

## Liquid Crystal Alignment on the Films of Polymethacrylate and Polyurethane Bearing an Aminonitroazobenzene Chromophore

Dong Hoon Choi\*, Jae Hyung Kim, and Kang Jin Cho

College of Environment and Applied Chemistry, Institute of Material Science and Technology,  
Kyung Hee University, Kyungki-do 449-701, Korea

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**Abstract :** We synthesized polymethacrylate and polyurethane bearing a photosensitive azobenzene chromophore. Photo-induced birefringence of the thin film was observed under a linearly polarized light ( $\lambda = 532$  nm). Dynamic behaviors of birefringence in two polymers were investigated in terms of the rate constants of growth and decay. An induced dichroism was observed from polarized UV-VIS absorption spectroscopy. Layers of two photosensitive polymers were used for aligning liquid crystal (LC) molecules instead of one of the rubbed polyimide layers in the conventional twisted nematic cell. For producing homogeneous alignment of a nematic LC molecule, a linearly polarized light was exposed to the films of two polymers. The stability of the LC alignment upon the linearly polarized light exposure was also studied.

### Introduction

Polymers containing azobenzene moieties have drawn much interest in the field of optical data storage, nonlinear optical, and holographic applications. A number of researchers have investigated the photo-induced anisotropic behavior through trans-cis-trans photoisomerization and molecular rearrangement under a linearly polarized light. Polar azobenzene groups show angular-dependent absorption of linearly polarized light.<sup>1-6</sup> An anisotropy can be induced by the orientation of the azobenzene groups. The induced anisotropy can be removed by irradiation with circularly polarized light or random polarized light. The control of the liquid crystal (LC) alignment by a linearly polarized light has attracted much attention from both fundamental and practical points of view. A photo-induced method of aligning LC molecules has several advantages over a conventional rubbing technique such as non-contact and no contaminants involved. It has been reported that some polyimides exhibit an irreversible anisotropic

chemical reaction induced by a linearly polarized visible light, which causes the change in the alignment of LC molecules.<sup>7-9</sup> Moreover, the nematic LC orientation on a dichroic dye-doped polyimide layer can be controlled by a linearly polarized laser beam<sup>10</sup> and the optical regulation of the alignment of nematic LCs can be achieved on a substrate attached with photoisomerizable azobenzene chromophores.<sup>11,12</sup>

In this work, we report on the synthesis and properties of two photosensitive polymers for the LC alignment controlled by a linearly polarized visible light ( $\lambda = 532$  nm). The photo-induced birefringence of the thin films as well as the optical anisotropy of LC cell was studied using two synthesized polymers.

### Experimental

Azobenzene chromophore was synthesized via diazotization and coupling reaction between 6-(methyl-phenyl-amino)-hexan-1-ol and 4-nitroaniline. 2-Methyl-acrylic acid 6-{methyl-[4-(4-nitrophenylazo)-phenyl]-amino}-hexyl ester was prepared by esterification between methacryloyl chlo-

\*e-mail : dhchoi@khu.ac.kr

ride and 6-{methyl-[4-(4-nitro-phenylazo)-phenyl]-amino}-hexan-1-ol.

**Synthesis of Polymethacrylate(PMA).** Homopolymer of 2-methyl-acrylic acid 6-{methyl-[4-(4-nitro-phenylazo)-phenyl]-amino}-hexyl ester was prepared by radical polymerization. The monomer (0.5 g, 1.18 mmole) was dissolved in dried NMP (5 mL) in the presence of AIBN(5.8 mg, 0.035 mmole). The solution was kept at 70 °C for 48 h under argon atmosphere. Red polymer was collected and purified by reprecipitation from tetrachloroethane/methanol until there is no monomer left and dried in vacuum at 90 °C for 48 h. Yield, 60%.  $T_g \sim 90^\circ\text{C}$ .

