Effect of Temperature on Photoinduced Reorientation of Azobenzene Chromophore in the Side Chain Copolymers

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We synthesized the photoresponsive side chain polymers containing aminonitro azobenzene for studying the effect of temperature on photoinduced birefringence. Four different copolymers were prepared using methacrylate, α-methylstyrene, and itaconate monomer. Photoisomerization was observed under the exposure of UV light using UV-VIS absorption spectroscopy. Reorientation of polar azobenzene molecules induced optical anisotropy under a linearly polarized light at 532 nm. The change of the birefringence was observed with increasing the sample temperature under a continuous irradiation of excitation light. We could estimate the activation energy of molecular motion in thermal and photochemical mode. Besides the effect of glass transition temperature on the activation energy, we focused our interests on the effect of geometrical hindrance of polar azobenzene molecules and cooperative motion of environmental mesogenic molecules in the vicinity of polar azobenzene molecules.

Introduction

Polymers containing an azobenzene moiety were highly attractive to investigate their unique optical and photochemical properties.[1-5] Besides the research in the direction of nonlinear optical properties, there is constantly increasing attention in the field of optical data storage and holographic applications. Photoinduced anisotropy is very promising property to be employed for optical information storage and erasing. The mechanism of writing information involves photoinduced excitation of the polar azobenzene group, which undergoes *trans-cis-trans* isomerization. This phenomenon was attributed to photoinduced anisotropy after reorientation of azobenzene molecules.

The photoinduced trans-cis isomerization of azobenzene and its derivatives has been studied in amorphous and liquid crystalline polymers.[6-10] The type of optically induced isomerization is also of particular interest because the induced changes in molecular orientation of polar azobenzene moiety can affect the surrounding molecules. In addition, the induced birefringence that results from molecular reorientation could potentially be used to investigate the molecular motion in polymer matrix and environment in the vicinity of the polar azobenzene molecules.

In the guest-host system, azobenzene guest molecules that have the structure of trans form are randomly oriented throughout the film. If the polymer film is then subjected to a linearly polarized light of an appropriate wavelength, the azobenzene molecules that have a nonvanishing transition dipole ($\Delta\mu$) component in the polarization direction of the pump beam can be photoisomerized to the *cis* form. After several repetitive photoexcitation and isomerization cycles, an excess of azobenzene molecules with transition dipole moments perpendicular to the polarization direction of the excitation light can be stabilized to new molecular direction. The azobenzene molecules placed in the perpendicular direction of polarization of pump light cannot interact with the excitation light and therefore become inert to the pump beam. The polymer matrix that was isotropic becomes anisotropic after irradiation under the excitation light. This behavior can be observed both in amorphous and liquid crystalline polymers. The anisotropic polar molecular distribution gives rise to birefringence and dichroism in the film. This phenomenon is strongly dependent on the molecular motion of azobenzene in the polymer matrix. During continuous irradiation at room temperature, molecular reorientation can be sustained in a locally ordered domain. However, increasing the sample temperature, thermal energy activates the fixed molecule to randomize and the optical anisotropy vanishes.

Usually, the induced birefringence increased under the light with the wavelength around λ_{max}. Without light, the birefringence will relax either fast or slow, which depends on the polymer structure. Since the relaxation behavior of induced birefringence depends on the mobility of the side chain and the main chain, we can have informations how the molecular motion was performed with the change of the temperature. Therefore, in order to investigate the thermal effect on the molecular motion, we have to fix the molecular reorientation under a continuous irradiation of the excitation light. The time required to reach maximum birefringence is expected to depend on the structure, polarity, environment of azobenzene molecules, the thickness of the film, and the wavelength of the excitation light. Additionally, the photoinduced birefringence is related to the structure of azo chromophore, the type of the polymer backbone, and the interaction between azobenzene dipoles. Therefore, photochemical activation energy in each system is dependent on many above structural factors. Photochemical reaction tends to reorient the molecules to the perpendicular direction of the polarization of the excitation light. On the other hand, thermal energy tends to disrupt the molecular ordering to make them dispersed in an isotropic state.

