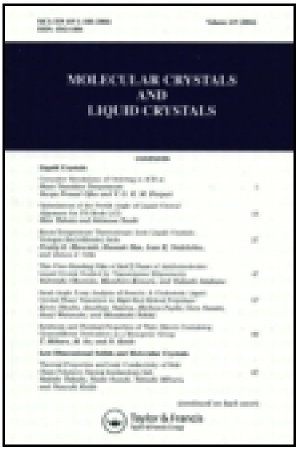

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Pretilt Angle of Nematic Liquid Crystals on Organic Solvent Soluble Polyimide

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Pretilt angles of various nematic liquid crystals (NLCs) aligned on the cured organic solvent soluble polyimide alignment film containing fluorine atoms have been measured. The relationship between obtained pretilt angles and physical properties of NLCs shows that the pretilt angle of NLCs increases linearly with the perpendicular component of permittivity of NLCs. This phenomenon suggests that the lateral substituents in NLC affects the generation of pretilt angles by the anisotropic-excluded-volume effect.

Keywords: Organic solvent soluble polyimide, alignment film, nematic liquid crystal, pretilt angle, perpendicular content of dielectric permittivity, anisotropic-excluded-volume effect

1. INTRODUCTION

The alignment of liquid crystals (NLCs) on alignment films is of great importance in both fundamental physical studies and technological applications.[1,2] Giving a pretilt angle of NLC is necessary to fabricate defect-free NLC cells. Therefore the creation of the pretilt angle is one of the phenomenon which characterize the interaction between NLCs and alignment films at the boundary surface. There is much effort to generate the high pretilt angle of NLCs on the rubbed alignment films.[3–5] However, the mechanism of the surface NLC alignment, in particular, the mechanism of the generation of the pretilt angle, has not been clearly understood yet.

In this research, we used a polyimide (PI) containing fluorine atoms synthesized by the author's group.[5] This PI is useful for NLC molecular orientation, in particular color-active matrix LC displays (LCDs) for its low curing temperature, say 180°C, below which dye-type color filters are stable. This research has been conducted with the aim of knowing how the nature of nematic NLC molecules affect the obtained values of the pretilt angle. The results show that the obtained pretilt angle changes linearly best with the perpendicular component of the dielectric constant ($\varepsilon\perp$) of NLCs. But for the anisotropy of the refractive index (Δn), the anisotropy of the dielectric permittivity ($\Delta\varepsilon$),

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and the parallel component of the dielectric permittivity ($\varepsilon\|$) of NLCs no such good linear dependencies are obtained.

2 EXPERIMENTS

2.1 Synthesis of Organic Solvent Soluble Polyimide

The organic solvent soluble PI was synthesized in terms of the chemical imidization of the precursor polyamic acid. The precursor polyamic acid was prepared from the reaction of 2,3,5-tricarboxycyclopentyl acetic dianhydride (TCA.AH) and p-phenylenediamine (*p*-PDA) and 2,2-bis(4-aminophenyl) hexafluoro propane (HFDA) at the mole fraction of diamines (*p*-PDA/HFDA = 75/25) in γ-butyrolactone at 60°C. The soluble (for simplicity, hereafter we omit the word "organic solvent") PI was obtained by chemical imidization of the corresponding polyamic acid at 120°C with catalysts of pyridine and acetic anhydride. The chemical structure of PI is shown in Figure 1.

2.2 Preparation of NLC Cells

NLC cells were prepared to measure the pretilt angles of NLCs aligned on the orientation films. The alignment films were deposited first with spin-coating of diluted solution of PI with γ-butyrolactone on the substrates and then cured at 180°C for an hour. The thickness of PI film was controlled at 100 nm. The PI films were rubbed with a rubbing machine using a rayon cloth. Sandwich-type cells where inner surfaces were treated by antiparallel rubbing in advance were used to measure pretilt angles of LC. The rubbing strength[6] (RS) was kept always the same, say RS = 300 mm. Nematic NLCs, ZLI-1132, 1565, 2293, 3086, 4338, 4540, 4792, MLC-2001 (E. Merck, Merck Japan), were used to measure the pretilt angles. The physical properties of NLCs (Δn, $\Delta\varepsilon$, $\varepsilon\|$, and $\varepsilon\perp$) are summarized in Table 1.

