



## 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 Relationship between the Conformation of Polyimide Films and the Magnitude of the Pretilt Angle

Bernt O. Myrvold <sup>a b</sup>, Katsumi Kondo <sup>a</sup> & Shuichi Oh-hara <sup>a</sup>

<sup>a</sup> Hitachi Research Laboratory, Hitachi Ltd, 1-1, Oh-mika-cho, 7-  
chome Hitachi-shi, Ibaraki-ken, 319-12, Japan

<sup>b</sup> Department of Chemistry, University of Oslo, P. O. Box 1033,  
Blindern, N-0314, Oslo, Norway

Version of record first published: 24 Sep 2006.

To cite this article: Bernt O. Myrvold , Katsumi Kondo & Shuichi Oh-hara (1995): The Relationship between the Conformation of Polyimide Films and the Magnitude of the Pretilt Angle, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 269:1, 99-110

To link to this article: <http://dx.doi.org/10.1080/10587259508037324>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# The Relationship between the Conformation of Polyimide Films and the Magnitude of the Pretilt Angle

BERNT O. MYRVOLD\*, KATSUMI KONDO and SHUICHI OH-HARA

Hitachi Research Laboratory, Hitachi Ltd 1-1, Oh-mika-cho, 7-chome Hitachi-shi Ibaraki-ken, 319-12 Japan

(Received October 27, 1993; in final form February 8, 1995)

Seven alkylene aromatic polyimides have been synthesised. FT-IR spectra for the polyimides show small regular changes. This shows that the bulk structure of these polyimides changes in a regular fashion, while SEM pictures do not reveal any difference in the surface topology.

The dispersive and polar parts of the surface tension have been calculated. Although the total surface tension shows only small variations, there is a large odd-even effect in the dispersive and polar parts of the surface tension. This shows that there is a regular change in the structure close to the surface for this series of polyimides.

We also found a clear odd-even effect in the pretilt angles with ZLI-1132, and other nematic liquid crystals. We find that there is a decrease in the angle between the surface and the first molecule with increasing alkylene chain length, while the in-plane order shows a weak odd-even effect.

**Keywords:** Polyimide, conformation, pretilt, in-plane-order

## 1. INTRODUCTION

The control of the alignment of liquid crystals on rubbed polymer surfaces is a problem of great practical importance. Unfortunately very little is known about the mechanisms and forces involved in this process. For practical applications of displays the control over the angle between the long axis of the molecules and their projection onto the surface with no electric field applied, the so called pretilt, is required.

That changes in the shapes of molecules in the alignment layer can change the alignment of liquid crystals has been dramatically demonstrated by using the photo-sensitive azobenzenes.<sup>1</sup> This group has recently proposed that not only changes in the configuration, but also the more subtle changes in conformation will influence the pretilt.<sup>2</sup>

The basis for this assumption is that for a series of polyimides based on biphenyltetracarboxylic acid and aliphatic alkylene diamines there is a clear odd-even effect in the pretilt angle as the number of methylene groups in the alkyl chain varies.<sup>2</sup> Calculation

\* Present address: Department of Chemistry, University of Oslo, P. O. Box 1033 Blindern, N-0314 Oslo, Norway

of the most stable conformer also shows that there is a regular change in the conformation of the polymer chain as the number of methylene groups varies. It thus seemed reasonable to explain the varying pretilt angles by nearest neighbour interactions with polymer chains of different shape.

Polyimides with a benzophenone tetra carboxylic acid unit and alkylene chains give good bistable alignment of ferroelectric smectic C\* liquid crystals for alkyl chains with both an odd and even number of methylene units in the chain.<sup>3</sup> As crystalline alignment layers are a requisite for bistable operations of the ferroelectric liquid crystalline devices<sup>4,5</sup> this shows that all the members of this series of polyimides are crystalline (at least for alkylene chain lengths between two and ten carbon atoms). In crystals there is normally only one conformation present. As the alkylene chain length increases in this series of polyimides we would thus expect there to be a regular change in the conformations.

We have already in a preliminary investigation found a regular change in the pretilt angles for this series of polyimides.<sup>6</sup> Although there is a quantitative difference between the odd-even effect found for the BTDA-series of poly(alkanimides)<sup>6</sup> and the s-BPDA-series of poly(alkanimides).<sup>2</sup> In the latter case there is an order of magnitude difference between the pretilt for the even members (around 5°) and the odd members (around 0.5°). For the BTDA-series, on the other hand, there is only a factor 2–3 between the highest and lowest pretilt found.

