

Ethyl Cellulose Films as Alignment Layers for Liquid Crystals

LIFENG YAN,¹ QINGSHI ZHU,¹ TOMIKI IKEDA²

¹ Open Laboratory of Bond Selective Chemistry, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, People's Republic of China

² Laboratory of Resource Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-Ku, Yokohama 226, Japan,

Received 12 May 2000; accepted 7 January 2001

ABSTRACT: Films were formed by coating hydroxypropyl cellulose (HPC) or ethyl cellulose (EC) with different kinds of solvents at high coating speeds and thin coating thicknesses. These films were used as alignment layers for liquid crystals. Atomic force microscopy (AFM) and polarizing optical microscopy (POM) were used to identify the banded texture structure of the films. The alignments of a nematic liquid crystal 5CB droplet on those films were observed by POM. Further, a novel cycle disclination line was recorded and studied. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2770–2774, 2001

Key words: ethyl cellulose; hydroxylpropyl cellulose; atomic force microscopy; liquid crystal alignment; disclination line

INTRODUCTION

A liquid crystal display (LCD) usually requires an alignment layer for liquid crystals (LCs). The most widely used alignment film is mechanically rubbed polyimide. It is well known that the polymer main chain orientation and microgrooves obtained by rubbing the polymer surface contribute to the LC alignment. However, the rubbing process produces dust and static electricity, which give rise to serious problems for the manufacturing process of LCDs. As a result, rubbing-free processes have received much more attention in

recent years. Many novel alignment layers have been proposed: Langmuir–Blodgett films,^{1,2} obliquely evaporated SiO films,³ polarized light alignment,^{4,5} UV curable polymer films,⁶ pulsed laser ablation,⁷ and so forth.

For rubbed polyimide films, there is a possible explanation for the alignment mechanism of LCs: the anisotropic molecular force between the rubbed polyimide surface and LCs causes the surface alignment of LCs.

A novel method was recently proposed to prepare rubbing-free alignment layers for LCs, hydroxypropyl cellulose (HPC) films were used.⁸ The HPC aqueous solution had a critical concentration of about 42 wt %. Above that concentration there is a phase transition, and the isotropic phase changed to a liquid crystalline one, which takes place in the aqueous solution of HPC. It showed the behavior of a liquid crystalline polymer (LCP). Usually, LCPs maintain a high degree of molecular orientation, which is induced by the flow in polymer processing until solidification, be-

Correspondence to: L. Yan (lfyan@ustc.edu.cn).
Contract grant sponsor: Japan Society for the Promotion of Science.

Contract grant sponsor: Foundation of the Chinese Academy of Science; contract grant number: KJ951-A1-510.

Contract grant sponsor: Natural Science Foundation of Anhui Province; contract grant number: 99041202.

Journal of Applied Polymer Science, Vol. 82, 2770–2774 (2001)
© 2001 John Wiley & Sons, Inc.

cause of the long relaxation time of orientation. Therefore, LCP films with flow-induced molecular orientation may induce the molecular alignment of LCs.

In this work we prepared flow-induced oriented HPC and ethyl cellulose (EC) films as alignment layers. The surface morphology of the films and alignment behavior for the LCs on these films were studied with different casting solvents.

EXPERIMENTAL

Film Preparation

Solutions of EC (10 cP viscosity in 49% ethoxy, Wako Pure Chemical Industries, Ltd.) were dissolved in chloroform, benzene, and acetone. Because EC tends to form a sticky, inhomogeneous paste if the concentration is too high, we initially prepared dilute solutions. Then the solutions were concentrated by evaporation until the desired concentration was reached. A solution was prepared at a concentration of 60 wt % for each system; at this concentration all the systems existed in an anisotropic liquid crystalline state. In cases where a significant amount of polymer adhered to the side of the container as the solvent evaporated, the sample vial was immersed in a heated water bath and small additional amounts of solvent were periodically used to flush the adhering material into the bulk solution.⁹ Solutions were homogenized in sealed vials for at least 1 week prior to use.

Glass substrates were coated with these solutions of EC at room temperature. The EC films were cast and sheared by a knife edge moving at a constant speed, which ranged from 0.5 to 5 mm/s. The coating thickness was controlled by the gap between the knife edge and the glass substrate, which was 20–60 μm . After the coating, the glass substrate was immediately placed in a desiccator with silica gel, and the coating film was dried for 2 days at the room temperature.

