

# Photoisomerization and Photo-induced Optical Anisotropy of Polymethacrylate Containing Aminonitroazobenzene Chromophores in the Side Chain

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**Abstract:** Photoresponsive side chain copolymer and homopolymer containing an aminonitroazobenzene were synthesized for studying photoisomerization behavior and photo-induced anisotropy. *Trans-to-cis* photoisomerization was observed under the exposure of a circularly polarized visible light with UV-Vis absorption spectroscopy. Reorientation of polar azobenzene molecules induced optical anisotropy under a linearly polarized light at 532 nm. Polarized absorption spectroscopy was employed to investigate the anisotropy of the polymer film during irradiation of the excitation light. 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.

**Keywords:** Azobenzene, Photo-induced birefringence, Photoisomerization, Linearly polarized light, Liquid crystal alignment layer

## Introduction

Polymers containing azobenzene moieties in the side chain received a considerable interest for several reasons as these materials possess unique optical properties[1-8]. In addition to the studies in the direction of nonlinear optical properties, there is constantly increasing attention in the field of optical data storage and holographic applications. Optically induced anisotropy is a very promising property for optical information storage and erasing. The mechanism of writing information involves photo-induced excitation of the azobenzene group, which undergoes *trans-cis-trans* isomerization. The polarized light induces an angular selective optical excitation followed by molecular reorientation during the *trans-cis* isomerization and *cis-trans* relaxation. This phenomena result in photo-induced anisotropy in the polymer matrix[9-15].

The final molecular distribution of the azobenzene groups with respect to the polarization direction of the excitation light is assumed to be uniaxial. This phenomenological approach explains the reorientation mechanisms of the azo molecules during photoisomerization cycles, and its predictions can be compared with experimental results of the time dependent orientation and relaxation process.

Several structural factors may be involved in the orientation mechanisms. Among these factors, the nature of the neighbors of an azobenzene unit in a functionalized polymer may be quite important. For copolymers containing azobenzene entities and methyl methacrylate structural units, birefringence measurements have shown that the degree and rate of

ordering are dependent on the distribution of the azobenzene side chains, indicating that azobenzene groups tend to move in concert with each other[13-15].

The control of the liquid crystal (LC) alignment by a linearly polarized light has also 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. 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[16-18]. Moreover, the nematic LC orientation on a dichroic dye-doped polyimide layer can be controlled by a linearly polarized laser beam[19] and the optical regulation of the alignment of nematic LCs can be achieved on a substrate attached with photoisomerizable azobenzene chromophores[20,21].

In this paper, we synthesized the homopolymer and copolymer containing aminonitroazobenzene moieties in the side chain and studied the dynamics of photoisomerization and the photo-induced anisotropy in the polymers using polarized visible absorption spectroscopy. Additionally, we report on the properties of these two photosensitive polymers for the LC alignment controlled by a linearly polarized visible light.

## Experimental

### UV/VIS spectroscopic study for photoisomerization

Hewlett Packard (PDA type, model 8453) spectrophotometer was employed to record the UV/Vis absorption spectrum from 190 to 1100 nm. Polymer films were used to perform

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this experiment. The films were prepared by spin coating from 2~5 wt% polymer solution in cyclohexanone and then, dried under vacuum at 70°C for 24 h. For studying the photoisomerization of the polymer, the films coated on glass slides were placed in the UV/Vis spectrophotometer. The samples were irradiated with a diode pumped laser that is circularly polarized ( $\lambda = 532$  nm,  $I = 50$  mW/cm<sup>2</sup>) and the absorption spectra were recorded simultaneously. The spectrum was taken every 0.5 second. Absorption spectra were recorded during *trans-to-cis* (pump beam on) and *cis-to-trans* (pump beam off) process.

