Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Thin Films of Liquid Crystalline Polymers as Alignment Layers for Liquid Crystal Displays

M. Murakami [a b] & H. Fujii [a c]

[a] GTC, Chuo-ku, Tokyo, 103, Japan

[b] Hoechst Japan Ltd., Advanced Technology Laboratories 3-2, Minamidai I-chome, Kawagoc, Saitama, 350, Japan

[c] Casio Computer Co., Ltd., Hachioji Research Center, 2951-5, Ishikawa-cho Hachioji, Tokyo, 192, Japan

Version of record first published: 24 Sep 2006.

To cite this article: M. Murakami & H. Fujii (1993): Thin Films of Liquid Crystalline Polymers as Alignment Layers for Liquid Crystal Displays, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 225:1, 259-268

To link to this article: http://dx.doi.org/10.1080/10587259308036232

Mol. Cryst. Liq. Cryst., 1993, Vol. 225, pp. 259–268
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Thin Films of Liquid Crystalline Polymers as Alignment Layers for Liquid Crystal Displays

M. MURAKAMI† and H. FUJII‡
GTC, Chuo-ku, Tokyo 103, Japan

(Received February 24, 1992; in final form June 2, 1992)

Thin films of main-chain and side-chain liquid crystalline polymers (LCP) formed by spincoating were investigated. The self-aligning effect of the rubbed main-chain LCP thin film after thermal annealing was observed. The thermal annealing at the onset temperature of the transition from the solid to liquid crystalline phase brings large optical anisotropy (delta $n > 0.07$) to the main-chain LCP film but not to the side-chain LCP film.

The effect of rubbing and annealing on the surface morphology of the main-chain LCP film is also discussed by means of a scanning electron microscope (SEM) and atomic force microscope (AFM). The surface roughness of the main-chain LCP film increased drastically after the annealing because of the recrystallization.

Nematic liquid crystals orient uniformly even on such a rough surface when the main-chain orientation of the LCP is in the rubbing direction. This indicates that the main-chain LCP can be used as an alignment layer with high performance for LCDs.

Keywords: liquid crystalline polymer, alignment layer, pretilt angle, rubbing

INTRODUCTION

There has been recent significant development for liquid crystal displays (LCD), especially the thin film transistor (TFT) type. The majority of the LCD is the twisted nematic type (TN), which requires uni-directional orientation of liquid crystal molecule on substrates. In order to align the liquid crystal molecules, polymer layers are usually formed on glass substrates. Since the polymer film itself has no capacity for the alignment of nematic liquid crystals, anisotropic rubbing by a buffing brush is required for the desired alignment. Polyimide (PI) or polyamide are commonly used because of their high thermal and chemical reliability and past good performances in other electronic devices.[1] Despite the large number of investigations on the alignment mechanism of the liquid crystals on the rubbed polymer surface,[2,3] the mechanism has not been understood very well. The topography of the surface may be one of the most coherent explanations for the alignment of the liquid crystals on rubbed polymers. Berreman, *et al.*, estimated that liquid

†Present address: Hoechst Japan Ltd., Advanced Technology Laboratories 3-2, Minamidai 1-chome Kawagoe Saitama 350, Japan.
‡Present address: Casio Computer Co., Ltd., Hachioji Research Center, 2951-5, Ishikawa-cho Hachioji Tokyo 192, Japan.

crystal molecules are stabilized by small grooves (depth: 1 nm, interval: 20 nm),[4] although such small grooves have not yet clearly been observed in the rubbed polymers. In addition to this explanation, van der Waals forces between the aligned molecular surface and liquid crystals is also a possible explanation. Moreover, some polymers can align on the long axes of liquid crystals perpendicular to the rubbing direction. For example, a rubbed polystyrene film orients the long axis of liquid crystal molecules perpendicular to the rubbing direction.[5] These studies suggest that both the surface topography and van der Walls effect contribute to the alignment of liquid crystal molecules on the rubbed surface of polymers.

LCP has been extensively investigated as a highly oriented material for polymer composites, fibers, and molded parts. Moreover, the highly oriented micro-structure has been well studied by Scanning Electron Microscopy (SEM) or Transmittive Electron Microscopy (TEM).[6] An LCP film with such a highly oriented micro-structure might align the liquid crystal molecules. Ohnuma, *et al.*, reported the polysiloxisane side chain type LCP as an alignment layer for a ferroelectric liquid crystal display.[7] Their LCP film coated on the rubbed polyimide orients ferroelectric liquid crystals uniformly after thermal annealing at the temperature range of the nematic phase of the corresponding polymer.

