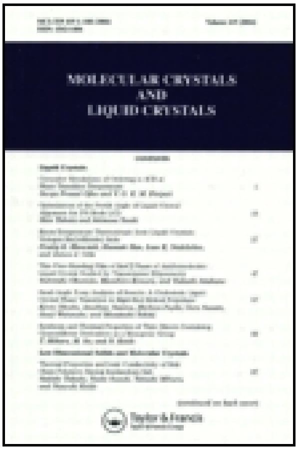

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Alignment of Liquid-Crystals on Rubbed Polyimide Films Prepared from Various Precursor Polymers

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Alignment of Liquid-Crystals on Rubbed Polyimide Films Prepared from Various Precursor Polymers

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For poly(*p*-phenylene biphenyltetracarboximide) (BPDA-PDA) and poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA) in films, surface topographies and molecular in-plane orientations were very sensitive to the precursor origins as well as the softbake and imidization processes. Poly(amic diethyl ester) precursor produced higher surface roughness and lower molecular in-plane orientation in the resultant polyimide than the corresponding poly(amic acid). Rapid softbake and imidization process caused relatively high surface roughness and low molecular in-plane orientation in the resultant film. Rougher surface in the film was more favorably rubbed by rubbing process, causing higher pretilt angle in liquid-crystal molecules in contact with the rubbed film.

Keywords: polyimide films, molecular orientation, surface roughness, rubbing, liquid-crystal, pretilt angle

INTRODUCTION

For full-color liquid-crystal display (LCD) devices, polyimide films rubbed with a cloth are widely used to control the alignment of liquid-crystals (LCs) in contact with the polymer. In the case, LCs are known to be oriented in the rubbing direction. This phenomenon has been previously proposed to be induced by microgrooves or scratches generated during rubbing the film surface[1],[2]. However, some of recent publications have suggested that the orientation of polymer chains near the surface, which are generated during rubbing, plays a key role in aligning LCs at the surface[3]-[5]. The others have proposed that both the mechanisms are operatively worked together[6],[7]. The mechanism of aligning LCs at the rubbed polymer surface is still one of the main subjects to be clarified in the field of LCDs. In this study, films of two representative polyimides, BPDA-PDA and PMDA-ODA, were prepared from their poly(amic acid) (PAA) and poly(amic diethyl ester) (PAE) precursors, respectively, by varying softbake and imidization conditions. For the polyimide films, we investigated molecular orientation, surface topographic characteristic, rubbing processability, and pretilt angle to LCs.

EXPERIMENTAL

PAA and PAE precursors of BPDA-PDA and PMDA-ODA polyimides were synthesized in *N*-methyl-2-pyrrolidone (NMP), respectively, as described previously in the literature[8],[9]: BPDA-PDA PAA, BPDA-PDA PAE, PMDA-ODA PAA, and PMDA-ODA PAE. The intrinsic viscosity measured in NMP at 25°C was 0.69 *dl*/g for BPDA-PDA PAA, 0.85 *dl*/g for BPDA-PDA PAE, 0.60 *dl*/g for PMDA-ODA PAA, and 0.80 *dl*/g for PMDA-ODA PAE. The precursors solutions were spin-coated onto glass substrates, followed by a rapid or slow softbake process (see Table I). And, the softbaked precursor films were thermally imidized rapidly or slowly under a N_2 flow as illustrated in Table I.

Some of the imidized films were taken off from the substrates and used for characterization. In-plane thermal expansion coefficient (TEC) was measured with a rate of 5.0 K/min using a thermomechanical analyzer (Seiko Instrument, Model 120CU) with a tension probe and then averaged over the range of 100-200°C. Out-of-plane birefringence (Δ) was estimated from refractive indices measured using a prism coupler[8]. The other polyimide films on substrates were rubbed with varying rubbing density (L/l)[10] using a rubbing machine with a roller covered by a rayon cloth (Yoshikawa Co., YA-20-R): Here, L is the total length of the rubbing cloth which contacts a certain point of the polymer film and l is the contact length of circumference of rubbing roller. Surface topographies of the films were examined before and after rubbing using an atomic force microscope (Digital Instrument). Two pieces of a rubbed film on the substrate were assembled together in the anti-parallel direction by using 10 μm thick poly(ethylene terephthalate) film spacers. A nematic LC, 4-*n*-pentyl-4'-cyanobiphenyl (5CB) was injected into the cell gap and then pretilt angle (α) of the LCs was measured by a crystal rotation technique[11].

