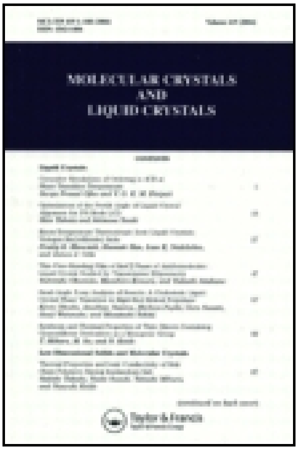

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Generation of Pretilt Angle of Liquid Crystals Aligned on Organic-Solvent-Soluble Polyimide Alignment Films for Active-Matrix TN-LCDs and its Mechanism Caused by the Micro-Surface Structure of Surfaces

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Generation of Pretilt Angle of Liquid Crystals Aligned on Organic-Solvent-Soluble Polyimide Alignment Films for Active-Matrix TN-LCDs and its Mechanism Caused by the Micro-Surface Structure of Surfaces

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The increasing of pretilt angles of liquid crystals (LCs) in active-matrix twisted nematic liquid crystal displays (AM-TN-LCDs) is one of the most important subjects to achieve high contrast and defect-free AM-TN-LCDs. We have developed the new generation method of the pretilt angle by using newly synthesized organic-solvent-soluble polyimides (PIs) containing two types of diamine. These PIs are useful in the production process of AM-TN-LCDs due to their low temperature process, say 180°C. The maximum pretilt angle of 2.8° for an NLC, ZLI-1565, is obtained using the PI containing two types of diamine with a mole fraction of 50/50. This phenomenon can be explained on the basis of the micro-topography of the PI surfaces and, in particular, the obtained pretilt angles may be attributed to the relative bulkiness of diamines used in the PIs.

Keywords: organic-solvent-soluble polyimide, alignment film, nematic liquid crystal, pretilt angle, surface energy, micro-surface structure

1. INTRODUCTION

Currently active-matrix twisted nematic liquid crystal displays (AM-TN-LCDs) are widely utilized for the computer and television screens due to their useful performance featuring good color display capability and high information content. However, there are some problems with the performance and characteristics of AM LCDs. Among them, the preventation of reverse tilt disclination appearing in twisted nematic (TN) LCDs has been one of the most significant problems to produce the LCDs with high contrast ratios. These disclinations are caused by the following factors: (1)

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The fluorinated LCs are useful for AM-TN-LCDs obtaining a good voltage-holding ratio but they generally give rise to a small pretilt angle,[1] (2) The pretilt angle generally decreases at high temperature, as exemplified in projection displays,[2] (3) The effect of the irregular electric field caused by the minuteness of thin-film transistor pixels.[3]

It is known that the reverse tilt disclination is prevented by the increase of the pretilt angle between LC and alignment film.[4] A pretilt angle of higher than 2° is needed for fabricating defect-free and higher contrast AM-TN-LCDs.[5] One approach to generate a high pretilt angle is to use appropriately rubbed alkyl-branched polyimide (PI) films.[6,7] This technology is being widely used for producing defect-free supertwisted nematic (STN) LCDs. However, an experiment conducted by the authors' group shows that the pretilt angles generated by using alkyl-branched PI films are shown to be largely influenced by the rubbing strength when the baking temperature is below 200 °C. This temperature is compatible with the process temperature of AM-TN-LCDs such as color filters.

In a previous paper[8] we reported that an organic-solvent-soluble PI, which is synthesized by ourselves, can be cured at a temperature below 200°C. However, the obtained pretilt angle using this PI film is about 1 degree for optimum rubbing strength. It is necessary to synthesize an organic-solvent-soluble PI which is capable of generating a high pretilt angle to prevent the reverse tilt disclination of TN-LCDs.

In this paper, we report newly synthesized organic-solvent-soluble PIs, containing two types of diamine, which are capable of producing the pretilt angle higher than 2°. The dependence of the LC pretilt angles and the mechanism of the generation of pretilt angles are also discussed.