In this study, we synthesized four different types of copolymer bearing the same aminonitro azobenzene molecule in the side chain. After reaching to the maximum value of birefringence under a linearly polarized excitation light, we increased the sample temperature during exposure to pump light (532 nm). From the relationship between the birefringence and sample temperature, we could investigate the molecular motion arising from the thermal energy. Among many factors to affect the reorientation of azobenzene molecule, we performed the study on the environmental effect of polar azobenzene molecules.

Experimental Section

Copolymer I (CP I) and copolymer II (CP II) were synthesized by following the literature methods[11,12]

4-Methoxyphenyl-4-methacryloyloxy hexyloxy benzoate (MMHB) (M-I). It was synthesized by following the method of Horvath *et al.*[13] using 4-hydroxy benzoic acid as the starting material. Yield: 56% ^{1}H NMR (200 MHz, DMSO-d$_6$): δ (ppm) 8.01 (d, 2H), 7.04 (m, 6H), 5.99 (s, 1H), 5.63 (s, 1H), 4.08 (d, 4H), 3.74 (s, 3H), 1.85 (s, 3H), 1.39-1.72 (m, 8H). Anal. Calcd. for $C_{24}H_{28}O_6$: C, 69.89, H, 6.84 Found: C, 69.51, H, 7.19

4-Nitrophenyl azophenyloxy-N-methylhexyl methacrylate (NAMM) (M-II). This monomer was synthesized in three steps by using the method described in literature.[12] ^{1}H NMR (200 MHz, DMSO-d$_6$): δ (ppm) 8.33 (d, 2H), 7.89 (m, 4H), 6.84 (d, 2H), 5.99 (s, 1H), 5.63 (s, 1H), 4.08 (t, 2H), 3.46 (t, 2H), 3.05 (s, 3H), 1.85 (s, 3H), 1.32-1.57 m, 8H). Anal. Calcd. for $C_{23}H_{28}N_4O_4$: C, 65.08, H, 6.65, N, 13.20. Found: C, 65.82, H, 6.24, N, 13.65.

2-Methylene-succinic acid bis-(6-{methyl-[4-[-(4-nitrophenylazo)-phenyl]-amino}-hexyl) ester (MSAE) (M-III). 4'-[(6-Hydroxyhexyl)methylamino]-4-nitroazobenzene (HMNA) was reacted with itaconic acid using a Mitsunobu reaction.[14,15] 7.12 g (0.02 mole) HMNA was dissolved in THF (100 mL). 13.1 g (0.050 mole) triphenyl phosphine, dissolved in THF (20 mL) was added. A solution containing 8.08 g (0.04 mole) diisopropyl azodicarboxylate and itaconic acid (1.44 g, 0.11 mole) in 20 mL THF was added dropwise over a period of 40 min. The progress of the reaction was checked by thin layer chromatography (TLC). The reaction was completed in 2 h. The solution was cooled in a deep freezer and the crude product was filtered. The residue was recrystallized from acetonitrile to get pure product. Yield: 70%. ^{1}H NMR (200 MHz, DMSO-d$_6$): δ (ppm) 8.34 (d, 4H), 7.93 (m, 8H), 6.85 (d, 4H), 6.23 (s, 1H), 5.73 (s, 1H), 4.06 (m, 6H), 3.50 (m, 4H), 3.11 (s, 4H), 2.87 (s, 2H), 1.39-2.04 m, 16H). Anal. Calcd. for $C_{43}H_{50}N_8O_8$: C, 64.01, H, 6.25, N, 13.89 Found: C, 64.98, H, 6.64, N, 13.11.

Synthesis of Copolymers. Equimolar mixture of M-I (mesogenic monomer) and M-II was dissolved in freshly distilled 1-methyl-2-pyrrolidinone (NMP) to a total monomer concentration of 10 wt%. Azobisisobutyronitrile (AIBN) (2 mole % with respect to total monomer) was added to the monomer solution. The solution was taken in glass ampoule and embedded gas was removed by a vacuum-freeze-thawing technique. The ampoule was placed at 70 °C and the solution kept stirring for 48 h. The copolymer was precipitated into hot ethanol. The precipitated copolymer was purified by successive reprecipitation from THF into ethanol. The pure copolymer (CP III) were filtered and dried under reduced pressure at 60 °C for 48 h. (Yield, 48%) Copolymer IV was also prepared by the same method (Yield, 35%).

