors for the core and the alkyl chain. As the birefringence of the liquid crystal changes, it is mostly due to changes in the core. This means that the orientation of the optical axis within the molecule changes. Thus even with all polar groups making the same angle with the surface, the observed pretilt angle will increase with increased birefringence. It should also be noted from Figure 10 that the pretilt of the optical axis is much larger than the pretilt of the "geometric" long axis of these molecules. Optical second harmonic generation has shown that the optical axis of 8CB is 19° relative to the surface,[18,19] even though the pretilt for the sample was rather low.

The splay of the optical axis is not on its own strong enough to explain all the difference in the pretilt between the different liquid crystalline materials. There must also be some differences in the interactions between the surfaces and the liquid crystals between different materials.

The surface used by Becker *et al.*[4] was the polyamide-imide AI-1130-L which has a regular structure. It is thus possible that the surface used in their investigation also was crystalline, and that the explanation given above is valid also for their samples. On the other hand this investigation used only five fluids, with a rather small change in the pretilt angles found. Their lowest pretilt was found for the

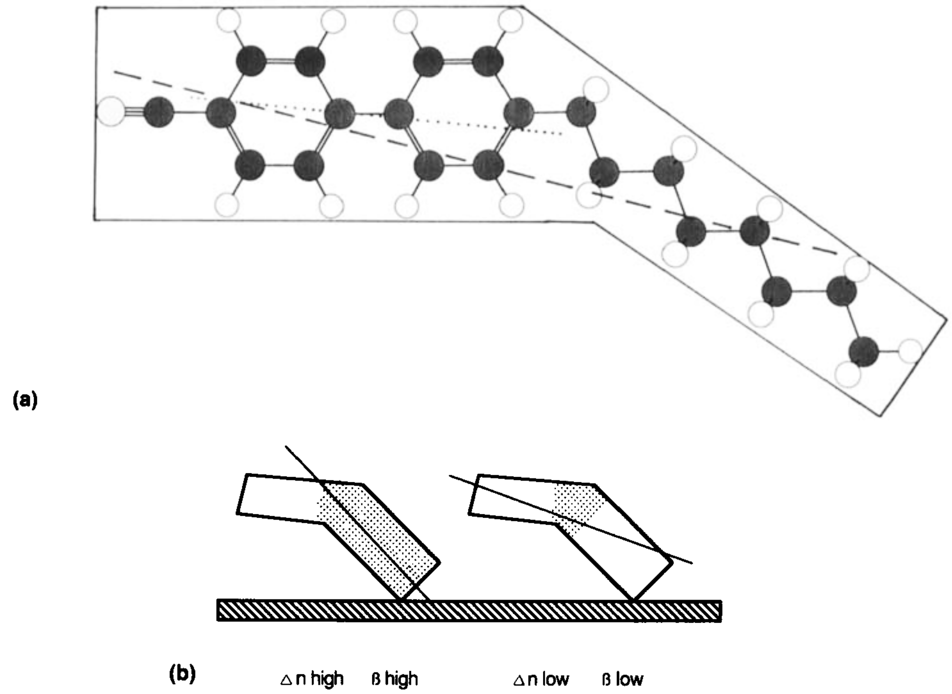

FIGURE 10 (a) The structure of the liquid crystal 4,4′-*n*-octyl-cyanobiphenyl (8CB) in its most stable conformation. The outline indicates the bent shape of the molecule. The dashed line shows the geometric long axis for this conformation (the axis of least moment of inertia), while the dotted line indicates the optical long axis (which is mostly a function of the aromatic core and thus rather independent of the conformation). (b) A schematic drawing showing how a material with high birefringence will show a higher pretilt of the optical axis than a material with a low birefringence as the contribution from the alkyl chain becomes more important.

mixture ZLI-1085 which has a negative dielectric anisotropy. As we have shown, this class of mixtures gives unusually low pretilts.

4.3. The Amorphous Surfaces

The group at Merck found a decrease in the pretilt with increasing dielectric anisotropy when the commercial polyimide SE-4110 was used as the alignment layer.[5] Most commercial polyimides are random copolymers, and thus are amorphous. Their result is thus in agreement with our finding that on an amorphous surface the pretilt will decrease with increasing dielectric anisotropy, when no effort is made to keep the birefringence constant.

The amorphous structure is less ordered than the crystalline structure. While all molecules are lined up nicely and regularly on the crystalline surface as illustrated in Figure 11, they will be much more disordered on an amorphous surface. Some of them will be leaning out of the plane of the paper, others into the plane. In other words, the amorphous surface imposes a much smaller order on the nematic phase. The symmetry will be bulk-like much closer to the surface. Thus the different long axes will also coincide over a larger part of the total cell thickness. This effect will also contribute to a low observed pretilt.