2. EXPERIMENTS

2.1 Synthesis of Organic-Solvent-Soluble PIs

The novel PIs were synthesized from the chemical imidization of the precursor polyamic acids. This method is basically the same as that reported in a previous paper except for the moieties used.[8] The precursor polyamic acids were prepared from the reaction of 2,3,5-tricarboxycyclopentyl acetic dianhydride (TCA·AH), 2,2-bis(4-aminophenyl) hexafluoropropane (HFDA), and four types of diamine in γ-butyrolactone at 60°C as shown in Figure 1. The novel soluble (for simplicity, here after we omit the word "organic solvent") PIs were obtained by chemical imidization of the corresponding polyamic acid at 120°C in the presence of pyridine and acetic anhydride.

2.2 Preparation of LC Cells

LC cells were fabricated to measure the pretilt angle of the LC aligned on the orientation films. The orientation films were deposited first by spin-coating of diluted solutions of PIs with γ-butyrolactone and then cured at 180°C for an hour. The thicknesses of polyimide films were kept at 100 nm. The PI films were rubbed by a rubbing machine using rayon cloth. Pairs of substrates were assembled in an

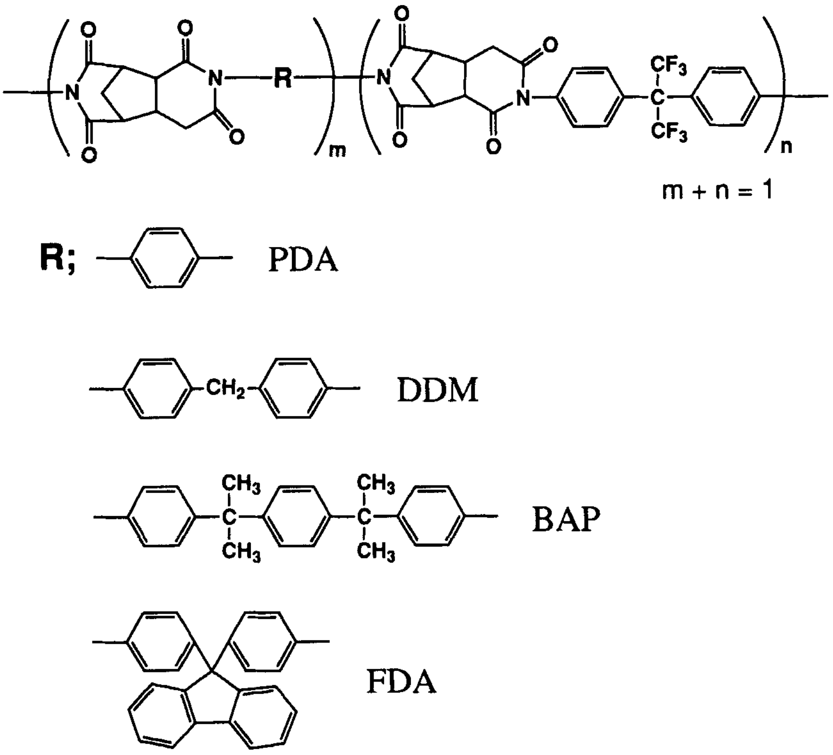


FIGURE 1 Chemical structure of soluble polyimides.

antiparallel configuration. The NLC used in the measurements was ZLI-1565 (E. Merck).