### Polarized absorption spectroscopy

Investigation of the molecular reorientation of azobenzene molecules was performed *in-situ* by irradiating the film sample with a s-polarized diode pumped laser ( $\lambda = 532$  nm,  $I = 50$  mW/cm<sup>2</sup>). The spectrophotometer was equipped with Glan-Taylor polarizer to provide a linearly polarized probe light in order to measure the absorbance of the sample in the parallel ( $A_{\parallel}$ ) and perpendicular direction ( $A_{\perp}$ ) with respect to the pump polarization direction. Measurements for absorption spectra were collected during the molecular

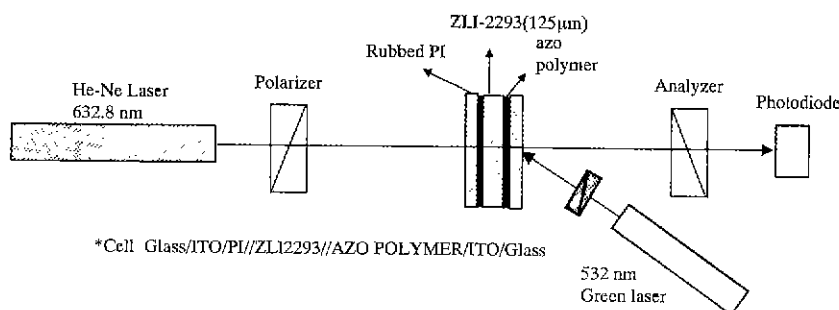
orientation (pump beam on) and the relaxation (pump beam off) process.

### Measurement of optically induced birefringences in polymer film and liquid crystal cell

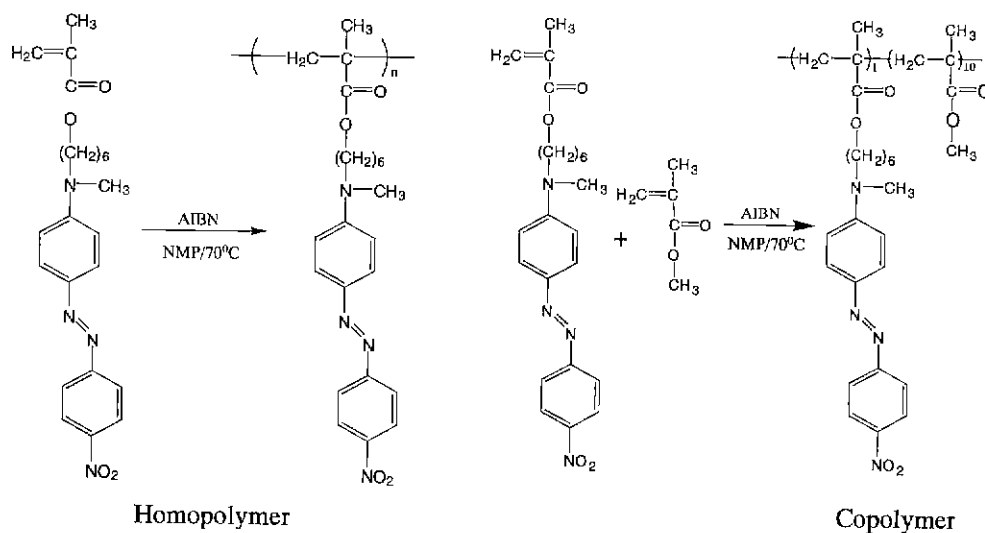
The setup for measuring optically induced birefringence is shown in Figure 1, where the change in transmission of the He-Ne laser through the polymer film between crossed polarizers is recorded as a function of time after irradiation of pumped diode laser ( $\lambda = 532$  nm, max. intensity 10 mW/cm<sup>2</sup>). He-Ne laser (~5 mW) at 632.8 nm was used as a probe light to measure the power that is transmitted. The wavelength of the pump beam is in the absorption range of the chromophore. 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 photosensitive polymer was coated. The transmission was detected with a photodiode detector (New Port 818-SL).

### Results and Discussion

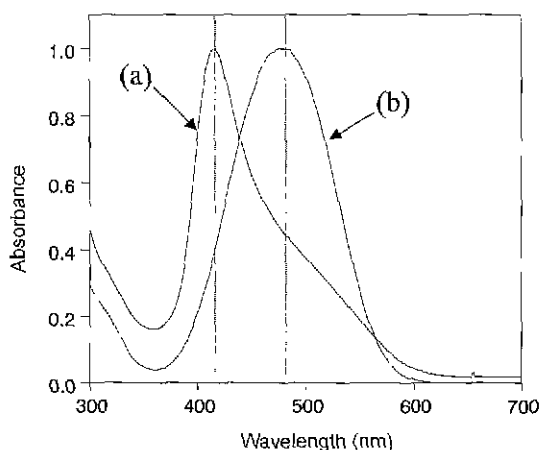
The polymers were prepared by radical polymerization



**Figure 1.** Optic setup for measuring the optical anisotropy in the liquid crystal cell under irradiation of a linearly polarized light.