Films of HPC and water (HPC/W), and HPC and ethanol (HPC/E) were prepared as described in the literature⁸ to compare the films formed by EC with HPC.

Measure of Surface Morphology and Alignment Behaviors

The surface morphology of the films was analyzed by using atomic force microscopy (AFM, SPM-9500 J2 microscope, Shimadzu, Tokyo). Silicon

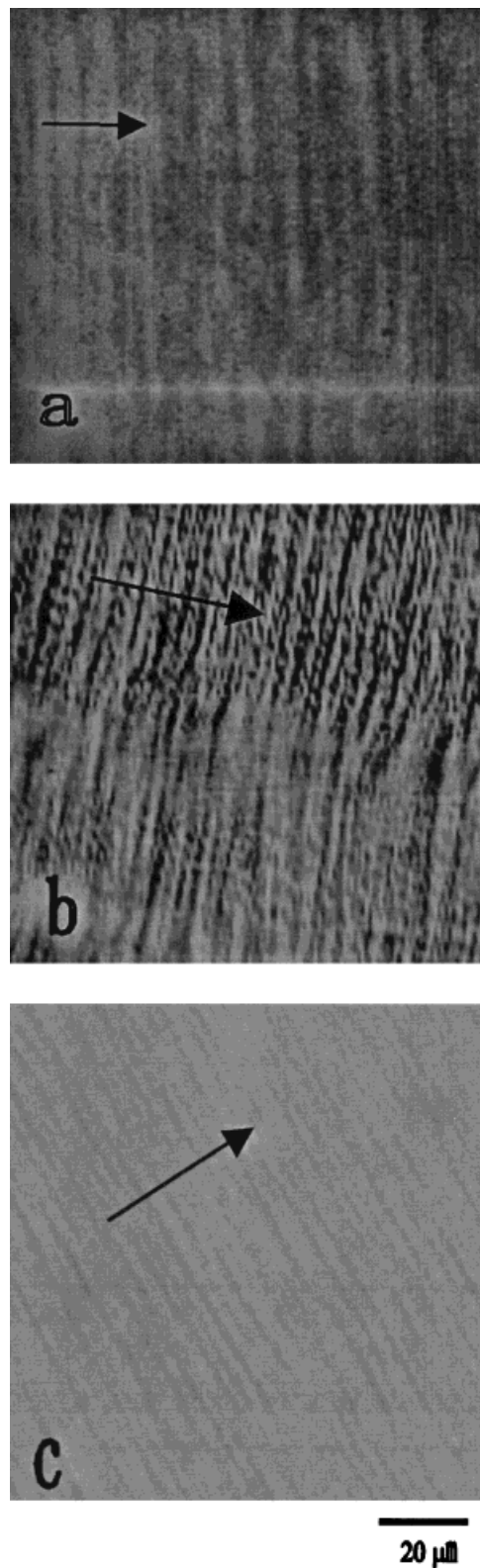


Figure 1 The banded-texture structure of the (a) HPC/W, (b) HPC/E, and (c) EC/C films observed by POM; the arrows show the casting direction.

nitride tips were purchased from the same manufacturer. A narrow cantilever was used that had a length of 200 μm , a spring constant of 0.16 N/m,