2.3 Measurement Method of Pretilt Angle and Surface Energy

For measuring the pretilt angle of aligned LCs in the cell, we adopted the crystal rotation method.[9] The surface energy of the PI films was measured with an instrument to measure the contact angles of water and methylene iodide on PI films.[10]

3. RESULTS AND DISCUSSION

3.1 Pretilt Angles of LCs on Soluble PIs

The relationship between the mole fraction of diamine (HFDA) in soluble PIs concerning the PDA/HFDA system and the pretilt angles of LCs is shown in Figure 2. The pretilt angle of an LC gradually increases with the mole fraction of HFDA in the region of lower than 50 mole%. On the other hand, the pretilt angle of an LC gradually

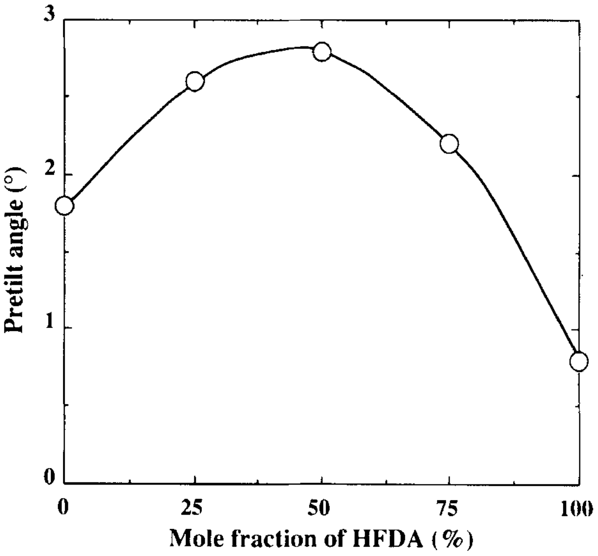


FIGURE 2 Relationship between mole fraction of HFDA in soluble polyimides (PDA/HFDA) and pretilt angles of LCs.

decreases with the mole fraction of HFDA in the region of higher than 50 mole%. The maximum pretilt angle of 2.8 degrees was obtained at the mole fraction of diamines (PDA/HFDA = 50/50). These results suggest that the difference in the PI structure largely affects the pretilt angles of LCs.

Dubois *et al.*, observed the molecular alignments of six types of LCs with different surface energies (γ_{LC}) on five kinds of polymeric material with different surface energy (γ_{AL}) of 22–44 dyne/cm.[11] In this report, when γ_{AL} was very low compared with γ_{LC}, the perpendicular alignment of LCs was effectively induced. Conversely, when γ_{AL} was very large, the parallel alignment of LCs was observed. This is generally known as the Friedel-Creagh-Kmetz (FCK) rule.[12]

The surface energies of PI films concerning the PDA/HFDA system were measured to elucidate the generation mechanism of the pretilt angles of LCs on PI films. The relationship between the surface energies of PI films and the pretilt angles of LCs on corresponding PIs is shown in Figure 3. The surface energies of PIs gradually decrease with the increase of the mole fraction of HFDA. This phenomenon is caused by the increase of fluorine atoms, which tend to lower the surface energy in PIs. However, in the case of our soluble PIs, no clear relationship between the surface energies of PI films and the pretilt angles of LCs was obtained as shown in Figure 3. This suggests that the surface energy of PI film may reflect the macroscopic condition of PI film, on the other hand, the pretilt angle of an LC on alignment film may be affected by the microscopic structure of the PI surface.

Next, we will discuss the steric structure of the diamines used in the soluble PIs. Three other types of soluble PI were synthesized using three other types of diamine, DDM, BAP and FDA, with different bulkiness as shown in Figure 4, instead of PDA. It

