Pretilt angle for BTDA, PMDA and CPDA series polyimides with various side chain lengths

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Polyamic acid precursors were prepared by mixing dianhydride of 3,3′,4,4′-benzophenone-tetracarboxylic dianhydride (BTDA), 1,2,3,4-benzene-tetracarboxylic dianhydride (pyrromellitic dianhydride PMDA), *cis*-1,2,3,4-cyclopentane-tetracarboxylic dianhydride (CPDA), the diamine (alkyl 3,5-diaminobenzoate) with side chain, and 4,4′-oxydianiline (ODA) without side chain. Copolyimide films with various side chain lengths were prepared by thermal imidization of polyamic acid precursors. The roughness of rubbed polyimide surface increased with increase in the side chain length. The pretilt angle for the BTDA and PMDA series polyimide (PI) increased exponentially with increase in side chain length. Various pretilt angles were obtained on the synthesized polyimides. In the case of CPDA series PI, the pretilt angle was nearly constant at 0° until the alkyl side chain length reached 12 (C12) and then increased markedly at C18. Models of pretilt angle generation were tested.

1. Introduction

Liquid crystal displays (LCDs) are widely used because of their portability, flatness, low voltage requirement, and low power consumption. For an optimal electro-optic LCD performance, it is essential to obtain a uniform alignment of the LC molecules. Various methods for liquid crystal alignment, such as oblique evaporating [1], rubbing [2–4] and non-rubbing methods [5–7] have been reported over many years. Rubbing is widely used in LCD production because of its high productivity. Pretilt angle is an important parameter in the display mode for wide viewing angle (such as the multi-domain TN effect), vertically aligned nematic LCDs, SSFLCDs, the in-plane switching (IPS) mode and others [8–10]. Various technologies for the generation of pretilt angle have therefore been reported [11–13]. In a previous paper [14], we reported on the pretilt angle in relation to rubbing strength on various commercial polyimides.

In this study, the characteristics of alignment layer and LC alignment have been studied by synthesizing various copolyimides. Polyamic acid precursors were prepared by mixing BTDA, PMDA and CPDA, the alkyl 3,5-diamino-benzoate with side chain, and 4,4′-oxydianiline (ODA) without side chain, in specified molar ratio. Finally, 12 kinds of a new copolymer with BTDA, PMDA and CPDA with various side chain lengths were synthesized by the thermal imidization of polyamic acid precursors.

The characteristics of alignment layer and LC alignment by rubbing, in terms of side chain length and nature of component anhydrides were examined.

## 2. Experimental
2.1. *Synthesis*

For the synthesis of alignment materials, the dianhydrides BTDA, PMDA, and CPDA were obtained from Aldrich and used after recrystallization from acetic anhydride. The reagents for the diamine were all obtained from Aldrich: 4,4′-oxydianiline (ODA) was recrystallized in tetrahydrofuran (THF), pyridine, 3,5-dinitrobenzoic acid, methanol, hexanol, dodecanol, and octadecanol were used as received.

As shown in figure 1, four kinds of alkyl 3,5-diamino-benzoate monomers were synthesized by catalytic hydro-genation of the alkyl 3,5-dinitrobenzoate, which had been obtained by esterification of 3,5-dinitrobenzoyl chloride with alcohols having 1, 6, 12 and 18 carbon atoms. The 12 kinds of polyamic acid synthesized from BTDA, PMDA, CPDA series dianhydride/diamine with side chain/ODA, in the mole ratio 2:1:1, are shown in figure 2. Polyimide films were prepared by thermal imidization at 260°C for 1.5 h.

2.1.1. *Methyl 3,5-dinitrobenzoate*

3,5-Dinitrobenzoyl chloride (10 g 0.043 mol) was dissolved in pyridine (60 ml) and stirred at 60°C for 30 min; methanol (1.39 g 0.043 mol) was then added dropwise. The reaction solution was poured into ice-water; the

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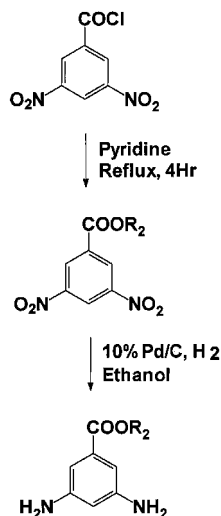
R₂: CH_3, C_6H_{13}, $C_{12}H_{25}$, $C_{18}H_{37}$