**Figure 2.** Synthetic procedure for homopolymer and copolymer.



**Figure 3.** UV-Vis absorption spectra of the polymer films: (a) homopolymer, (b) copolymer.

technique to give a good yield (65%). The synthetic procedure was simply illustrated in Figure 2. In the case of copolymer, the composition of azobenzene-monomer and methylmethacrylate was determined to be 9% and 91%, respectively by elemental analysis and peak integration in NMR spectrum.

#### Photoisomerization behavior of homopolymer and copolymer

Figure 3 shows the absorption spectra of the synthesized homopolymer and copolymer films. In the case of copolymer, the absorption spectrum displays a symmetrical intense band at 480 nm due to the vibronically coupled  $n - \pi^*$  and  $\pi - \pi^*$  electronic transitions. However, in the case of the film of homopolymer, a large blue-shift of  $\lambda_{\text{max}}$  was observed compared to that of the copolymer. Absorption maximum appeared around 415–420 nm.

In a linear polymer structure, dye aggregation can usually be observed when the concentration of the polar dye increased in the matrix. Particularly, polar chromophores were observed

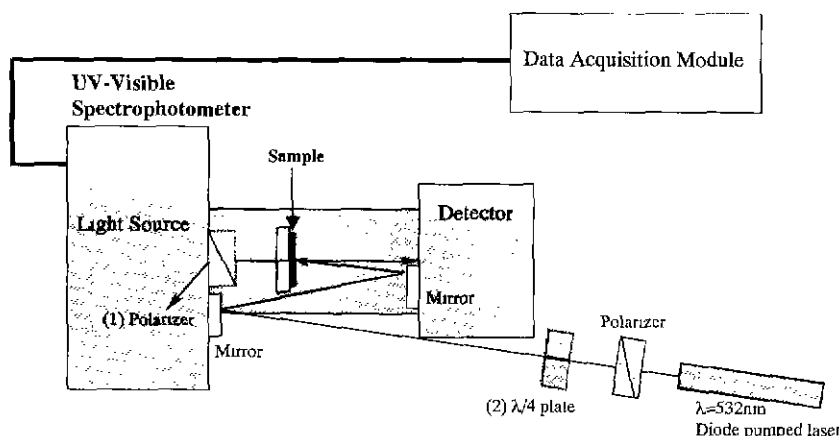
to be arranged in an antiparallel way[13]. When the dipoles are aligned antiparallel, the resulting local electric field will be in the opposite direction as the dipoles. The absorption maximum of the film appeared at the lower wavelength compared to that in the solution state. Usually, the aggregation of the chromophores in the film could be destroyed under thermal annealing. Therefore, we heated and quenched the film of homopolymer. The spectrum of thermally treated film showed  $\lambda_{\text{max}}$  around 460 nm and this sample was used for investigating the kinetics of photoisomerization. The schematic diagram of measuring setup was shown in Figure 4. In Figure 4, we introduced the  $\lambda/4$  wave plate (2) in front of the linearly polarized pump beam without the polarizer (1) for this experiment. The pump beam was circularly polarized to irradiate the film.

The curves from the change of absorbance from  $\pi - \pi^*$  transition were well fitted to double exponential functions (equations 1 and 2).