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) 1.65~0.88 (5H,  $\text{CH}_3\text{C}-$ ,  $-\text{CH}_2-$  in the main chain; 8H,  $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}-$ ), 3.00 (3H,  $\text{CH}_3\text{N}-$ ), 3.34 (2H,  $-\text{CH}_2\text{N}-$ ), 3.90 (2H,  $-\text{CH}_2\text{O}-$ ), 6.64 (2H, aromatic), 7.84 (4H, aromatic), 8.26 (2H, aromatic).

**Synthesis of Polyurethane(PU).** 2-{(2-Hydroxy-ethyl)-[4-(4-nitro-phenylazo)-phenyl]-amino}-ethanol (MI)(3 g, 9.1 mmole) and tetramethyl-1,3-xylene diisocyanate (*m*-TMXDI, 2.22 g, 9.1 mmole) were dissolved in freshly dried dimethylformamide (DMF, 47.2 mL) under argon atmosphere. Dibutyltin dilaurate (DBTDL, 0.012 g, 0.018 mmole) was added into the solution and the reaction mixture was kept under stirring at 85 °C for 72 h. The product was precipitated into hot ethanol and filtered. It was dried under vacuum at 95 °C for 72 h. Yield, 53.7%.  $T_g \sim 103^\circ\text{C}$ .

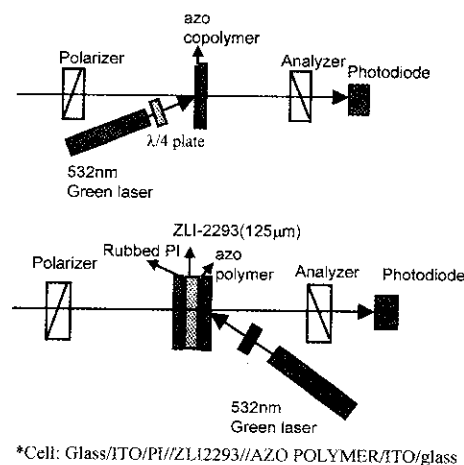
$^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ )  $\delta$  (ppm) 1.49 (12H, aliphatic  $\text{CH}_3$  in *m*-TMXDI unit), 3.67 (4H,  $-\text{O}-\text{CH}_2\text{CH}_2\text{N}-$ ), 4.1 (4H,  $-\text{N}-\text{CH}_2\text{CH}_2\text{O}-\text{CO}-$ ), 6.25 (1H, aromatic), 8.0-6.7 (9H, aromatic), 8.34 (2H, aromatic).

**Characterization.** IR spectra were taken by absorbance on a Bruker IFS66V FT-IR spectrometer.  $^1\text{H}$  NMR spectra were recorded with a Bruker 200 MHz spectrometer.  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  were used as solvents for polymers. Differential scanning calorimetry (DSC) measurement was performed on a Perkin-Elmer DSC 4 under heating rate of 10 °C/min. UV-visible spectra were measured on Hewlett Packard 8453(Photodiode Array Type, 190-1100 nm) spectrophotometer.

**Film Fabrication.** The films of PMA and PU were prepared by spin-coating from tetrachloro-

ethane and cyclohexanone onto the proper substrates respectively and dried in vacuum at 100 °C for 48 h. The film thickness was measured by surface profilometer (Tenco P10).

**Measurement of Optically Induced Birefringence.** The setup for measuring optically induced birefringence is shown in Figure 1, where the change in transmission of the He-Ne laser through the film between crossed polarizers is recorded as a function of time after irradiation of pumped diode laser ( $\lambda = 532$  nm, max. intensity 10  $\text{mW}/\text{cm}^2$ ). Under the maximum light intensity, the temperature of the surface of the sample increased by 5-6 °C for measuring period. All the samples underwent identical thermal effect. He-Ne laser ( $\sim 5$  mW) at 632.8 nm was used as a probe light to measure the power that is transmitted. Optical anisotropy was induced in the polymer film using a polarized light emitted by pumped diode laser. The wavelength of the pump beam is in the absorption range of the polymers. To remove the birefringence that had been induced, a quarter waveplate ( $\lambda/4$ ) was inserted into the optical path before the sample. The transmission was detected with a photodiode detector (New Port 818-SL). The transmitted signal  $I(t)$  due to birefringence can be shown to be proportional to  $\sin^2(\pi d \Delta n / \lambda)$  where  $d$  and  $\Delta n$  are thickness and birefringence of the film, respectively.  $\lambda$  is the wavelength of the probe beam (the He-Ne laser