Figure 1.   Scheme for synthesis of diamines with side chain.
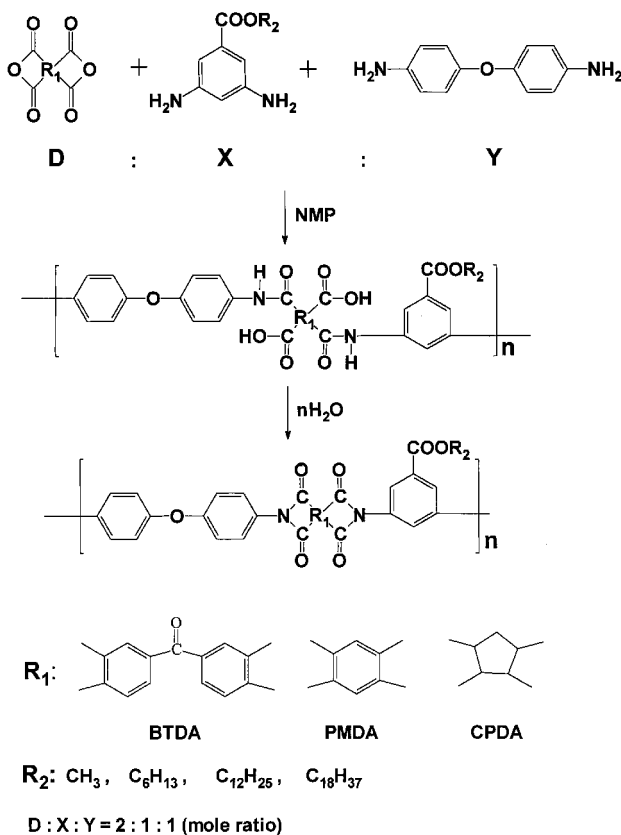

D : X : Y = 2 : 1 : 1 (mole ratio)

Figure 2.   Scheme for synthesis of the copolyimides.

resulting solid was filtered, washed with cold water until the smell of pyridine disappeared, and dried. A white solid (8.85 g 90%) was obtained by recrystallization from ethanol.

Similar methods were used to obtain the compounds hexyl 3,5-dinitrobenzoate (yellow solid, 85%), dodecyl 3,5-dinitrobenzoate (yellow solid, 89%), and octadecyl 3,5-dinitrobenzoate (white solid, 89%).

2.1.2. *Methyl 3,5-diaminobenzoate*

Methyl 3,5-dinitrobenzoate was dissolved in methanol with 10% Pd/C in high pressure equipment. The mixture was stirred at 25°C for 2 h, starting with $10 \, kg \, cm^{-2}$ pressure of hydrogen gas. When the (falling) pressure remained constant, the reaction was ended. A brown solid was obtained after filtering off the Pd/C and removing solvent.

Similar methods were used to obtain hexyl 3,5-diaminobenzoate, dodecyl 3,5-diaminobenzoate, and octadecyl 3,5-diaminobenzoate.

2.1.3. *Synthesis of copolyimide*
(dianhydride : diamine : ODA = 2 : 1 : 1 mole ratio)

PMDA was dissolved in NMP under nitrogen in a 50 ml 3-neck rounded bottom flask fitted with magnetic stirrer; a solution of diamine and ODA in NMP, was then added dropwise. The dianhydride : diamine : ODA mole ratio was 2 : 1 : 1. The polymerization of polyamic acid containing 10 wt % solids was run for 24 h and the polyamic acid was stored at 0°C ∼ 10°C. 12 types of copolymer were synthesized with BTDA, PMDA, and CPDA as dianhydrides, diamines with normal alkyl chains of 1,6,12,18 carbons, and ODA. These were:

2BTDA-DA1-ODA, 2BTDA-DA6-ODA,
2BTDA-DA12-ODA, 2BTDA-DA18-ODA
2PMDA-DA1-ODA, 2PMDA-DA6-ODA,
2PMDA-DA12-ODA, 2PMDA-DA18-ODA
2CPDA-DA1-ODA, 2CPDA-DA6-ODA,
2CPDA-DA12-ODA, 2CPDA-DA18-ODA.

2.2.   *Processing and measurements*

The identification of reaction products and their structures was by means of F254 TLC plates from Merck, Hitachi R-24B (60 MHz) ¹H NMR, Hewlett Packard series 6890GC/MSD and IFS-66 (Bruker) FTIR.