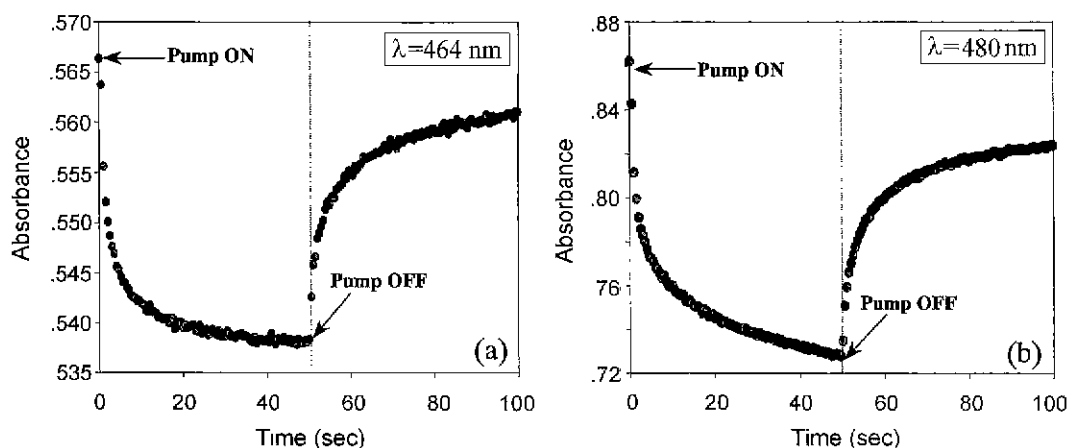
$$\text{Decay: } A(t) = A_1 \exp(-k_1 t) + B_1 \exp(-k_2 t) + C \quad (1)$$

$$\text{Growth: } A(t) = A_2 [1 - \exp(-k_3 t)] + B_2 [1 - \exp(-k_4 t)] \quad (2)$$

When the circularly polarized pump beam is turned on, the absorbance at  $\lambda_{\text{max}}$  decreases and without light, it increases (See Figure 5). Those curves can be analyzed into the fast and slow process. The rate constant,  $k_1$  in copolymer is larger than that in homopolymer. For the same exposure time, therefore the decrement of absorbance is smaller in homopolymer compared to that in copolymer. This implies that the strong dipolar coupling interaction in homopolymer induces the higher activation energy for *trans-cis* isomerization so that the isomerization was much more retarded. Then, without light, the *cis* molecules in homopolymer recovered faster than that in copolymer. The rate constant,  $k_3$  of *cis-to-trans* thermal back relaxation in homopolymer is 0.715 that is larger than that in copolymer ( $k_3 = 0.502$ ). It is attributable to that the life time of *cis* isomer in homopolymer is shorter



**Figure 4.** Schematic diagram of measurement for photoisomerization and photo-induced anisotropy.



**Figure 5.** Change of the absorbance at  $\lambda_{\max}$  in absorption spectra of the polymer films: (a) homopolymer, (b) copolymer.

**Table 1.** Calculated parameters for dynamic behavior of photoisomerization

Polymer	Decay		Rise	
	$k_1$ (/sec)	$k_2$ (/sec)	$k_3$ (/sec)	$k_4$ (/sec)
Homopolymer	0.126	0.012	0.350	0.010
Copolymer	0.121	0.012	0.140	0.008

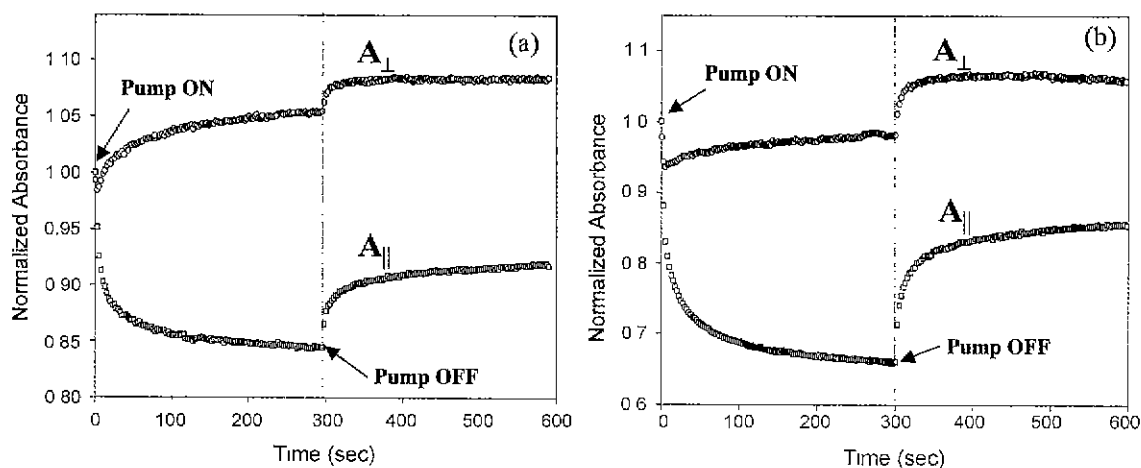
than that in copolymer. The rate constants determined in this experiment were shown in Table 1.

