

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

Suk Gyu Hahm, Taek Joon Lee, Dongmin Kim, Taihyun Chang, Jin Chul Jung,
Wang-Cheol Zin, and Moonhor Ree*

Polymer Research Institute, Dept. of Chemistry, Dept. of Materials Science & Engineering, National Research Lab for Polymer Synthesis & Physics, Center for Integrated Molecular Systems, and BK21 Program, , and Pohang University of Science & Technology,
Pohang 790-784, Republic of Korea
Fax, +82-54-279-3399; Tel, +82-54-279-2120; E-mail, ree@postech.edu

ABSTRACT

We synthesized two polyimides (PIs), poly(4,4'-(9,9-fluorenyl)diphenylene cyclobutanyltetracarboximide) and poly(4,4'-(9,9-fluorenyl)diphenylene pyromellitimide), and investigated in detail the surface morphology, molecular orientation, and nematic liquid crystal alignments of rubbed PI films. This study found that both the PIs are promising alignment layer materials for the fabrication of advanced LC display devices.

Keywords: polyimides, rubbing process, Surface morphology, Molecular orientation, liquid crystal alignment

1 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 [1,2]. 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 [3-8]. Such PI film surfaces need to be treated if they are to produce uniform alignments of LC molecules [3-8]. 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 [3-8]. The rubbing of all PI films reported so far has been found to create microgrooves along the rubbing direction and to orient polymer main chains along the rubbing direction [3-8]. For most rubbed PI films, the unidirectional microgrooves and oriented polymer main chains cooperatively align LC molecules along the rubbing direction because of their anisotropic interactions with the LC molecules [3-8]. However, in two cases the rubbed films of PIs have been found to align LCs perpendicular to the rubbing direction [7,8]. The mechanism of their perpendicular LC alignment was

recently investigated in detail [7]. The second case is poly(4,4'-(9,9-fluorenyl)diphenylene cyclobutanyltetracarboximide) (CBDA-FDA) [8]. Despite the interesting perpendicular LC alignment behavior of rubbed films of this PI, the LC alignment mechanism has not yet been determined. If the exact mechanism of such an unusual LC alignment is to be found, the rubbing-induced orientations of all CBDA-FDA chain segments and the rubbed film surface morphology must be quantitatively and comprehensively investigated. In the present study, we synthesized CBDA-FDA and its analogue, poly(4,4'-(9,9-fluorenyl)diphenylene pyromellitimide) (PMDA-FDA), and then we 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 by taking into account the interactions of the LC molecules with the oriented polymer chain segments and the surface morphologies.

2 EXPERIMENTAL

CBDA-FDA poly(amic acid) (PAA) was prepared in a round bottom flask filled with dry nitrogen gas by slowly adding the equivalent mol of CBDA into the FDA dissolved in dry NMP by stirring vigorously. Once the CBDA addition was complete, the reaction flask was sealed tightly and stirring was continued for 2 days to make the polymerization mixture completely homogeneous. In the same manner, PMDA-FDA PAA was prepared in NMP from PMDA and FDA monomer. Solid contents of the synthesized PAA solutions were 10% (w/v). Each PAA solution was filtered with PTFE membranes of 1.0-mm pore size. For the synthesized PAA precursors, inherent viscosity measurements were performed at a concentration of 0.1 g/dL in NMP at 25.0 °C: 0.98 for CBDA-FDA PAA and 0.96 for PMDA-FDA PAA.

