Polymer Cluster Orientation and Optical Phase Retardation of the Rubbed Polyimide Surfaces

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ABSTRACT: In an atomic force microscopic image of the main-chain- and the side-chain-type polyimide surfaces, we have observed a variation of the surface morphology to use the rubbing depths and the rubbing times. On the rubbed polyimide surface, the polymer clusters are aligned in long chains along the rubbing direction. The topology of the polyimide surface is weakly changed at a lower rubbing depth, but it is greatly changed at a deeper rubbing depth. Once the polished string structure is obtained, no considerable changes in the surface topography of the polyimide are visible, although rubbing times are increased from 1 to 8 at constant rubbing depths (0.3 mm). The rubbed polyimide films show optical phase retardation, which was steeply increased with increasing rubbing depth; but it was increased very little with increasing rubbing times. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1728–1734, 2000

Key words: atomic force microscopy; main-chain-type polyimide; side-chain-type polyimide; polymer cluster

INTRODUCTION

It is well known that the liquid crystal molecules would be aligned on the rubbed polyimide surface or on the elongated polymer films.[1] Although many theoretical and experimental studies have been done on this subject, the actual alignment mechanism has not been clarified.[2–4]

One possibility is that the alignment is induced by grooves or scratches mechanically formed on the polymer surface by the rubbing process.[2]

An alternative concept is that alignment acts through the orientation of polymer molecules.[3–4] Obviously, the surface morphology at the nanometer level is important for understanding the alignment mechanism of liquid crystal molecules. On these very flat surfaces, it is difficult to use ordinary electron microscopy due to the low height resolution. Atomic force microscopy (AFM) studies of rubbed polymers show that grooves are presented on the surface.[5–10] Recently Zhu et al.[11] used AFM to investigate rubbed polymers and found, on a large scale, oriented scratches and microstructure, while on a nanometer scale, oriented polyimide aggregates were visible. However, only one rubbing-strength was used for these experiments.

In this work, we will describe the surface morphology at the nanometer level and the optical phase retardation of the rubbed polyimide films as a function of the rubbing parameters and polyimide materials.

EXPERIMENTAL

AL-1051 (film hardness, HB; decomposition temperature, 448°C) as a main-chain-type polyimide

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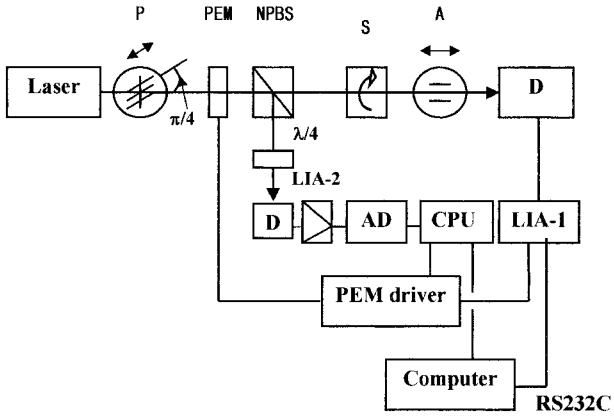

Figure 1 System setup for the measurement of optical phase retardation of the rubbed polyimide films: laser, He–Ne laser; P, polarizer; PEM, photoelastic modulator; NPBS, nonpolarized beam splitter (mirror); S, rateable sample; A, analyzer; D, detector; LIA-1, dc amplifier; LIA-2, ac amplifier; CPU, computer; AD, A/D converter.

and AL-8044 (film hardness, HB; decomposition temperature, 440°C) as a side-chain-type polyimide type from JSR Co. (Tokyo, Japan) was used. The polyimide films were spin-coated (spinner: 800 rpm; 60 s) on the glass coated with ITO film, precured at 80°C for 30 min, and main-cured at 180°C for 1 h. The approximate thickness of the resulting polyimide films was about 800Å ± 50Å. Rubbing was done with the rubbing machine, and wounded nylon velvet (subfiber diameter, 2 μm; length, 1.8 mm) on the roller. The rubbing strength (RS) was calculated using the following expression[6]:

$$RS = \gamma \times L \tag{1}$$

where γ is a characteristic of the rubbing process, including the rubbing pressure, the fiber density in the rubbing material, and the coefficient of friction. L is the total length of the rubbing fiber in contact with a certain point of the substrate and is expressed by

$$L = N \times l\left(1 + \frac{2\pi rn}{60\nu}\right) \tag{2}$$

where N is the rubbing time, l is the contact length (m) of rubbing fiber, n is the number of revolutions per minute (rpm), r is the radius (m) of the roller, and ν is the velocity (m s) of the substrate stage. In this study, rubbing was controlled with the rubbing depth and rubbing times.