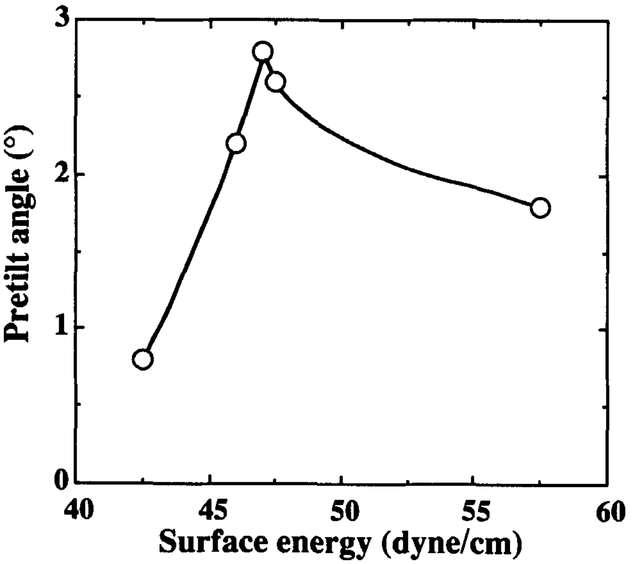
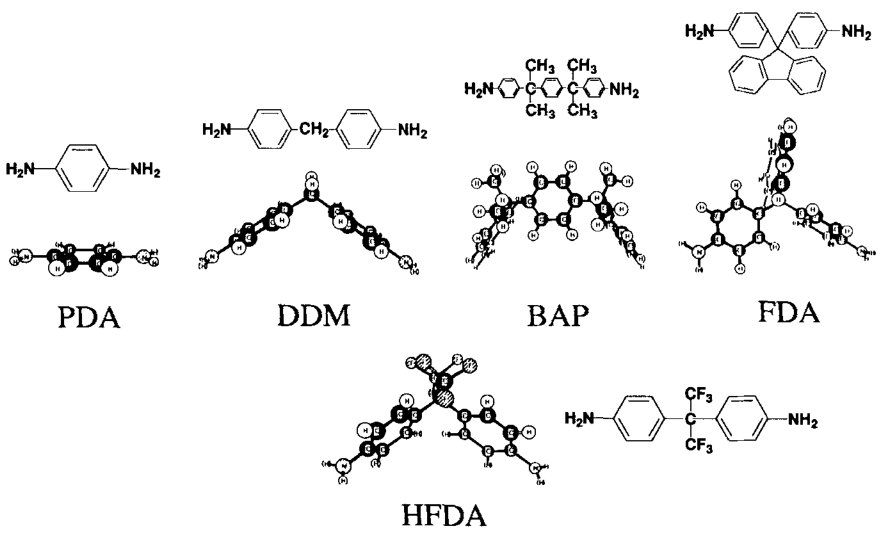


FIGURE 3 Relationship between surface energy of soluble polyimide films (PDA/HFDA) and pretilt angles of LCs.



PDA DDM BAP FDA

HFDA

FIGURE 4 Chemical and steric structure of diamines used in soluble polyimides.

is clear that PDA has the planar benzene ring. On the other hand, HFDA has the tilted benzene ring and bulky trifluoromethyl group with a large van der Waals radius. From the point of view of the steric structure of the diamines shown in Figure 4, the order of bulkiness of diamines used in soluble PIs is

HFDA > FDA > BAP > DDM > PDA

The pretilt angles of other soluble PIs were measured in comparison with those of the PI films containing PDA and HFDA moieties. The obtained pretilt angles of LCs on PIs are shown in Figure 5. The pretilt angles of LCs largely decrease by using other types of diamines (DDM, BAP and FDA). It is clear that the order of bulkiness of the diamines used in PIs corresponds to the decrease of the pretilt angles of the LC. In our experiments, the high pretilt angles are obtained by using both of the plane diamine (PDA) and the bulky trifluoromethyl group containing diamine (HFDA) in the PI.

Seo *et al.* discussed the mechanism of the pretilt angle and suggested that microscopic asymmetric triangles formed on the PI by rubbing may contributed to generating the pretilt angle of an LC.[13] In the case of our soluble PIs, it is expected that the use of the plane diamine and the bulky trifluoromethyl group containing diamine causes the micro-surface roughness in the polyimide film as shown in Figure 6(a). On the other hand, the use of the bulky diamine and bulky trifluoromethyl group containing diamine forms a rather flat surface of PI film as shown in Figure 6(b), The pretilt angle of an LC is probably reflected in the three-dimensional surface structure of the PI surface. From these experimental results, we claim that a useful way to generate a high pretilt angle is first to prepare a hard PI having a zigzag main chain structure[14] by introducing appropriate moieties, and second to perform rubbing to produce microscopic surface structure featuring an assembly of asymmetric triangles, whose dimension is almost comparable to that of LC molecules. The steric interaction between these asymmetric triangles and LC molecules may be the dominant mechanism of the angles.