Imidization was followed by FTIR. The thermal stability of polyimides was measured using Perkin-Elmer 7 series thermogravimetric analysis (TGA). Soluble polyimide was dried under vacuum at 100°C for 4 h and analysed by TGA with a heating rate of $10°C \, min^{-1}$ from 100°C to 500°C. The standard of thermal stability was the temperature (T_0) at which thermal decomposition started and the temperature (T_{10}) corresponding to 10% weight loss.

Rubbing of the copolyimide films was done with nylon velvet [15]. Rubbing conditions include the number of the revolution per minute (500 rpm), the moving speed of the roller (32 mm s^{-1}), the radius of the roller (67 mm), and the depth of rubbing (0.3 mm). For this work, the synthesized copolyimide films were spin coated from dilute solution (4–6 wt%) onto indium tin oxide coated glass, then precured for 0.5 h at 100°C (to evaporate the solvent), and cured at 260°C for 1.5 h. The approximate thickness of the resulting polyimide films was 800 Å ± 50 Å.

The image of the rubbed polyimide surfaces was measured using atomic force microscopy (AFM) using a Scientific Instrument type 352. Standard Si$_3$N$_4$ AFM tips, with a force constant of 0.0032 N m^{-1} were used in the commercial AFM. The force applied for all images was about 5 nN and the scanning frequency was kept in the interval 0.5–1 Hz. The images were tilt corrected and low-pass filtered.

For the measurement of alignment characteristics of nematic liquid crystals, the cell was assembled by controlling the rubbing direction to anti-parallel, and then injecting the LCs. The LC alignment condition was observed using a polarizing microscope BH-2 of Olympus Co. under crossed nicols with ×100 magnifications. Pretilt angles of the nematic liquid crystal (MJ951160, E. Merck) were measured with a TBA101 instrument (Autronic).

3. Result and discussion
3.1. *FTIR evaluation of copolyimide*
The imidization ratio of the synthesized polyamic acid (PAA) was monitored from the IR spectra of PMDA series PI (2PMDA-DA1-ODA) cured at 170°C, 200°C, 230°C and 260°C, as shown in figure 3. The broad O−H stretching at 2400–3600 cm^{-1} and the symmetrical C=O
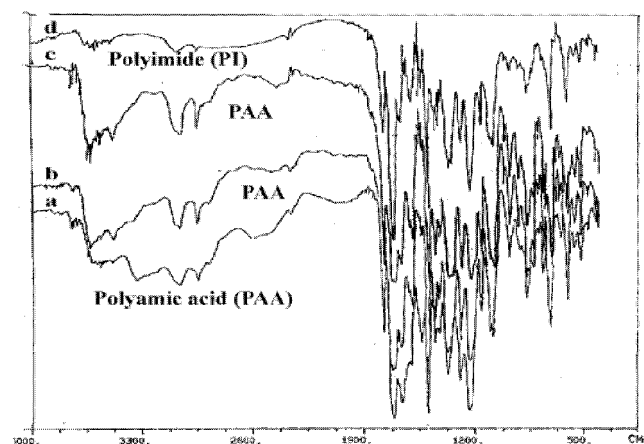
of polyamic acid at 1720 cm^{-1} decreased as the curing temperature increased. On the other hand, C=O asymmetric stretching at 1780 cm^{-1} and C−N stretching of polyimide at 1380–1385 cm^{-1} increased systematically with the increase of temperature. As shown in figure 3, we supposed that imidization was complete because O−H stretching corresponding to the acid peak of polyamic acid almost disappeared in a 260°C-cured PI film [16].

3.2. *AFM image of rubbed polyimide surfaces*
The AFM images of PMDA series polyimide surfaces are shown in figure 4. Polymer clusters of various size on the unrubbed polyimide surface were very irregularly distributed (*a*), while the polymer clusters of the rubbed polyimide surface were aligned along the rubbing direction (*b*). We suppose that local friction and simultaneous shearing forces cause the formation and alignment of cluster chains, as proposed by Geary *et al.* [17] and Kim *et al.* [3]; this leads to microgrooves. The surface roughness increased with the increase of side chain length. This may be due to the size and structure differences in the polyimide monomers. The size of polymer clusters tended to be larger as the side chain lengthened. Clusters involving short side chains were generally aligned along the rubbing direction, while as the side chain length increased the clusters aligned partly along the rubbing direction. This may be due to the steric hindrance effect of the PI side chain.

