

강유전성 액정 디스플레이의 배향을 위한 액정성 고분자

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Liquid Crystalline Polymer for the Alignment of Ferroelectric Liquid Crystal Display

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초 록 강유전성 액정 분자 배향을 위해 열방성 고분자 액정물질을 배향막으로 사용하고 그 표면 morphology를 AFM (Atomic Force Microscope)으로 관찰한 결과 잘 배향된 sample cell에서도 microgroove 구조가 나타나지 않았음을 관찰하였다. 잘 배향된 sample cell은 23:1의 contrast ratio를 보이면서 memory 효과를 나타내었다. 또한 20V의 AC field로 안정화시키자 전형적인 stripe-shaped 무늬가 나타났다.

Abstract Thermotropic liquid crystalline polymer(LCP) has been used for the alignment of ferroelectric liquid crystal (FLC) molecules and the surface morphology of the resulting polymeric thin film has been observed by atomic force microscope.

The uniform alignment of FLC molecules on the surface of thermotropic LCP thin film was obtained even though microgroove structures were not formed. The contrast ratio of sample cell was about 23:1 including two polarizers and a good memory capability due to the bistability of FLC was obtained. After AC field stabilization at 20 V, the typical stripe-shaped patterns appeared.

Key words : Polymers, Ferroelectricity, Optical materials, Atomic force microscopy(AFM)

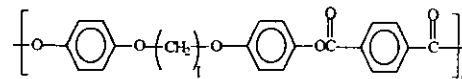
1. Introduction

Since the discovery of a ferroelectricity of chiral smectic C phase molecules¹⁾, many researches and developments have been focused on the realization of surface stabilized ferroelectric liquid crystal displays (SSFLCD) to the high information content, high contrast ratio, wide viewing angle, and fast switching speed as compared with an ordinary nematic displays.^{2~4)}

Although the SSFLCD has many attractive characteristics, a commercialized SSFLCD is still not available. Several problems are still left to realize a practical SSFLCD. Among the problems which should be solved, an uniform alignment of liquid crystal molecules is the most important to obtain a high quality screen image. In order to align the liquid crystal molecules, the rubbing treatment of polymeric thin films by appropriate cloth is required. According to many previ-

ous studies, the morphological changes including the chain elongation of polymeric alignment film along the rubbing direction may be one of the most reasonable explanations for the alignment of liquid crystals on the rubbed polymeric thin films.^{5~7)} But the mechanism has not been understood very well.

We are focusing on the alignment of ferroelectric liquid crystal molecules using the thermotropic liquid



I=6 and 10

I=6:	T _g is not observed,	T _m =300°C,	T _d =435°C
I=10:	T _g =182°C,	T _m =270°C,	T _d =450°C
Mol(I=6)/Mol(I=10)=1/1:	T _g is not observed,	T _m =230°C,	T _d =410°C

Fig. 1. The chemical structure of LCP for the alignment of FLC molecules. T_g is glass transition temperature, T_m is melting temperature, and T_d is decomposition temperature.

crystalline polymer (LCP) as an alignment film because the thermotropic LCPs have properties of self-orientation by appropriate external forces such as mechanical or thermal treatment. In present research, we first describe the results of uniform FLC molecular alignment on the thermotropic LCP film by rubbing process that show a good cell performance even though any grooves or scratches are not formed.