The present paper addresses the utilization of LCPs as alignment layers. The mechanism of alignment by means of an investigation of optical anisotropy caused by rubbing and annealing of the LCP and surface morphology observation by SEM and AFM will also be discussed.

EXPERIMENTAL

Two kinds of LCPs were used in this study. One LCP was a rigid aromatic type copolyester (LCP-1) obtained from *p*-hydroxy benzoic acid, hydroquinone, and isophtalic acid. This polymer was the main chain thermotropic liquid crystalline polymer.[8] The other LCP was poly[6-(4′-nitrostilbene-oxy)-hexyl]methacrylate (LCP-2). These materials were provided by Hoechst Celanese Corporation. The thermal properties of the materials were analyzed using a differential scanning calorimetry (a Perkin Elmer DSC7) under nitrogen atmosphere. The samples were heated and cooled at the rate of 10°C/min.

The as-received LCP-1 pellets were dissolved in *N*-methyl pyrrolidone (4 wt% polymer) at 130°C. LCP-1 was dissolved in *N*-methyl pyrrolidone easily and completely. LCP-2 powders were dissolved in γ-butyrolactone in 3 wt% concentration at 100°C. The solutions were spin-coated on glass substrates or silicon wafers at 2000 rpm and then baked at 180°C. The thickness of the obtained films was ca. 100 nm. Afterwards the substrates were rubbed with a nylon brush under various rubbing strengths. Finally the substrates were annealed at various temperatures within the liquid crystal phase range.

The surface morphology of these samples was analyzed using a scanning electron microscopy (SEM: Hitachi S-4000) and atomic force microscope (AFM: Digital Instruments NanoScope AFM). For the SEM observations, silicon wafers were used as the substrates. Pt-Pd was sputter-coated on the LCP surface for the SEM observation.

Optical retardation of LCP film on glass substrates and the direction of the fast-axis were measured by the "Automatic birefringence measurement system" (Oak ADR-100XY)." The light source of the probe ray was a He-Ne laser (632.8 nm). The molecular alignment of the LCP was also investigated by FT-IR (Bruker IFS-120 HR) with a wire grid polarizer.

Test LC cells (cell gap: 20 μm) were fabricated in order to evaluate the alignment capability of the LCPs for nematic liquid crystals (Chisso Corporation: GT5001). Pre-tilt angles were measured by the crystal rotation method. Alignment of liquid crystals was also evaluted by measuring dichroic ratio of the guest dye (Showa Kako KT2bd) mixed into host nematic liquid crystals. The dye was dichroic and has peak absorption at 550 nm in a liquid crystal. The polarized absorption spectra were measured by a UV/VIS photometer (Hitachi U3410).

RESULTS AND DISCUSSIONS

The DSC measurement was carried out in order to find the appropriate temperature for a thermal treatment of LCP film. Figures 1a and 1b show the DSC curves of LCP-1 and LCP-2 respectively. They were obtained by DSC for 2nd heating and cooling. The specimens were pellets for LCP-1 and powder for LCP-2 as received. In the 2nd heating of LCP-1, besides the glass transition at 135°C, a broad endothermic peak with a discernible shoulder and a small peak can be observed at Tm 286°C and Tm 322°C (Tm: melting transition temperature). The phase transition of LCP-1 from nematic to isotropic could not be observed because of the decomposition of the LCP. As compared with the main-chain liquid crystalline polymer, LCP-2 has clear isotropization at 152°C. The transition from solid to nematic is observed at 70°C. As the solid to nematic phase is a second order change, the DSC thermograph shows a subtle change around 70°C. However no peak for Tm could be observed because LCP-2 is an amorphous polymer.

Optical retardation of polymer film shows the direction and degree of orientation of the polymer molecules. In the case of LCP-1 and polyimide, there is a large local electronic polarization associated with phenyl groups in the main chains. On the other hand, the polarization of LCP-2 is in the side chain mesogen groups.