3.3. *Alignment of LCs and pretilt angle*
The alignment states of LCs on rubbed PMDA series copolyimide films were generally good, regardless of the side chain length (figure 5). The alignment states of LCs on BTDA and CPDA series copolyimide films were also good, regardless of the side chain length. As shown in figure 6, the pretilt angle increased exponentially, regardless of the type of polyimide, as the side chain length increased, with the rubbing depth fixed at 0.3 mm. However, in the case of CPDA series PI, the pretilt angle was nearly constant at 0° until the alkyl side chain length reached 12 (C12, dodecyl) and then increased markedly at C18. Here, the pretilt angles on BTDA and PMDA series PI were higer than on CPDA series PI. It seems that π-electrons of the benzene ring in BTDA and PMDA series PI occupied a larger volume than those in CPDA series PI, contributing to force out LC molecules (non-polar part). Furthermore, all three types showed a sudden increase of pretilt angle at C18 (octadecyl) and it is expected that there might be a certain critical point at 12 carbon atoms length.

From consideration of AFM images of the rubbed polyimide layers, models of the influence of PI clusters on NLC molecule alignment are shown in figure 7.
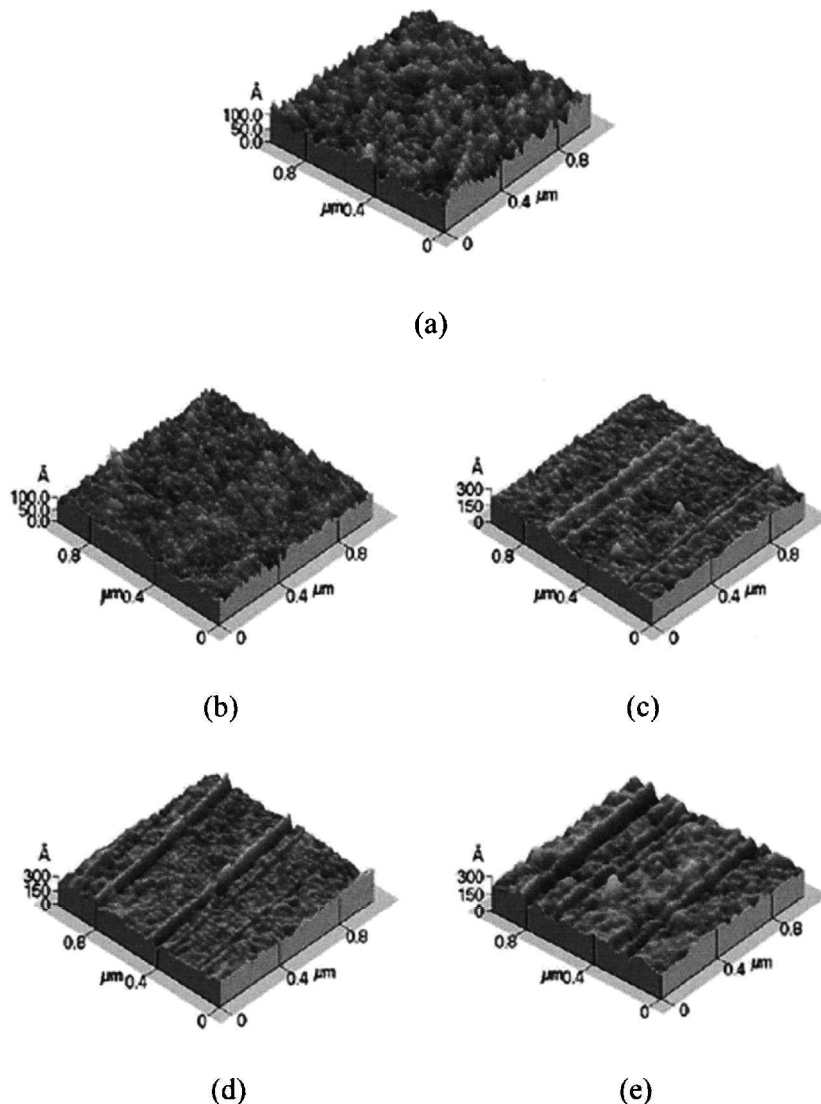

Figure 3. FTIR spectra as a function of curing temperature of the polyamic acid (2PMDA-DA1-ODA). (*a*) 170°C, (*b*) 200°C, (*c*) 230°C, (*d*) 260°C.