Characterization

NMR Spectroscopy. Proton NMR spectrum was recorded with Varian 200 NMR spectrometer using tetramethylsilane as an internal standard. Dimethylsulfoxide-d$_6$ was used as a solvent for recording NMR spectra.

UV/VIS absorption spectroscopic study. Hewlett Packard (PDA type, model 8453) spectrophotometer was employed to record the UV/VIS absorption spectrum from 190 nm to 1100 nm.

Gel permeation chromatography. The number average molecular weight (M_n) and molecular weight distributions were determined by using Waters gel permeation chromatography (model 440) attached with 410 diffraction refractometer. Spectral grade THF was used as a solvent and molecular weight calibration was done using polystyrene standard.

Differential Scanning Calorimetry. Thermal transition temperatures were examined by using differential scanning calorimeter (Perkin Elmer, DSC 4) at a scan rate of 10 °C/min under nitrogen atmosphere. Both heating and cooling

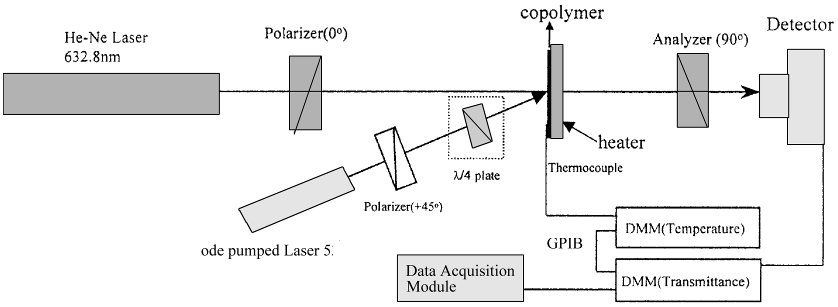


Figure 1. Schematic diagram for the measurement of optically induced birefringence.

scans were repeated three times.

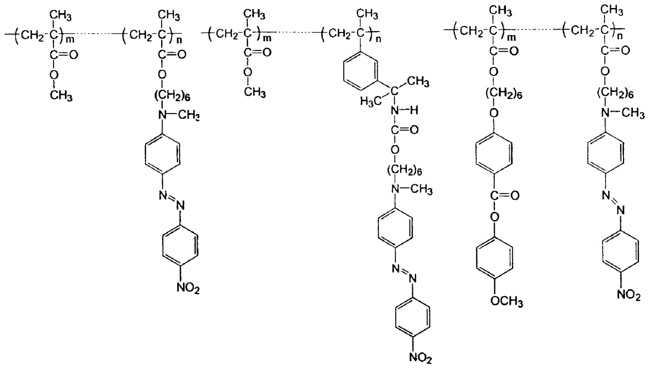
Optically Induced Birefringence. The optic setup for measuring optically induced birefringence is shown in Figure 1, where the change in transmittance of the He-Ne laser through the film between crossed polarizers is recorded as a function of time after irradiation of pumped diode laser (λ=532 nm, intensity: 216 mW/cm^2). He-Ne laser (~10 mW) at 632 nm was used as a probe light to measure the power which is transmitted. Optical anisotropy was induced in the polymer film using a polarized pumped diode beam at a polarization angle of 45° with the respect to the polarizer direction. The transmittance was detected with a photodiode detector (New Port 818-SL). The transmitted signal $I(t)$ due to birefringence is proportional to $\sin^2(\pi d\ \Delta n/\lambda)$ where d and Δn are thickness and birefringence of the film, respectively. λ is the wavelength of the probe beam (He-Ne laser radiation at 632 nm). We measured the thickness of the films using Tencor P10 to convert from transmittance to birefringence using the following equation (1).

