

# 이온빔을 조사한 폴리스타일렌 기판에서의 액정의 배향특성

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## Investigation of Liquid Crystal Alignment on ion beam exposed polystyrene surface

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### 요약

본 연구에서는 이온빔을 조사한 폴리스타일렌 기판에 일정강도의 이온빔을 조사한 경우에 발생되는 액정배향의 특성에 대해서 연구하였다. 폴리스타일렌은 기계적강도 및 절연성에서 액정표시소자의 배향막으로 사용되는 폴리이미드 계열의 대체 물질로서 주목받고 있으며, 특히 비접촉 배향에서의 가능성이 새롭게 평가되고 있는 소재이다. 이온빔을 조사하여 이방성을 발생시킨 박막의 표면에서의 액정배향상태를 편광현미경으로 관찰하고, 액정배향에 기여한 메커니즘의 규명을 위해서 XPS(X-ray photoelectron spectroscopy) 분석을 사용하였다. 분석한 결과 15초까지의 이온빔 조사는 액정의 배향을 유발하는 중요한 원인으로 작용함을 알 수 있었으며, 이온빔조사에 의한 액정의 배향방법은 고온안정성도 겸비하고 있는 것을 실험을 통해서 알 수 있었다.

**Key Words :** liquid crystal, orientation, ion beam, polystyrene, x-ray photoelectron spectroscopy

### ABSTRACT

This paper introduces homogeneous liquid crystal (LC) orientations on chemically modulated polystyrene (PS) surfaces using various ion beam (IB) exposure time. Transparent PS was replaced with conventional polyimide material. As a non-contact process, IB bombardment process induced LC orientation in the direction parallel to the IB process. Through x-ray photoelectron spectroscopy, it was shown that the chemical compositional changes of the IB-irradiated PS surfaces were determined as a function of IB exposure time. Using this analysis, the optimal IB bombardment condition was determined at IB exposure time of up to 15 s. Moreover, thermal stability on IB-irradiated PS surfaces were carried out which showed that a relatively high IB exposure time induced a thermally stable LC alignment property.

## I. 서 론

Interactions between liquid crystal (LC) molecules and LC alignment surfaces have significant meaning in both fundamental research and liquid-crystal display (LCD) applications [1,2]. Organic and inorganic LC alignment layers have been widely studied by several groups [3-6]. Although inorganic LC alignment layers have attracted wide attention in these days [4,5], organic materials for LC alignment layers such as polyimide (PI) and polystyrene (PS) should be studied because it is easy to coat organic materials on glass substrates. Moreover, with the many disadvantages associated with mechanical rubbing,

non-contact LC alignment method has become the most promising substitute for this conventional method [3-x]. A rubbed polymer surface includes debris left by the cloth, and the generation of electrostatic charges during rubbing induces local defects, streaks, and a gratinglike wavy surface due to nonuniform microgrooves that degrade the display resolution. Non-contact alternatives, including ultraviolet (UV) exposure [4,7,8], ion beam (IB) bombardment [3,5,6], and nanoimprinting lithography [9], have been reported. Of these, the UV alignment method has the advantages of a clean process, large-scale manufacturing and multidomain capability, although UV stability, low anchoring energy, and alignment materials

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must be considered carefully. In contrast, the IB alignment method has none of the drawbacks of the UV alignment method.

As a LC alignment material, the refractive index of PS is nearly the same as that of glass substrate, implying that the transparent PS material is a candidate for an organic alignment material. PS material was studied by another group, which shows that IB treatment broke phenyl rings of the PS material selectively. However, further studies are needed using IB treatment for applying PS material. Our study will provide a more detailed investigation under various IB experimental conditions. To align the homogeneous LC molecules on the PS layers, IB irradiation as a function of IB exposure time was used. Observing the conditions of the homogeneously aligned LC molecules helped to determine the optimal IB exposure time. Additionally, the chemical changes before and after the IB irradiation process on the PS surfaces were examined using X-ray photoelectron spectroscopy (XPS) analysis.

## II. Experimental

PS (from Aldrich) was used as alignment layers. PS was dissolved in toluene to form a solution of 1.4 wt% concentration. Indium tin oxide (ITO)-coated glass substrates were cleaned supersonically in a trichloroethylene-acetone-methanol-deionized water solution sequentially for 15 min and then dried with N<sub>2</sub> gas. The PS solution is spin-coated onto ITO-coated glass and the coated substrates were soft-baked at 80 °C for 10 min and imidized at 230 °C for 1 h. The PS surfaces were irradiated with an Ar IB plasma using a DuoPIGatron-type IB system [6]. The IB chamber was initially evacuated to a base pressure of approximately 10<sup>-6</sup> Torr, and the working pressure was maintained at approximately 10<sup>-4</sup> Torr with an Ar gas flow of 1.4 sccm. The IB bombardment was conducted at times of 15, 30, 45, and 60 s with exposure energy and angle of 2 keV and 45°, respectively. These substrates were fabricated in an antiparallel configuration with cell gap of 60 μ, were used to measure the pretilt angle and thermal stability. A positive LC ( $T_c = 72$  °C,  $\eta_M = 8.2$ ,  $\eta = 0.777$ ; Merck MJ001929) was injected into the cell and assembled. To measure the pretilt angles of homogeneous LC molecules on the IB-irradiated PS surfaces, a crystal rotation method