Each PAA solution was diluted to 2% (w/v) with dried NMP and then the diluted PAA solution was spin-coated onto silicone substrates for AFM images, and indium tin oxide (ITO) glass substrates for optical retardations and LC

cell assemblies, followed by drying on a hot plate at 80°C for 1 h. The dried PAA films were thermally imidized in an oven with a dry nitrogen gas flow by a three-step imidization protocol: 150 °C/60 min, 200 °C/60 min, and 250 °C/120 min with a ramping rate of 2.0 °C/min. After the thermal imidization, the samples were cooled to room temperature with a rate of 10 °C/min. The resulting PI films were measured to have a thickness of around 100 nm, using a spectroscopic ellipsometer and an α -stepper. The PI films coated onto the substrates were rubbed at various rubbing strengths using a laboratory rubbing machine (Wande) with a roller covered with a rayon velvet fabric (model YA-20-R, Yoshikawa, Japan). The rubbing strength was varied by changing the cumulative rubbing time for a constant rubbing depth, 0.25 mm. Some of the rubbed PI films on glass substrates were cut into 2.5 cm \times 2.5 cm pieces and then used for assembling two different LC cells as follows. First, paired pieces cut from each glass substrate were assembled together antiparallel with respect to the rubbing direction by using 50 μ m thick spacers, injected with a nematic LC, 4-*n*-pentyl-4'-cyanobiphenyl (5CB) (n_e (extraordinary refractive index)= 1.717 and n_o (ordinary refractive index) = 1.53) containing 1.0 wt% Disperse Blue 1 as a dichroic dye, and then sealed with an epoxy glue, giving antiparallel nematic LC cells. Second, paired pieces from each glass substrate were assembled together orthogonal to the rubbing direction by using silica balls of 4.0 μ m diameter as spacers, injected with the LC and then sealed with an epoxy glue, giving 90°-twisted nematic LC cells (TN LC cells). All the prepared LC cells were found to be uniform and homogeneous throughout by optical microscopy.

The surface morphology of the PI films was measured before and after rubbing, using an atomic force microscope (Digital Instruments, model Multimode AFM Nanoscope IIIa) in contact mode. Optical phase retardations were measured using an optical set up equipped with either a photoelastic modulator with a fused silica head or a quarter plate. The optical phase retardation measurements were calibrated with a $\lambda/30$ plate standard. Samples were installed perpendicular to the incident beam direction. Optical phase retardations were measured as a function of the angle of rotation of the samples. The LC alignment of antiparallel LC cells was examined using an optical setup that was equipped with a He-Ne laser (632.8 nm wavelength), a polarizer, a photodiode detector, and a goniometer. In the measurement, the laser beam was incident perpendicular to the surface of the LC cell mounted on the goniometer, and these components were placed between the polarizer and the detector. Light absorption of the dichroic dye aligned together with the LC molecules in the cell was then monitored as a function of the angle of rotation of the cell. The pretilt angle α of the LC molecules was measured using a crystal rotation apparatus [5]. For the TN LC cells, azimuthal anchoring energy was measured by using an ultraviolet-visible (UV-vis) spectrophotometer equipped with two Glan-Laser

prisms; the analyzer was mounted on a motorized goniometer. Each TN cell was placed between the polarizer and the analyzer. UV-vis spectra were recorded at 0.8 cm⁻¹ resolution as a function of the angle of rotation of the analyzer in the range 0–180° with an interval of 1.0°. In these measurements, the rotation angles giving a minimum transmittance in the UV-vis spectra were determined. Of the rotation angles for which measurements were carried out, one angle was chosen by considering the nature of the birefringence dispersion of the LC and used for determining the twist angle at which the easy axes of the upper and lower substrates of the cell occur [9]. The azimuthal anchoring energies of the LCs on the rubbed PI film surfaces were estimated from the twist angle using the optical parameters of the LC [9].

3 RESULTS AND DISCUSSION

Using the AFM technique, we examined the surfaces of the PI films in detail before and after they had been rubbed with various rubbing strengths. Figures 1a and c show AFM images of unrubbed CBDA-FDA and PMDA-FDA films respectively. Figures 1c and d show representative AFM images of the PI films after rubbing at a rubbing strength of 129.6. As can be seen in Figure 1b, the rubbed CBDA-FDA film has weakly developed microgrooves that run parallel to the rubbing direction, which resemble those reported for rubbed films of conventional PIs used in the LCD industry [3,4]. In contrast, a new type of meandering microgroove structure that runs in a direction perpendicular to the rubbing direction can be seen in the rubbed PMDA-FDA film (Figure 1d). This is the first report of such structures in a rubbed PI film. The observed surface morphology might be due to the characteristic deformation response of PMDA-FDA to the shear force caused by contact of fibers with the surface during the rubbing process.