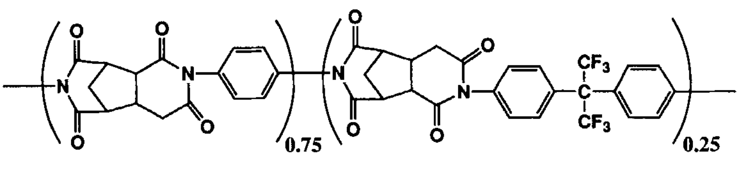

FIGURE 1 Chemical structure of soluble polyimide.

TABLE I
Physical properties of NLCs

NLC	Δn	$\Delta\varepsilon$	$\varepsilon\|$	$\varepsilon\perp$
ZLI-1132	0.14	10.3	15.0	4.7
ZLI-1565	0.13	7.0	10.7	3.7
ZLI-2293	0.13	10.0	14.1	4.1
ZLI-3086	0.11	0.06	2.9	2.8
ZLI-4338	0.11	8.2	13.3	5.1
ZLI-4540	0.14	11.1	15.3	4.2
ZLI-4792	0.09	5.2	8.3	3.1
MLC-2001	0.09	6.8	10.2	3.4

2.3 Measurement Method of Pretilt Angle

For measuring the pretilt angles of aligned NLCs in the cells, we used the crystal rotation method.[7]

3 RESULTS AND DISCUSSION

3.1 Pretilt Angles of NLCs on Soluble Polyimide

The pretilt angle of NLCs aligned on the soluble PI are summarized in Table 2. Pretilt angles of cyano containing NLCs are generally higher than those of fluorine containing NLCs.

The dependence of the pretilt angle of NLC on Δn, $\Delta\varepsilon$ and $\varepsilon\|$ of NLCs on the soluble PI are shown in Figures 2, 3 and 4, respectively. The lines in these figures are drawn

TABLE II
Pretilt angles of NLCs on soluble polyimide

NLC	Pretilt angle (°)
ZLI-1132	3.4
ZLI-1565	2.6
ZLI-2293	2.6
ZLI-3086	1.7
ZLI-4338	3.4
ZLI-4540	3.0
ZLI-4792	2.1
MLC-2001	2.4

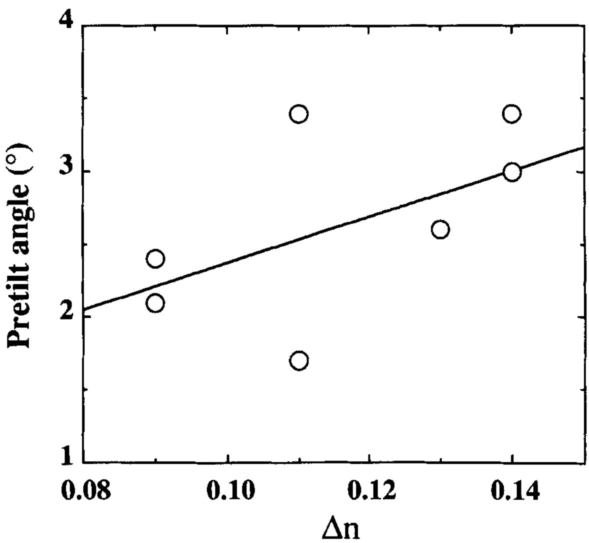

FIGURE 2 Relationship between Δn of NLCs and pretilt angles on organic solvent soluble polyimide.

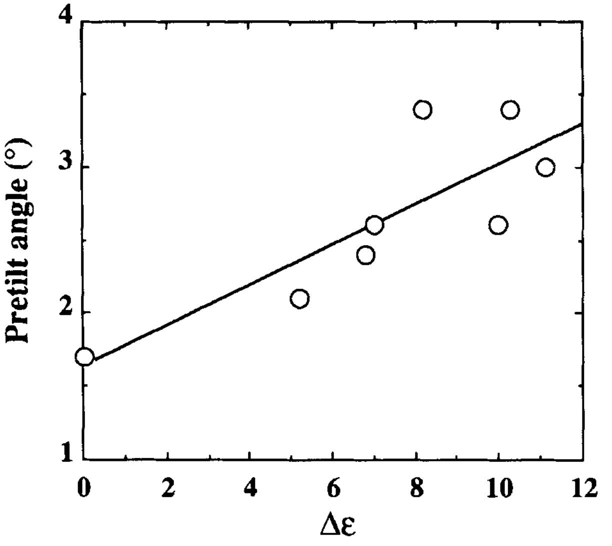

FIGURE 3 Relationship between Δε of NLCs and pretilt angles on organic solvent soluble polyimide.