TABLE I Properties of polyimide films prepared by rapid and slow softbake and imidization processes

Polyimide film	Precursor	Softbake process	Imidization process	TEC (ppm/°C)	Δ	Thickness (μm)
BPDA-PDA (#1)	PAA	slow[a]	slow[c]	4	0.2528	11.1
BPDA-PDA (#2)	PAA	slow	rapid[d]	5	0.2340	10.3
BPDA-PDA (#3)	PAA	rapid[b]	rapid	16	0.1310	10.1
BPDA-PDA (#4)	PAE	slow	slow	21	0.1759	11.1
PMDA-ODA (#1)	PAA	slow	slow	29	0.0787	8.3
PMDA-ODA (#2)	PAE	slow	slow	34	0.0664	11.1

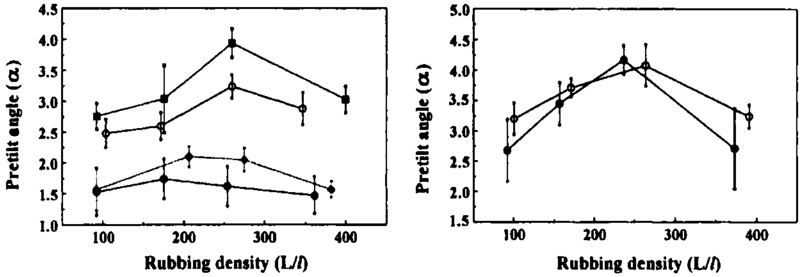
[a] Slow softbake: 80°C/60 min.
[b] Rapid softbake: 80°C/10 min, 115°C/2 min, and 185°C/2 min.
[c] Slow imidization: 150°C/30 min and 230°C/30 min with a ramping rate of 2.0 K/min and 380°C/1 h with a ramping rate of 5.0 K/min.
[d] Rapid imidization: 380°C/2 h with a ramping rate of 10.0 K/min.

RESULTS AND DISCUSSION

For BPDA-PDA PAA precursor, the rapid imidization produced a slightly high TEC and low Δ in the resultant polyimide film, compared to the slow process. The rapid imidization process coupled with the rapid softbake caused much higher TEC and lower Δ in the resultant film. In comparison to the PAA precursor, the PAE produced relatively high TEC and low Δ in the resultant polyimide film. Overall, both TEC and Δ in the BPDA-PDA polyimide film are dependent strongly upon the softbake and imidization processes as well as the history of precursor origin (see Table I).

In comparison to the pseudo-rodlike BPDA-PDA, semi-flexible PMDA-ODA polyimide exhibited relatively high TEC and low Δ even though it was slowly imidized, regardless of the precursor origin. The PAE precursor caused slightly higher TEC and lower Δ in the resultant polyimide film than the PAA.

For LC cells prepared with the rubbed BPDA-PDA films, pretilt angle (α) of LCs initially increased to a certain level with increasing rubbing density and then declined with further increasing rubbing density. However, the level of α and its dependency to the rubbing density were dependent strongly upon the history of film formation process and the precursor origin: α varied in the range of 1.4-3.9°. That is, the film, which was prepared by the rapid softbake and imidization, exhibited a relatively higher α than that prepared by the slow process. And, the film prepared from the PAE gave a higher α than that from



(a) ●, BPDA-PDA (#1); ◆, BPDA-PDA (#2);
■, BPDA-PDA (#3); o, BPDA-PDA (#4)

(b) ●, PMDA-ODA (#1);
o, PMDA-ODA (#2)

FIGURE 1 Variations of the pretilt angle of LC molecules in contact with rubbed polyimide films as function of rubbing density.

the PAA. Consequently, a film exhibiting higher TEC and lower Δ provides higher α. From this, it is suggested that lower in-plane chain orientation in a film causes higher α to the LC molecules in contact with the rubbed film.

Similar dependency of α to the rubbing density was observed for LC cells prepared with PMDA-ODA films. However, α was measured to be relatively less sensitive to the precursor origin: α varied in the range of 2.7-4.2°.

The mean surface roughness was measured by AFM to be 0.085 nm for BPDA-PDA (#1), 0.152 nm for BPDA-PDA (#3), 0.112 nm for BPDA-PDA (#4), 0.165 nm for PMDA-ODA (#1), and 0.179 nm for PMDA-ODA (#2). These films were rubbed at a rubbing density which gives the maximum α and then examined again by AFM. Figure 2-(a) shows the surface topography of BPDA-PDA (#1) film which exhibited a relatively small α. Its surface roughness is reatively small and microgrooves are not easily found. In contrast, the BPDA-PDA (#3) with a high α exhibited a reatively rough surface and microgrooves were detected in the rubbing direction [see Figure 2-(b)]. On the other hand, the BPDA-PDA (#4) with a high α, which was slowly imidized from the poly(amic diethyl ester), also exhibited a rough surface and microgrooves were shown clearly [see Figure 2-(c)].

PMDA-ODA films show quite different surface topographies from those of BPDA-PDA films. As shown in Figure 3-(a), the PMDA-ODA (#1) prepared from the PAA exhibited a relatively rough surface with microgrooves. In comparison, the PMDA-ODA (#2) from the PAE showed much rougher surface and microgrooves appeared more clearly.