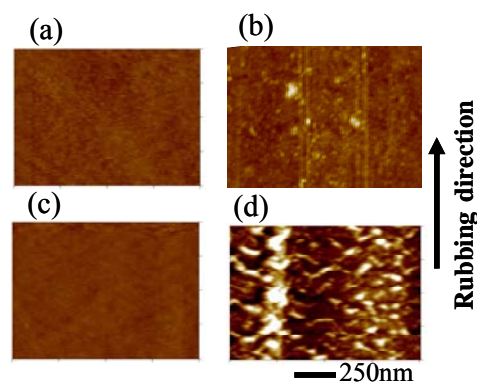


Figure 1: Surface AFM images of PI films before and after rubbing at a rubbing strength parameter of 129.6 cm: (a) unrubbed CBDAFDA PI; (b) rubbed CBDA-FDA PI; (c) unrubbed PMDA-FDA PI; (d) rubbed PMDA-FDA PI. The arrow in the AFM image denotes the rubbing direction.

To obtain information about the optical properties of the polymer chains in the rubbed PI films, an optical phase retardation technique was used. Figure 2 displays polar diagrams of the variations of the transmitted light intensity [= (in-plane birefringence) \times (phase)] with the angle of rotation of PI films rubbed at a rubbing density of 129.6. As can be seen in Figure 2a, for the rubbed CBDA-FDA film the maximum transmitted light intensity arises for the direction $270^\circ \leftrightarrow 90^\circ$, which is perpendicular to the rubbing direction, and the minimum light intensity arises for the direction $0^\circ \leftrightarrow 180^\circ$, which is parallel to the rubbing direction. As discussed above, the polymer main chains in the rubbed films are oriented parallel to the rubbing direction and the fluorene side groups are oriented orthogonally to the polymer main chain. Thus Figure 2a 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.

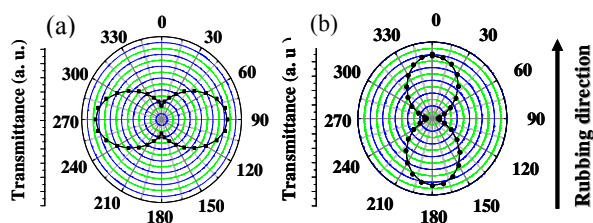


Figure 2: Polar diagrams of the variation of the retardation with the angle of rotation of the film in optical phase retardation measurements of PI films rubbed at a rubbing strength parameter of 129.6 cm; (a) rubbed CBDA-FDA PI; (b) rubbed PMDA-FDA PI.

In contrast, the maximum intensity of transmitted light for the rubbed PMDA-FDA film arises for the direction $0^\circ \leftrightarrow 180^\circ$, and the minimum light intensity arises for the direction $270^\circ \leftrightarrow 90^\circ$ (Figure 2b). Thus the anisotropic polar diagram indicates that the refractive index in the direction along the polymer main chains is higher than that orthogonal to the polymer main chains, i.e., 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.

For the CBDA-FDA film, the magnitude of in-plane birefringence Δ_{xy} rapidly increases with rubbing strength up to 129.6, and then levels off with further increases in the rubbing strength (data not shown). For the PMDA-FDA film, Δ_{xy} rapidly increases with rubbing strength up to 86.4, and then levels off with further increases in the rubbing strength (data not shown). Overall, the absolute value of Δ_{xy} is slightly larger for the PMDA-FDA film than for the CBDA-FDA film when the films are rubbed at the same rubbing strength. These results confirm that the polymer

chains in the surfaces of the PI films are oriented along the rubbing direction by the rubbing process, and that preferential orientation can be achieved by rubbing at rubbing strengths greater than 86.4 for PMDA-FDA and 129.6 for CBDA-FDA.

