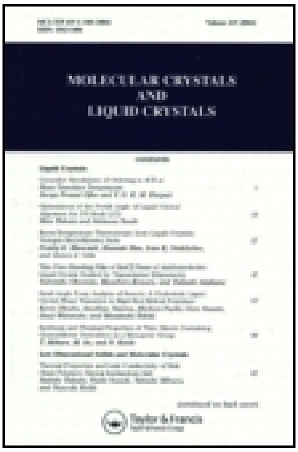

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Polyimides with Fluorinated Side Chains for Liquid Crystal Alignment

Shigeki Ishibashi [a], Misako Hirayama [a] & Tohru Matsuura [a]
[a] NTT Interdisciplinary Research Laboratories, Nippon Telegraph and Telephone Corporation, 3-9-11 Midori-Cho Musashino-shi, Tokyo, 180, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Shigeki Ishibashi , Misako Hirayama & Tohru Matsuura (1993): Polyimides with Fluorinated Side Chains for Liquid Crystal Alignment, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 225:1, 99-105

To link to this article: http://dx.doi.org/10.1080/10587259308036221

Mol. Cryst. Liq. Cryst., 1993, Vol. 225, pp. 99–105
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Polyimides with Fluorinated Side Chains for Liquid Crystal Alignment

SHIGEKI ISHIBASHI, MISAKO HIRAYAMA, and TOHRU MATSUURA
NTT Interdisciplinary Research Laboratories, Nippon Telegraph and Telephone Corporation, 3-9-11 Midori-Cho Musashino-shi, Tokyo 180, Japan

(Received March 5, 1992; in final form May 6, 1992)

The surface properties of a series of polyimides with fluorinated alkyl side chains are studied by contact angle and pretilt angle measurements. The contact angles depend on the fluorine content of the polyimides. Higher pretilt angles are obtained for polyimides with longer fluorinated side chains. The pretilt angles, however, not only depend on the side chain length, but also on the main chain structure of the polyimides. Polyimides prepared from benzophenone tetracarboxylic dianhydride are found to show higher pretilt angles than those prepared from 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride. The anisotropic interaction between polyimide molecules and liquid crystal molecules is discussed.

Keywords: liquid crystal, pretilt, polyimide, fluorinated polyimide, surface tension

INTRODUCTION

The alignment of liquid crystal molecules is one of the most important technologies in liquid crystal device fabrication. It is generally a simpler matter to produce either homogeneous or homeotropic alignment. For example, rubbed polyimides have been widely used for homogeneous alignment. However, it is rather complicated to obtain an alignment layer with a high, optimised pretilt surface, which is necessary for high performance liquid crystal devices, such as the Scheffer supertwisted birefringent effect liquid crystal display,[1] and the Clark-Lagerwall ferroelectric liquid crystal display.[2,3]

The conventional method for producing high pretilt surfaces has been to employ oblique evaporation of silicon monoxide. However, this method is time-consuming and can limit the substrate size. A preferable method is to use a chemical process. A few chemical methods have been proposed: Filas and Patel[4] proposed aliphatic silane treatment. The use of silane coupling reagents for high pretilt surfaces, however, tends to result in instability. Fukuro and Kobayashi[5] used alkyl-branched polyimides to obtain high pretilt surfaces and have suggested that the pretilt can be attributed to steric interactions between liquid crystal molecules and neatly aligned branched alkyl chains. However, the alkylamines reacted with polyimide precursors left amide groups in their alkyl-branched polyimides. These amide groups could be the source of the pretilt, because imide and amide groups differ in the strength of their interaction with liquid crystal molecules.

Here we report the study of polyimides with fluorinated alkyl side chains, in which no amide groups are expected to be left. Their contact angles, critical surface tensions, and pretilt angles will be reported, and the pretilt mechanisms will be discussed.

EXPERIMENTAL

The molecular structure of fluorinated polyimides[6] are shown in Figure 1. The dianhydride moieties tested were 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BTDA). The diamines used were 1H,1H-perfluoroethoxy-2,4-diaminobenzene (3F), 1H,1H-perfluorobutoxy-2,4-diaminobenzene (7F), and 1H,1H-perfluorooctoxy-2,4-diaminobenzene (15F).

Equal amounts of diamines and tetracarboxylic dianhydrides were reacted in *N*-methyl-2-pyrrolidinone at room temperature in a standard manner.[6] The resulting poly(amic acid) solution was filtered to 0.4 μm. The solid content was adjusted to give a 60-nm polyimide layer after spin-coating onto indium-tin-oxide coated glass plates. The plates were prebaked at 150°C for 1 h and then hardbaked at 300°C for 2 h.