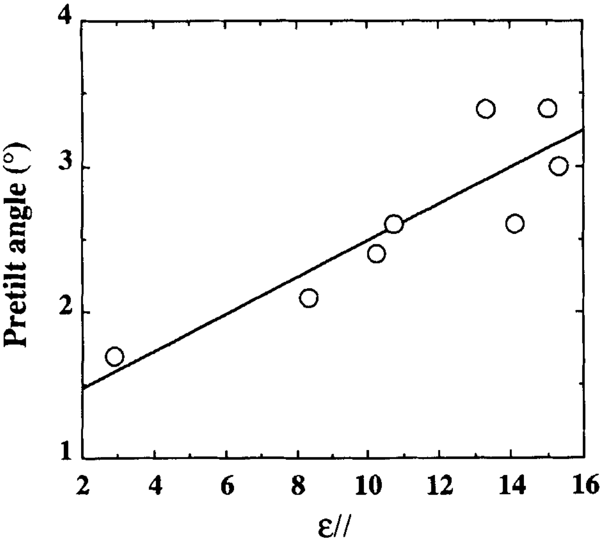

FIGURE 4 Relationship between ε|| of NLCs and pretilt angles on organic solvent soluble polyimide.

from the minimum square method of plots in each figure. The obtained data scatter for Δn, $\Delta\varepsilon$, $\varepsilon\|$ of NLCs are shown in these figures.

Figure 5 shows the relationship between $\varepsilon\perp$ of NLC and the pretilt angle for these for these NLCs. It is clear that the obtained pretilt angle shows a good linear relationship with $\varepsilon\perp$ of NLCs.

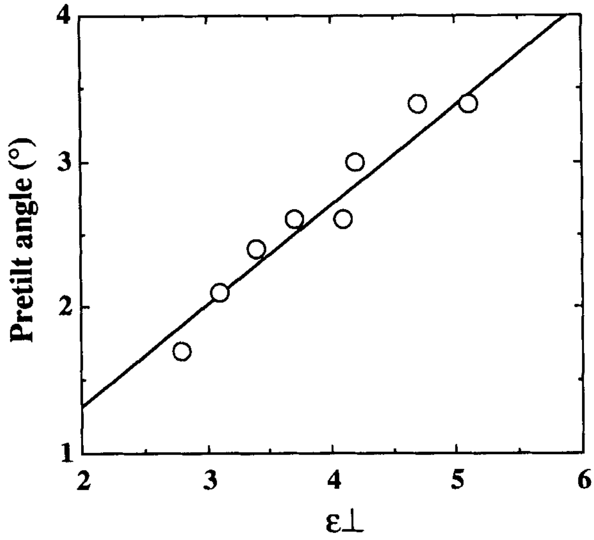

FIGURE 5 Relationship between ε⊥ of NLCs and pretilt angles on organic solvent soluble polyimide.

Several authors reported the experimental results of the pretilt angle. Becker *et al.* reported that the pretilt angle of NLCs increases with Δε of NLCs.[8] They suggested that this effect is due to the interaction between the permanent and the induced electric dipole moments in the NLCs. Nakayama *et al.*, reported that the pretilt angle of NLCs increases with Δn of NLCs.[9] They suggested that this effect is due to π-π* interaction, or dispersion force, between NLCs and alignment films. Sawada *et al.* reported that the pretilt angle of NLCs related with ε|| of NLC.[10] They suggested that this effect is due to the dipole-dipole interaction between NLCs and alignment films.