Before rubbing there is almost no optical anisotropy apart from shear-induced anisotropy from spin-coating or from the original anisotropy from the glass substrate. After rubbing unidirectional optical anisotropy can be observed in both LCP samples. The slow axes of the rubbing-induced retardation of LCP-1 film, the LCP-2, and polyimide film are parallel to the rubbing direction. Therefore, one can say that the large electronic polarization of the LCPs orients in the rubbing direction in the same manner as that of main-chain type polymers. Since LCP-2 is a side-chain type polymer, we expected that LCP-2 would show the slow axis perpendicular to the rubbing direction, like polystyrene film. However, LCP-2 shows the slow axis parallel to the rubbing direction. One difference between polystyrene and LCP-2 is the length of the flexible spacer between the main chain and the core. Since the polystyrene has no flexible spacer, the polymer main chain tends to orient in the rubbing direction and the mesogen aligns perpendicular to the rubbing

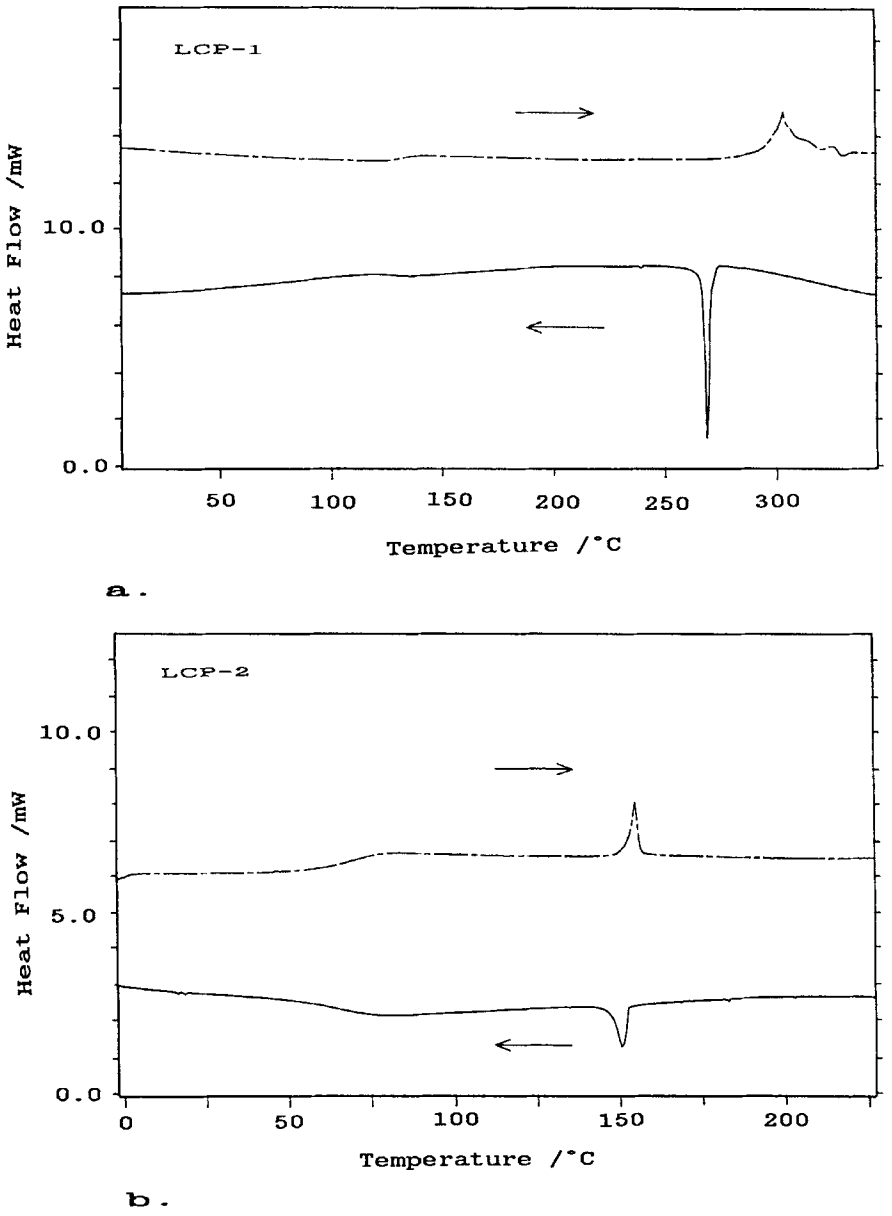

FIGURE 1 DSC second heating and cooling curves of the samples of (a) LCP-1 pellet and (b) LCP-2 powder, at a heating and cooling rate of 10°C/min.

direction. On the other hand, LCP-2 has a long alkyl side chain, and the mesogen might be able to align parallel to the rubbing direction.