Figure 4. AFM image of the rubbed PMDA series copolyimide film. (*a*) Unrubbed polyimide film (2PMDA-DA6-ODA); (*b*) 1C, (*c*) 6C, (*d*) 12C, (*e*) 18C side chain length of PMDA series PI. Rubbing depth = 0.3 mm.

In the case of short side chain length, their resistance becomes weak during rubbing and cluster elongation arises easily. Therefore, LC molecules may aligned flat along the cluster chain with a small curve, figure 7 (*a*). In the case of long side chains, on the other hand, elongation does not arise easily because of strong resistance to rubbing. Therefore, LC molecules may align slantwise along the cluster chain with a large curve, figure 7 (*b*). We therefore assume that the pretilt angle in (*b*) is higher than that in (*a*), as shown in figure 7.

An attractive model for the generation of pretilt angle is presented in figure 8. In this case, only structural considerations of the lengthening polymer chains are made. We consider the side chain length as it increases from 1 to 18. The side chain interval within (2:1:1) copolyimides is 26–36 Å. We suppose that LC molecules (the length of the long axis of the LC molecules is 17 Å, the short axis is 5 Å) enter into the interval in two ways: one in which a LC molecule enters horizontally within the 26–36 Å of side chain interval; the other in which three or four molecules enter side by side between the side chains. In the latter case, if the side chain length were smaller than the length of LC molecules, the LC molecules would disperse because the side chains would not support them. The pretilt angle becomes zero or smaller at this point, figure 8 (*a*). If the side chain length is similar to the length of the LC molecules, they would be angled together rather than lying parallel to the polymer chain. The pretilt angle therefore becomes larger, figure 8 (*b, c*). However, if the side chain exceeds critical length, the LC molecules would be at a greater angle because the side chains can support more molecules.
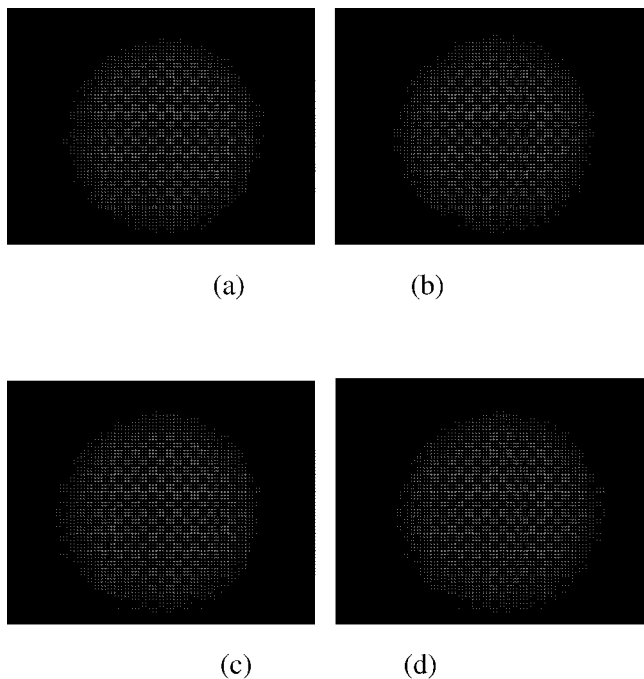
(a)   (b)

(c)   (d)

Figure 5. Polarizing microscopic textures of nematic liquid crystal in anti-paralleled cells. (*a*) 1C, (*b*) 6C, (*c*) 12C, (*d*) 18C side chain length of PMDA series PI. Rubbing depth = 0.3 mm, LC: MJ951160 (nematic liquid crystal).
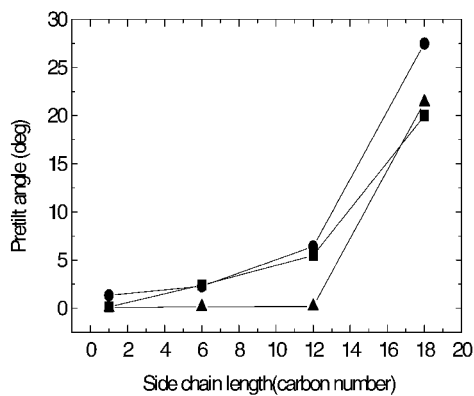

Figure 6. The side chain length dependence of the pretilt angle. ■ BTDA series, ● PMDA series, ▲ CPDA series: rubbing depth = 0.3 mm, temperature = 20°C.