Standard Si_3N_4 AFM tips, with a force constant of 0.032 nm^{-1}, were used in a commercial AFM (Park Science Instruments) operated in the contact mode with constant-force. The tip-sample force in all images was about 10 nN, and the scan frequency was kept in the interval of 0.5–1 Hz. The images were tilt-corrected and low-pass-filtered. The system for measuring optical phase retardation on the rubbed polyimide films is shown in Figure 1.

RESULTS AND DISCUSSION

The spherical clusters of different size are randomly distributed in unrubbed surface. This im-

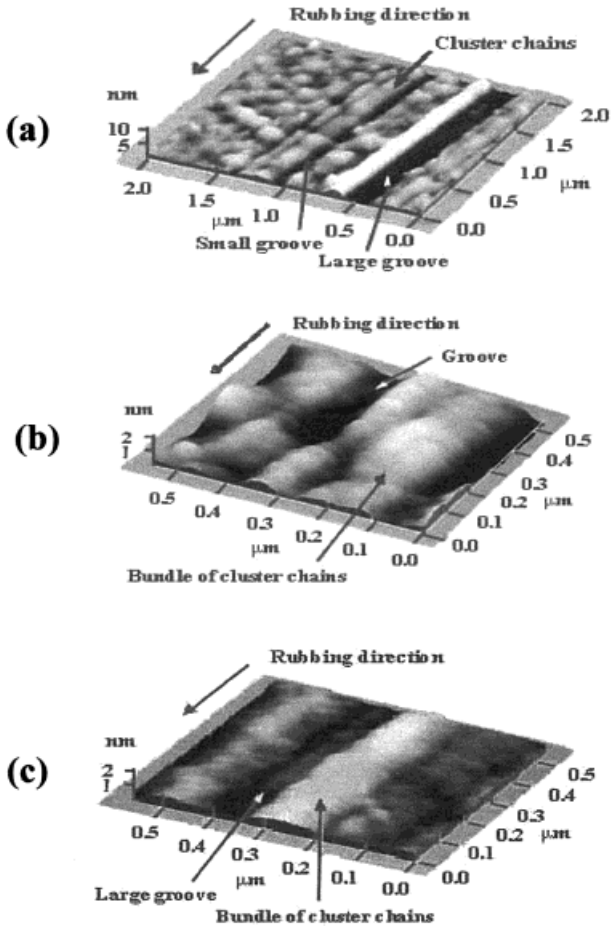

Figure 2 Typical AFM image of the rubbed polyimide surfaces

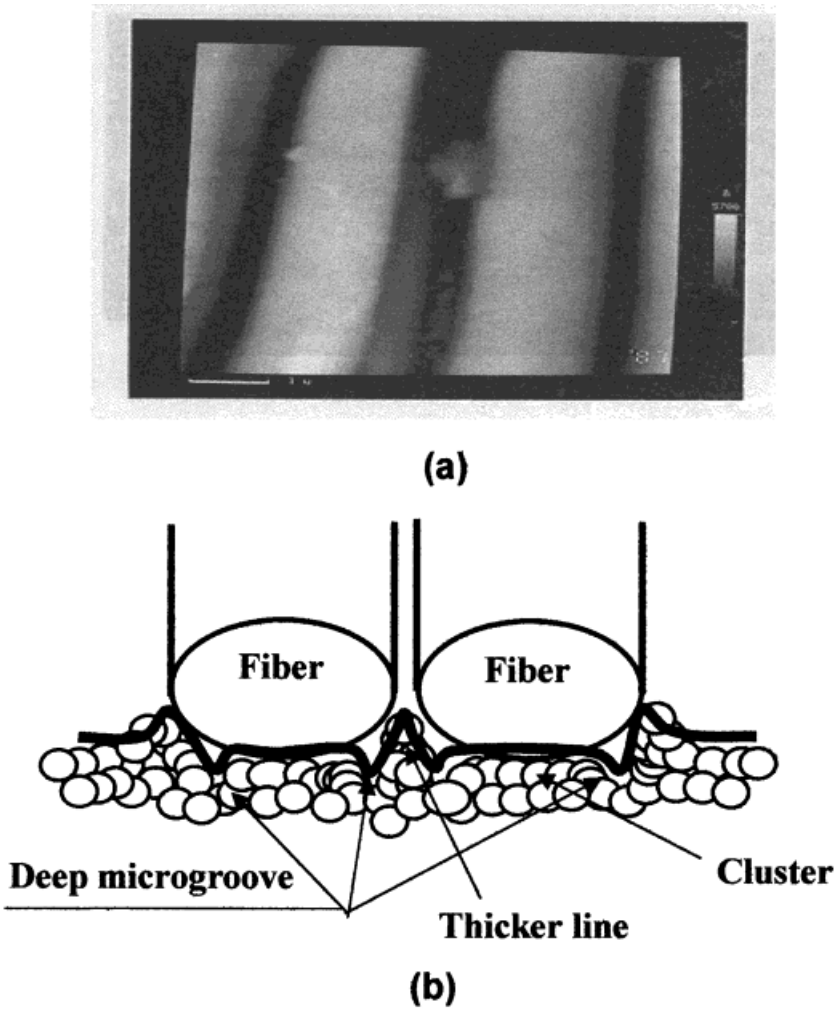

Figure 3 (a) AFM image of rubbing fiber (approximately 20 μm in diameter). (b) Cross-sectional view of a polyimide film in contact with a fiber of rubbing material.

age is not surprising since the polymer chain forms a spherical cluster in the solvent.[6–9]

Figure 2 shows that the spherical cluster becomes elongated to the rubbing direction in the rubbed surface, and small groove and large grooves are presented between alignment of the cluster.

A larger view of the rubbed surface (scan size: 0.5×0.5 μm) has obviously shown a row of the ellipsoidal clusters lines along the rubbing direction. Here, we suggest calling the ellipsoidal cluster line the cluster chain. We observed that the bend with a rippling pattern is composed of the number of cluster chains, and the linear grooves were located between those bends. These line grooves were not found in the bends, but the discontinuous line grooves were observed between the cluster chains. It is an important to understand the elongation and alignment mechanism of the polyimide chain by the rubbing process. We suggest that there are two factors acting on the polyimide surface, as follows: a local heating and a simultaneous shearing force during the rubbing process, respectively. Both factors have contributed to the elongating of the polyimide chain in the cluster and the alignment of ellipsoidal clusters along the rubbing direction.

Figure 3 shows the AFM image of the fiber from the rubbing cloth and the mechanism suggested to explain the process of forming the deep groove.[7] The fibers of rubbing material are a bundle of fine fibers of approximately 2 μm diameter, as shown in Figure 3(a). These fibers make contacted with the polyimide surface, as described in