## 2. EXPERIMENTAL

The polyamic acids were synthesized as described earlier.<sup>3</sup> The polyamic acid solutions were spin-coated onto cleaned indium tin oxide coated glasses, and the polyamic acids were imidized at 300°C for 2 hours. The polyimide surface was buffed with a rotating speed of 500 rpm and a translational speed of 16.7 mm/sec. The penetration depth of the rubbing cloth ( $d_{\max}$ ) was 0.4 μm. 120 μm Mylar spacers were used to separate the two glass plates with an antiparallel rubbing direction. The cells were assembled using Loktite 352 UV curing glue. All the cells were vacuum filled with the nematic mixture ZLI-1132 from E. Merck.

The surface pretilt angle was determined by the crystal rotation method,<sup>8</sup> in an automated experimental set up. Contact angles were determined with a Face Q1 contact angle meter (Kyowa Kaimen Kagaku Co., Ltd.). Water, glycerol, diiodomethane and 1,1,2,2-tetrachloroethane were used as the probing fluids allowing us to determine the dispersive, polar and hydrogen bonding parts of the surface tension. Contact angles are a sensitive measure of the changes of the structure of the top 5 Å of the surface.<sup>7</sup> By measuring the contact angles we should thus be able to probe any changes in the structure of the surface.

FT-IR spectra were recorded on a Nicolet 170 SX Fourier transform infrared spectrometer. Infrared spectroscopy is a technique that is sensitive to changes in the conformation of the molecules probed. But with transmission spectroscopy we measure changes not only in the surface layer, but also throughout the bulk of the sample.

SEM photographs were obtained by a Hitachi S-650 scanning electron microscope. This technique gives us direct access to changes in surface topology.

### 3. RESULTS AND DISCUSSION

#### 3.1 Contact Angles and Pretilt Angles

When the contact angles were measured there was a small difference between the contact angles for a drop advancing parallel to the rubbing direction and for drops advancing perpendicular to the rubbing direction. This difference was most marked for water which has the highest surface tension. The differences were also largest for the surfaces with an even number of methylene units in the alkylene chain. The contact angles for all four fluids used are shown in Figure 1.

From the data in Figure 1 we have extracted the dispersive and polar part of the surface tension, both parallel and perpendicular to the rubbing direction. We have defined the anisotropy of the surface tension as surface tension perpendicular to the rubbing minus the surface tension parallel to the rubbing. In Figure 2 we have plotted the anisotropy of the surface tension as a function of the alkylene chain length. The polyimides with an even number of methylene groups show a strong anisotropy in the surface tension, while those with an odd number are nearly isotropic.

There was also a clear odd-even effect in the pretilt angles in the alkylene aromatic polyimides based on BTDA, as can be seen from Figure 3. The polyimides with an even number of methylene units gave the highest pretilt. The regular change in the pretilt clearly corresponds to a regular change in the surface.

The surface tension data clearly shows that there is a regular change in the surface across this series of polyimides, with all the polyimides with an even number of methylene units giving very similar surface tensions and all those with an odd number of methylene units clustering around another set of values. This clearly shows that there

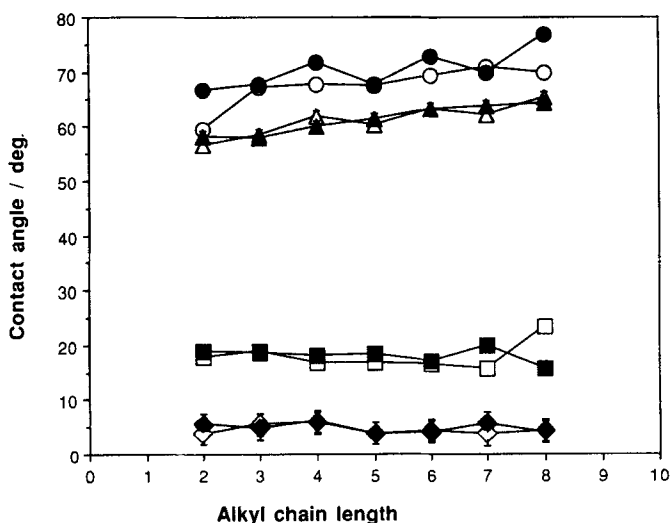


FIGURE 1 Contact angles with water (circles), glycerol (triangles), diiodomethane (squares) and tetrachloromethane (diamonds), filled symbols parallel to the rubbing, open symbols perpendicular to the rubbing direction.