### Real-time polarized UV-Vis absorption spectroscopy for investigating optical anisotropy

The absorption maxima in the visible absorption spectra of two polymers appeared around 460–488 nm due to a  $\pi-\pi^*$  transition of the aminonitroazobenzene. Usually, aminoazobenzene type molecules are characterized spectroscopically by a close proximity of  $n-\pi^*$  and  $\pi-\pi^*$  bands. Often the former is buried beneath that intense  $\pi-\pi^*$  absorption[22].

When we irradiate the 532 nm linear polarized light to the sample,  $\pi-\pi^*$  and  $n-\pi^*$  transition are all activated to absorb the light so that *trans-cis-trans* isomerization and angular molecular reorientation can occur. Typical perpendicular and parallel absorbance variations of polymer films during growth and decay periods are presented in Figure 6. To compare the time dependence of the two polarized spectra, we used the normalized absorbances obtained by dividing  $A_{\parallel}$  and  $A_{\perp}$  by the absorbance,  $A_0$  of the film before irradiation.

In the writing process, the fast one is due to the pump efficiency and depends on both the intensity of the excitation beam and the angle between the polarization direction of the excitation beam and long molecular axis of azobenzene groups. This selective optical pumping from the *trans-to-cis* isomers produces an “angular hole burning” in the distribution of the *trans* isomers. This fast process is clearly shown in Figure 6 by instant decrease of absorbance for very short period. The decrease of the perpendicular absorbance during the first few seconds shows that the absorbance of the *cis*



**Figure 6.** Time dependence of the normalized perpendicular and parallel absorbances: (a) homopolymer, (b) copolymer

isomer at  $\lambda_{\text{max}}$  is smaller than that of the *trans* isomer[12]. In addition, upon irradiation and during the *trans-cis-trans* isomerization cycles, a slow molecular redistribution of the azobenzene molecules can occur and diffuse by thermal back relaxation. Consequently, during the writing period, the above two reactions occur simultaneously producing a slight increase in the concentration of the azobenzene molecules oriented perpendicularly to the pump beam polarization direction, as shown by the time variations of the  $A_{\parallel}$  and  $A_{\perp}$  components.

When the laser is turned off, the thermal *cis-trans* relaxation, which depends on the life time of the *cis* isomer, is the main factor in the first few seconds and is at the origin of the increase of both  $A_{\parallel}$  and  $A_{\perp}$  components. During the molecular relaxation period, the redistribution process affects the perpendicular and parallel absorbance significantly but the initial isotropic state of the azobenzene molecules is never recovered even after a long time delay.

The molecular orientation in these polymer matrices can be expressed by the molecular order parameter,  $P_2$ . The order parameter, associated with the orientation of the transition dipole moments of the electronic transition, is given by the following equation:

$$P_2 = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp}) \quad (3)$$

The values of  $P_2$  are in the range of +1.0 and -0.5 if the transition dipole moment is perfectly oriented parallel or perpendicular to the polarization direction of the pump beam, respectively. In azo-functional polymers, Natansohn *et al.*[12,14], have shown that the time dependence of the birefringence during the orientation and relaxation periods can be well described by biexponential functions. The fast modes were associated with dipole reorientations through *trans-cis-trans* isomerization for the orientation process and with the thermal *cis-trans* back-relaxation and the angular redistribution of dipoles for the relaxation processes. The slow mode for both the orientation and relaxation processes

was associated with the dipole reorientations involving motions of the main chain of the polymer[9-15]. According to their results, we can explain the changing behavior of the order parameter to classify into two stages. The fast and slow process can be applied to our decaying and rising curves (equations (1) and (2)). The dynamic parameters from the curves were shown in Table 2.