There were measured polar diagrams of the absorbances of LC cells fabricated with PI films rubbed at a rubbing strength of 129.6. The LC cell of the rubbed CBDA-FDA film was found to exhibit maximum absorbance along the direction $270^\circ \leftrightarrow 90^\circ$, which is perpendicular to the rubbing direction. The anisotropy of this polar diagram indicates that the LC molecules in contact with the rubbed CBDA-FDA film surface are induced homogeneously to align perpendicular to the rubbing direction. This LC alignment is quite different from those observed for conventional PI alignment layer materials [3-6]. In contrast, the LC cell of the rubbed PMDA-FDA film was found to reveal maximum absorbance along the direction $0^\circ \leftrightarrow 180^\circ$, which is parallel to the rubbing direction. 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. Thus the LC molecules align parallel to the polymer main chains, which are oriented along the rubbing direction. So the alignment of the LCs in this case is directly induced by their strong anisotropic molecular interactions with the oriented polymer main chains, which override the interactions with the meandering microgrooves that are created perpendicular to the rubbing direction.

The pretilt angles of the LCs in the LC cells were measured by using the crystal-rotation method. For both the LC cells fabricated with the rubbed films of the two PIs, the measured LC pretilt angles were found to be in the range $0-1.0^\circ$, depending on the rubbing strengths employed in the rubbing process. Overall, both PI films induce LC molecules to align with low pretilt angles on the rubbed film surfaces. TN cells were then prepared and found to be very stable and homogeneous throughout. These TN LC cells were used in measurements with a UV-Visible spectroscopic technique of the twist angles of the LC molecules. The twist angles were found to be 90° for all the LC cells, regardless of the rubbing strength and the type of PI polymer. From this measured twist angle, the anchoring energies of the LC molecules on the rubbed films of both the PIs were estimated to be much greater than $1 \times 10^{-3} \text{ J/m}^2$. This anchoring energy is very high, and comparable to those of LC cells fabricated with rubbed films of conventional PIs currently used in the LCD industry.

This work was supported by Korea Research Foundation Grant (Contract No: KRF-2006-005-J01301) funded by the Korean Government (MOEHRD), by the Korea Science and Engineering Foundation (KOSEF) (National Research Lab Program and Science Research Center Program), and by the Ministry of Education (BK21 Program).

REFERENCES

- [1] M. Ree, *Macromol. Res.* 14, 1, 2006.
- [2] S. I. Kim, S. M. Pyo, and M. Ree, *Macromolecules*, 30, 7890, 1997.
- [3] S. M. Pyo, S. I. Kim, T. J. Shin, M. Ree, K. H. Park, and J. S. Kang, *Macromolecules*, 31, 4777, 1998.
- [4] M. Ree, K. Kim, S. H. Woo, H. Chang, *J. Appl. Phys.*, 81, 698, 1997.
- [5] Y. Kim, M. Ree, T. Chang, C. S. Ha, T. L. Nunes, and J. S. Lin, *J. Polym. Sci.: Part B: Polym. Phys. Ed.*, 33, 2075, 1995.
- [6] M. Ree, T. J. Shin, and S. W. Lee, *Kor. Polym. J.*, 9, 1, 2001.
- [7] S. W. Lee, S. J. Lee, S. G. Hahm, T. J. Lee, B. Lee, B. Chae, S. B. Kim, J. C. Jung, W. C. Zin, B. H. Sohn, and M. Ree, *Macromolecules*, 38, 4331, 2005.
- [8] M. Nishikawa, B. Taheri, and J. L. West, *Appl. Phys. Lett.*, 72, 2403, 1998
- [9] S. W. Lee, B. Chae, H. C. Kim, B. Lee, W. Choi, S. B. Kim, T. Chang, and M. Ree, *Langmuir*, 19, 8735, 2003.