Figure 2 shows the annealing temperature dependence of the optical retardation of LCP-1, 2 and PI. The optical retardation of LCP-1 started to increase at 250°C, peaking at 300°C. At 350°C the optical retardation of LCP-1 decreased. This in-

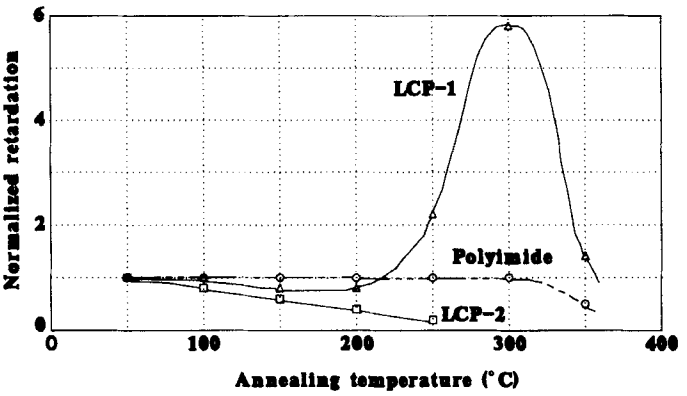

FIGURE 2 Temperature dependence of optical retardation of the films rubbed and annealed at each temperature for 10 min. The retardation values are normalized to that for the film without annealing.

dicated that the LCP-1 film orients better by thermal annealing at an adequate temperature. On the other hand, LCP-2 showed a decrease of optical retardation by any thermal annealing. This phenomena is similar to that of PI but more pronounced. Although LCP-2 has a nematic phase, this phase does not enhance the orienting property of the polymer film.

In the following, we describe the properties of LCP-1 film, which exhibits unusual phenomena in the measurement of optical retardation.

Optical retardation measurement reveals that the thermal annealing improves main-chain orientation of the LCP-1 film. However, from the measurement more detailed information like carbonyl group orientation can not be obtained. Figures 3a and 3b show FT-IR subtraction spectra of the rubbed LCP-1 before and after annealing, respectively. The subtraction spectrum is obtained by subtracting the absorption spectra measured with light polarized parallel with the rubbing direction from that polarized perpendicular. Since we used a different silicon wafer for the reference, the baseline of the spectrum is inclined. However, if a peak appears on the upperside of the baseline, the absorbance is anisotropically oriented perpendicular to the rubbing direction. As shown in Figure 3a, no strong difference between absorbance parallel and absorbance perpendicular can be observed before annealing. However, as shown in Figure 3b, characteristic peaks appeared after annealing. The carbonyl stretching peak (1740 cm^{-1}) is on the upperside of the baseline, while the phenyl ring vibration peak (1605 and 1510 cm^{-1}) is on the lowerside. This result by the measurement of FT-IR also indicates that the LCP-1 molecules in the layer orient more in the rubbing direction after the thermal annealing.

Surface observations of rubbing alignment layers have been studied by SEM and AFM in order to understand the relationship between the quality of the alignment of liquid crystals and the rubbing condition. Suzuki, *et al.*, investigated a rubbed polyimide surface by STM and concluded that only soft rubbing created highly aligned grain structure.[9] However, the molecular orientation in the grain was not determined in this STM investigation.

