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Surface Morphology of Photo-Crosslinkable Polyimide after Irradiation of Polarized UV Light

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Photo-crosslinkable polyimide(PI) which contains CF_3 moiety was synthesized. Polarized UV light transformed ketone group of PI to hydroxyl group, which was confirmed by IR and UV-visible spectroscopy. We investigated the dichroic UV-absorption before and after photo-reaction with linearly polarized light. The grooves were formed on the surface of PI film after irradiation with polarized UV-light. It was interesting to observe that the alignment of grooves was perpendicular to the polarized director, while the orientation of LC was parallel to the groove alignment.

Keywords: polyimide; photo-crosslink; surface morphology

INTRODUCTION

Liquid crystal(LC) alignment plays an important role in attaining high-quality device performance. To align liquid crystals, rubbing has been carried out for the polymer on the substrates in liquid crystal display(LCD) panel fabrication. This technique is the most widely used, but it has some problems such as the dust and static charge due to the mechanical contact of rubbing cloth on the alignment layer. The photo-alignment technique was proposed to improve the resolution of LCDs instead of the rubbing method. Schadt et al. reported the alignment of the poly(vinyl 4-methoxy cinnamate) films[1]. We have studied new photo-crosslinkable and soluble polyimide

with CF_3 functional group. In this paper we investigated photo reaction with FT-IR spectrophotometer, UV/visible spectrophotometer and the surface morphology by atomic force microscopy(AFM).

EXPERIMENT

The synthesis of soluble polyimide(PI) was reported in the previous paper[2]. The molecular structure is shown in Figure 1.

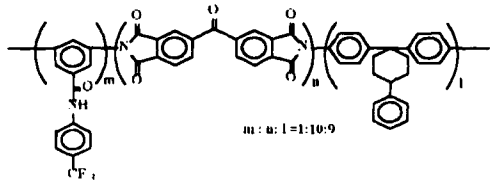


FIGURE 1. Molecular structure of polyimide, BTDA/BAPH/4FAM.

PI dissolved in γ-butyrolactone was spin-coated on Si-wafer or quartz plate. The coated films were baked at 240 ℃ for 30min to evaporate the solvent. The films were irradiated with 500W high pressure mercury lamp equipped with Glan-Laser polarizer.

Infrared spectra were obtained from the Nicolet Magna IR 560 FT-IR spectrophotometer. The UV dichroic ratio and absorption spectra were measured with HITACHI U-2000 UV/visible spectrophotometer and HP 8452 spectrophotometer. The AFM experiments were performed with Autoprobe CP, Park Scientific Instruments. All the AFM images of PI films were taken non-contact mode at ambient temperature in air. To measure the pretilt angle of LC, one of substrates had conventionally rubbed PI layer which produced pretilt angle of 1.33°. The pretilt angle of the LC cell was determined by crystal rotation method.

RESULTS AND DISCUSSION

Figure 2 shows IR absorption spectra of BTDA/BAPH/4FAM on Si-wafer before and after polarized irradiation for 90 min. The OH group absorption clearly appears at 3500 cm^{-1}. The ketone peak(1678cm^{-1}) of BTDA slightly shifted(1680cm^{-1}) and decreased. This indicated that ketone group in BTDA was converted to hydroxyl group. The conversion of ketone was also

confirmed by the decrease in 270 nm UV absorption band.

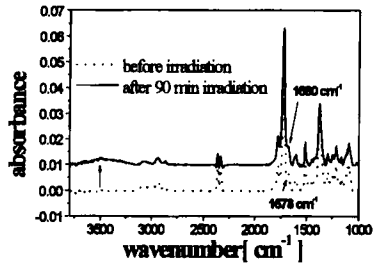
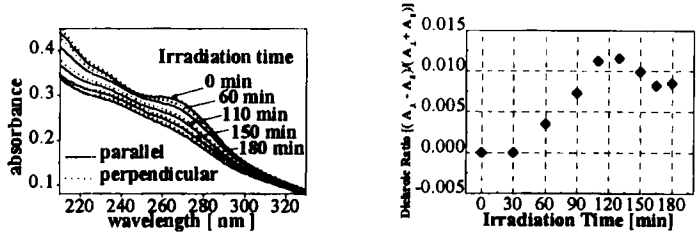


FIGURE 2. FT-IR spectra of PI films with polarized UV irradiation.

The dichroic ratio of PI films was obtained as a function of irradiation time to determine the optimum irradiation condition. As the photo-reaction proceeded, the whole spectral absorption decreased and isobestic points do not appear in Figure 3. This indicates that the crosslinking with free radical reaction progresses by more than one mechanism. Longer irradiation makes pronounced decrease in 270 nm peak and increase in dichroic ratio($A_{\perp} - A_{\parallel}$)/($A_{\perp} + A_{\parallel}$). It supports that the photo-selection by polarizer induces an oriented photo-crosslinking. This clearly shows that polarized photo-reaction indeed leads to the anisotropic UV absorption in PI films.



(a) (b)

FIGURE 3 (a) The dichroic UV absorption spectra (b) The dichroic ratio of BTDA/BAPH/4FAM film.

LC alignment is known to be influenced by surface morphology and polymer chain orientation[3]. In particular, the resolution of surface

morphology for rubbed and oriented polymer films can be obtained with Scanning Tunnel Microscopy (STM) and AFM[4]. We investigated the AFM images of PI films before and after irradiation as illustrated in Figure 4. As the photo-reaction progressed, average roughness was increased by two times. PI film showed an aggregate structure whose size was of few tens nm, which was formed by the photo-crosslinking reaction. It is also interesting to observe that the linear grooves are formed perpendicular to the polarization direction, while LCs were aligned along the grooves. The depth of the grooves is roughly about 4.0 nm. The pretilt angle was 0° for PI with 60 min photo-irradiation, and this became 1° after the 120min irradiation. As the roughness of film increased significantly with photo-irradiation, the pretilt angle was increased relatively small amount. The increase in pretilt angle can be achieved by tilt photo-irradiation.

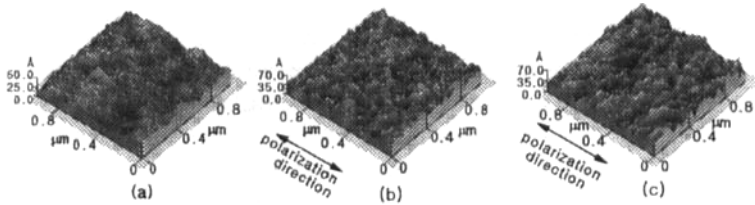


FIGURE 4 AFM images of PI films. (a) no irradiation (b) after 120 min irradiation (c) after 180 min irradiation.

Acknowledgments

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