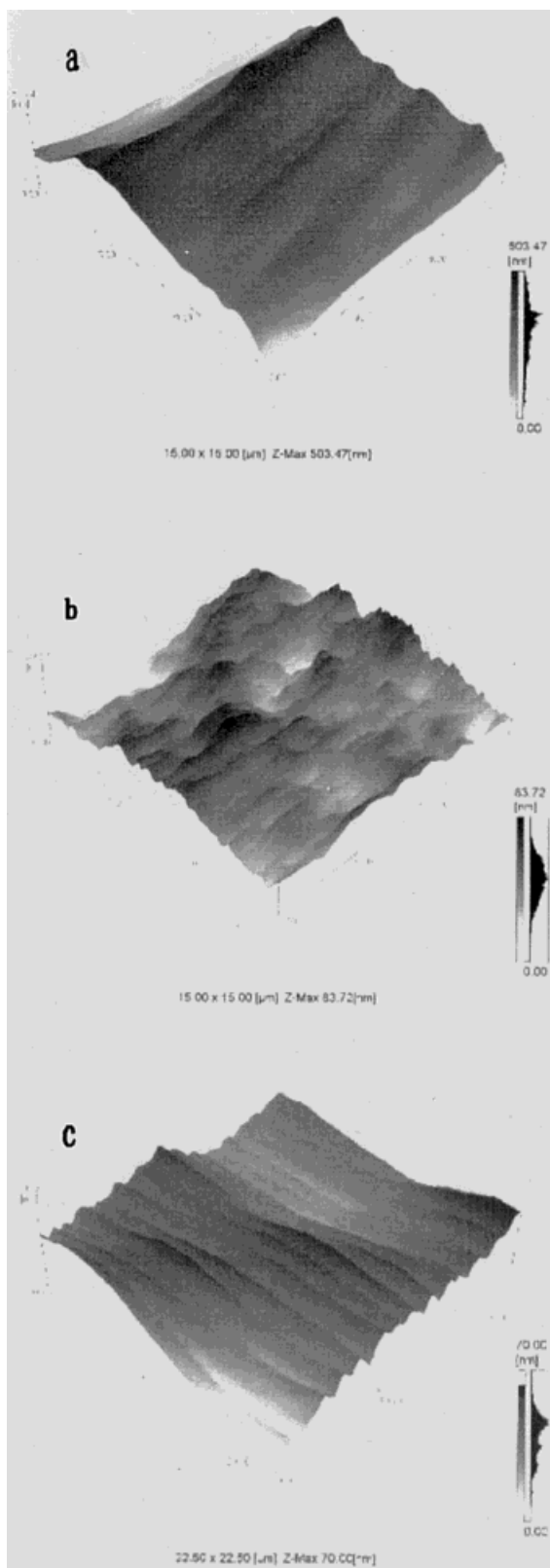
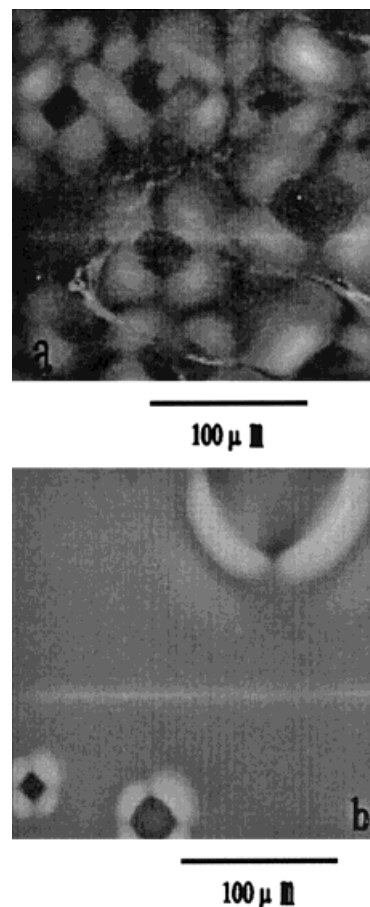


Figure 3 The texture structure of EC films prepared in (a) benzene and (b) acetone as observed by POM.



and a resonance frequency of 27. The texture of the films was measured by polarizing optical microscopy (POM, Olympus BH-2 microscope), and it was also used to measure the alignment behavior of the LC droplet on the surface of the film. A Sony CCD camera was used to record the optical images.

RESULTS AND DISCUSSION

Surface Morphology of Films

Figure 1(a–c) shows the banded texture of the HPC/W, HPC/E, and EC/chloroform (EC/C) films,

Figure 2 The surface morphology of the (a) HPC/W ($15.0 \times 15.0 \mu\text{m}$, $Z\text{-max} = 503.47 \text{ nm}$), (b) HPC/E ($15.0 \times 15.0 \mu\text{m}$, $Z\text{-max} = 83.72 \text{ nm}$), and (c) EC/C ($22.50 \times 22.50 \mu\text{m}$, $Z\text{-max} = 70.0 \text{ nm}$) films measured by AFM; the arrows show the casting direction.