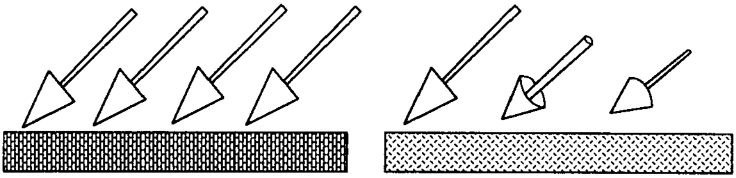

FIGURE 11 Left side shows mesogens on a regular, crystalline surface all pointing in the same direction and averaging a higher pretilt. On the right side an unordered, amorphous surface is shown. Here the situation is less ordered. The average pretilt angle in the bulk will be low.

On crystalline surfaces we have a regular ordering on a large scale. Over large areas all the dipoles of the surface will point in the same direction and we might obtain a higher pretilt. However, as long as the exact orientation of the dipoles on the crystalline surface is unknown, we cannot predict the pretilt angles with certainty on the crystalline surfaces. As we mentioned under 4.2. crystalline polymers do not show complete order. There will thus be local variations of the pretilt across the surface. Depending on the length scale of these variations they will average in the bulk (for short scale variations) or show up as unevenness in the pretilt angles (long scale variations).

4.4. The Balance of Forces

The two different situations on crystalline and amorphous surfaces can both be explained by an underlying balance of forces. In the bulk of the nematic material most liquid crystals will form dimeric pair of two molecules oriented in an anti-parallel fashion.[14,19] To break up this pair requires energy. The regular arrangement of the mesogenic molecules at a crystalline surface together with polar interactions with the surface supplies the energy needed. The surface layer will consist of essentially single molecules. This has already been shown for highly crystalline inorganic surfaces by STM observations.[15]

On amorphous surfaces the surface structure will be less ordered and there will be a smaller gain in energy. It will thus be less favorable to break up the dimeric pairs.[20] The stronger the pairs are bound together, the more difficult it is to break them up.

Our model suggests that when the energy released by organizing the mesogenic molecules on a surface is larger than the energy holding the dimers together, the pairs will break up. The difference in the concentration of single molecules on a surface has been observed by SHG and related to the polarity of the surface[21,22] or the crystallinity and polarity of the polymers.[20]

We have so far explained all differences between the different surfaces in terms of the differences between crystalline and amorphous structures. This change in the packing, and long range order, of the polymers will of course also alter most of the physical properties. It should thus be mentioned that all the differences we have observed could be due to a difference in some of the physical properties of the alignment layer and not directly related to the crystallinity at all. There exists at least the possibility that future investigations will find amorphous polymers behaving like our crystalline polyimides or *vice versa*.

It should be noted that the birefringence and dielectric data for the different nematic fluids are bulk data. The properties are actually for the dimeric species that exist in the bulk for most of these materials. On the other hand, as the SHG measurements show, the dimeric pairs will break up at the surface. When the pretilt is plotted as a function of bulk properties, the exact nature of the species at the surface is unknown. The different components of the nematic mixtures will also have different affinities for the surface, and bound in dimeric pairs with different strength. The actual composition of the liquid crystalline mixture at the surface might thus also be different from the bulk composition. This effect has already been observed on inorganic surfaces.[23]

The polyimides used in this study contains diaminoalkylene groups. With incomplete reaction we could thus have short chains pointing out of the surface. It has been found that incorporating 10% long chain alkylamines (7–15 carbons) in a polyimide will give a high pretilt angle,[24] presumably due to the steric effect of alkyl chains pointing out of the surface. The alignment of ferroelectric liquid crystals on the other hand is insensitive to the diacid:diamine ratio for the PMDA-derivatives.[25] We conclude that number of possible free alkyl chains for the polyimides used in this study is too small, and their length too short to explain the differences found between the different surfaces.

5. CONCLUSIONS

We have investigated possible correlations between the pretilt angles and the bulk properties of nematic liquid crystalline materials on five different polyimide alignment layers, and found that.

—There are no correlations between the pretilt and clearing temperature or elastic ratios of the liquid crystalline materials used.

—On both crystalline and amorphous surfaces the pretilt seems to increase with increasing dielectric anisotropy of the liquid crystalline materials, when the birefringence is kept constant.

—On the crystalline surfaces the pretilt seems to increase with increasing birefringence of the liquid crystalline materials, while on the amorphous surfaces it decreases, when the dielectric anisotropy is kept constant.

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