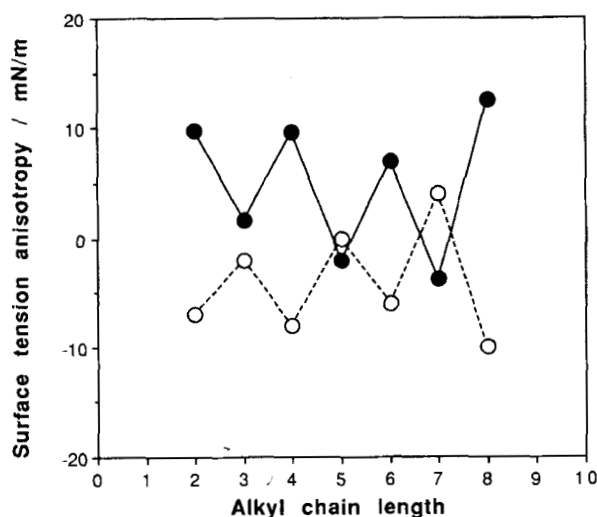


FIGURE 2 Anisotropy in dispersive (filled circles) and polar (open circles) part of the surface tension. Error bars omitted for clarity.

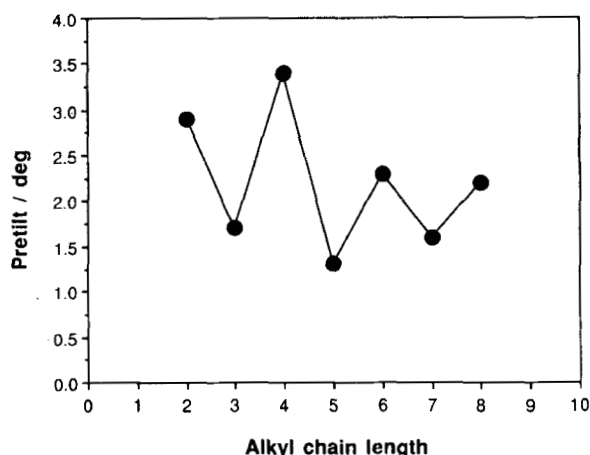


FIGURE 3 Surface pretilt with ZLI-1132 as a function of the alkylene chain length.

is a difference in the structure of the top few Angstroms between the different members of the series. The differences could be due to either a different packing of the chains in the polyimides or different conformations of the polymer chains. In any case, we also clearly see that these subtle differences in the conformations of the polyimides give clear differences in the pretilts found when these polyimides are used as alignment layers for nematic liquid crystals. On the other hand no such difference has been found when they were used as alignment layers for ferroelectric smectic C\* liquid crystals.<sup>3</sup>

### 3.2 Infra-Red Spectra

Infrared (and Raman) spectroscopy is sensitive to the vibrational frequencies of chemical bonds. In the first approximation this can be treated as a harmonic vibration. The vibrational frequency is a function of the mass of the atoms (or groups) vibrating relative to each other, and the force constant (strength of the bond connecting them). The vibrational frequencies are sensitive to the environment and thus tell us about the conformation of the molecules involved. Different conformations will have slightly different vibrational frequencies. On the other hand, many chemical groups will have a characteristic frequency which changes only weakly with the environment. This is called a group frequency and can be used to aid identification of unknown compounds, or parts of an unknown compound.

The IR spectrum of BTDA-5 is given in Figure 4. The spectra for all the other polyimides are nearly identical to this. As Table 1 shows there are only small shifts in the position of some of the bands. We will thus discuss the assignment of all seven spectra at once.

Bands 1 and 3 are typical group frequencies for the imide-group. Band 1 is for the symmetrical C=O stretching while band 3 is for the unsymmetrical stretching. Band 1 is normally found around  $1770\text{--}1780\text{ cm}^{-1}$  and band 3 at  $1720\text{ to }1730\text{ cm}^{-1}$ , the intensity of the former is 10–80% of the latter.<sup>9</sup> Collectively these two bands are known as Imide I.