**Figure 1.** Schematic diagram for the measurement of optically induced birefringence.

radiation at 632 nm). We measured the thickness of the films using the surface profilometer in order to calculate absolute birefringence ( $\Delta n(t)$ ) using the following equation (1).

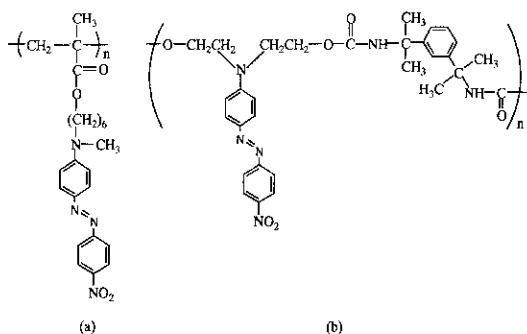
$$\Delta n(t) = [\lambda/\pi d] \arcsin [(I(t)/I_0)^{0.5}] \quad (1)$$

When we investigated the induced birefringence of LC cell, we only replaced the film with the LC cell. In this case we irradiated the pump beam on the glass substrate on which the photo-sensitive polymer was coated.

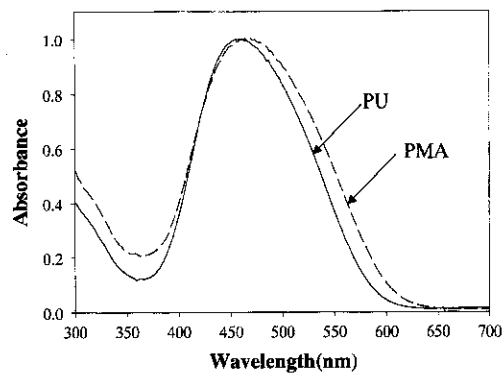
## Results and Discussion

**Synthesis and Characterization.** NMR and IR spectral analysis confirmed the structures of the synthesized monomers and polymers. The synthesized polymer structures are shown in Scheme 1. The obtained PMA was well soluble only in 1,1,2,2-tetrachloroethane and PU showed good solubility in acetone, chloroform, and tetrahydrofuran. Glass transition temperatures of PMA and PU were measured to be 90 and 103°C, respectively. The UV-VIS absorption spectra of two polymers were shown in Figure 2. The absorption maximal of PMA and PU appeared at 465 and 462 nm respectively, which can be assigned to  $\pi$ - $\pi^*$  transition in azobenzene unit. Cutoff wavelength was found around 650 nm.

**Photo-induced Optical Anisotropy of the Polymer Thin Films.** We first examined the photo-induced optical anisotropy of the two polymer films that were exposed to a linearly polarized