Figure 7 shows the time dependence of the order parameter  $P_2$  associated with the absorption band at 480 nm. Before irradiation, all the azobenzene molecules are randomly distributed in the film and  $P_2$  is equal to zero. When the linearly polarized laser is turned on,  $P_2$  becomes negative, showing that the transition dipole moment of the electronic absorption starts moving toward a direction perpendicular to the polarization direction of the pump beam. Since the direction of this transition moment is nearly along the long molecular axis of the azobenzene molecules, the polarized light induces a perpendicular orientation of the chromophores as expected. When the pump beam is turned off, the orderness of the molecules was reduced as shown by the increase of  $P_2$  values.

When we compare the dynamic behavior of the order parameters,  $P_2$  in two polymers, the structural effect can be considered. The copolymer contains only 9% of azo-repeating unit and the others are all methylmethacrylate. Therefore, less molecular interaction gave rise to induce the larger rate of reorientation in copolymer. The  $k_1$  value (= 0.824) is larger than that in homopolymer. After 300 sec exposure of linear polarized light to the film of homopolymer, the order parameter was observed to be -0.071. In comparison, the copolymer showed -0.123 after the identical exposure time. Therefore, homopolymer showed lower orderness in the orientation of the polar azobenzene molecules. This is also attributed to the strong dipolar coupling between the polar azobenzene group in the side chains of homopolymer. The reoriented dipoles were stabilized in a new position and then the dipolar coupling was also re-formed. Therefore, when

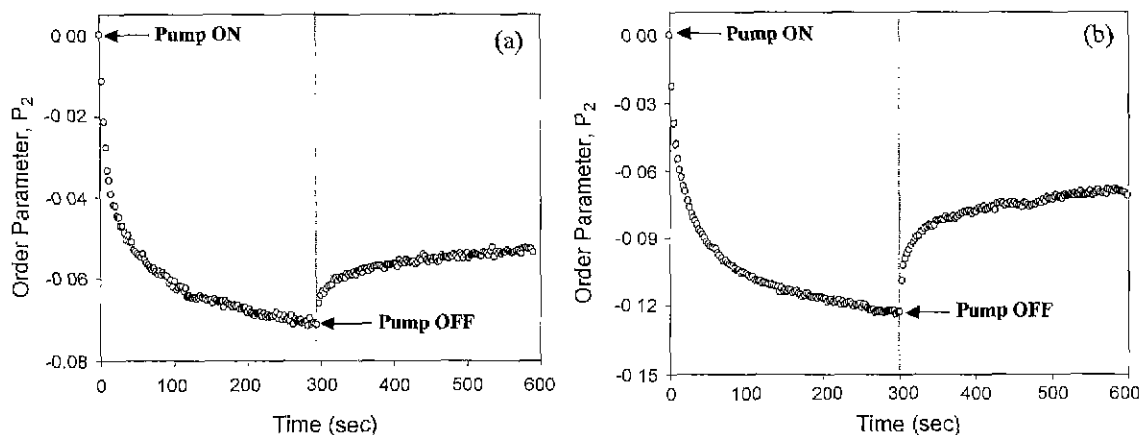


Figure 7. Time dependence of the order parameter,  $P_2$ : (a) homopolymer, (b) copolymer.

**Table 2.** Calculated parameters for dynamic behavior of optical anisotropy

Polymer	Decay		Rise	
	$k_1$ (/sec)	$k_2$ (/sec)	$k_3$ (/sec)	$k_4$ (/sec)
Homopolymer	0.703	0.084	0.715	0.064
Copolymer	0.824	0.050	0.502	0.061

the pump beam was turned off, the order parameter of homopolymer film recovered slower than that in copolymer. The copolymer provides a higher degree of freedom to enhance the mobility of the azobenzene groups. The  $k_3$  value in homopolymer is larger than that in copolymer resulting from the dipole-dipole interaction between the oriented and unoriented molecules. The dynamic parameters obtained from the decaying and rising curves were illustrated in Table 2.