In the case of our soluble PI, the pretilt angle of NLCs show also a fairly good correlation with ε⊥ of NLCs. The concrete composition of NLCs used in this experiment is unkown. However, the NLC mixtures with large ε⊥ generally contain the NLCs with lateral substituents that give a large ε⊥.[11] Typical chemical structures of NLCs with large ε⊥ are shown in Figure 6. In Figure 6, NLC molecules have the cyano groups in the lateral site of NLC structures. Suggested schematic drawings of the

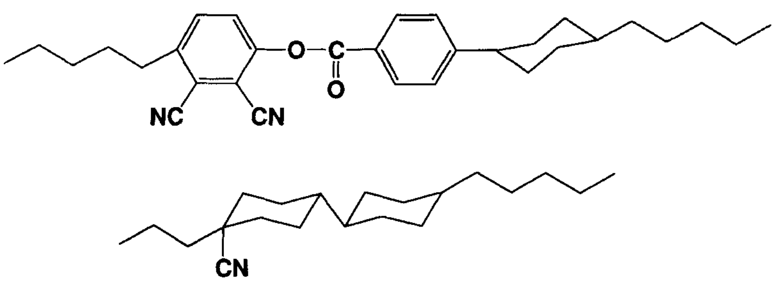

FIGURE 6 Typical chemical structures of NLCs with large ε⊥.

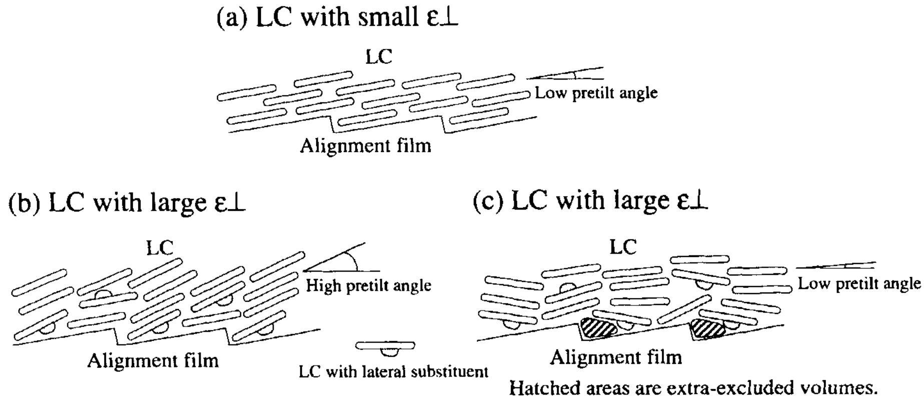

FIGURE 7 Schematic drawings of generation mechanism of pretilt angles on alignment film.

generation mechanism of the pretilt angle are shown in Figure 7. The rubbed PI surface used in this experiment has a zigzag main chain structure[12] as drawn in Figure 7. This drawing was made based on a computer simulation using MOPAC.[13] Seo *et al.*, discussed the generation mechanism of the pretilt angle and suggested that the rubbing gives rise to an unidirectional alignment of NLC and asymmetric triangles of the PI surface formed by rubbing may attribute to the generation of the pretilt angle of NLC.[14] The occurrence of the pretilt angle, in our proposal, is assumed to be attributable to the steric interaction between rod-like NLC molecules having lateral substituents and the triangular PI surface. When the NLC with small $\varepsilon\perp$ is put on the rubbed triangular PI surface, the NLC is probably aligned along the PI surface by the anisotropic-excluded-volume effect[15,16] as shown in Figure 7(a). On the other hand, when the NLC with large $\varepsilon\perp$ is put on the rubbed triangular PI surface, two types of NLC alignment could be proposed as shown in Figure 7 (b) and (c). Shen observed that 8CB molecules are oriented with their hydrophilic cyano group absorbed on the homogeneous alignment from the second harmonic generation experiment.[17] This paper claims that the cyano group of 8CB directly touches the PI surface. Therefore, we suppose that the lateral substituents in the NLCs with large $\varepsilon\perp$ tend to absorb selectively on the PI surface. We compare two possible NLC conformations shown in Figure 7 (b) and (c), respectively. The NLCs favor the conformation (b) rather than (c), since the latter contains extra exclusive spaces as shown by hatching. Therefore, it may be claimed that the conformation (b) gives rise to a higher pretilt angle than that of (a) and (c). These figures may support why NLCs with larger $\varepsilon\perp$ give rise to a high pretilt angle.

4 CONCLUSION

We report the pretilt angle of nematic liquid crystals (NLCs) on soluble polyimide alignment film. The obtained pretilt angles of NLCs increase linearly as the perpendicular component of the dielectric constant of NLCs. This phenomenon suggests that the lateral substituents in NLC affect the generation of the pretilt angle by the anisotropic-excluded-volume effect.

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