As we described above, the molecules of LCP-1 orient highly by the thermal

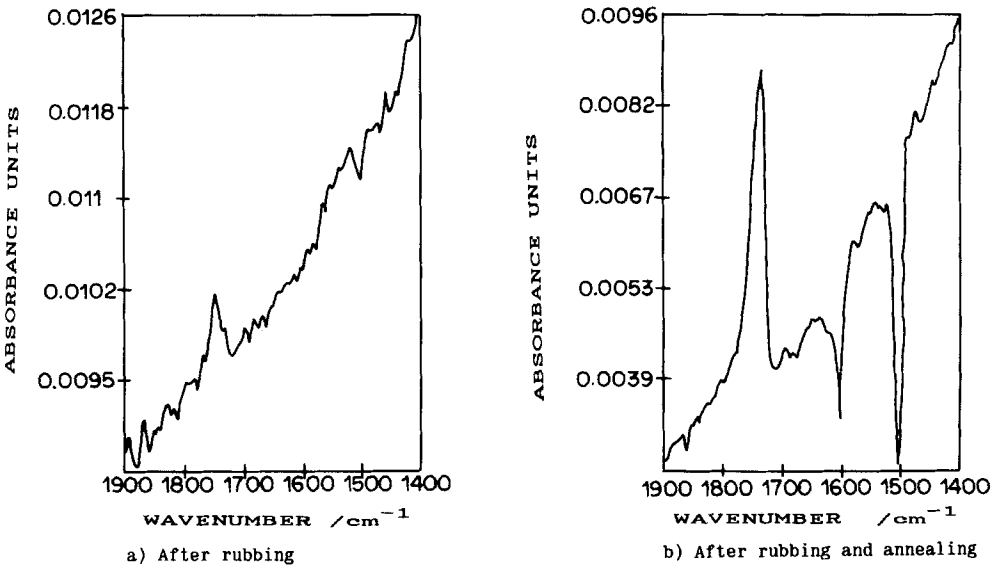

FIGURE 3 FT-IR subtraction spectrums (a) after rubbing and (b) after rubbing and thermal annealing at 300°C for 10 min. The spectra were obtained by subtracting absorbance parallel to rubbing direction from that perpendicular.

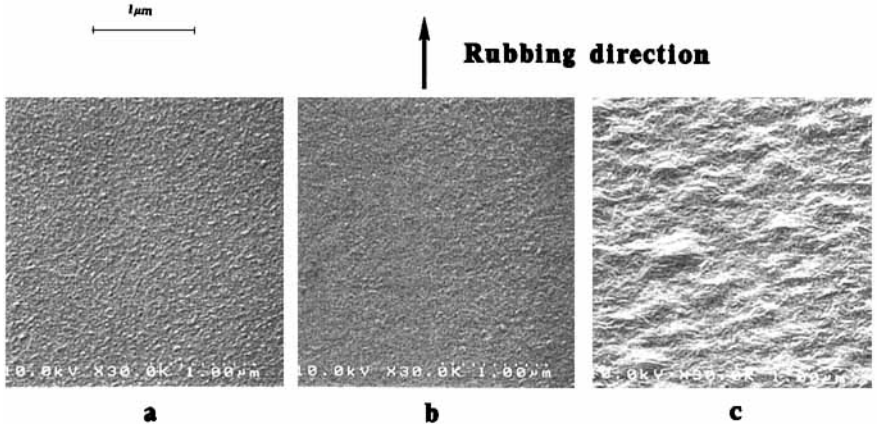

FIGURE 4 The surface of an untreated, LCP-1 film, after spin-coating on silicone wafer is shown in the scanning electron micrograph (a). The rubbed surface (b) and the rubbed and annealed surface (c) are shown.

annealing after rubbing. The treated surfaces were observed by both SEM and AFM. Since AFM does not need a conductive layer for insulation layers, a finer surface structure can be investigated.

Figure 4 shows scanning electron micrographs of the spin-coated film of LCP-1. As shown in Figure 4a, the surface coated by LCP-1 is relatively smooth although there exist hilly structures and some scratches. When the LCP film was rubbed by a nylon brush, the hill-like structures became flat (Figure 4b). After the rubbed film was annealed at 300°C for 10 minutes, the surface structure of LCP film changed

to the structure as in Figure 4c. A wavy pattern with short fibril-like structures clearly appeared. The short fibril-like structures are assumed to be crystallites.

AFM observations revealed a more detailed surface morphological change. Figure 5a shows that the cotton-like structure of the LCP-1 surface after coating is more easily observed with AFM than by SEM. The flattened spherical grain structure after rubbing can be observed cleary in Figure 5b. The annealed surface consists of many worm-like structures, which look fibrillar or needle-like in SEM observation. According to SEM observation, the length of fibril-like structures seems to vary between 50 nm and 400 nm. However AFM observation reveals that the dimensions of the worm-like structure are almost the same; ca. 150 nm by 40 nm. Because of the coating of the conductive materials used for SEM observation, fine patterns might not be distinguishable.

The surface of the oriented LCP-1 film annealed after rubbing consists of the long-range wavy patterns and short-range worm-like patterns. The wavy pattern can be explained by unwetting of the polymer layer on the glass substrates. That is, there is a tendency to minimize the surface-to-volume ratio by increasing the thickness and decreasing the surface area since the as-cast film has excess surface energy. The worm-like structure could be crystallites recrystallized at 300°C. HBA containing copolymers seems to form nonperiodic layer crystals with three dimensional order.[10] Since the annealing temperature (300°C) is not high enough for the residual high melt crystallites, the crystallites would be a nucleation of the worm-like crystallites keeping the molecular orientation created by the rubbing.