The contact angles of these polyimides were measured both before and after

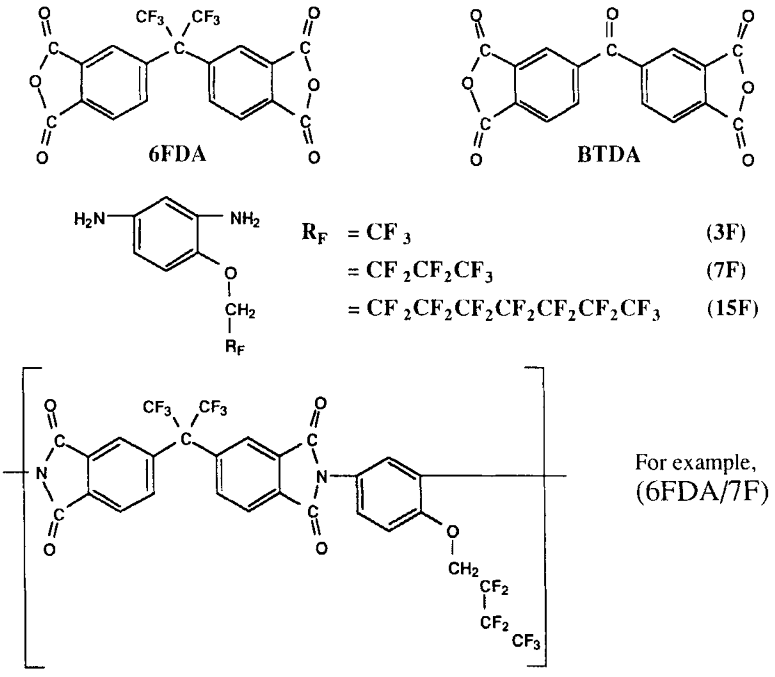

FIGURE 1 Structures of polyimide with fluorinated alkyl side chains.

rubbing with a nylon roll, using an automatic contact angle meter (Kyowa Interface Science, CA-Z). The critical surface tension was determined from the contact angles with water, ethyleneglycol, and cyclohexanol. The pretilt angles were measured with cells sealed in antiparallel rubbing directions on two pieces of glass to produce a parallel tilt configuration. These cells were filled with a nematic mixture (Merck ZLI-2293), using capillarity in the isotropic phase. The magnetocapacitive method[7] was used for pretilt angle measurements with a magnetic field of 14.6 kOe.

RESULTS AND DISCUSSION

The fluorinated polyimides have large contact angles with water. Figure 2 shows the contact angle dependence on the rubbing strength parameter L.[8] L is given by:

$$L = Nl(1 + 2\pi rn/60v),$$

where N is the cumulative number of rubbings, l is the contact length of the rubbing roller circumference, n is the number of revolutions per minute of the roller, r is its radius and v is the speed of the substrate stage.

For almost all of the polyimides, the angle decreased sharply with rubbing strength until $L = 50$ cm, decreasing more slowly thereafter. The polyimides with the diamine 3F, with the shortest side chains, exhibited the least change in contact angle with rubbing. In particular, the contact angle of polyimide (6FDA/3F) showed very little change. These facts imply that alignment of the side chains plays an important role in the contact angle and it can be affected by rubbing.

The polyimides with dianhydride 6FDA had higher contact angles than those with BTDA. The differing fluorine contents of these polyimides may be the origin of the angle difference. Figure 3 shows the variation of contact angle with the fluorine content of the fluorinated polyimides, at a rubbing strength L of 75.5 cm. The figure clearly shows that, in these samples, the contact angles are proportional to the fluorine contents. The contact angle, which is a macroscopic physical property, depends on the amount of hydrophobic groups, such as fluorine substituents,

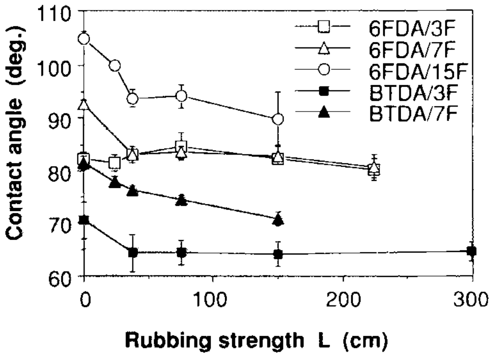

FIGURE 2 Dependence of contact angle (with water) on rubbing strength L.