(TBA 107 Tilt-bias Angle Evaluation Device; Autotronic) was used, observing the oscillation of the transmittance of LC cells (60 μ cell gap) with a latitudinal rotation from -70° to 70° through the variation of the birefringence produced by LC cell rotation. Thermal stabilities for LC cells were observed to estimate LC anchoring energy. After the LC cell was annealed by specific heat and cooled gradually, the LC alignment effect was observed by photomicroscope. All IB-irradiated PS surfaces were examined using XPS (ESCA LAB 220-XL, VG Scientific, USA) analysis. The measured bindings were referred to the C1s signal at 284.6 eV, and the composition of each sample was determined to compare the normalized area intensities of the C1s peaks.

## III. Results and Discussion

Figure 1 shows the transmittance characteristics as a function of exposure time for measuring the pretilt angles of LCs on the PS surface. Figures 1(b), 1(c) and 1(d) show stable graphs of the pretilt angles of LC on the PS surface. The error ratios, which are represented by the difference between the blue and red curves in Fig. 1, were low, indicating well-aligned homogeneous LC orientation. However, Fig. 1(a) shows high error ratio. This indicates that well-aligned LC on PS surfaces achieved when IB exposure time is up to 30 s. Table 1 shows the measured pretilt angles of homogeneous LCs on IB-irradiated PS surfaces. As seen, all pretilt angles were 0–1°. However, it could be confirmed that LCs were randomly aligned on PS surface at exposure time of 15 s. Here, the important thing is that LCs align parallel to the direction of IB exposure while using an IB process. Generally, the LC orientation achieved is in a direction orthogonal to the rubbing process [10,11]. This difference arises because IB irradiation produces very dominant dipole-dipole interactions that induce the LCs on the PS surface to align in a direction parallel to the direction of IB irradiation.

**Table 1. The measured pretilt angles of homogeneous LC molecules on IB-irradiated PS surfaces.**

IB irradiation time (s)	Pretilet angle (°)	Error
15	0.20986	0.02472
30	0.153854	0.0025
45	0.142633	0.002789
60	0.559771	0.005537

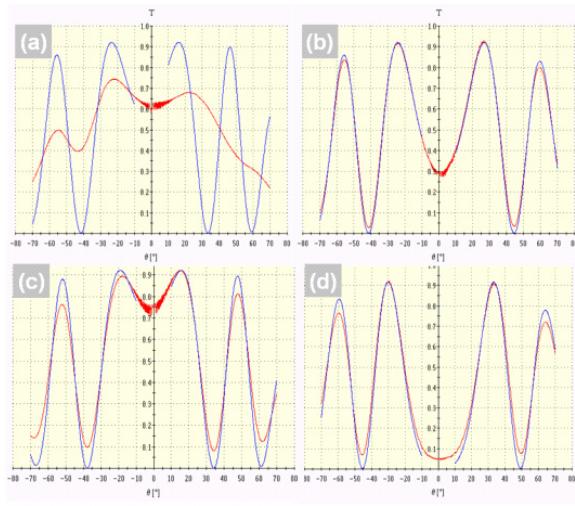


Fig. 1. Transmittance as a function of incident angle on the PS surface with various IB exposure time: (a) 15 s, (b) 30 s, (c) 45 s, and (d) 60 s.

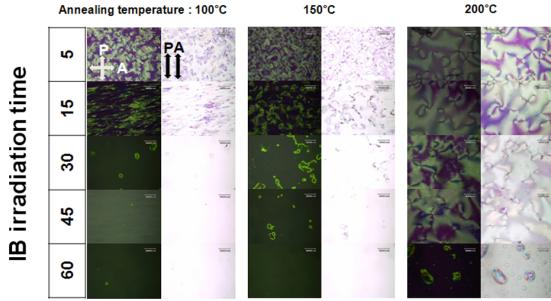


Fig. 2. Photomicroscopic images of each LC cell for thermal stability using various IB exposure time. Each cell was annealed using three different annealing temperatures of 100, 150, and 200 °C.