### Optical anisotropy of LC cell fabricated with a photo-sensitive polymer

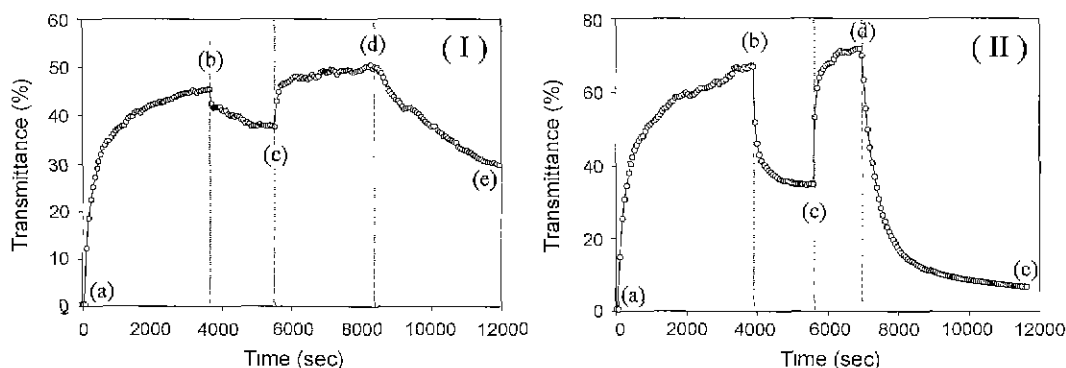
In order to prepare a LC alignment layer, the polymer solutions of 5% by weight were spin coated on an ITO glass at room temperature. The film thickness was determined to be around 0.1~0.2  $\mu\text{m}$ . The LC used was ZLI-2293 of E. Merck that has the nematic phase at room temperature. One substrate 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. The polarization direction of the pump beam was set to be parallel to the rubbing axis of one polyimide layer.

First of all, we investigated the effect of birefringence in polymer film on the birefringence of liquid crystal cell. In Figure 8, typical traces of induced birefringence were illustrated. The transmittance starts to increase due to the

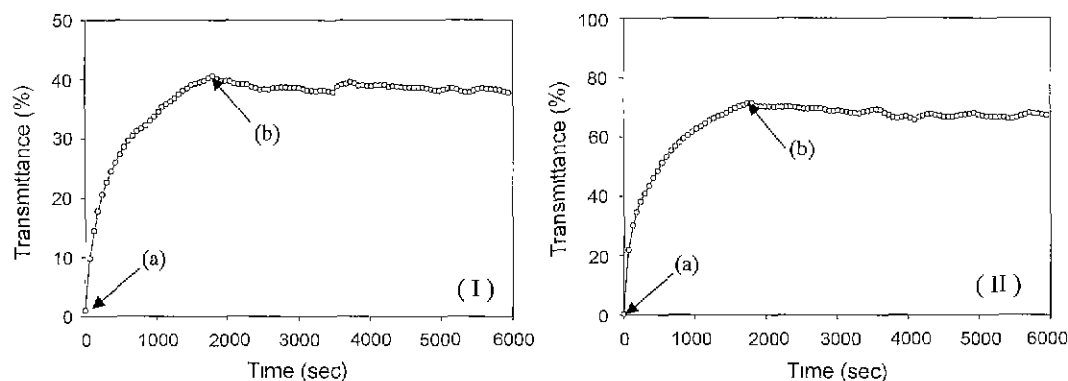
interaction between the liquid crystal molecules and reoriented azobenzene molecules when the pump beam was turned on (point (a)). In Figure 8, the transmission through the cell was observed to increase fast just after the pump beam was irradiated on the surface of the polymer film. This indicates that the LC on the photosensitive polymer films oriented, whose director is perpendicular to that of the LC on the rubbed polyimide. At point (b), we inserted quarter wave plate ( $\lambda/4$ ) to make the linear polarized light of the pump beam to the circularly polarized light. The induced birefringence of the alignment layer reduced due to randomization of the molecular orientation of the azobenzene moieties. Simultaneously, the birefringence of the LC cell also decreased. At point (c), we irradiate the linearly polarized light to the sample again. Finally, at point (d), we inserted half wave plate ( $\lambda/2$ ) in front of the pump beam to rotate  $90^\circ$  of its polarization. At this stage, similar to the region (b)-(c), the transmittance also decreased and the decrement, however, is relatively larger. This implies that in region (b)-(c), under the circularly polarized light, the azobenzene molecules will be distributed in an isotropic manner. Therefore, some of the LC molecules will remain to align in the perpendicular direction of the rubbing direction of the polyimide layer. However, in the region (d)-(e), we irradiate the linearly polarized light to the sample and the polarization direction of the pump beam is orthogonal to that of the incident linearly polarized light. The molecular reorientation of the azobenzene molecules occurred and the resultant orientation direction could be parallel to the rubbing direction of the polyimide film.

