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Alkylene Polyimides for Aligning Nematic Liquid Crystals: Anomalous Odd-Even Effect in Tilt Bias Angles as a Function of Chain Length of Alkylenes

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Measurements of tilt bias angles of a nematic liquid crystal were carried out, by using several alkylene polyimides synthesized from 3,3′,4,4′-biphenyltetracarboxylic dianhydrides and diamines with different chain lengths as alignment layers. The tilt bias angle dependence on the alkylene chain length of polyimides shows an anomalous odd-even effect. Small tilt bias angles, less than one degree, were observed with odd-number alkylene chain lengths. Relatively high tilt bias angles, however, were observed with even-number lengths.

We have made an attempt to explain this effect from X-ray diffraction and scanning electron microscope measurements and molecular mechanics calculations of the polyimides with alkylene chain. As a result, this odd-even effect of the tilt bias angle is due to the difference of surface structures between alkylene polyimides with odd alkylene lengths and those with even ones.

INTRODUCTION

Alignment control of liquid crystal molecules is one of the most important key techniques for producing liquid crystal displays. Particularly, precise control of the tilt bias angle, defined as the angle made between the long axis of the liquid crystal molecules and the plane of the surface, is strongly required with super-twisted nematic liquid crystal displays (STN-LCDs). It is very important to realize chemical structure effect on the tilt bias angle in order to reveal the mechanism for the generation of the tilt bias. There are several well-known relationships between the tilt bias angle and the chemical structure of the alignment layer. Chemical structures of some polymers which induce relatively high tilt bias angles have been reported.[1–5] For instance, alkyl-branched polyimides and introduction of fluoro groups as substituents lead to higher tilt bias angles.[6,7] But the number of polyimides for which the relationship between chemical structures and tilt bias angles has been discussed is quite limited.

In this paper, we report experimental results for the relationship between alkylene length of polyimides and tilt bias angles. Then we propose a model to explain the mechanisms of liquid crystal tilting orientation.

EXPERIMENTAL

Alkylene polyamic acids were synthesized by the reaction between 3,3′,4,4′-biphenyltetracarboxylic dianhydride and appropriate diamines with different numbers of methylene groups. The numbers were varied from five to twelve, as shown in Figure 1. These polyamic acids were coated onto solid plates with indium tin oxide (ITO). Alkylene polyimide films having a thickness of about 500 Å were obtained by heat treatments of polyamic acids on the solid plates at 200°C for 30 minutes. Film thicknesses was controlled by rotation speed of solid plates when polyamic acids were coated. The rubbing process was carried out under the following conditions: cylinder rotation speed, 750 rpm, cylinder diameter, 50 mmϕ; moving speed of solid plate, 240 mm/min. Two solid plates were set in the opposite direction to obtain a uniformly tilted liquid crystal orientation. The gap between them was controlled to about 25 μm. The liquid crystal used in these experiments was ZLI-1132 (from Merck) which includes cyanophenylcyclohexane derivatives.

Tilt bias angles were measured by the crystal rotation method.[8] An incident angle dependence on transmittance leads to an average angle between the long axis of the liquid crystal molecules and the substrate surface.

A scanning electron microscope (Hitachi S-650; 20 kv) was used to observe the polyimide film surfaces. The sample thicknesses were set to 1–2 μm. X-ray diffraction measurements were performed with a Rigaku RU-200 (40 kV, 150 mA).

RESULTS AND DISCUSSION

Figure 2 shows the tilt bias angle dependence on the alkylene chain length of polyimides. Tilt bias angles produced by a different number of methylene groups of alkylene polyimides were found to vary systematically. This series of tilt bias angle dependence on the alkylene length showed a clear odd-even effect. Small tilt bias angles, less than one degree, were obtained with odd numbers of methylene groups. Relatively higher tilt bias angles, however, were observed with even numbers of methylene groups. A similar odd-even effect has been seen in cone angles which correspond to apparent tilt angles of chiral smectic liquid crystal molecules.[9]

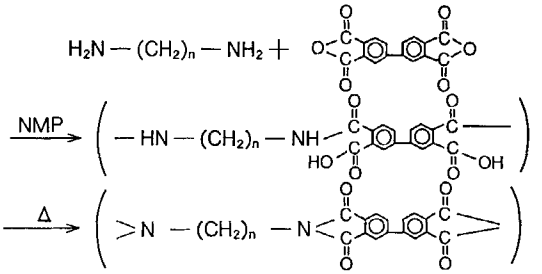

FIGURE 1 Procedure for synthesis of alkylene polyimides.