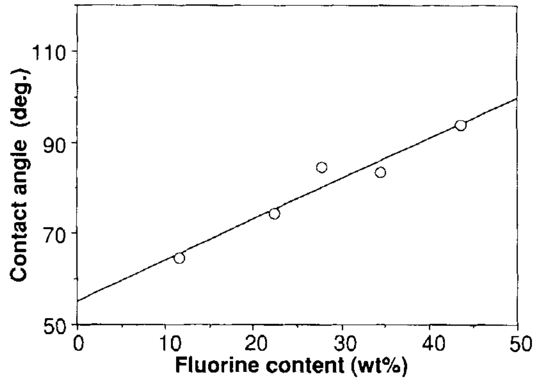

FIGURE 3 Contact angle dependence on fluorine content.

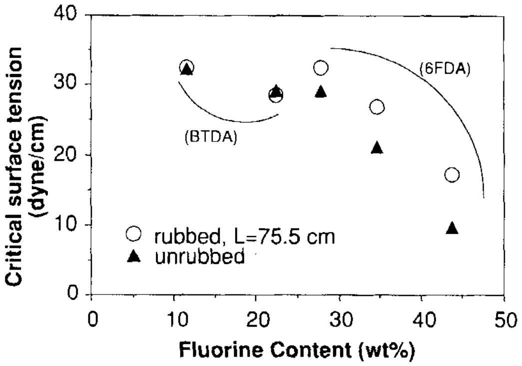

FIGURE 4 Critical surface tension dependence on fluorine content, with and without rubbing.

at least in this series of polyimides. Though the contact angle should also be affected by the main chain structure, this effect was not observed.

The critical surface tension is also affected by the fluorine content. Figure 4 shows the dependences of the critical surface tension on the fluorine content with and without rubbing. The surface tension of unrubbed samples decreased steadily with increasing fluorine content. After rubbing, however, the relationship was far from proportional. The rubbing process causes an increase in the critical surface tension of polyimides with 6FDA, but not for polyimides with BTDA. This difference may indicate that the surface density of CF_3 groups in 6FDA polyimides is decreased by rubbing. The decrease in the CF_3 group surface density after rubbing has been reported for polyimides with CF_3 groups using X-ray photoelectron spectroscopy.[9]

The pretilt angles of the fluorinated polyimide surfaces rubbed at a density of 75.5 cm are plotted against their fluorine contents in Figure 5. It is obvious that the pretilt angles are not proportional to the fluorine content, in contrast to the contact angles and the critical surface tensions. A large difference in pretilt angles was observed between polyimides with 6FDA and BTDA, the higher pretilt being obtained for BTDA polyimides whose fluorine content is lower than 6FDA poly-

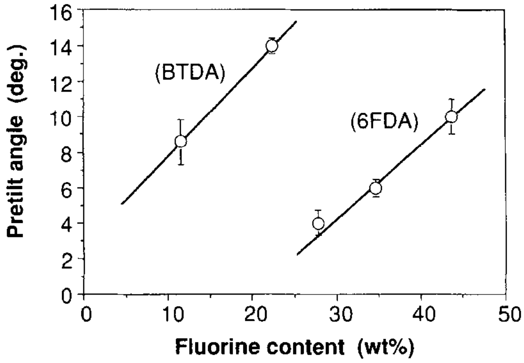

FIGURE 5 Pretilt angle dependence on fluorine content, at rubbing strength L = 75.5 cm.

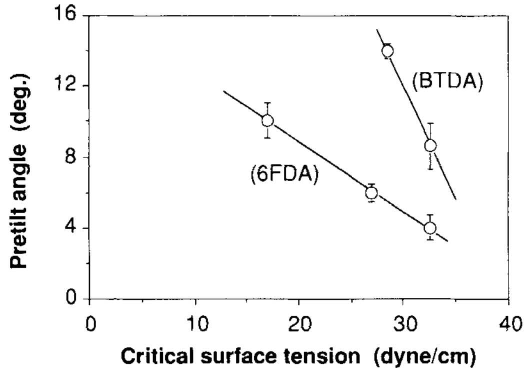

FIGURE 6 Pretilt angles vs critical surface tension, at rubbing strength L = 75.5 cm.

imides. However, within a polyimide series, those with larger fluorine contents always have higher pretilts.