Band 4 is an interesting band. The frequency varies between  $1670\text{ and }1684\text{ cm}^{-1}$ , and shows a clear odd-even effect. This band is due to the C=O stretching of the benzophenone carbonyl group. This band is found at  $1681\text{ cm}^{-1}$  for benzophenone in the gas phase, and at slightly lower frequencies in the liquid or solid phases.<sup>10</sup> For several polyimides and model compounds based on BTDA the band has been found at  $1660\text{--}1670\text{ cm}^{-1}$  together with a band near  $1620\text{ cm}^{-1}$  (Ref. 11). The second band is

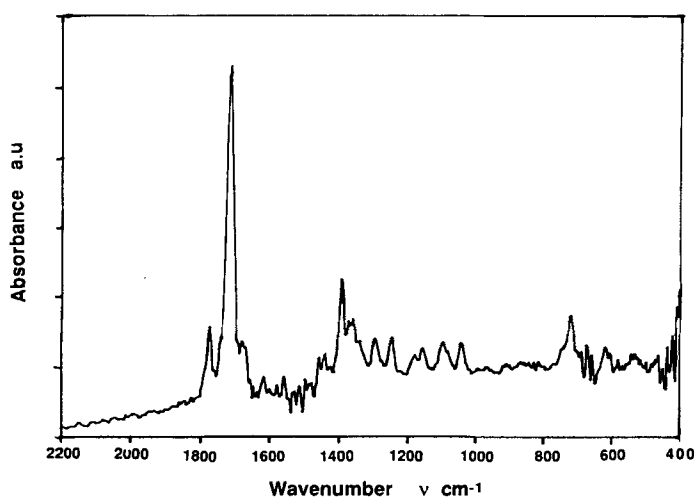


FIGURE 4 IR-spectrum BTDA-5.

TABLE 1

The vibrational frequencies for BTDA-5 together with our assignation.

Band no.	Wavenumber <sup>#</sup> cm <sup>-1</sup>	Assignation
1	1774 m	Imide I
2	1740 sh	
3	1711 s	Imide I
4	1678 m	C=O benzophenone
5	1670 sh	
6	1658 sh	
7	1617 w	C=O benzophenone
8	1575 w	
9	1558 w	
10	1456 m	
11	1440 m	
12	1390 s	Imide II
13	1370 m	Imide II
14	1360 m	Imide II
15	1340 w	<i>trans</i> -alkylene
16	1296 s	
17	1248 s	
18	1180 m	
19	1158 m	Imide III
20	1098 m	Imide III
21	1085 sh	
22	1059 m	
23	750 sh	
24	727 s	Imide IV

<sup>#</sup> s = strong, m = medium, w = weak, sh = shoulder

our band 7 at 1613–1618 cm<sup>-1</sup>. This band is weaker and does not show any clear odd-even effect.

Bands 8–10 at 1575, 1558 and 1456 cm<sup>-1</sup> respectively can all be attributed to the aromatic rings.<sup>10</sup> The symmetric scissoring of the alkylene chain will also give a band in the region of 1463–1473 cm. In the amorphous phase there will be one band, while this will split into two for the crystalline phase.<sup>12</sup> Unfortunately we can not separate this band from the aromatic bands and are not able to tell whether this polymer is crystalline or not from this transition.

Bands 12, 13 and 14 at 1390, 1370 and 1360 cm<sup>-1</sup> are due to imide II, the axial stretching of the N-C(carbonyl) bonds.<sup>9</sup>

*Trans*-alkyl chains<sup>13</sup> have bands at 1470 and 1340 cm<sup>-1</sup>. The band at 1470 cm<sup>-1</sup> is close to the strong aromatic ring bands and can not be seen clearly. The weak bands at 1339–1341 cm<sup>-1</sup> (band 15) could be due to the *trans* conformation of the alkyl chains.

Imide III is due to the transverse vibration of the N atom relative to the two carbonyl groups. These bands are found at 1120–1140 and 1100–1120 cm<sup>-1</sup> for aromatic polyimides.<sup>9</sup> For the more flexible alkanimides we find these two vibrations at 1156–60 and 1096–1099 cm<sup>-1</sup> respectively (bands 19 and 20)

Band 22 shows a regular increase in wavenumber from 1060 to 1053 cm<sup>-1</sup> as the alkylene chain length increases. The band is thus probably related to the alkylene chain, but we have not found any typical group frequencies for the alkyl or alkylene chains in this region.