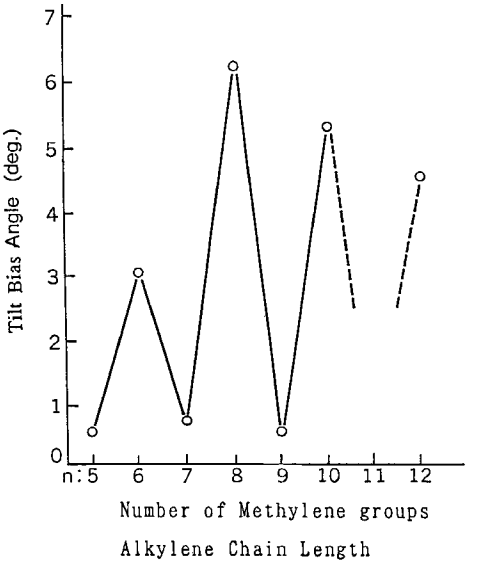

FIGURE 2 Tilt bias angle dependence on alkylene chain length.

But it is very interesting that not only cone angles of chiral smectic liquid crystals, but also tilt bias angles of nematic liquid crystals show the odd-even effect on alignment layer structures.

Although a mechanism for the origin of the tilt bias is not clear so far, the conformational structures of alkylene polyimides near the surface and interaction of liquid crystals with the surface are considered to be essential factors. Original dipole-dipole interactions between liquid crystals and polyimide molecules are not thought to be so different, because the difference in polyimide structures is only the length of their alkylene group chain. Therefore, the difference in steric interaction due to conformational changes with the number of methylene groups is considered to play a significant role in the odd-even effect of tilt bias angles.

First, in order to elucidate the difference of alignment layer structures, these surfaces were observed by SEM and by X-ray diffraction measurements. Figures 3 and 4 show the SEM photographs and the results of X-ray diffraction measurements, respectively. These two techniques reveal that polyimides with even numbers of methylene groups built up crystallized films, and that polyimides with odd numbers form amorphous films.

Second, molecular mechanics calculations were carried out, supposing the polyimides were crystalline. The results of these calculations indicate the stable conformational structures of alkylene polyimide chains with odd and even numbers of methylene groups, as shown in Figure 5. Those polyimide chains consist of rigid parts corresponding to imide cycles and of flexible parts corresponding to alkylene groups. The tilt bias angles are induced by the surface shape of the polymer layer.[10] This surface effect is considered to depend on conformational differences of polymer chains. According to our models, the conformation of polyimides with odd numbers of methylene groups is symmetric against vertical direction to the sub-

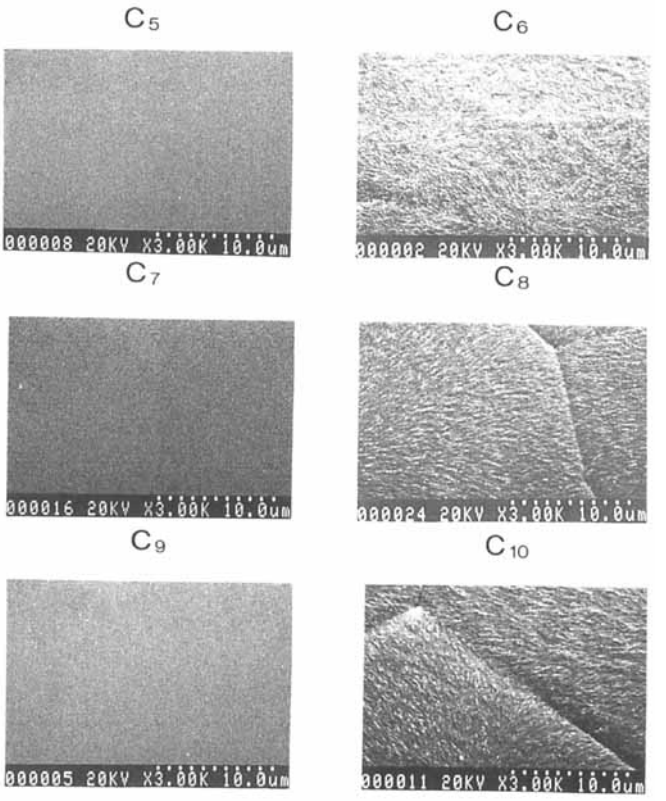

FIGURE 3 SEM photographs of alkylene polyimide surfaces with odd and even numbers of methylene groups.