In Figure 6, the pretilt angles are plotted against the critical surface tension. The straight lines indicate the polyimides with 6FDA and BTDA. In both cases, the polyimides with larger critical surface tensions have reduced pretilt angles. The empirical FCK rule states that a surface with a smaller critical surface tension than that of the liquid crystal will favour homeotropic alignment, in which the pretilt angle is 90 degrees. The same trends can be seen in Figure 6, for each of the polyimides. In these plots there is an obvious difference between 6FDA and BTDA polyimides. The BTDA polyimides have higher pretilt angles than those with 6FDA, even when they have almost the same critical surface tensions. The difference in the pretilt of the polyimides is also shown in the Figure 7, where the pretilt is plotted against the length of the fluoroalkyl side chain at rubbing strength of 75.5 cm. The pretilt was found to be proportional to the chain length.

In order to clarify the results of the pretilt angle measurement, we should take into account the partial interactions between polyimide molecules and liquid crystal molecules. The attractive forces which should be considered are mainly the dispersion forces between the aromatic moieties in the polyimide and liquid crystal

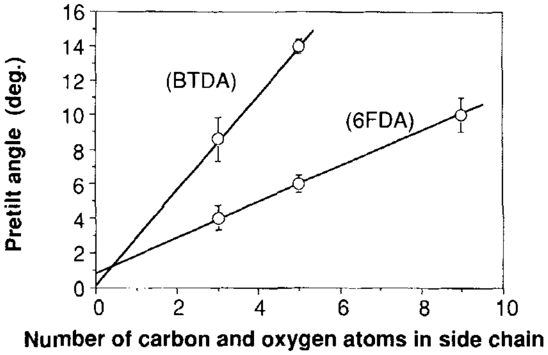

FIGURE 7 Pretilt angle dependence on side chain length.

molecules. The repulsion may be chiefly attributed to the fluoroalkyl side chain of the polyimides—the longer the fluoroalkyl chain, the larger the repulsion. The overall situation is that a liquid crystal molecule is withdrawn by the polyimide molecule especially at the aromatic moiety, and at the same time it receives a repulsive force from the fluoroalkyl side chains. When a rod-like liquid crystal molecule is partially withdrawn and partially repulsed, it tends to tilt from the polyimide surface, thus causing pretilt.

In 6FDA polyimides, there are fluorine substituents in both the dianhydride and diamine moieties. These fluorine substituents are more or less repulsive to the liquid crystal molecules over the entire polyimide molecular structure. Thus these polyimides show a small pretilt. The longer the fluoralkyl side chain in the diamine moiety, the larger the repulsion to this moiety becomes. This enlarged repulsion makes the liquid crystal molecule more apart from the diamine moiety, thus making the pretilt higher. In BTDA polyimides, however, the fluorine substituents exist only in the diamine moiety, and the dianhydride moiety remains attractive to the liquid crystal molecule. The large difference in the repulsive force of a single polymer unit causes higher pretilt in BTDA polyimides than in those with 6FDA.

CONCLUSION

The surface properties of polyimides with fluorinated alkyl side chains have been presented. The contact angles are found to depend linearly on the fluorine contents, although the pretilt angles are found to be closely related to the molecular structure of the polyimides. The interactions between liquid crystal molecules and polyimide molecules may be partly attractive due to the aromatic cores and partly repulsive due to the fluorinated alkyl side chains in the polyimides. Local differences in intermolecular interactions could be the cause of pretilt. This assumption will be tested for a variety of liquid crystals and polyimides, and could be a guideline in the design of future polymers for liquid crystal alignment.

Acknowledgment

Drs. S. Sasaki and F. Yamamoto are acknowledged for their valuable discussion. Mr. N. Yamada is also acknowledged for his experimental advice.

References

1. T. J. Scheffer, J. Nehring, M. Kaufmann, H. Amstutz, D. Heimgartner, and P. Eglin, *SID85 Digest* (Palisades Institute for Research Services, New York, 1985), p. 120.
2. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
3. J. Kanbe, H. Inoue, A. Mizutome, Y. Hanyuu, K. Katagiri, and S. Yoshihara, *Ferroelectrics*, **114**, 3 (1991).
4. R. W. Filas and J. S. Patel, *Appl. Phys. Lett.*, **50**, 1426 (1987).
5. H. Fukuro and S. Kobayashi, *Mol. Cryst. Liq. Cryst.*, **163**, 157 (1988).
6. T. Ichino, S. Sasaki, T. Matsuura, and S. Nishi, *J. Polym. Sci. Polym. Chem. Ed.*, **28**, 323 (1990).
7. T. J. Scheffer and J. Nehring, *J. Appl. Phys.*, **48**, 1783 (1977).
8. T. Uchida, M. Hirano and H. Sakai, *Liq. Cryst.*, **5**, 1127 (1989).
9. H. Kurai, H. Mochizuki, S. Satoh, and S. Ozaki, presented at 16th Liquid Crystal Colloquium (Japan), 1L307 (1990).