The AFM results indicate that when a polyimide film is rubbed, microgrooves are generated more favorably on the rough surface than the smooth surface, providing high pretilt angle α in LCs in contact with the

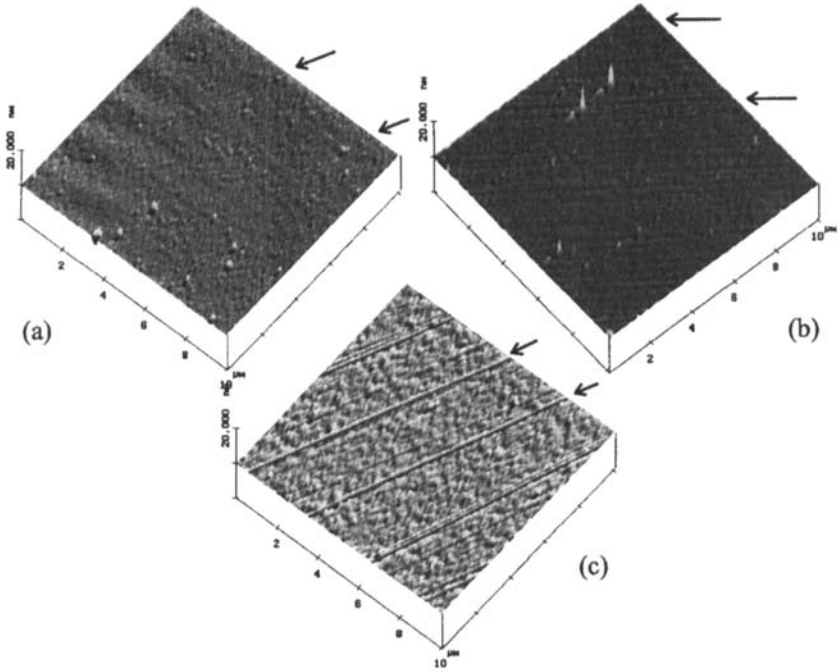


FIGURE 2 Surface topographies of rubbed BPDA-PDA films : (a), BPDA-PDA (#1) (rubbing density is 253.7); (b), BPDA-PDA (#3) (rubbing density is 259.4); (c), BPDA-PDA (#4) (rubbing density is 259.4). Arrows indicate rubbing direction.

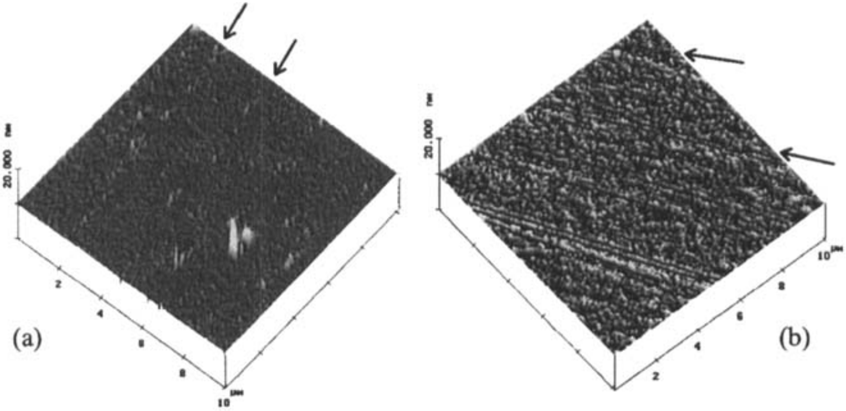


FIGURE 3 Surface topographies of rubbed PMDA-ODA films : (a), PMDA-ODA (#1) (rubbing density is 236.6); (b), PMDA-ODA (#2) (rubbing density is 263.2). Arrows indicate rubbing direction.

rubbed film. Therefore, although microgrooves may not play a role directly to align LCs in contact with the film surface, the degree of microgroove formation might be an indication how polymer chains and their segments on the surface are favorably oriented in the rubbing direction by the rubbing process.

CONCLUSION

For pseudo-rodlike BPDA-PDA polyimide, its surface topography and molecular in-plane orientation in bulk were dependent strongly upon both the film formation process and the precursor origin. Rapid softbake and imidization porcess produces the polyimide film with a relatively rough surface and a low degree of molecular in-plane orientation, compared to slow softbake and imidization. The PAE precursor generates a higher surface roughness and a lower molecular in-plane orientation in the resultant polyimide film than the PAA. For semi-flexible PMDA-ODA polyimide, it has also been found that the PAE precursor produces a relatively higher surface roughness and a lower molecular in-plane orientation than the PAA. Overall, lower molecular in-plane orientation in a bulk film exhibits higher roughness on its surface. Higher surface roughness is more favorably rubbed, consequently providing higher pretilt angle α of LC molecules in contact with the rubbed surface.

Acknowledgments

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