$$\Delta n = [\lambda_o/\pi d] \arcsin [(I(t)/I_o)^{0.5}] \qquad (1)$$

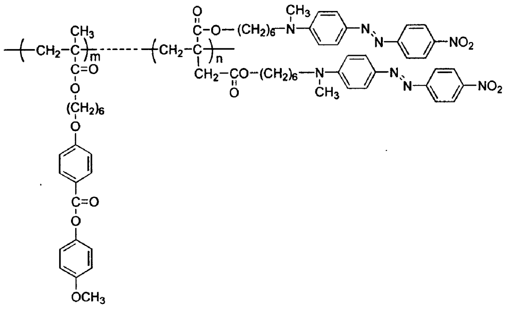
For studying the effect of sample temperature on photoinduced reorientation of azobenzene molecules, we irradiate the pump light to the sample continuously preserving the maximum birefringence at room temperature. In order to increase the sample temperature, we placed the sample on the hot stage whose temperature was being monitored with K-type thermocouple and all the data was transmitted to the data acquisition module. The rate of temperature was set to be 5 °C/min. Temperature of hot stage was precisely controlled by programmable thermo-controller P100 (Hanyoung, Korea).

Results and Discussion

Four different copolymers were prepared by a free radical polymerization method under a small amount of AIBN ([M]/[I]=50). The structures of synthesized copolymers were illustrated in Figure 2. Copolymer I (CP I) was prepared using the methacrylate (M-II) bearing the aminonitro azobenzene and methylmethacrylate (MMA). Copolymer II (CP II) was also prepared using the α-methylstyrene containing an aminonitro azobenzene and MMA. Copolymer III (CP III) consists of MMHB (M-I) and NAMM (M-II) units, whereas copolymer IV (CP IV) consists of MMHB (M-I) and MSME (M-III) units. All the copolymers are well soluble in organic solvents such as tetrahydrofuran, dimethylformamide, chlorinated hydrocarbon etc. Composition ratio of each copolymer was determined by NMR and elemental analysis. The details about monomer feeding ratio, copolymer composition, molecular weight, and glass transition temperature are listed in Table 1.



Copolymer I (CP I) Copolymer II (CP II) Copolymer III (CP III)



Copolymer IV (CP IV)

Figure 2. Structures of copolymers used in this study.

Thin films were obtained by dissolving the copolymers in THF and casting the solution onto a clean glass slide. We dried the films thoroughly at room temperature under vacuum for 48 h.

UV-Vis absorption spectroscopic study. Aminonitro azobenzene chromophore shows the highest absorbance at 483 nm. In Figure 3, the representative UV-VIS absorption spectrum of CP I was shown to observed the absorption behavior of the azo chromophore and the absorption maximum was found at 483 nm, which can be assigned to π–π* transition in a polar azobenzene unit. The wavelength of used excitation light (532 nm) is in the range of the absorption. We could observe the clear photoisomerization process and that the reverse reaction also is very quickly performed.[16]

Table 1. Molar composition, molecular weight, polydispersity, and glass transition temperature of the synthesized each copolymer

	Monomer Feeding Mole Ratio		Resultant Mole Composition		Molecular Weight (M_n)	Polydispersity	Glass Transition Temperature (°C)
	A	B	A	B			
CP I	1	1.5	1	0.7	9300	2.90	115.0
CP II	1	2	1	1	10000	2.10	118.0
CP III	1	1	1	0.9	7000	2.23	56.0
CP IV	1	1	1	0.2	5300	2.50	37.5

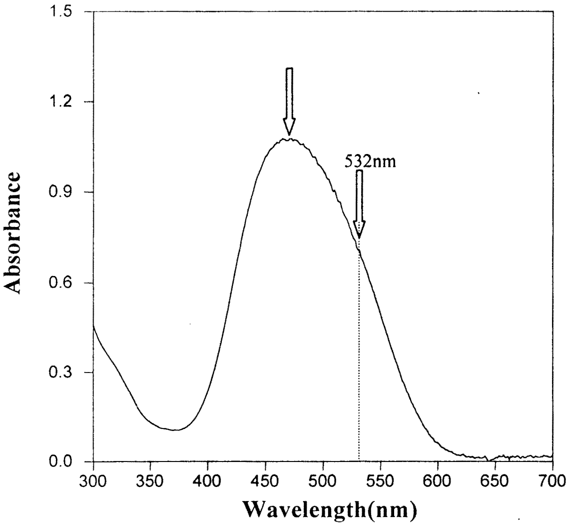


Figure 3. UV-VIS absorption spectrum of copolymer I (CP I).