**Scheme 1.** Structures of the synthesized (a) poly-methacrylate (PMA) and (b) polyurethane (PU).

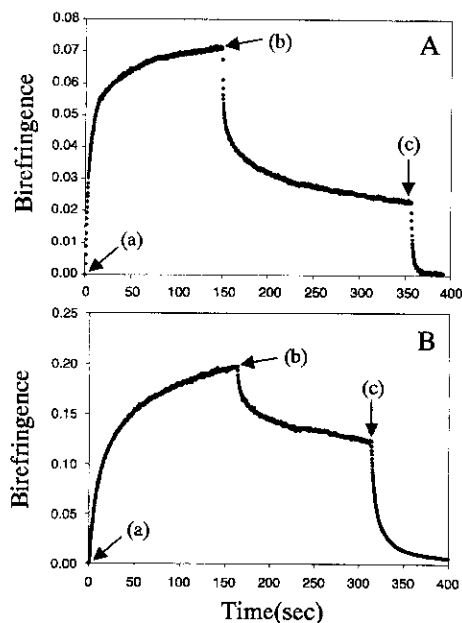


**Figure 2.** UV-VIS absorption spectra of PMA and PU film.

light from a diode pumped laser ( $\lambda = 532$  nm, 10 mW/cm<sup>2</sup>). The optical anisotropy in the two polymers was measured with a probe beam of a He-Ne laser ( $\lambda = 632$  nm, 5 mW) under crossed polarizers. One of the crossed polarizers was arranged to make an angle of 45° with respect to the polarization direction of the pump beam.

We compared the dynamic behaviors of photo-induced birefringence in two polymers. In Figure 3, two plots showed the relationship between the induced birefringence and the elapsed exposure time. No transmission of the probe beam is detected through the crossed polarizers before pumping. When optical anisotropy is induced in the polymer film, the probe light is partially transmitted through the optical setup and then transmission reaches to the high level. Trans-cis-trans isomerization occurred and consequently the preferential orientation of the azobenzene moieties became perpendicular to the polarization of the pump beam. At the second stage, the excitation light is turned off and the transmission was observed to decrease to a certain level. The decrease has been associated with the thermal reorientation of some azobenzene moieties. When we insert the quarter waveplate in front of the pump beam, the polarization of the excitation light changed to be circular. Under the exposure to circularly polarized light, the induced birefringence vanished at all, arising from randomization of oriented polar azobenzene molecules.

The data of birefringence were fitted to the double exponential functions (equation 2 and 3).



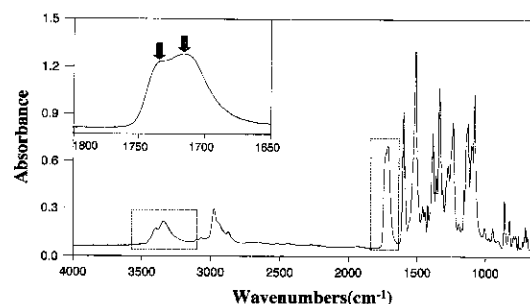
**Figure 3.** Dynamic behaviors of photoinduced birefringence of PMA (A) and PU (B). (a) pump beam on; (b) pump beam off; (c) circularly polarized light on.

$$\text{Growth : } \Delta n(t) = A[1 - \exp(-k_1 t)] + B[1 - \exp(-k_2 t)] \quad (2)$$

$$\text{Decay : } \Delta n(t) = C \exp(-k_3 t) + D \exp(-k_4 t) + R \quad (3)$$

The rate constants and the induced birefringence after the exposure for 120 sec are tabulated in Table I. In the rising curve,  $k_1$  and  $k_2$  were calculated to be 0.109 and 0.014/sec in polyurethane (PU). Compared to those in PMA, the growth and decay are relatively very slow in PU. The absolute value of birefringence after 2 min exposure in PU is much higher than that in PMA.

The IR spectrum of PU film shows the existence of hydrogen bonds between the main chains (see Figure 4). The hydrogen bonded and the isolated carbonyl stretching band appeared at 1713 and 1734  $\text{cm}^{-1}$ , respectively. Simultaneously, two bands



**Figure 4.** Infrared spectrum of polyurethane (PU) film.

from secondary amine stretching vibration were overlapped and appeared around 3341-3396  $\text{cm}^{-1}$ . It can be analyzed into the hydrogen bonded and the isolated mode. Therefore, inter-chain molecular specific interaction retards the rate of growth in the induced birefringence. Although PU takes much longer to induce the maximum birefringence due to hydrogen bonds between the main chains themselves, those can create a microscopic local ordering that contributes to the higher induced birefringence. If there is strong specific interaction between the main chains, the photo-induced molecular organization is reinforced including the cooperative reorientation of the carbamate units and the values of birefringence are significantly higher than in totally amorphous polymer films (PMA). Although PU has disadvantages for optical data storage arising from slow writing and erasing properties, it can show better functionality for LC alignment layer with an aid of the high optical anisotropy in the thin film.