strate. On the other hand, the counterpart with even numbers of methylene groups is antisymmetric. The symmetric surface shape is considered to produce an average zero-degree tilt bias angle, while the antisymmetric one is expected to give a relatively high tilt bias angle.

Actually X-ray data show alignment layers with even numbers of methylene groups form crystal layers. Therefore, the results of molecular mechanics calculations can support our model depicted in Figure 5 (b). On the other hand, the conformational model of the odd-number homologues, however, cannot apply to the results of low pretilt angles, because X-ray data show the odd-number homologues form amorphous layers. But the tilt bias angle on the amorphous surface can be averaged due to the amorphous structure.

These results show the presence of the structural difference between alignment layers with odd numbers and those with even numbers. This fact implies the difference of reorientation by rubbing process between alignment layers with odd numbers and even-number homologous. This difference might be caused by the difference of activation energy for reorientation or of the stability between the crystalline of odd-number and even-number homologous. The mechanism of this relation between the crystallinity and alkylene chain length has not been clarified. This is the future problem to be solved.

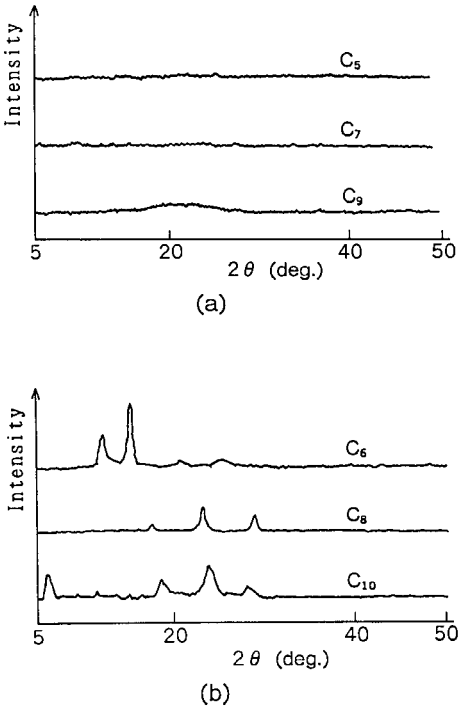

FIGURE 4 The results of X-ray diffraction measurements of alkylene polyimides with odd and even numbers of methylene groups.

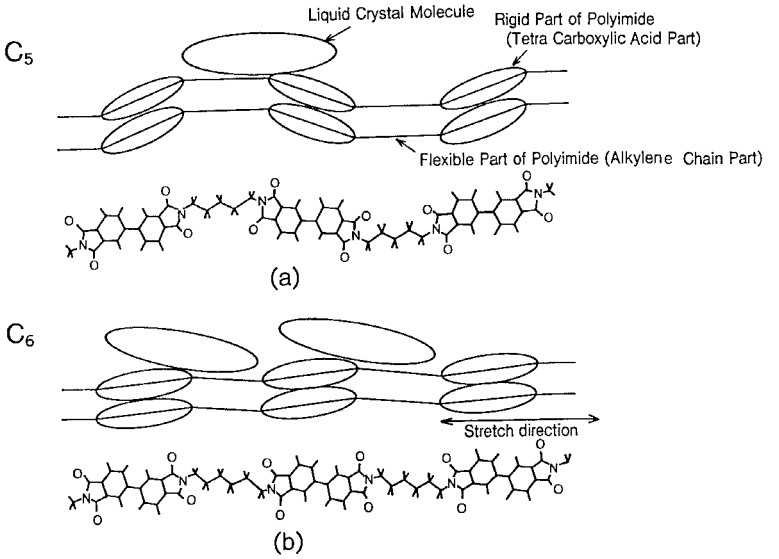

FIGURE 5 Conformational model for alkylene polyimide molecules with odd (C_5) and even (C_6) numbers of methylene groups.

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