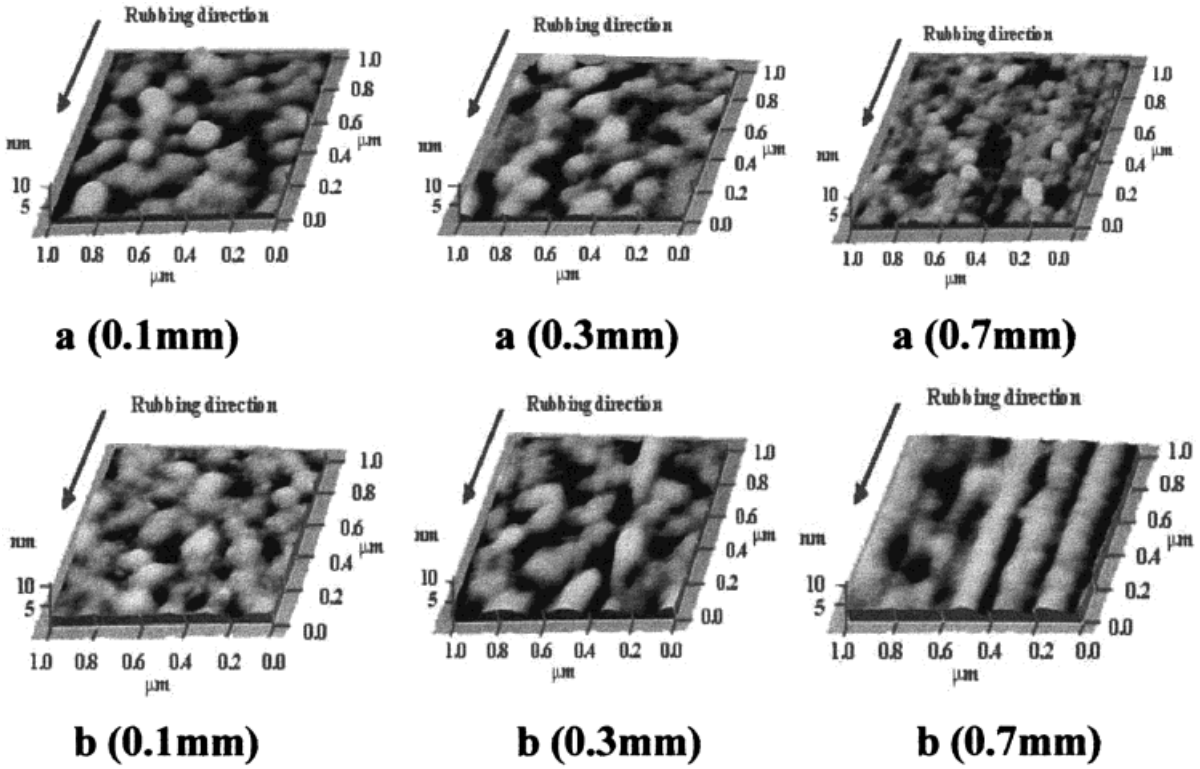

Figure 4 AFM images illustrating the influence of increasing rubbing depths at a rubbing time 1 and a scan size 1 × 1 μm: (a) AL-1051; (b) AL-8044 (the rubbing depths are given in parentheses).

Figure 3(b). The unidirectional motion of fibrous material, which is pressed into contact with the surface, accomplishes rubbing of the polyimide surface. The contact area between the fiber and the surface of the polyimide that is created by the rubbing pressure, while substantially less than the fiber diameter, can reasonably be expected to be substantially broader than the film thickness. Hence, during the rubbing, the polyimide film is caught between two broad planes, one stationary (substrate), and the other moving (the fiber contact area). The polyimide surface will experience a shearing force and a local heating; and, if the friction exerted by the fiber contact area is great enough, a permanent shearing deformation can be generated. Thus, through the action of shearing, the polyimide surface will be deformed much as if it had first been aligned and had elongated the cluster of the polyimide chain by cold drawing and then placed upon the substrate. During this process, the rubbing depths throw some cluster chains up on the V- or U-shaped area between fibers and then make a thick line of the bundle of cluster chains.

In comparative experiments of the main-chain- and side-chain-type polyimide, we have observed a variation of the surface morphology to use the rubbing depths and times. As the rubbing depth is increased from 0.05 to 0.7 mm at constant rubbing times, the orientation degree of polyimide clusters is better aligned to the rubbing direction (Fig. 4). Even at a weak rubbing strength (lower rubbing depth), some degree of the anisotropic alignment of clusters can be noticed. At an increased rubbing depth, independent clusters coalesced with the neighboring ones, resulting in row-like cluster structures and formation of microgrooves. The cluster chains are almost periodically aligned. For a strong rubbing strength (higher rubbing depth), the neighboring chains could be coalesced with each other. Thus, the cluster chains have formed the thicker bundles because of the local heating and simultaneous shearing forces during the rubbing process. We can observe here microgrooves running along strings of cluster chains. The surface topology on the side-chain-type polyimide films is changed larger than that on the main-chain-type poly-