Figure 2 shows the microscope images of the fabricated LC cells as a function of annealing temperatures to examine the relationship between the ability of the LCs to maintain their orientation and thermal stability. To examine the thermal stability of the LC cells, the cells were annealed at 100, 150, 200 oC for 10 min. All images were same until annealing temperature of 100 oC. As mentioned above, randomly aligned LCs were obtained on IB-irradiated PS surfaces with IB exposure time of 5 and 15 s. Destruction of the LC orientation on the IB-irradiated PS surface with an IB exposure time of 30 s started at an annealing temperature of 100 oC. In contrast, the LC orientations of the other cells obtained using IB exposure times of 45 and 60 s were stable at a temperature of 100 oC. As the annealing temperature was increased up to 150 oC, the LC orientation induced by the IB exposure time of 45 s destroyed. Eventually, the LC orientations on all LC cells were destroyed at annealing temperature of 200 oC. These results mean that a relatively high IB exposure

time resulted in strong thermal dipole-dipole interactions between PS surfaces and homogeneous LC molecules allowing them to maintain their LC orientation with a stable thermal property. Also, we can see that LC cells fabricated by IB-irradiated PS surface have good thermal stability comparable to PI-based LC cell.

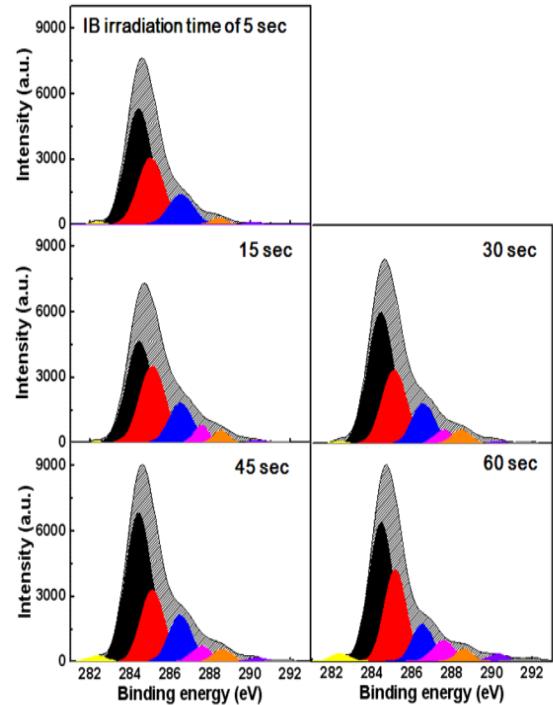


Fig. 3. XPS spectra of IB-irradiated PS surfaces for C 1s at various IB exposure time.

The chemical binding characteristics of the atoms on the PS surfaces were analyzed by a series of XPS spectra of C 1s core levels [13–15], and the changes in composition of the LC alignment layers before and after IB irradiation are shown in Fig. 3. Figure 3 shows the measured C 1s spectra, in which the dominant peak component of the aromatic carbon area was located at  $284.5 \pm 0.1$  eV. The component peak at  $285 \pm 0.1$  eV is related to the CH atoms, and the low binding energy at  $282.3 \pm 0.1$  eV is due to the surface contamination of C 1s. The component peak located at  $286.4 \pm 0.1$  eV is related to the C-OR bonds, the component peak centered at  $288.6 \pm 0.1$  eV corresponds to the O-C=O bonds and the component peak at the  $291.5 \pm 0.1$  eV is from the broad aromatic shake up. In Fig. 3, the peak corresponds to the carbons on the phenyl ring, which increase and is saturated over IB exposure time of 15 s. Also, we observed the newly produced C=O bonds centered at  $287.6 \pm 0.1$  eV between the IB exposure times of 15 s and 60 s,

although the production was scant at 5 s. The increment of C=O peak indicates the reformation of the phenyl ring. That is, IB bombardment transformed carbon oxide bonds on the PS surfaces into C=O bonds in the direction of the anisotropic IB exposure process via surface oxidization [13].

Although the breaking phenomena of aromatic carbon and CH were noticeably detected, the produced C=O bonds strongly contributed to the LC alignment properties on the PS surfaces. Therefore, the produced C=O and the selective bonding breaking could induce anisotropic dipole fields to align the LC molecules.

## IV. Summary and Conclusion

In this study, the homogeneous PS material for the LC alignment layer was modified by IB irradiation at various IB exposure time with fixed IB bombardment energy and exposure angle to replace conventional rubbing technology and PI material for LCD applications. An increase in IB exposure time resulted in a stable and clear LC orientation with matching of experimental crystal rotation graphs. Uniformly aligned LC molecules on IB irradiated PS surface achieved for IB exposure time up to 15 s. Moreover, the thermal stability of the LC cells also increased as the IB exposure time increased, which means that the IB bombardment method can result in a uniform thermally stable surface on an IB-irradiated PS alignment layer by inducing anisotropic dipole-dipole interactions due to bond reformations and breakages. This means IB-irradiated PS materials can help to extend the lifetime of LCD devices with a highly stable thermal property.

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