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

Relationship between Pretilt Angles of Liquid Crystals and Surface Energies of Polyimides Containing Fluorine Atoms

M. Nishikawa [a c], T. Miyamoto [a], S. Kawamura [a], Y. Tsuda [a], N. Bessho [a], D.-S. Seo [b], Y. Iimura [b] & S. Kobayashi [b]

[a] Tokyo Research Laboratory, Japan Synthetic Rubber Co. Ltd., 3-5-1 Higashi-yurigaoka, Asao-ku, Kawasaki, 215, Japan

[b] Division of Electronic and Information Engineering, The Graduate School of Technology, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganel, Tokyo, 184, Japan

[c] Graduate School of Technology, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganel, Tokyo, 184, Japan

Version of record first published: 23 Sep 2006.

Mol. Cryst. Liq. Cryst., 1995, Vol. 258, pp. 285–290
Reprints available directly form the publisher
Photocopying permitted by license only

Relationship between Pretilt Angles of Liquid Crystals and Surface Energies of Polyimides Containing Fluorine Atoms

M. NISHIKAWA*,T. MIYAMOTO, S. KAWAMURA, Y. TSUDA, N. BESSHO, D.-S. SEO[1], Y. IIMURA[1], and S. KOBAYASHI[1]

Tokyo Research Laboratory, Japan Synthetic Rubber Co. Ltd. 3-5-1 Higashi-yurigaoka, Asao-ku, Kawasaki 215, Japan

[1] *Division of Electronic and Information Engineering, The Graduate School of Technology, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei, Tokyo 184, Japan*

(Received May 2, 1994)

We have synthesized the novel organic-solvent-soluble polyimides having helix backbone structure and containing four different types of diamine with trifluoromethyl groups as alignment films for liquid crystal displays. These alignment films show the pretilt angles of liquid crystal from 2° up to 40°. The surface energies of these polyimide films show a monotonic decrease with the increase of concentration of fluorine atoms in polyimide films. This tendency commonly occurs for four different fluorine containing diamines. A clear relationship between the surface energy of polyimide films and the pretilt angles of liquid crystal on polyimide films was not obtained. The dependence of the obtained pretilt angles on the chemical structure of the polyimides is as follows: the polyimides with fluorine atoms in the lateral benzene rings, which are capable of generating a high pretilt angle of up to 40°, show the linear increasing of pretilt angles with the decreasing of the surface energies. On the other hand, the polyimides with fluorine atoms in polymer backbones show a maximum value of pretilt angles in the medium ranges. These results suggest that the microscopic surface structure of polyimides largely affect the generation of the pretilt angle at the boundary surface between liquid crystals and alignment films.

Keywords: organic-solvent-soluble polyimides, alignment film, nematic liquid crystal, pretilt angle, fluorine atoms, surface energy.

1. INTRODUCTION

The unidirectional alignment of liquid crystal (LC) molecules is of scientific and industrial importance in fabricating LC cells. It is rather easy to produce just unidirectional homogeneous or homeotropic LC molecular alignment without having an accompanying pretilt angle. The generation of an appropriate angle is necessary to fabricate defect-free and high-performance LC displays (LCDs), such as twisted nematic (TN) LCDs,[1,2] supertwisted nematic (STN) LCD,[3] and ferroelectric LCDs.[4,5] However, the generation of a stable high pretilt angle is a complicated matter. Several approaches to increase the pretilt angle of LC molecules aligned on rubbed polyimide (PI) films have been demonstrated.[6,7] However, the relationship between properties of

* M. Nishikawa is also in the Graduate School of Technology, Tokyo University of Agriculture and Technology.

the pretilt angles and the chemical structure of the alignment film has not been fully clarified yet.

In this paper, we report the synthesis of the novel organic-solvent-soluble PIs containing fluorine atoms, which show a high pretilt angle from 2° up to 40°, and then properties of the LC molecular pretilt angles on the PI films are discussed in terms of their surface energies and chemical structures. The PI films synthesized in this research are useful for their low curing temperature, say 180°C, which is very compatible with the process temperature of color active matrix TN LCDs.

2. EXPERIMENTS

2.1. Synthesis of Organic-Solvent-Soluble PI Containing Fluorine Atoms

The novel PIs were synthesized in terms of the chemical imidization of the precursor polyamic acids. This method is basically the same as that reported in a previous paper[8] expect for the moieties used. The precursor polyamic acids were prepared from the reaction of 2,3,5-tricarboxycyclopentyl acetic dianhydride (TCA·AH), p-phenylenediamine (p-PDA), and four types of diamine containing trifluoromethyl groups (DA-1-DA-4) as shown in Figure 1. The novel soluble (for simplicity, here after we omit the word "organic-solvent".) PIs were obtained from chemical imidization of polyamic acids at 120°C with catalysts of pyridine and acetic anhydride.