Band 24 is largely due to imide IV, or the out-of-plane vibration of the nitrogen atom. The alkyl chain with three or more methylene groups will also have vibrations in the area of 722–725 (Ref. 14), or 720–731  $\text{cm}^{-1}$  (Ref. 12) due to the methylene group rocking. For the ethylene group this vibration is in the region of 734–743  $\text{cm}^{-1}$  (Ref. 14) These vibrations will split into two bands in the crystalline phase, while there will be only one band in the amorphous phase. Due to the proximity to the imide IV band we are unable to judge the crystallinity from this band, either.

So far we have focused on the similarity between the spectra of the different polyimides. There are, however, also subtle differences in the band positions. Data for the four easily identified bands with the largest differences are shown in Figure 5.

Band 4 is due to the vibration of the  $\text{C}=\text{O}$  group in the benzophenone moiety. These vibrations show a weak but clear odd-even effect. In a planar conformation this group will be conjugated with both neighbouring phenyl groups. For conformations with twisting around the bond joining the aromatic group and the carbonyl group the conjugation will be less efficient. This means that the electron density of the carbonyl group will change, and thus also the force constant. The odd-even effect in the vibrational frequency for the carbonyl group can thus be interpreted as a regular change in the amount of conjugation—in other words a regular change in the twisting around the phenyl-carbonyl bond.

Band 3, the imide I band and band 19, the imide III band both show a small odd-even effect. As the imide group is connected both to the aromatic ring and the alkyl chain, the odd-even effect here could be a result of different conjugation between the imide groups and the carbonyl group through the phenyl group, or a more direct effect from the different shape and flexibility of the alkyl chain.

A band at 1297  $\text{cm}^{-1}$  has been attributed to NMP.<sup>9</sup> This is close to our band 16 at 1297  $\text{cm}^{-1}$ . But we do not believe this band is due to NMP left in the samples. This band is one of the strongest in the sample which would require a very large amount of NMP to be retained. In PMDA-based polyimides this band is absent, even in films that

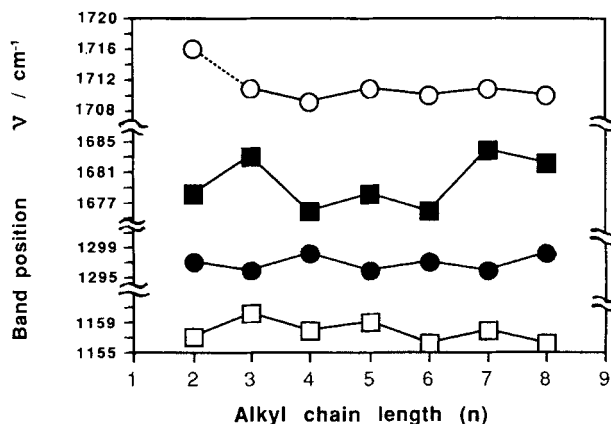


FIGURE 5 Shift in band positions for  $\text{C}=\text{O}$  (circles), imide I (filled squares), the unidentified band 16 (filled circles), and imide III (squares).



have been cured at a temperature of 100°C lower than our BTDA-films. We thus firmly believe that this band is a band intrinsic to the alkylene-BTDA polyimides. This band also shows an odd-even effect. The most notable feature with the odd-even effect for this band is the frequency shift in the opposite direction from the other three bands, thus excluding possible off-set in the zero point as the source of the odd-even effect.

Figure 5 summarizes the regular shifts in band positions we have found. We have chosen to discuss primarily the bands that can be regarded as group frequencies. The advantages of choosing group frequencies is that these bands are normally strong and well defined. Their assignation is also usually straightforward, and the bands will normally be connected with only one vibrational transition. It is thus clear which part of the molecules the changes seen in the spectra are connected. The disadvantage is that these bands are designed group frequencies for precisely the reason that they are not very sensitive to changes in the molecular structure. These bands can thus also be used to identify functional groups in molecules of unknown structure.

### 3.3 Scanning Electron Microscopy

Three sets of polyimide films were investigated by scanning electron microscopy (SEM). (1) Thin films as used for alignment, and FT-IR spectra, (2) thick films, (3) films that were rubbed and annealed.

The thin films are uniform and featureless, except for BTDA-5, BTDA-6 and BTDA-7 which show some structure indicating crystallinity. Thicker samples were virtually indistinguishable from the thinner ones when studied by SEM.