#### Polarized Absorption Spectroscopic Study.

**Dichroism:** We investigated the anisotropy of polymer films using polarized pump and probe method. In order to estimate the degree of molecular orientation, we employed the polarized UV-VIS absorption spectroscopy. The spectrometer was equipped with Glan-Taylor polarizer. The pump beam was used in an identical way to measure the induced birefringence except for the irradiation

**Table I.** Rate Constants, Induced Birefringence, Dichroic Ratio, and Order Parameter of PMA and PU

	$k_1$	$k_2$	$\Delta n$	$k_3$	$k_4$	$R$	$S$
Polymethacrylate	0.200	0.018	0.072	0.688	0.028	1.182	0.057
Polyurethane	0.109	0.014	0.188	0.362	0.028	1.565	0.158

of s-polarized green light. Angular-dependent absorbance of the polar azobenzene molecules at 463 nm was measured before and after irradiation. The irradiation time was set to be 10 minutes to get a saturation value of birefringence. The absorbances at 463 nm as a function of the rotation angle of polarized probe beam are shown in Figure 5. When the direction of polarization of the probe beam was perpendicular to that of the excitation light, the absorbance reached to the maximum value. When the polarization directions of irradiation light and probe beam were parallel, the absorbance was observed to be minimum. Therefore, we could confirm that the orientation of the azobenzene moieties is perpendicular to the electric vector of pump light. If the transition dipole moment is oriented to parallel to the molecular long axis, the order parameter has the following relationship with dichroic ratio,  $R$ .

$$S = (R-1)/(R+2) \quad (4)$$

If the dichroic ratio can be determined by polarized UV-VIS spectroscopy and given by the following equation.<sup>13,14</sup>

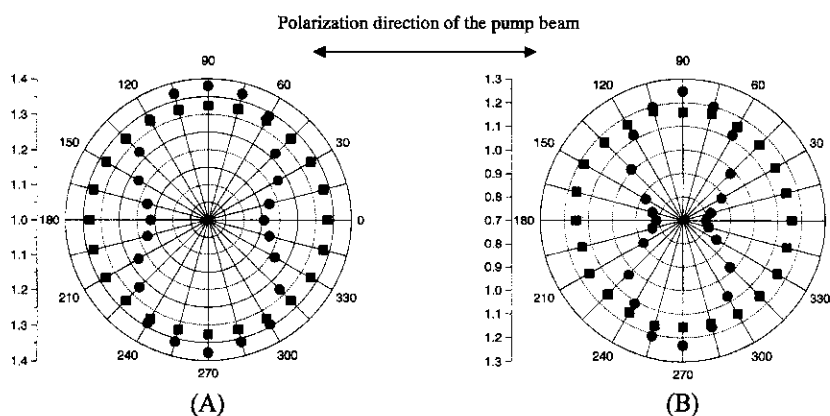
$$R = A_0/A_{90} \quad (5)$$

$A_0$  and  $A_{90}$  are the absorbances measured with the polarized beam parallel and perpendicular to the optic axis of the azobenzene molecule, respectively.