Effect of sample temperature on photoinduced birefringence. A typical sequence for inducing birefringence and relaxation in copolymer IV are presented in Figure 4. The sample is homogeneous and optically isotropic. No transmission of the probe beam is detected through the crossed polarizers. Optical anisotropy is induced by exposure to a linearly polarized pumped diode laser beam (λ=532 nm). Using CP III and CP IV, we measured the maximum value of transmittance with the change of the difference between polarization of pump beam and analyzer axis. We increased the angle of difference from 0° to 45° to obtain the maximum birefringence at each step. These experimental results were shown in Figure 5. At 45° angle difference between the polarization of pump beam and analyzer axis, the transmittance was observed to be the highest level in both cases. Therefore, we set the angle difference to be 45° when we did pump the azobenzene molecules in polymer film. When optical anisotropy is induced in the polymer film, the probe light is partially transmitted through the optical setup and transmittance reaches to the maximum level.

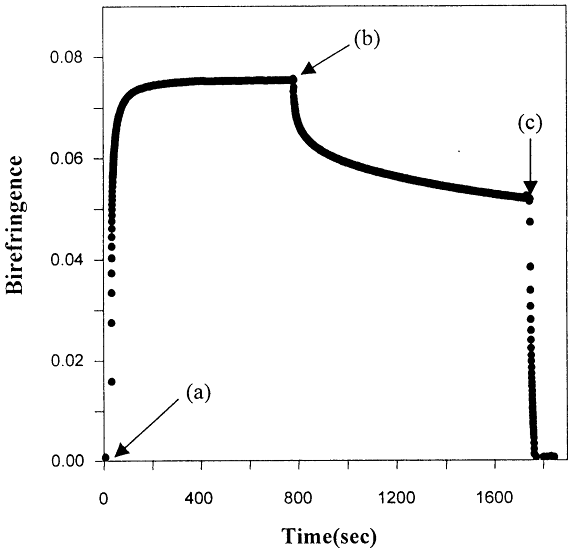


Figure 4. Growth and decay of birefringence on a copolymer IV (CP IV) film: (a) The writing beam is turned on. (b) The writing beam is turned off. (c) Circularly polarized light on. *Pump beam intensity 216 mW/cm^2.

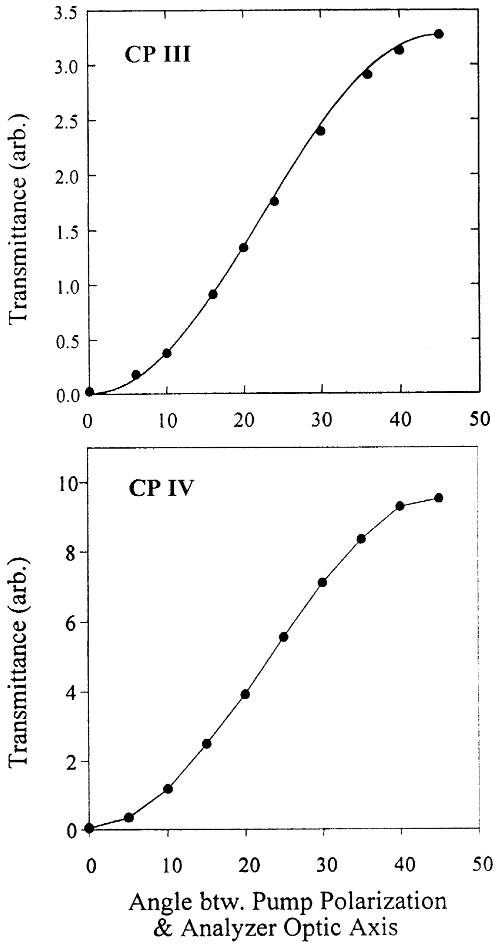


Figure 5. Change of the transmittance with respect to angle between pump polarization and analyzer optic axis. *Sample: Copolymer III(CP III), Copolymer IV(CP IV); Pump beam intensity 216 mW/cm^2.