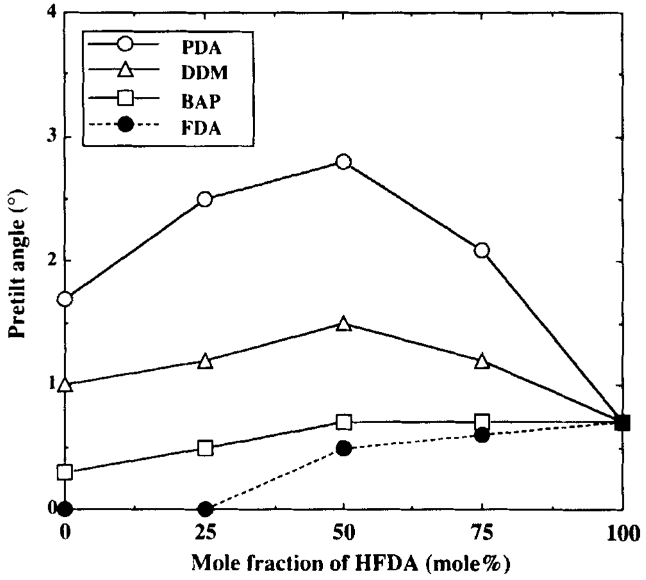
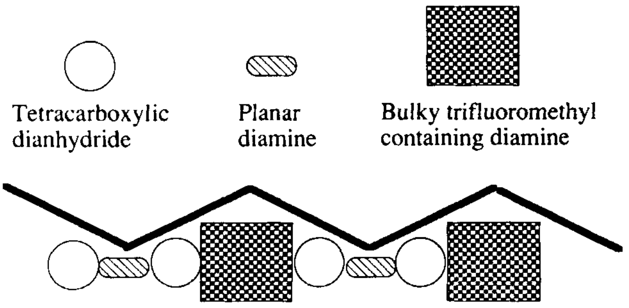
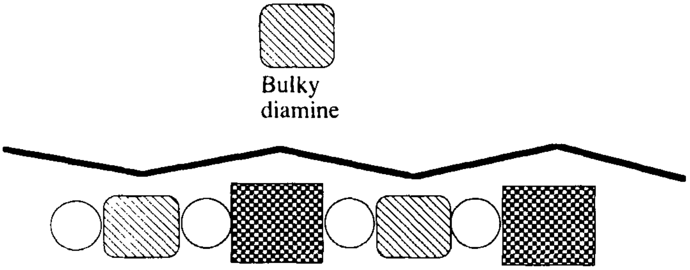


FIGURE 5 Relationship between mole fraction of HFDA in soluble polyimides and pretilt angles of LCs in the case of varying the bulkiness of diamine used in polyimides.



(a) Surface micro-topography of polyimide from planar diamine and bulky trifluoromethyl diamine



(b) Surface micro-topography of polyimide from bulky diamine and bulky trifluoromethyl containing diamine

FIGURE 6 Schematic drawing of surface models of soluble polyimides.

4. CONCLUSION

We developed the new generation method of the pretilt angle of an LC by using organic-solvent-soluble PIs containing the planar diamine and the bulky diamine. The maximum pretilt angle of 2.8° was obtained from the PI containing two types of diamine with the mole fraction of 50/50. The obtained pretilt angle is probably caused by the micro-roughness of the PI surface, featuring the assembly of asymmetric triangles formed by rubbing.

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