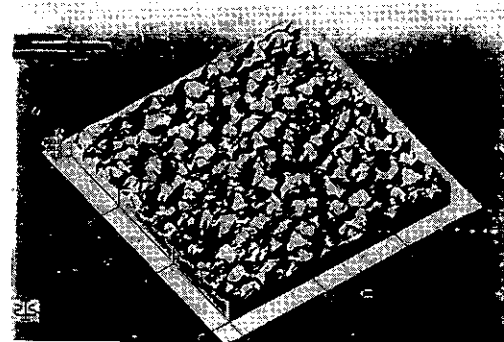
2. Experimental

In this experiment, two kinds of polymeric thin films were used. One is the well-known polyimide RN-715 that is provided by Nissan Chemical Co. and the other is the thermotropic LCP that was directly synthesized from the mixture of 1,6-di(4-hydroxyphenyl)hexane and 1,10-di(4-hydroxyphenyl)decane for aromatic diol and terephthaloyl chloride for acid chloride. The 1,6-di(4-hydroxyphenyl)hexane was synthesized from hydroquinone and 1,6-dibromohexane. And also the 1,10-di(4-hydroxyphenyl)decane was synthesized from hydroquinone and 1,10-dibromodecane. The detailed synthetic method is described in reference.⁹⁾ The thermotropic LCP structure is shown in Fig. 1. The thermal properties of this thermotropic LCP was controlled by changing the mole ratio of the two diols with different methylene length ($l=6$ and 10). When the mole ratio of the diols is 1:1, the thermotropic LCP has melting temperature at 230°C but the glass transition temperature was not observed at all. In this experiment we used the thermotropic LCP as an alignment film because of a relatively low melting temperature and an easy processibility. This polymer is aromatic main chain type thermotropic liquid crystalline polymer. The thermotropic LCP was dissolved in dimethylsulfoxide (1 wt%) at 25°C and then filtered through $0.5\mu\text{m}$ pore size. The solution was spin coated on glass substrated at 3000 rpm and then baked at 110°C for 10 min and 260°C for 30 min. The RN-715 solution (1 wt%) was coated by the same method as that of thermotropic LCP solution, and baked at 80°C for 15 min and 260°C for 30 min. The thicknesses of the obtained films were about 500\AA . Afterwards the substrates were rubbed with a rayon cloth under appropriate rubbing strength. The sample cell was prepared by sandwiching the FLC materials, FELIX-T250 provided by Hoechst Japan Ltd. between two glass substrates with indium-tin oxide electrode was controlled to $1.7\mu\text{m}$ by using silica spacers. A good alignment was obtained by slow cooling of the cell from the isotropic (85°C) to the SmA phase (62°C) and electro-optical measurements were carried out under opti-

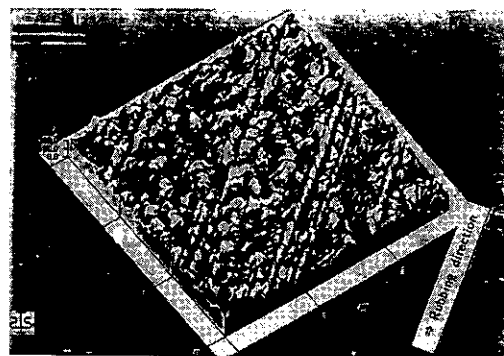
cal polarized microscope after the application of bipolar electric field of $\pm 20\text{ V}$ that has pulse width of $67.5\mu\text{s}$ and cycle of 16.7 msec. The cell was between crossed polarizers and rotated to the angle of minimum transmission for one of the states. The surface morphology of alignment layers has been studied by atomic force microscope in order to investigate the relationship between the rubbing treatment and the capability of alignment of FLC materials.^{9,10)}

3. Result and Discussion

In order to compare the morphological changes of thermotropic LCP with those of RN-715 before and after rubbing treatment, the surface was observed by atomic force microscope. When the surface of RN-715 is not rubbed, the hill-like structures having about 100\AA height are formed and randomly located through the surface as shown on Fig. 2. (a). By rubbing treatment these peaks are oriented in the rubbing direction and result in forming microgrooves as shown in Fig. 2. (b). The width between the microgrooves is approximately $1\mu\text{m}$ and the surface of thermotropic LCP is rather flattened. Fig. 3. shows the electro-optical measurement



(a)



(b)

Fig. 2. The surface morphology of RN-715 film is shown in the atomic force micrograph. (a) untreated surface, (b) rubbed surface

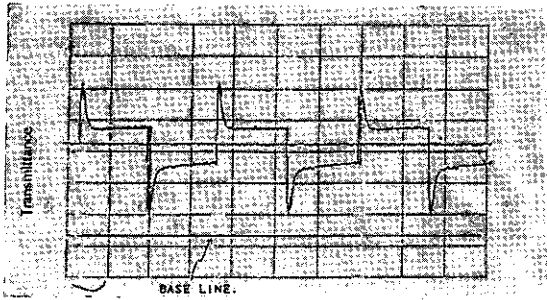


Fig. 3. The electric-optical response of the cell coated with RN-715 to ± 20 V bipolar pulse.