The pretilt angle shows a sudden increase at this point, figure 8 (*d*). It is supposed that this critical point corresponds to a C12 side chain length. The critical pretilt angle occurs as LC molecules try to align in their most stable states as the two models co-operatively interact with each other. However, the two models have the following limits: they ignore the various interactions between LC-molecules and polyimide surfaces, and consider only a structural view of side length and polymer cluster size.
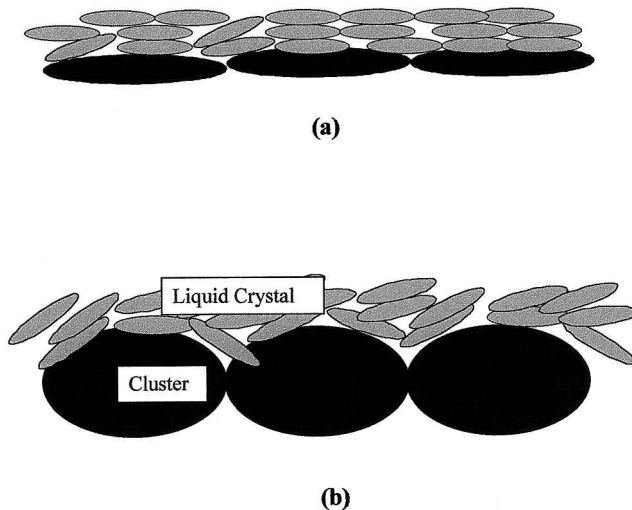

Figure 7. Alignment model for dependence of pretilt angle on cluster chain size. (*a*) small cluster chain (*b*) large cluster chain.
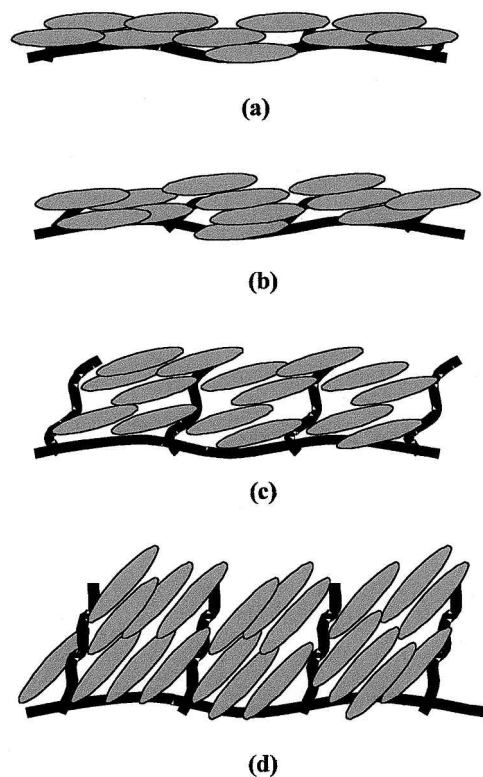

(a)

(b)

(c)

(d)

Figure 8. Alignment model for the dependence of the LC molecule arrangement on side chain length. (*a*) 2PMDA-DA1-ODA, (*b*) 2PMDA-DA6-ODA, (*c*) 2PMDA-DA12-ODA, (*d*) 2PMDA-DA18-ODA; 1, 6, 12, 18 denote side chain length of the diamine.

4. Conclusion

We have synthesized 12 types of copolyimide by thermal imidization from the dianhydrides of BTDA, PMDA and CPDA, a diamine with various side chain lengths, and ODA.

Various size polymer clusters were irregularly aligned on the unrubbed polyimide surface. However, in rubbed polyimide surfaces the clusters were arranged linearly and formed grooves. The surface of rubbed polyimides showed greater roughness as the side chain length increased, as did clusters. This may be due to the size and the structure differences in the polyimide monomers.

The NLC alignment was good, regardless of side chain length within the copolyimides. The pretilt angle on BTDA and PMDA series PI increased exponentially with increase in side chain length, but the CPDA series PI behaved differently. Models for the generation of pretilt angle are proposed on the basis of side chain length and PI cluster.

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