Unusual Alignment of Liquid Crystals on Rubbed Films of Polyimides with Fluorenyl Side Groups

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Introduction
Polyimides (PIs) have been widely used in the microelectronics industry as dielectric materials because of their advantageous properties, including their excellent optical transparency, adhesion, heat resistance, dimensional stability, mechanical and dielectric properties, and adhesion. One of the most recently developed applications of PIs is their use as liquid crystal (LC) alignment layers for flat-panel LC display (LCD) devices. Such PI film surfaces need to be treated if they are to produce uniform alignments of LC molecules. A rubbing process using a velvet fabric is currently the only technique adopted in the LCD industry for treating PI film surfaces in the mass-production of flat-panel LCD devices. This process has become the method of choice because of its simplicity and the control with this method of both the LC anchoring energy and the pretilt angle. The rubbing of all PI films reported so far has been found to create microcracks along the rubbing direction and to orient polymer main chains along the rubbing direction. For most rubbed PI films, the unidirectional microcracks and oriented polymer main chains cooperatively align LC molecules along the rubbing direction because of their anisotropic interactions with the LC molecules [1-6].

Experimental
In the present study, we synthesized CBDA-FDA and its analogue, poly(4,4'-9-fluorenylidiphenylepyromellitimide) (PMDA-FDA) and then investigated quantitatively the orientational distributions of the polymer chain segments in the surfaces of their films by using linearly polarized Fourier transform infrared (FTIR) spectroscopy and optical retardation analysis. We also examined the films' surface topographies using high spatial resolution atomic force microscopy (AFM). Further, rubbed films were used to assemble antiparallel and 90° twisted nematic (TN) LC cells, and the alignment behaviors, pretilt angles and anchoring energies of the LC molecules in the cells were determined. The films were found to have very interesting surface morphologies and LC alignment behaviors, which have not previously been reported. The observed LC alignments, pretilt angles and anchoring energies are discussed by taking into account the interactions of the LC molecules with the oriented polymer chain segments and the surface morphologies.

Results and Discussion
We examined the surfaces of the PI films in detail before and after they had been rubbed with various rubbing strength parameters using the AFM technique. The rubbed CBDA-FDA film has weakly developed microcracks that run parallel to the rubbing direction, which resemble those reported for rubbed films of conventional PIs used in the LCD industry. In contrast, a new type of meandering microcrack structure that runs in a direction perpendicular to the rubbing direction can be seen in the rubbed PMDA-FDA film. This is the first report of such structures in a rubbed PI film. Thus the observed surface morphology is a significant departure from the surface morphologies reported so far for all other PI alignment layers.

Dichroic IR spectral analyses were conducted for the CBDA-FDA and PMDA-FDA films before and after rubbing by using polarized transmission and reflection FTIR spectroscopy. IR results indicate that in CBDA-FDA and PMDA-FDA rubbed films the main chain segments lie in the film plane and are oriented preferentially along the rubbing direction, and the fluorenyl side groups lie in the out-of-plane of the films and are preferentially oriented perpendicular to the rubbing direction.

An optical phase retardation technique was used to obtain information about the optical properties of the polymer chains in the rubbed PI films. The polymer main chains in the rubbed films are oriented parallel to the rubbing direction and the fluorenyl side groups are oriented orthogonally to the polymer main chain. Thus Figure 1 indicates that the refractive index in the direction along the polymer main chains is lower than that orthogonal to the polymer main chains, i.e., CBDA-FDA is a negative birefringent polymer while PMDA-FDA is a positive birefringent polymer. This difference in the optical properties of the PIs is attributed to the difference in their chemical structures. The optical retardation results indicate that the polarization of the aliphatic CBDA unit along its long axis is lower than that of the aromatic PMDA unit along its long axis. The anisotropy of this polar diagram indicates that the LC molecules in contact with the rubbed PMDA-FDA film surface are induced homogeneously to align parallel to the rubbing direction. In contrast, the LC alignment of the rubbed CBDA-FDA PI films is quite different from that observed at the rubbed PMDA-FDA film surface as shown in Figure 2.

Conclusion
The unusual tendency of LC molecules to align perpendicular to the microcracks developed at the rubbed PI film surface is primarily driven by directionally anisotropic interactions of the LC molecules with the preferentially oriented phenyl rings whose number is higher than that of the phenyl rings oriented to the other direction. When the number of the phenyl rings oriented to one direction is same with that of the phenyl rings oriented to the other direction, the LC alignment is governed by cooperatively anisotropic interactions of the LC molecules with the other film surface components, in particular, other polymer segments (for example, imide carbonate group) oriented to the coincident direction.

References

Figure 1. Optical birefringence of the rubbed PMDA and CBDA-FDA film, respectively

Figure 2. Polar diagrams of the light absorbance of the dichroic dye aligned together with the LC molecules in antiparallel LC cells; (a) rubbed CBDA-FDA (b) rubbed PMDA-FDA film, respectively