2.2. Preparation of LC Cells

LC cells were prepared to measure the pretilt angle of LC molecules aligned on the PI films. The alignment films were deposited first with spin-coating of a diluted solution of

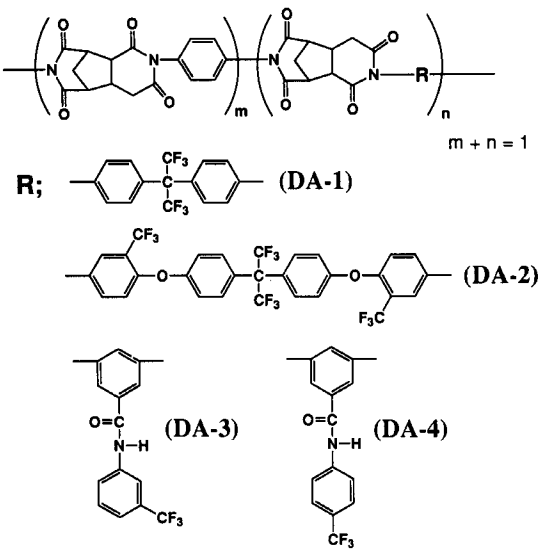

FIGURE 1 Chemical structures of soluble polyimides containing trifluoromethyl groups.

PI with γ-butyrolactone on the substrates and then cured at 180°C for an hour. The thickness of the PI films were controlled at 100 nm. The PI films were rubbed with a rubbing machine using a rayon cloth. The inner surfaces of sandwich cells were treated by antiparallel rubbing in advance. The nematic LC used to investigate the pretilt angle was ZLI-2293 (E. Merck).

2.3. Measurement Method of Pretilt Angle and Surface Energy

For measuring the pretilt angles of the aligned LC in the cells, we adopted the crystal rotation method.[9] The surface energy of each PI film was obtained from the measurement of the contact angles of water and methylene iodide on the PI films.[10]

3. RESULTS AND DISCUSSION

3.1. Pretilt Angles of LC on PI Films

The relationship between the mole fraction of four different diamines with trifluoromethyl groups (from DA-1 to DA-4) in the soluble PIs and the pretilt angles of the LC is shown in Figure 2. The PIs containing DA-1 and DA-2 show relatively low pretilt angles exhibiting broad maxima; while the PIs containing DA-3 and DA-4 are shown to be capable of generating pretilt angles that increase almost monotonously from 2° up to 40° with the increase of the mole fraction of these diamines. These results suggest that the difference of the PI structure largely affects the pretilt angles of the LC.

Dubois *et al.* found that the molecular alignments of six types of LCs with different surface energies (γ_{LC}) aligned on five kinds of polymeric materials with different surface

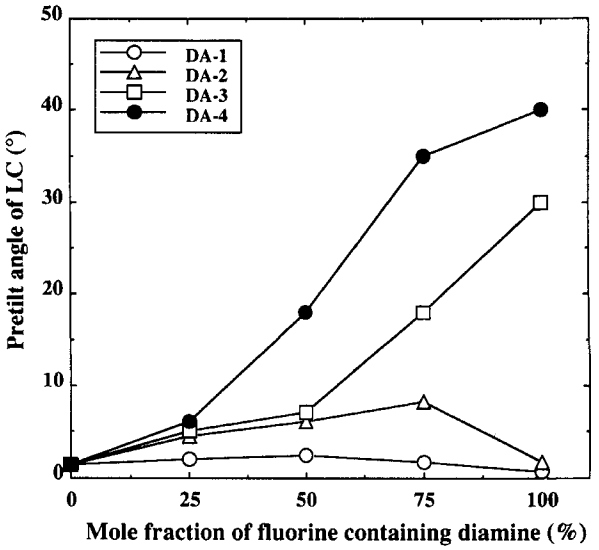

FIGURE 2 Relationship between mole fraction of fluorine atoms containing diamines and pretilt angles of LC on polyimide films.

energies (γ_{AL}) of 22–44 dyne/cm[11] and claimed that when γ_{AL} was very low compared with γ_{LC}, homeotropic alignment of LC was effectively induced; conversely, when γ_{AL} was very large, homogeneous alignment of the LC was observed. This is generally known as the Friedel-Creagh-Kmetz (FCK) rule.