We fabricated test cells using LCP-1 as alignment layer and evaluated them after filling them with GT5001. Figure 6 shows the liquid crystal orientation under the polarizing microscope. A rubbed cell with 20 μm spacing shows relatively good orientation in the rubbing direction although the pattern from the screen plate which was used for sealing the test cells can be observed. The test cells fabricated from substrates after annealing show better orientation without the pattern from the screen plate. This indicates that annealing makes the surface of LCP-1 harder than the original surface.

The dichroic ratio of the guest/host liquid crystal in test cells was measured for the evaluation of the annealing effect on the LCP-1 alignment layer. Figure 7 shows the rubbing strength dependence of the dichroic ratio before and after thermal

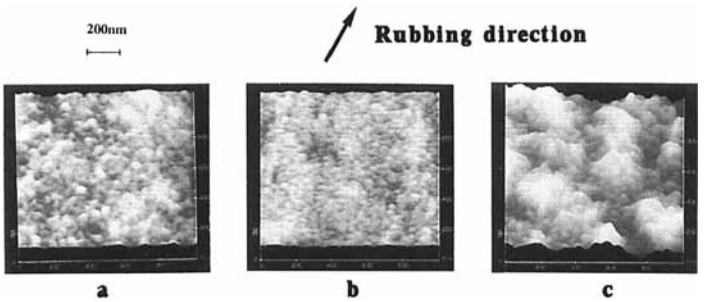

FIGURE 5 The surface morphological structures of LCP-1 film are shown in the atomic force micrographs. The untreated surface (a), the rubbed surface (b) and the rubbed and annealed surface (c) are shown.

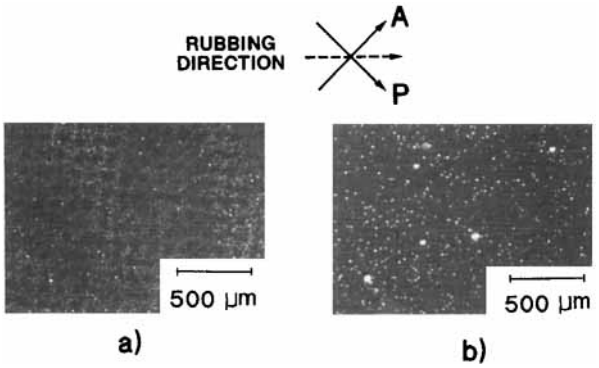

FIGURE 6 Observation of the alignment of a liquid crystal mixture under a polarising microscope shows patterns from a silk screen for the printing of sealing materials in the cell with a rubbed LCP-1 layer (a). The patterns disappeared in the cell with a rubbed and annealed LCP-1 layer (b). *A* and *P* mean the direction of analyzer and polarizer, respectively.

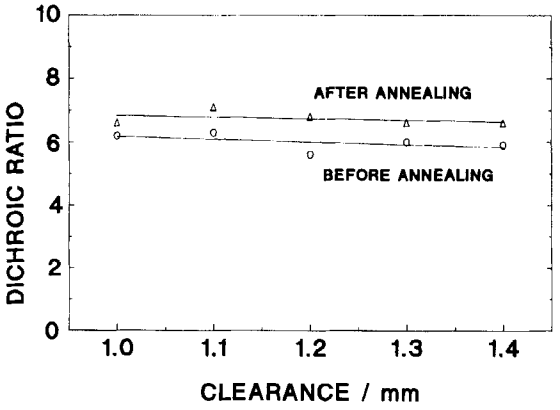

FIGURE 7 The clearance dependence of dichroic ratio of the dichroic dye in the liquid crystal mixture in the cell using substrates with and without annealing is shown. The rubbing strength is in reverse ratio to the clearance between the rubbing roll and glass surface in the rubbing machine.

annealing. In Figure 7 clearance means the distance between the running roll and glass surface in the rubbing machine. When the clearance becomes smaller, the rubbing strength becomes stronger. The dichroic ratio in the annealed cell is larger than that in the non-annealed cells regardless of rubbing strength. The alignment capacity of the LCP layer after annealing can be said to be superior to that before rubbing. This means that the rough surface after annealing could align nematic liquid crystals in the rubbing direction since molecules of LCPs are oriented in that direction.