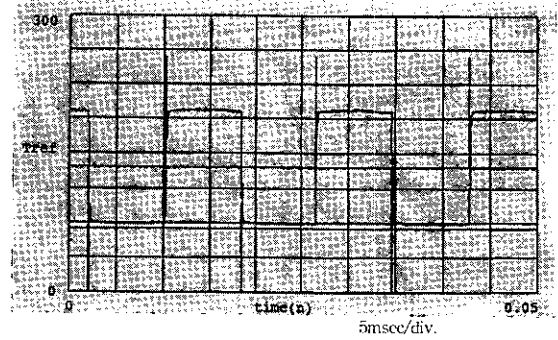
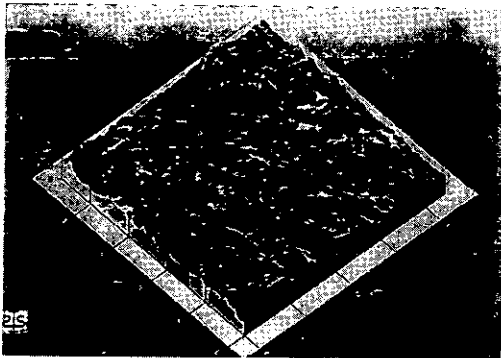
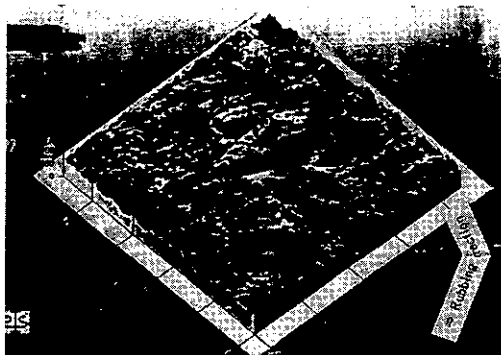


Fig. 5. The electric-optical response of the sample cell to 20V square wave. The horizontal dark line mark 0% level.



(a)



(b)

Fig. 4. The surface morphology of LCP thin film is shown in the atomic forced micrograph. (a) untreated surface, (b) rubbed surface

of the resulting sample cell. The memory capability due to the bistability of FLC molecules is not good. Transmittance is decreased to about 30% of maximum value just after switching off the applied voltage.

Fig. 4. (a) and Fig. 4. (b) show atomic forced microscope of the surface of thermotropic LCP before and after rubbing treatment. Before the surface is rubbed by rayon cloth, the irregular thread-like structures are observed as shown in Fig. 4. (a). However, after rubbing treatment of the surface of thermotropic LCP, the morphological changes are not observed at all, but the surface is relatively smooth as shown in Fig. 4. (b). Fig. 5. is the results of electro-optical measurement of the

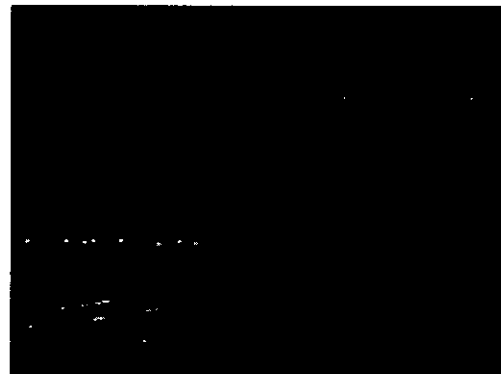


Fig. 6. The stripe pattern of the sample cell is shown in the polarized optical microscope.

sample cell coated with thermotropic LCP thin film. The memory capability is very good. Even though the applied voltage is off, transmittance is not decreased. Recently, M. Murakami et al. reported the similar results that show the fibril-like structure after annealing of the rubbed surface of main chain thermotropic LCP thin film.¹¹⁾ According to their results, the morphology of the surface of thermotropic LCP is drastically changed and thermotropic LCP orient more in the rubbing direction after annealing. However, in our experiment the morphological changes are not observed despite annealing at 200°C for 1 hour. This result may be due to the chain rigidity of the thermotropic LCP, in order words, the difficult thermal movement of polymer chains. When the annealing temperature is slowly increased to about 350°C, the polymer chains started to be decomposed. We are further researching on the relationship between the thermal treatment of thermotropic LCP thin films and the alignment of FLC molecules according to the various thermotropic LCPs with different chain rigidity.

Fig. 6. shows an optical polarized micrograph of the sample cell filled with FELIX-T250 after AC field treatment at 20 V. The typical stripe-shaped texture is

obtained. It has been previously reported that the stripes are aligned perpendicular to the smectic layers with a period proportional to the FLC cell thickness as observed under a polarizing microscope but the mechanism of the formation of stripes is being studied by many research groups.¹²⁾

From these experiments, it may be concluded that the chain orientation as well as the formation of micro-grooves affects the uniform alignment of ferroelectric liquid crystals on the surface of liquid crystalline polymeric thin films and resulting in a good electro-optical performance.

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