A few samples were investigated after rubbing. They were still featureless except for the polyimides with the two shortest alkylene chains (BTDA-2 and BTDA-3), which showed some stripes in the polyimide films 15–20 micron apart and 3–5 micron wide. Along these stripes there are irregular structures strongly reminiscent of the structures found in crystalline polyimides. After annealing at 120°C the stripes are still there, but the irregular areas found were larger.

After rubbing and annealing at 120°C for 1 hour all the polyimides showed clearly developed patterns (Fig. 6). These irregular structures are typical for crystalline polyimides.<sup>2</sup> In this case the rubbing mechanically forces the polyimide chains to be parallel, which promotes the crystallization. A short heating is thus all that is required for the crystals to form and the visual patterns to develop.

As we can see only minor differences in their behaviour we conclude that all these polyimides are crystalline. This is also what we expected as they all give identical results when used as alignment layers for ferroelectric smectic C\* materials. The SEM micrographs do not reveal any systematic differences in structure that can explain the odd-even effect in the pretilt angles. BTDA-5, BTDA-6 and BTDA-7 seem to have a higher degree of crystallinity, as evidenced by them showing patterns even before annealing.

### 3.4 The Population Distribution Model

We have proposed a population distribution model for the observed pretilt angles in nematic liquid crystal cells.<sup>15</sup> For thick cells ( $> 20\mu\text{m}$ ) the pretilt can be expressed by

$$\beta_{\text{obs}} = a_1(\beta_0 - \alpha)$$

where  $\beta_{\text{obs}}$  is the observed pretilt of the sample,  $a_1$  is the in-plane order,  $\beta_0$  is the angle between the surface and the optical axis of the mesogens in the first monolayer, and  $\alpha$  is the angle between the optical and mechanical axes of the mesogens. The relationship between the in-plane order and the pretilt was first discussed by Barmentlo and