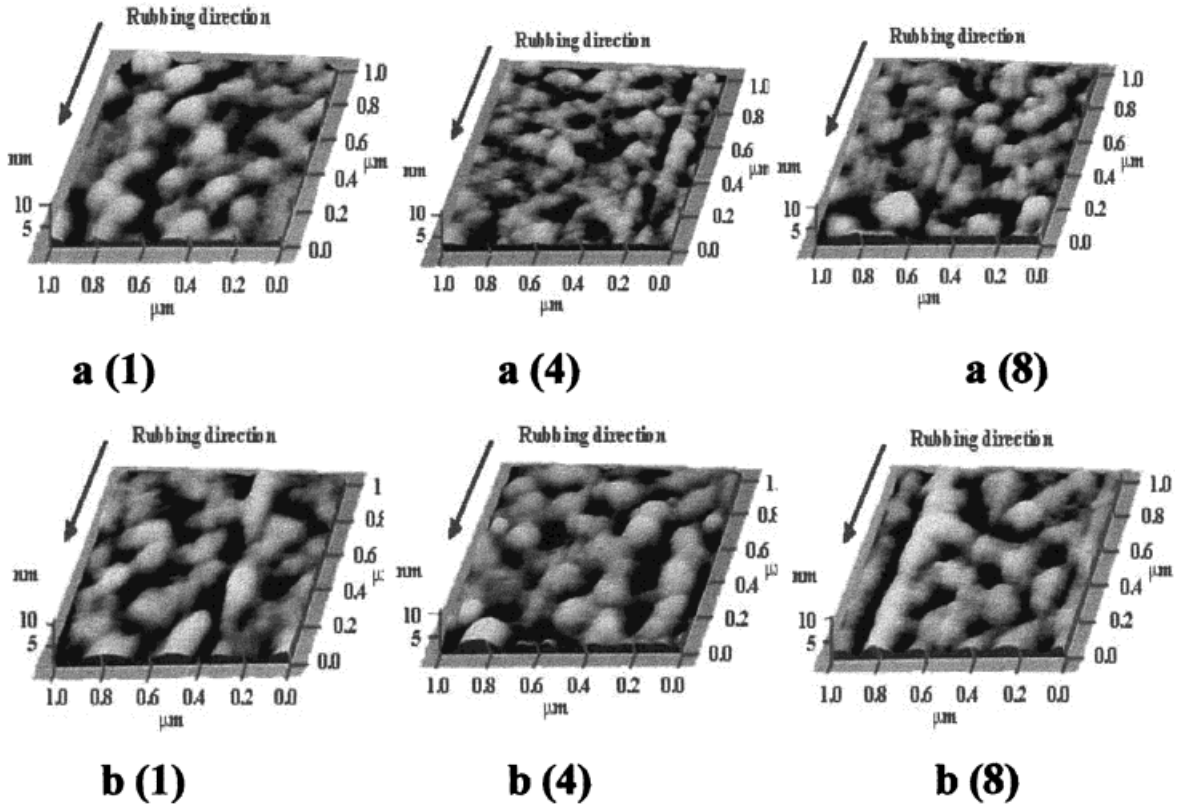

Figure 5 AFM images illustrating the influence of increasing rubbing times at a constant rubbing depth (0.3mm) and scan size (1×1 μm: (a): AL-1051; (b) AL-8044 (the rubbing times are given in parentheses).

imide films. Perhaps it is due to the size of monomer of polyimide. On the other hand, once the polished string structure is obtained, no considerable changes in the surface topography are visible, although rubbing times are increased from 1 to 8 at constant rubbing depths, as illustrated in Figure 5.