In the present research, the surface energies of PI films were measured to elucidate the generation mechanism of the pretilt angles of LCs on PI films. The relationship between the concentration of fluorine atoms in the soluble PIs and the surface energies of various PI films is shown in Figure 3. The surface energies of PI films gradually decrease with the increase of the concentration of fluorine atoms in the soluble PIs as shown in Figure 3. This trend is common for the different diamine species. The decreasing rate in the surface energy of each PI film is nearly in proportion to the concentration of fluorine atoms in the PI film. This phenomenon is thought to be caused by the increase of fluorine atoms, which tend to lower the surface energies in PI films.

The relationship between the surface energies of PI films and the obtained pretilt angles of the LC aligned on the corresponding PI films is shown in Figure 4. The pretilt angles of the LC gradually increase with the lowering of the surface energies of PI films containing DA-3 and DA-4. On the other hand, the behavior of PI films containing DA-1 and DA-2 show the maxima in the pretilt angles with the decrease of the surface energies of PI films.

In the case of our soluble PIs, a clear relationship between surface energies of PI films and pretilt angles of the LC was not obtained as shown in Figure 4. This suggests that the surface energy of PI film may reflect the macroscopic nature of the surface of the PI film or, on the other hand, the pretilt angles of LC on alignment films may be affected by the microscopic nature of the PI film surface.[12]

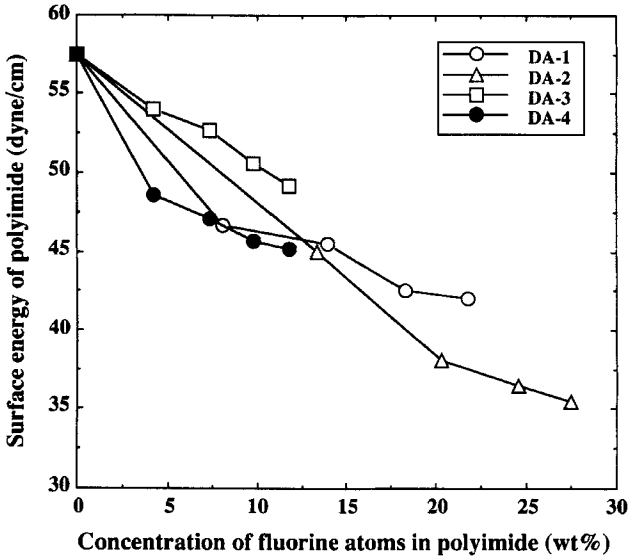

FIGURE 3 Relationship between concentration of fluorine atoms in polyimides and surface energies of polyimide films.

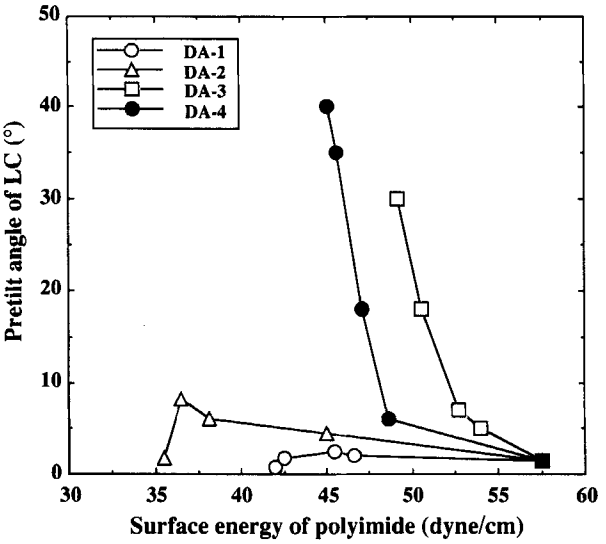

FIGURE 4 Relationship between surface energies of polyimide films and pretilt angles of LC on polyimide films.

Our soluble PIs are classified into two categories. The first one, type (A), is the PI with trifluoromethyl groups in polymer backbones (DA-1, -2). The other, type (B), is the PI with trifluoromethyl groups in lateral benzene rings (DA-3, -4). Schematic diagrams of these PI surfaces,[13] which are drawn based on a computer simulation using MOPAC,[14] are shown in Figure 5. Trifluoromethyl groups in type (A) PIs are directly attached with polymer backbones. On the other hand, trifluoromethyl groups in type (B) PIs are attached with polymer backbones via benzene rings as a linking group between polymer backbones and trifluoromethyl groups. These models may suggest that type (B) PIs have a larger roughness of PI surface than those of type (A) PIs. It is thought that the lateral benzene rings in type (B) PI are the origin of the three-dimensional structure of the PI surface that gives rise to the generation of a high pretilt angle, while this three-dimensional structure has no significant influence on the surface energies of the PI films.