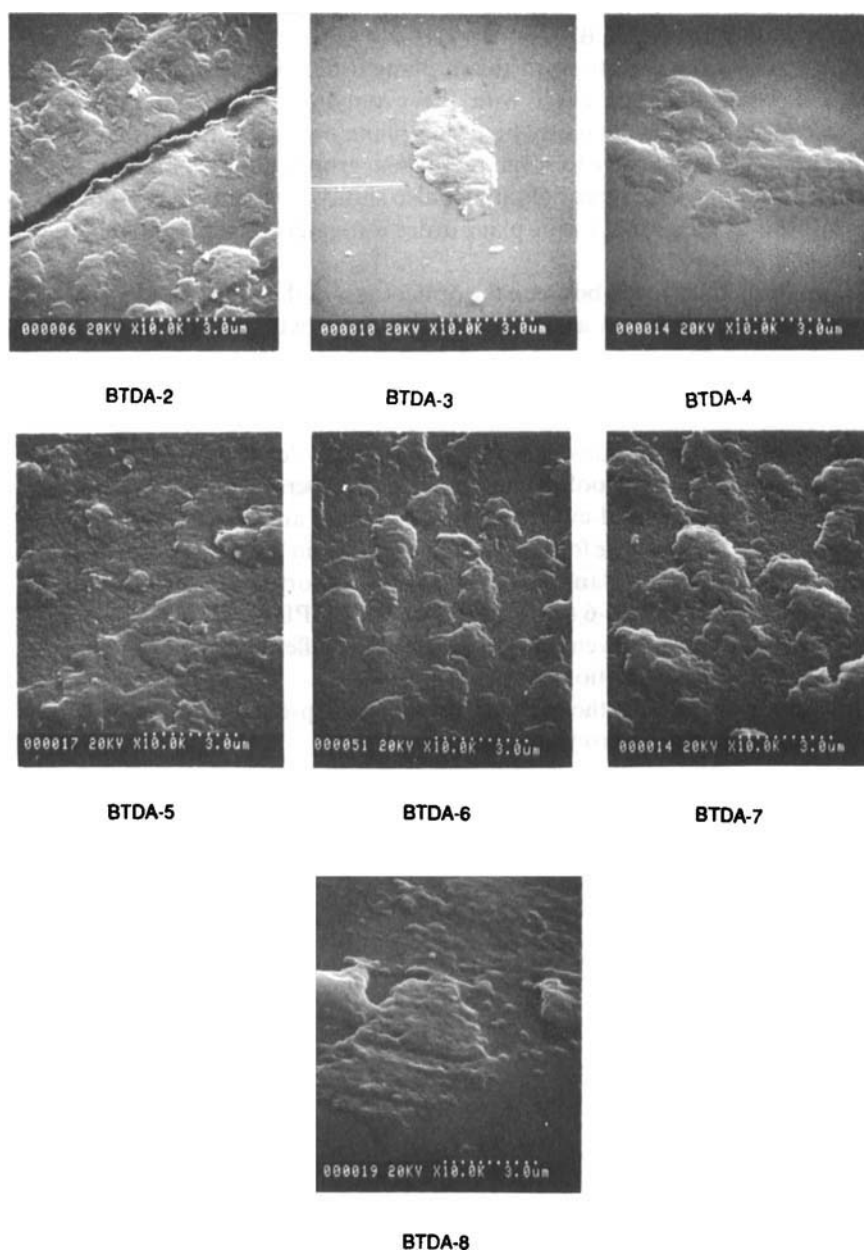


FIGURE 6 SEM micrographs of samples that have been rubbed and then heated at 120°C for 1 hour.

co-workers.<sup>16</sup>  $a_1$  measures the preference of the mesogens in the surface layer to be parallel (as opposed to anti-parallel) to the rubbing direction.

By choosing liquid crystals with known shapes ( $\alpha$ ), and similar groups interacting with the surface (thus giving the same  $\beta_0$ ), we were able to obtain values for  $\beta_0$  and  $a_1$  for the surfaces investigated here. The details will be published elsewhere.<sup>17</sup> As the in-plane distribution  $a_1$  also depends on the mesogens used, all values refer to 4'-pentyl-cyanobiphenyl (5CB).

Figure 7 shows the variations in the in-plane order. There seem to be two effects. There is a weak odd-even effect with those polyimides with an even number of methylene groups giving a slightly higher in-plane order. There is also a strong peak with the polyimides with five to seven methylene groups giving a high in-plane order. As we saw in 3.3 the same three polyimides also showed evidence of crystallinity before annealing. It thus seems that the in-plane order is strongly related to the crystallinity of the samples.

The variation in the angle between the optical axis of the molecules and the surface is shown in Figure 8. There is a decrease in this angle with increasing alkylene chain length, possibly with slightly higher angles for BTDA-5, -6 and -7.

For the BTDA-series the odd-even effect in the pretilt angle is consistent with the variation in the in-plane order. As all polyimides in this series are crystalline there are comparatively small variations in both the in-plane order and pretilt angles.

For comparison we also looked at two of the members of the s-BPDA-series where a much more dramatic odd-even effect in the pretilt angle has been reported.<sup>2</sup> For s-BPDA-5 and s-BPDA-6 we found the same  $\beta_0$  of  $16^\circ$  in both cases. There is, however, a large difference in the in-plane order between the amorphous s-BPDA-5 ( $a_1 = 0.045$ ) and the crystalline s-BPDA-6 ( $a_1 = 0.29$ ). For the s-BPDA-series it is probably most correct to say that the odd-even effect arises from the differences in crystallinity and not from the different conformations *per se*.

The relationship between the in-plane order and the pretilt angle has also been found for the series of alkylene-pyromellitimides.<sup>17,18</sup>

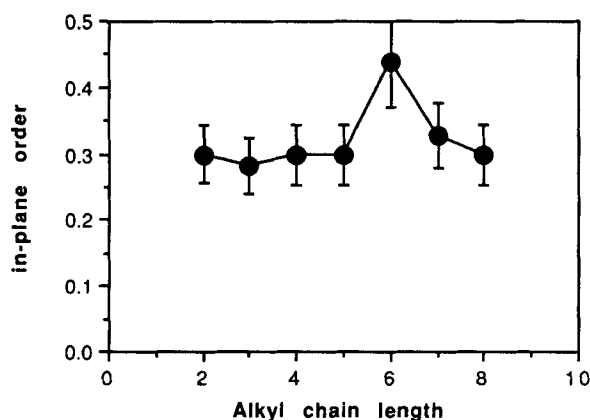


FIGURE 7 The in-plane order  $a_1$  as a function of alkylene chain length for SCB on the polyimides in the BTDA-series.