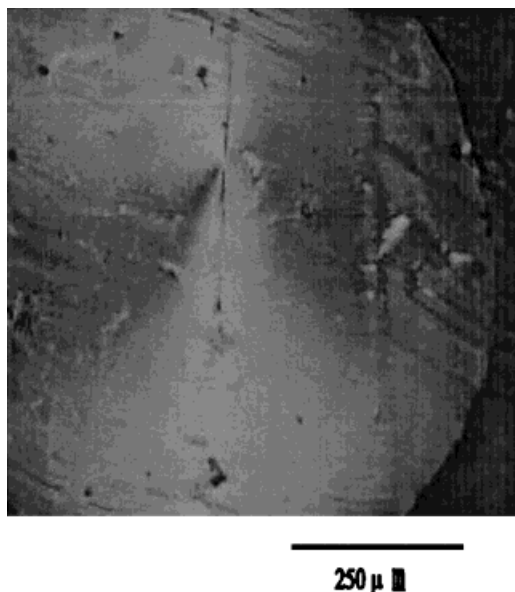


Figure 4 The alignment behavior of a 5CB droplet on EC/C film.

respectively. All three systems formed a banded-texture structure. Fine dark lines separated the bands homogeneously. However, the bandwidth in the three systems was different; HPC/E had the lowest bandwidth, and HPC/W had the highest one. The bandwidth is half of the period of the sinusoidal or zigzag packing structure. Figure 2 shows the relative morphology measured by AFM. The results were similar: the bandwidths of HPC/W, HPC/E, and EC/C were 3, 0.73, and 1.80 μm , respectively.

The band formation mechanism was proposed by several researchers.¹⁰ A common feature of this mechanism is that the banded texture is a transient structure in the relaxation of the oriented polymers that releases the stored energy as fast as possible. Zhao et al.¹⁰ concluded that during the shearing process there is some elastic energy stored in the rigid/semirigid polymer LCs. After cessation of shear, the oriented polymers begin to relax. However, because the rigid polymers are concentrated and highly aligned, their individual thermal relaxation is difficult; they must relax cooperatively and collectively to some degree. As a result, the inner stress induces a more or less intense periodical contraction in the polymer LCs and the macromolecules pack in a sinusoidal or zigzag fashion. Subsequently, an increasing individual thermal relaxation takes place. Finally, the banded texture is completely destroyed and the equilibrium state texture forms.

However, when we measured the EC/benzene (EC/B) and EC/acetone (EC/A) systems, which were prepared with the same method as that of EC/C films, the banded texture was not observed. Instead, we observed another liquid crystalline texture as shown in Figure 3. This texture may have been the effect of solvent polarity. Because EC/C is a better solvent than benzene and acetone, the inner stress of EC in benzene or acetone was low, which was not enough to form the banded-texture structure.

Observation of Droplets of LC 4-Cyano-4'-*n*-Pentylbiphenyl (5CB) Alignment on EC/C Film

Figure 4 shows the microphotographs of droplets of 5CB on the EC/C film after balance. A clear disclination line with crossed dark and bright regions is shown. Yamaguchi and Sato¹¹ suggested that if nematic LCs (NLCs) uniformly align parallel to the alignment layer, the directed distribution in the droplet causes a straight disclination line perpendicular to the easy axis across the center of the droplet. When the molecules of NLCs tilt at the surface, a curved disclination line appears. Figure 4 shows this behavior, which confirmed that 5CB NLC molecules aligned parallel to the direction of the banded-texture structure. Thus, the EC/C film was a suitable layer for LC alignment.

Mori et al.⁸ reported that homogeneous surface alignment of LC 5CB was observed for films formed by HPC/W and HPC/E systems. A similar disclination line was found in the 5CB droplets.

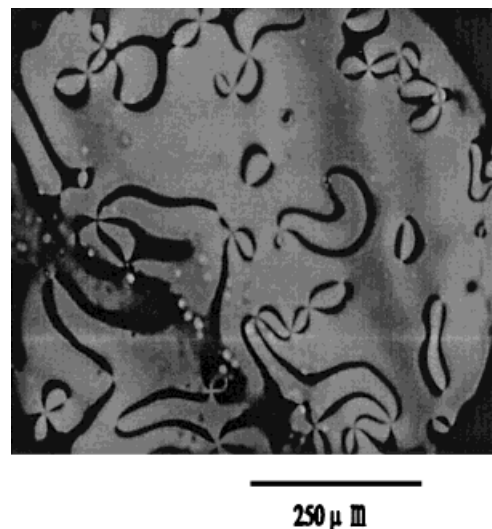


Figure 5 The texture of a 5CB droplet on a glass surface.