Kobayashi *et al.* discussed the mechanism of the pretilt angle and suggested that asymmetric microscopic triangles of the PI surface formed by rubbing may generate the

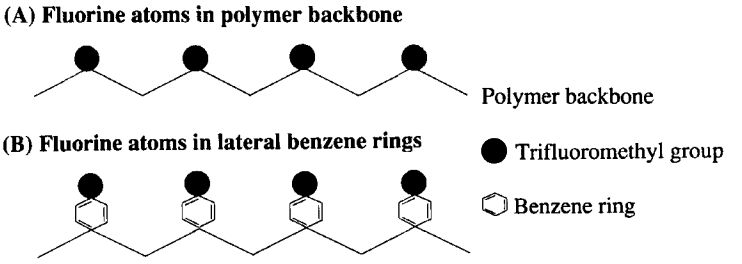

FIGURE 5 Schematic diagrams of polyimide surface.

pretilt angle of the LC.[15] In the case of our soluble PIs, it is expected that the use of the diamines with fluorine atoms in lateral benzene rings causes the micro-surface roughness in the PI film as shown in Figure 5. The pretilt angles of the LCs are probably reflected by the microscopic three-dimensional surface structure of the PI surface. When the roughness of the PI surface is small, the obtained small pretilt angle of the LC may be affected by just the hard zigzag backbone of the helix PI (type (A) PI). On the other hand, when the roughness of the PI surface is large, the obtained high pretilt angle of the LC may be affected by attaching trifluoromethyl groups on the lateral benzene rings which are located at the appropriate position in the helix PI (type (B) PI).

4. CONCLUSION

We have synthesized the novel organic-solvents-soluble PIs containing four types of diamine with trifluoromethyl groups as alignment films for LCDs. These alignment films show the pretilt angles of the LC from 2° up to 40°, depending on their chemical structures. The surface energies of PI films show a linear decrease with the increase of concentration of fluorine atoms in PI films. This phenomenon commonly occurs for four different trifluoromethyl containing diamines. No clear relationship between the surface energies of PI films and the pretilt angles of the LC on PI films has been obtained in these systems. It is shown that the PIs with trifluoromethyl groups in the lateral benzene rings exhibit a linear increase of the pretilt angle with the decrease of surface energy; on the other hand, the PIs with trifluoromethyl groups in the polymer backbone show maximum values for the pretilt angles. These results suggest that the microscopic structures of PIs affect the generation of the pretilt angle at the boundary surface between LCs and alignment films.

References

1. M. Schadt and W. Helfrich, *Appl. Phys. Lett.*, **18**, 127 (1971).
2. A. Miyaji, M. Yamaguchi, A. Toda, H. Mada, and S. Kobayashi, IEEE Tr. ED., **ED-24**, 811 (1977).
3. T. J. Scheffer, J. Nehring, M. Kaufmann, H. Amstutz, D. Heimgartner, and Péglin, SID 85 Digest of Technical Papers, 120 (1985).
4. J. Kanbe, H. Inoue, A. Mizutome, Y. Hanyuu, K. Katagiri, and S. Yoshihara, *Ferroelectrics*, **111**, 3 (1991).
5. M. Koden, T. Shinomiya, N. Itoh, T. Kuratake, T. Taniguchi, A. Awane, and T, Wada, *Jpn. J. Appl. Phys.*, **30**, 1823 (1991).
6. H. Fukuro and S. Kobayashi, *Mol. Cryst. Liq. Cryst.*, **163**, 157 (1988).
7. D. -S. Seo, M. Nishikawa, and S. Kobayashi, *Appl. Phys. Lett.*, **61**, 2392 (1992).
8. M. Nishikawa, Y. Yokoyama, N. Bessho, D. -S. Seo, Y. Iimura, and S. Kobayashi., *Jpn. J. Appl. Phys.*, **33**, L810 (1994).
9. T. J. Scheffer and J. Nehring, *J. Appl. Phys.*, **48**, 1783 (1977).
10. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, **13**, 1714 (1969).
11. M. Gazardand, A. Zann, and J. C. Dubois, *J. Appl. Phys.*, **47**, 1270 (1976).
12. M. Nishikawa, Y. Tsuda, and N. Bessho, *Display and Imaging*, **1**, 217 (1993) (in Japanese).
13. T. Miyamoto, S. Kawamura, M. Nishikawa, Y. Tsuda, T. Natsui, and Y. Ohta, Proceeding of the 19th LC Conference, 106 (1993) (in Japanese).
14. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1988).
15. D. -S. Seo, H. Matsuda, J. Ishizaki, Y. Iimura, and S. Kobayashi, SID 93 Digest of Technical Papers, 953 (1993).