In order to study the effect of thermal and photochemical stimuli on induced birefringence, we placed the sample on the hot stage to increase the sample temperature. We irradiated the excitation light on the sample continuously during heating. In this case, we can expect two different kinds of molecular behavior inside the polymer matrix. One is to increase the mobility of azobenzene molecule due to the thermal effect. Sample temperature can affect the increase of the molecular mobility to diminish the optical anisotropy. On the while, the photo-irradiation tends to make the azobenzene molecules reorient to induce the molecular anisotropy. Therefore, over a whole temperature range, both thermal and photochemical effect can be undergone in the polymer matrix. However, photochemical and thermal effect can be competitive to retain the optical birefringence and to disrupt the molecular ordering. Generally, at the temperature higher than T_g, azobenzene molecules cannot retain the local ordering from molecular reorientation due to large induced free volume arising from the main chain motion. Thermal effect is dominant to randomize the molecular ordering in the temperature range. On the contrary, far below T_g, thermal and photochemical effects are all available to induce the optical anisotropy and sequentially to randomize the molecular arrangement. At room temperature, photochemical effect is predominant to retain the optical birefringence built under the exposure to pump beam.

Generally, it was thought that the temporal stability of birefringence in a high T_g polymer is much better than that in a low T_g polymer. However, induction of optical birefringence is strongly dependent on the mobility of the side chain bearing the azobenzene unit. Therefore, the geometrical hindrance around azobenzene moiety will be another important factor to improve the stability of optical anisotropy.

First of all, we recorded the transmittance and sample temperature during irradiation of excitation light (216 mW/cm^2). We converted the transmittance to birefringence using the equation (1). The induced birefringence was gradually decreased and finally fell down to zero even though the irradiation kept going. In CP I and CP II, birefringence vanished totally in the vicinity of the glass transition temperature. Using the above data of birefringence (Δn) and sample temperature (T), we derived the relationship between ln (Δn) and 1000/T according to the Arrhenius relationship. The curve can be interpreted by following equation (2) employing the step function, 1(T-T') (= 1, T < T'; = 0, T > T').

$$\ln \Delta n = \ln \Delta n_o + (E_{a2}/R)\,(1/T) + 1(T-T')\,[(E_{a2}-E_{a1})/R] \times (1/T-1/T') \qquad (2)$$

T' is the temperature at which the inflection point is observed in birefringence. Δn_o is the maximum birefringence we observed. E_{a1} and E_{a2} are the activation energies at T < T' and T > T', respectively.

The molecular motion was wholly attributed to thermal effect over a full temperature range and the change of the reorientation of azobenzene is strongly dependent of side chain and main chain motion. Two different slopes (E_a/R) can be observed in Figure 6-10. The first slope, E_{a2}/R is due to disruption of optical birefringence and increase of the main chain mobility. As the temperature rises, one inflection point was observed in every case. This temperature can be explained that the main chain begins to move and then the mobility was added to the side chain mobility. In the case of CP I and CP II, this temperature is also likely to be consistent with the onset temperature of T_g in a heating cycle.