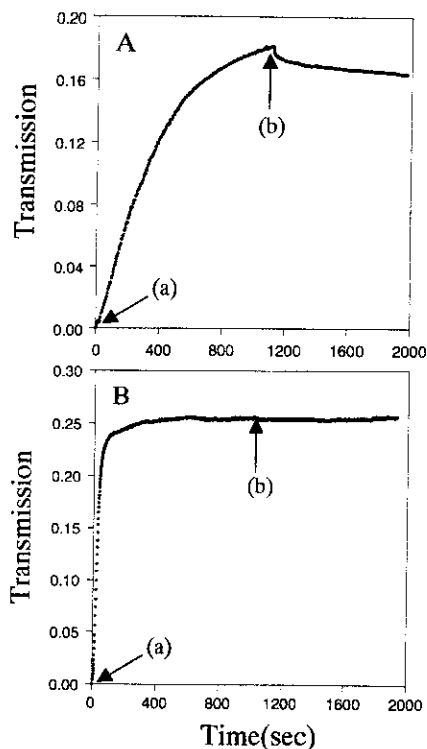
According to the above equations, we determined  $R$  and  $S$  resulting from Figure 5. The data were tabulated in Table I. Under irradiation of pump beam, PU showed higher dichroic ratio,  $R$  and order parameter,  $S$ . This is well consistent with the higher induced birefringence ( $\Delta n$ ) in the previous experiment.

**Optical Anisotropy of LC Cell Fabricated with a Photosensitive Polymer.** In order to prepare a LC alignment layer, the polymer solutions of 5% by weight were spin coated on an ITO glass at room temperature. The film thickness was determined to be around 0.2-0.3  $\mu\text{m}$ . The LC used was ZLI-2293 of E. Merck that has the nematic phase at room temperature. One substrate of the LC cell has the photosensitive polymer layer to control the LC alignment and the other has a rubbed polyimide layer to promote the homogeneous alignment. The cell thickness was maintained as 125  $\mu\text{m}$  using film spacers.

The LC alignment in the cell with one photosensitive polymer surface and one rubbed polyimide surface was observed when the polarization of the pump beam was rotated with respect to the rubbing axis of polyimide layer. Based on the results in Figure 3, the appropriate exposure time to a linearly polarized pump beam for stable LC alignment in the cell was determined to be about 10 minutes. The polarization direction of the pump beam was set to be parallel to the rubbing axis of one polyimide layer. In Figure 6, the transmission through the cell was observed to increase fast just



**Figure 5.** Angular-dependent absorbance of polar azobenzene molecules at 463 nm. (A) PMA; (B) PU; (square) before irradiation; (circle) after irradiation for 10 minutes.



**Figure 6.** Change of transmission due to the LC alignment on PMA (A) and PU (B) film. (a) pump beam on; (b) pump beam off.

after the pump beam was irradiated on the surface of the PMA or PU film. As the pump beam is turned on, the light transmission increased to a certain level. This indicates that the LC on the photosensitive polymer films oriented, whose director is perpendicular to that of the LC on the rubbed polyimide. In the case of PU, the transmission reached to the maximum relatively very fast compared to that in PMA. During the exposure for the same period, PU film showed much higher birefringence as can be seen in Figure 3. We could obtain the order parameter to be 0.057 and 0.158 in PMA and PU respectively, which was investigated by means of polarized UV-VIS absorption spectroscopy. High optical anisotropy of the thin alignment layer provides the fast alignment of LC molecules in the cell. The decay of transmission was not observed at all in PU although the pump beam turned off. Therefore, LC molecules on the PU layer were aligned faster and long-term stability of LC alignment is much

better than that on the layer of PMA.

Shortly, as the higher value of photo-induced birefringence is, the LC alignment is much faster when we fabricate the alignment layer with PU. Additionally, the long-term stability of LC alignment was also improved due to high optical anisotropy and the stability of the induced birefringence of the thin PU film.

## Conclusion

We have synthesized two photosensitive polymers and demonstrated that the stable LC alignment can be obtained on a polymethacrylate (PMA) and polyurethane (PU) layers upon a linearly polarized excitation light. The reorientation of photoisomerizable azobenzene group mainly achieves the collective homogeneous alignment of the LC molecules while the alignment stability is governed by the degree of optical anisotropy in an alignment layer and its stability.

A basic understanding of the physical mechanism for the LC alignment on other photoresponsive systems at a molecular level remains to be carried out.

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