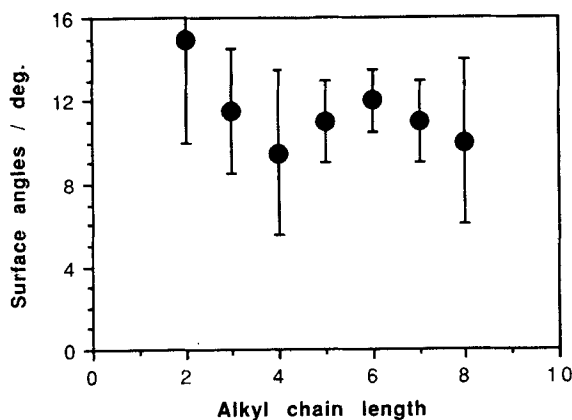


FIGURE 8 The angle between optical axis of the mesogens and the surface as a function of the alkylene chain length for polyimides in the BTDA-series.

To obtain uniform displays with good switching characteristics a uniform pretilt is required. As the performance of the displays rises the allowed non-uniformity of the pretilt becomes less. As the pretilt is sensitive to extremely small variations in the surface this might imply a need to control the conformational distribution of the polymer chains on the surface.

#### 4. CONCLUSION

We find small systematic variations in the conformation in the bulk of the different unrubbed samples indicating an odd-even effect in the polyimide conformation. There are corresponding variations in the dispersive and polar parts of the surface tension, but we can not see any differences in topology.

The pretilt angles of nematic liquid crystals oriented on these alkyl-aromatic polyimides show a clear odd-even, and is sensitive to small changes in the surface, as determined by changes in the surface tension.

The changes in the in-plane order is most important in determining the odd-even effect in the observed pretilt angle. While the angle between the optical axis of the molecules and the surface only shows small variations.

#### Acknowledgments

We wish to thank Mr. Hirakata for automating the pretilt angle measurement system, Mr. Yokota for assistance in the cell construction and Mr. Morooka of the 44th section of HRL for help with the contact angle measurements. We also thank Miss Y. Ishijima from the MCR center for recording the FT-IR spectra, and Miss M. Haniu of the MCR centre for recording the SEM photographs.

#### References

1. K. Aoki, T. Tamaki, T. Seki, Y. Kawanishi and K. Ichimura, *Langmuir* **8**, 1014 (1992).
2. H. Yokokura, M. Oh-e, K. Kondo and S. Oh-hara, *Mol. Cryst. Liq. Cryst.* **225**, 253 (1993).

3. B. O. Myrvold, *Liq. Cryst.* **4**, 367 (1989).
4. J. M. Geary, J. W. Goodby, A. R. Kmetz and J. S. Patel, *J. Appl. Phys.* **62**, 4100 (1987).
5. B. O. Myrvold, *Liq. Cryst.*, **3**, 1255 (1988).
6. B. O. Myrvold, K. Kondo and S. Oh-hara, *Liq. Cryst.* **15**, 429 (1993).
7. C. D. Bain and G. M. Whitesides, *J. Am. Chem. Soc.* **110**, 5897 (1988).
8. A. Mosley, B. M. Nicholas and P. A. Gass, *Displays* **8**, 17 (1987).
9. C. Johnson, J. Mao and S. L. Wunder in *Polyimides: Materials, Chemistry and Characterisation*, ed. C. Feger, M. M. Khojasteh and J. E. McGrath, (Elsevier, Amsterdam, 1989) pg. 347.
10. H. A. Szymanski, *IR Theory and Practice of Infrared Spectroscopy*, (Plenum Press, New York, 1964).
11. J. Gagliani, K. Daniels and P. Straub, in *Recent Advances in Polyimide Science and Technology*, ed. W. D. Weber and M. R. Gupta, (SPE, 1987).
12. C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, (Academic Press, New York, 1963).
13. R. Zbinden, *Infrared spectroscopy of high polymers*, (Academic Press, New York, 1964).
14. M. St. C. Flett, *Characteristic Frequencies of the Chemical Groups in the infra-red*, (Elsevier Amsterdam, 1963).
15. B. O. Myrvold and K. Kondo, *Liq. Cryst.* **17**, 437 (1994).
16. M. Barmantlo, R. W. J. Hollering and N. A. J. M. van Aerle, *Phys. Rev. A* **46**, R4490 (1992).
17. B. O. Myrvold, K. Kondo and S. Oh-hara, *Mol. Cryst. Liq. Cryst.*, in the press (LC-GH-5161).
18. D. Johannsmann, H. Zhou, P. Sonderkaer, H. Wierenga, B. O. Myrvold and Y. R. Shen. *Phys. Rev. E* **48**, 1889 (1993).