Resulting from the above phenomena, we could confirm that there is strong interaction between the photo-induced birefringence of the polymer film and the birefringence of the LC cell.

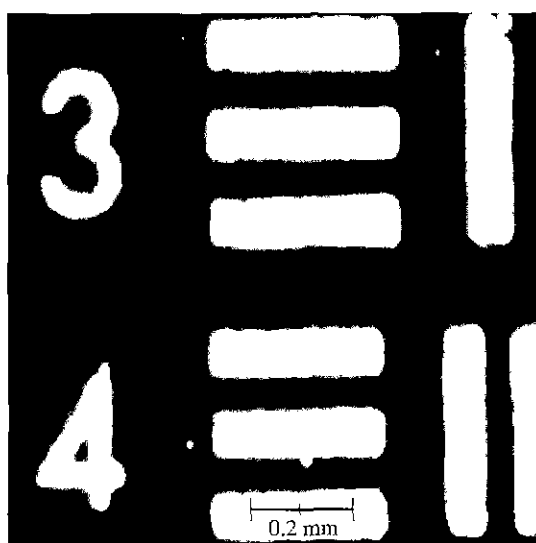
When we compare the writing and erasing behaviors in two LC cells fabricated with two polymers, the difference in the erasing behavior was shown significantly. In the two regions (b)-(c) and (d)-(e), the LC cell fabricated with alignment layer of the copolymer showed larger decrement



**Figure 8.** Change of the optical transmittance in the liquid crystal cell with the change of the polarization of the pump beam: (I) homopolymer, (II) copolymer.



**Figure 9.** Change of transmission due to the LC alignment on homopolymer (I) and copolymer (II) film: (a) pump beam on, (b) pump beam off.



**Figure 10.** Optical micrograph of the liquid crystal cell after exposure to a linearly polarized light. Photomask was placed on the surface of the substrate on which the pump beam was irradiated.

compared to those in homopolymer. This indicates that the strong dipolar coupling interaction in homopolymer can retard the decaying behavior of the anisotropy in polymer films.

We irradiated the linearly polarized light to the LC cell fabricated with photosensitive polymers. The transmittance was recorded under the identical period of the irradiation time and the stability was observed after turning off the pump light (see Figure 9). The transmittance of the LC cell reached to 70% within 1500 sec, which contains the alignment layer of the copolymer. On the while, the LC cell with the alignment layer of the homopolymer showed only 40% of transmittance in the LC cell. In the previous experiment to measure the order parameter,  $P_2$  we observed the higher  $P_2$  ( $= -0.123$ ) of the copolymer film. This indicates that the higher optically anisotropic layer can induce the higher birefringence in the LC cell. In both cases, after turning off

the pump beam, the stability of the induced birefringence in the LC cell was observed to be much better than that in the polymer film.

After inserting the photomask on the surface of the LC cell, we irradiated the linearly polarized light on the sample for 5 minutes. The optical image in Figure 10 was well illustrated by photo-patterning method using the LC cell with photosensitive azobenzene-polymer alignment layer.

## Conclusion

We synthesized homopolymer and copolymer bearing an aminonitroazobenzene chromophore in the side chain. Aminonitroazobenzene was synthesized to be introduced to side chain copolymers through the flexible methylene spacers. *Trans-to-cis* photoisomerization was clarified under the exposure of visible light ( $\lambda = 532$  nm) with the real time UV-Vis absorption spectroscopy. The dynamics of photo-induced orderness led to compare the effect of polymer structure on the rate of growth and decay of the anisotropy. The strong dipolar interaction of azobenzene molecules is found to be important factor to affect the rate of relaxation and the stability of anisotropy. 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.

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