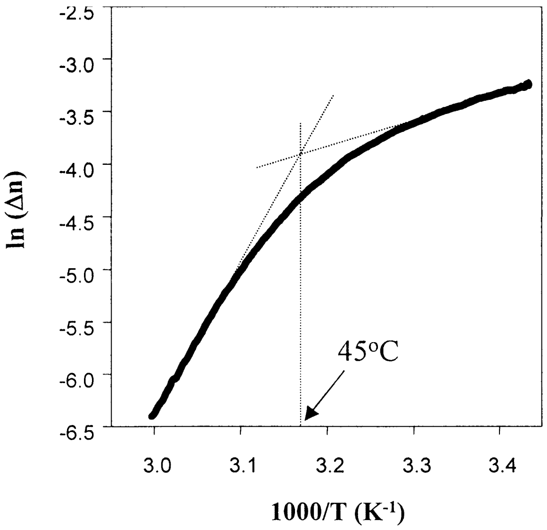


Figure 6. Arrhenius Relationship between the logarithmic birefringence and the measured temperatures. *Sample: PMMA/10 wt% DR1.

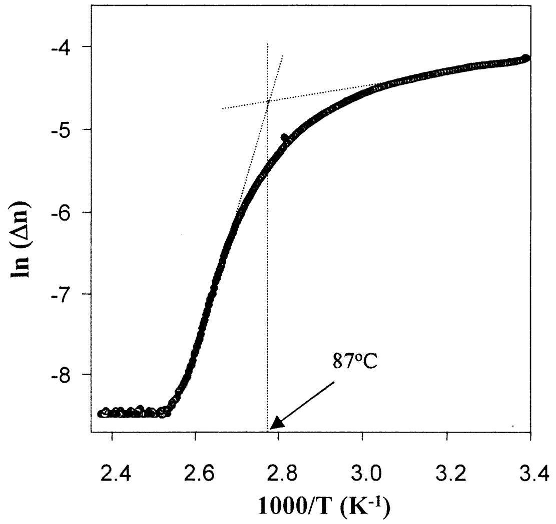


Figure 7. Arrhenius Relationship between the logarithmic birefringence and the measured temperatures. *Sample: Copolymer I (CP I).

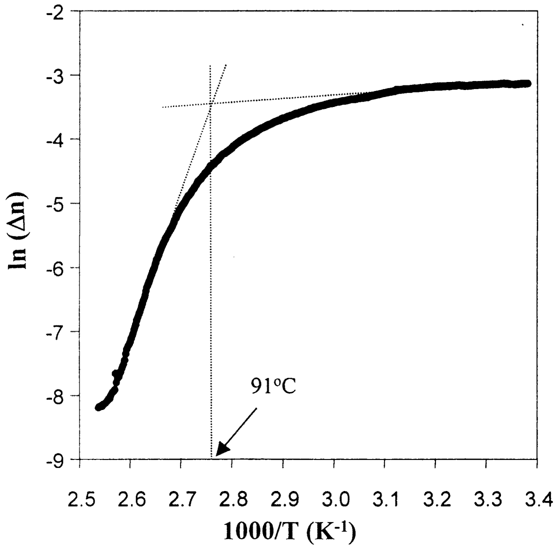


Figure 8. Arrhenius Relationship between the logarithmic birefringence and the measured temperatures. *Sample: Copolymer II (CP II).

In this experiment, we could observe two different slopes either in below T' and over T'. In the lower temperature range, the slope (E_{a1}/R) is comparably smaller than that (E_{a2}/R) in a high temperature range. This implies that in the low temperature range (T < T'), the photo energy and thermal energy contribution are quite competitive and mainly the side chain mobility can make the reoriented azo molecules

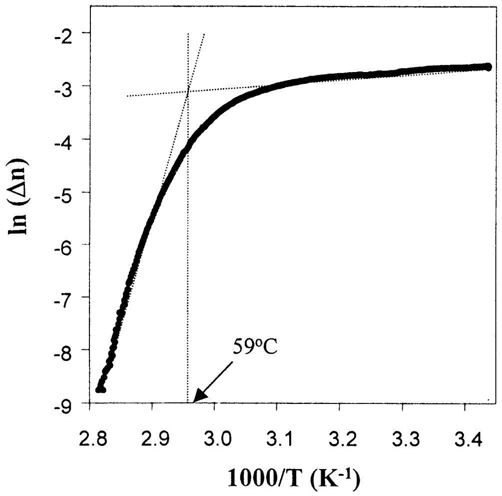


Figure 9. Arrhenius Relationship between the logarithmic birefringence and the measured temperatures. *Sample: Copolymer III (CP III).