Figure 8 shows the rubbing strength dependence of the pre-tilt angle of GT5001 on the LCP film before and after annealing. Before annealing the pre-tilt on the LCP-1 film is as high as that of the conventional PI. When the rubbing becomes stronger, the pre-tilt becomes higher. However, after annealing the pre-tilt of the liquid crystal is reduced to ca. 0° regardless of rubbing strength, while the orien-

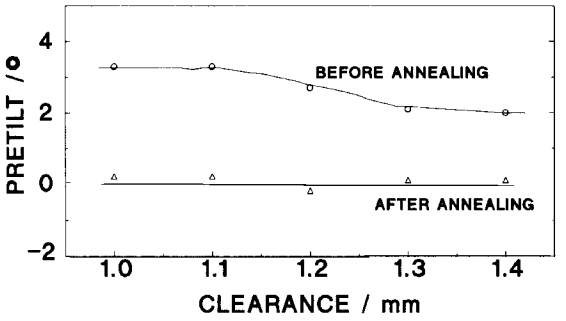

FIGURE 8 The rubbing strength dependence of pre-tilt angle of the liquid crystal mixture on LCP-1 film with and without the annealing is shown.

tation of the liquid crystal along the rubbing direction remains unchanged. Thus, the surface morphology of LCP-1 strongly affects only the pre-tilt angle.

CONCLUSION

The order of molecular orientation of main-chain LCP investigated by birefringence measurement and FT-IR is enhanced by annealing at the onset temperature of nematic transition.

The surface morphology of the LCP alignment layer, investigated by SEM and AFM, is changed drastically by the annealing. Despite the drastic change of the surface, nematic liquid crystal on the surface orient in the direction of the rubbing treatment before annealing. This result indicates that grooves do no play a role as had been expected by topographic effect arguments, and that the van der Waals force is more important for ordering the nematic liquid crystal. On the other hand, the pre-tilt of liquid crystals on the LCP layer disappeared after annealing. Since the LCP-1 does not contain any alkyl branches but consists of the rigid aromatic main-chain, the special steric interaction between LC molecules and the polymer surface for the high pre-tilt generation can not be expected as alignment layers for the STN devices.[11,12] Instead of such interaction, the specific surface morphology, such as spherical grain structure, is necessary for the emergence of pre-tilt for the rigid polymer.

Since the molecular orientation of the LCP is retained in the thin film after the thermal annealing at 300°C, it would be interesting to apply weak external force at that temperature to orient the LCP without rubbing.

Acknowledgment

We are grateful to Drs. T. M. Leslie and T. East from Hoechst Celanese Cooperation for LCP samples. We also thank Ms. Ubukata (Hoechst Japan Ltd.) for the SEM observation and Dr. Johnson and Dr. Yudasaka for the kind discussion. This work was supported by the Japan Key Technology Center.

References

1. Uchida, *et al.*, "Handbook of liquid crystal devices" (Ekishou device handbook), Nikkan Kogyo, 248 (1989).
2. J. Cognard, *Mol. Cryst. Liq. Cryst., Supplement* **1,** 1 (1982).
3. H. Yokoyama, *Mol. Cryst. Liq. Cryst.,* **165,** 265 (1988).
4. D. W. Berreman, *Phys. Rev. Lett.,* **28,** 1683 (1972).
5. K. Nakajima, H. Wakemoto, S. Sato, F. Yokotani, S. Ishihara and Y. Matsuo, *Mol. Cryst. Liq. Cryst.,* **180B,** 223 (1990).
6. L. C. Sawyer and M. Jaffe, *Journal of Material Science,* **21,** 1897 (1986).
7. T. Ohmura, Y. Sakon, T. Suzuki and T. Okawa, Presented at the 14th Liquid Crystal Conference in Japan (Sept. 27–29, Tohoku Univ.) 3B120 (1988).
8. S. G. Cotties and J. Economy, U. S. Pat. 3637595.
9. M. Suzuki, T. Maruo, F. Umemoto and K. Nagai, *J. Vac. Sci. Technol.,* **A8,** 631 (1990).
10. Y. G. Lin and H. H. Winter, *Macromolecules,* **1991,** 24, 2877–2882.
11. H. Fukuro and S. Kobayashi, *Mol. Cryst. Liq. Cryst.,* **163,** 157 (1988).
12. T. Sugiyama, S. Kuniyasu, D. Seo, H. Fukuro and S. Kobayashi, *Jpn. J. Appl. Phys.,* **29,** 2045 (1990).