We have varied the rubbing depths and the rubbing times for studying the rubbing influence on the polymimide surfaces. The optical phase retardation steeply rises as the rubbing depth at a rubbing time rises (Fig. 6). Also, no rigidly fixed limit is seen in Figure 6. The retardation, that is, was steeply increased and not saturated from about 0.1 o 1.0 nm for AL-1051 and from about 0.1 to 0.8 nm for AL-8044. Also, the retardation was smaller with side chains than without them; but the optical phase retardation was increased little with increasing rubbing times at a constant rubbing depth of 0.3 mm (Fig. 7). As shown in Figure 8, we propose that the overall retardation of unrubbed polyimide films is close to zero because it has no regular direction, even if it is aligned partly; but clusters are realigned to the rubbing direction due to the elongation of the alignment layers by rubbing. If the rubbing depth is increased, the polyimide clusters on rubbed polyimide films

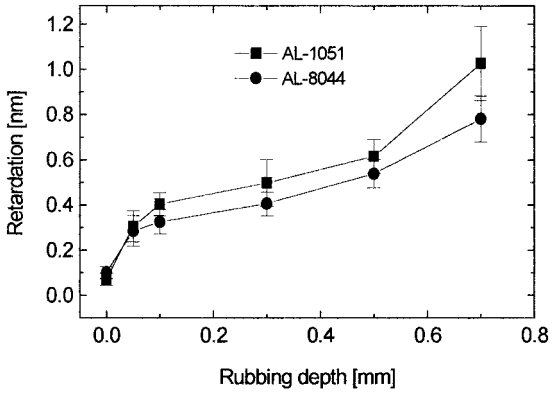

Figure 6 Retardartion of the rubbed polyimide films as a function of rubbing depth.

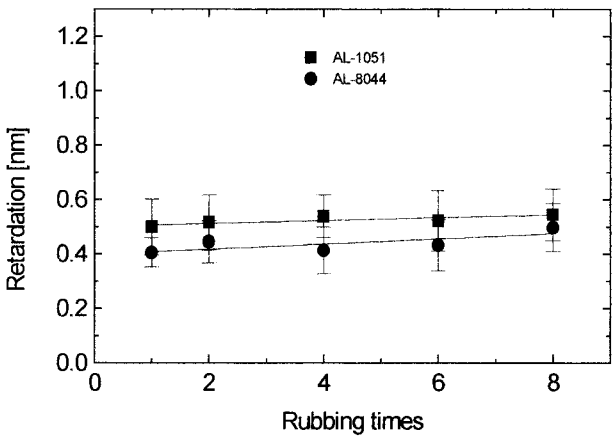

Figure 7 Retardation of the rubbed polyimide films as a function of rubbing times.

align better to the rubbing direction, and more retardation results because smaller clusters are coalesced and become bigger clusters. Retardation of AL-1051 is better than that of AL-8044 at a constant rubbing condition [Fig. 8(a) AL-1051; (b) AL-8044]. It may be the side-chain effect. This effect is understandable if one considers that the tiny areas of contact between the fibrous rubbing material and the polyimide surface constitute only a minute fraction of the surface's area. As rubbing proceeds, these isolated contact areas will leave behind narrow streaks of deformation in the polyimide surface [Fig. 4(b)], and the clusters located in the contact areas will be elongated and aligned along the rubbing direction. Therefore, the anisotropy elongation of cluster will create the optical phase retardation of polymer film and the microgrooves. At first, the contact areas will encounter only virgin surface, and the alignment density of cluster will increase as the fraction of the total area that has been affected by rubbing increases. But as the rubbing times accumulates, the streaks will begin to overlap, and the anisotropy elongation and the alignment density of clusters will not show a further increase. Assuming that most of the deformation that the shearing force and the frictional heat at contact areas can cause will occur on first contact, it is then clear that the observed optical phase retardation will increase rapidly, as more and more of the surface is rubbed.