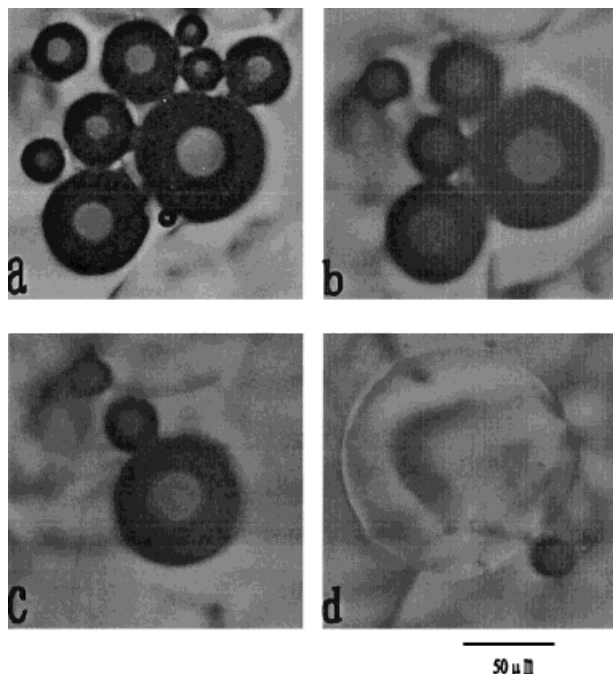


Figure 6 The cycles in the alignment process of 5CB on the surface of an EC/C film.

The relationship between the texture of LCP films and the alignment of the LCs on these films was discussed by many researchers. Yamaguchi and Sato¹¹ demonstrated that anisotropic surface morphology increases the anchoring energy of LCs, which means that the banded texture of the films is favorable for good alignment for LCs.

The texture of 5CB on a normal glass slide was measured to clearly identify the effect of the LCP film on the alignment of 5CB. Figure 5 shows the POM microphotograph of the 5CB droplet in which no disclination line was formed. Compared to Figure 4, the banded texture of the film was the main factor in the LC alignment.

However, we used the same EC/C film as the alignment layer and observed a different alignment behavior of 5CB on the film. There were several cycles in the droplet, as shown in Figure 6. The different sized cycles slowly connected with each other, and the little cycle combined into a bigger one. Finally, the big cycle broke and a cycle

disclination line appeared. This behavior was unclear. It seemed that these cycles were air bubbles formed in the droplet process. The cycle disclination line indicated a tilt alignment of the LCs on the surface.

CONCLUSION

Rubbing-free EC films were prepared by flow-induced orientation of LCP EC with chloroform as a solvent. A banded texture was observed by AFM and POM characterizations. As an alignment layer, this film showed wonderful alignment properties for LC 5CB. Moreover, a novel alignment behavior was found and a cycle disclination line was recorded in this study.

We are grateful to the Japan Society for the Promotion of Science for the support of the Core University Programme in Asia. This work was also supported by the Foundation of the Chinese Academy of Science and the Natural Science Foundation of Anhui Province. We would also like to express our sincere gratitude for the help given by Associate Professor Kanazawa, Dr. Hai-chao Zhang, and Dr. Kanayama in the Laboratory of Resource Utilization, Tokyo Institute of Technology.

REFERENCES

1. Chizaki, M.; Abe, H.; Iwa, H.; Tomokiyo, R.; Shigehara, K.; Amaya, N.; Kaiya, N.; Iimure, Y.; Kobayashi, S. *Jpn J Appl Phys* 1995, 34, 2411.
2. Sasaki, T.; Fujii, H.; Nishikawa, M. *Jpn J Appl Phys* 1992, 31, L632.
3. Janning, J. L. *Appl Phys Lett* 1972, 21, 1039.
4. Gibbons, N. M.; Shannon, P. J.; Sun, S. T.; Swetlin, B. J. *Nature* 1991, 351, 49.
5. Schadt, M.; Schmitt, K.; Kozinkov, V.; Chiqrinor, V. *Jpn J Appl Phys* 1992, 31, 2155.
6. Yamaguchi, R.; Sato, S. *Jpn J Appl Phys* 1996, 35, 937.
7. Luo, Q.; Xiong, S.; Wu, H.; Sun, Z.; Ming, N. *Mol Cryst Liq Cryst* 1996, 289A, 69.
8. Mori, N.; Morimoto, M.; Nakamura, K. *Macromolecules* 1999, 32, 1488.
9. Viney, C.; Putnam, W. S. *Polymer* 1955, 36, 1731.
10. Zhao, C.; Zhang, G.; Cai, B.; Xu, M. *Macromol Chem Phys* 1998, 199, 1485.
11. Yamaguchi, R.; Sato, S. *Jpn J Appl Phys* 1996, 35, L117.