CONCLUSION

The unrubbed polyimide surface consists of randomly distributed clusters, the sizes of which are much higher than of an individual molecule. Rubbing induced the cluster chain and grooves, which are aligned along the rubbing direction, drastically

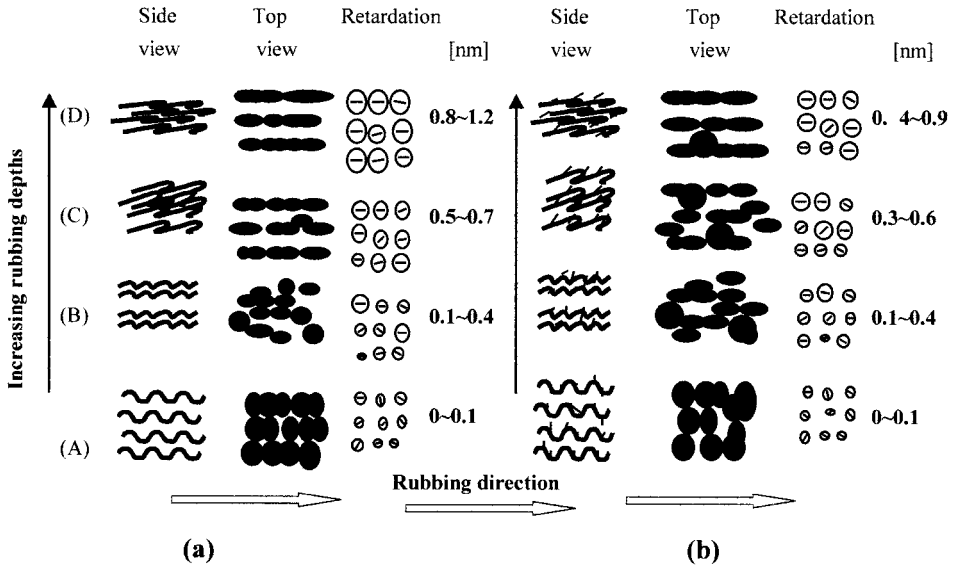

Figure 8 Realignment of the polyimide as a function of the rubbing depth: (a) AL-1051; (b) AL-8044. The arrow indicates the direction of the polyimide cluster alignment, the size of the circle indicates the optical phase retardation; (A) indicates nonrubbing, and (B)–(E) indicate increasing rubbing depths.

changing the surface. The deeper the rubbing depth, the better the clusters align on the alignment layer to the rubbing direction, and the larger the retardation because smaller clusters are coalesced and become bigger clusters. As the rubbing times accumulates, the streaks will begin to overlap, and the anisotropic elongation and the alignment density of clusters will not show a further increase.

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REFERENCES

1. Cognard, J. Mol Cryst Liq Cryst, Suppl 1982, 1, 1.
2. Berreman, D. W. Phys Rev Lett 1972, 28, 1683.
3. Castello, J. A. Mol Cryst Liq Cryst 1983, 94, 33.
4. Geary, J. A.; Goodby, J. W.; Kmetz, A. R.; Patel, J. S. J Appl Phys 1987, 2, 4100.
5. Suzuki, M.; Maruilo, T.; Yamamoto, F.; Nagai, K. J Vac Sci, Technol 1990, A8, 631.
6. Kim, Y. B.; Kim, H. S.; Choi, J. S.; Matuszcsyk, M.; Olin, H.; Buivydas, M.; Rudquist, P. Mol Cryst Liq Cryst 1995, 262, 89.
7. Kim, Y. B.; Olin, H.; Park, S. Y.; Choi, J. W.; Komitov, L.; Matuszcsyk, M.; Largerwall, S. T. J Appl Phys Lett 1995, 66, 2218.
8. Kim, Y. B.; Ban, B. S.; Olin, H. in Proceedings of the 16th International Liquid Crystal Crystal Conference, Kent State Univ., Kent, OH, 1996; p. 111.
9. Ban, B. S.; Jeon, Y. J.; Kim, Y. B. in Proceedings of the 50th Anniversary Conference and the 77th Congress of the Korean Chem Society, Program and Abstract, Yonsei Univ., Seoul, Korea, 1996; p. 181.
10. Matuszcsyk, M.; Matuszczyk, T.; Largerwall, S. T.; Kim, Y. B.; Wnek, M.; Maltese, P. Ferroelectrics 1996, 178, 41.
11. Zhu, Y. M.; Wang, L.; Lu, Z. H.; Wei, Y.; Hen, X. X.; Tang, J. H. J Appl Phys Lett 1994, 65, 49.