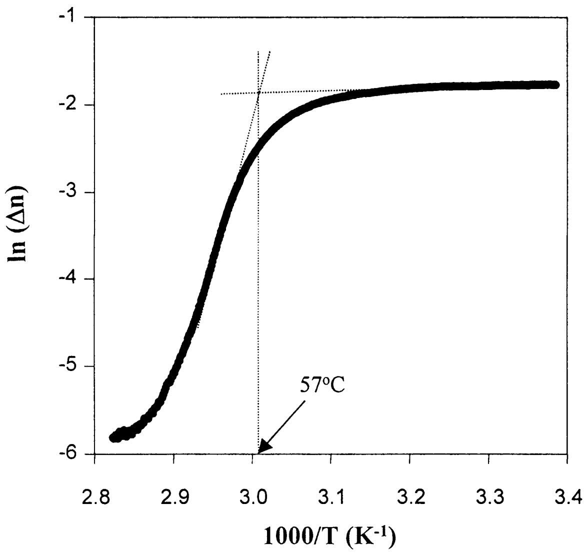


Figure 10. Arrhenius relationship between the logarithmic birefringence and the measured temperatures. *Sample: Copolymer IV (CP IV).

isrupt.

In a high temperature range (T > T'), photoinduced molecular reorientation cannot be sustained since the thermal energy is fully adequate to make the main chain move and randomize the local ordering that can induce the optical anisotropy. Two slopes are the important parameters to estimate the rate of induction and temporal stability of birefringence in each polymer system. The slopes were calculated and shown in Table 2. We focused our interests to what the structural effect to retard and accelerate the relaxation of birefringence is.

Five figures describe the relationship between ln (Δ*n*) and 1000/T, where T is the sample temperature, in five polymeric systems. As we mentioned in the experimental section, four different kinds of copolymer were used including the PMMA doped with 10 wt% disperse red 1. In the guest-host system the azobenzene molecule was not tethered through chemical bond in any side of azobenzene molecule. The time to reach the maximum birefringence is the shortest and the relaxation of birefringence is the fastest without pump light. In Figure 6, the two different slopes were observed and can be calculated in the plot. E_{a1}/R is the largest among the polymers used in this study. In the low temperature range (T < T'), the larger excluded volume of disperse red 1 provides the guest molecules to move more freely. Additionally, in the temperature higher than 45 °C (= T'), the larger slope was obtained. About 45 °C is the onset temperature at which the main chain starts to move. The birefringence totally vanished around 70 °C because the glass transition temperature of PMMA was lowered with plasticizer of 10 wt% disperse red 1.

In the case of CP I, the slope, E_{a1}/R is smaller than that in PMMA/DR1 system since the azobenzene molecule was bound to the polymer backbone. Therefore, the activation energy to disrupt the reorientation of the azobenzene molecules is relatively smaller. The birefringence disappeared around 110-115 °C, which is well consistent with T_g measured by DSC. The inflection point (T') was observed around 86 °C at which the main chain begins to move.

In the case of CP II, we could also observe two different slopes with the change of temperature. In the low temperature range (T < T'), the slope is smaller than that in CP I. This can be explained that there is high density of hydrogen bond between carbonyl and secondary amine in the carbamate groups in the side chain. That hydrogen bond formation was confirmed in IR spectral analysis.[16] The fraction of hydrogen bond and isolated mode was calculated to be 56% and 44% respectively. The side chain motion was restricted from hydrogen bond between the side chains themselves. Therefore, the rates of induction and relaxation of birefringence were smaller than those of CP I in the initial period.[16]

In the case of CP III, mesogenic monomer, M-I was copolymerized with methacrylate containing a polar azobenzene moiety. As was reported, when polar azobenzene was photo-

Table 2. Parameters obtained by Arrhenius relationship between the logarithmic birefringence and the measured temperatures

	Thickness (μm)	Max. Δ*n*	Temp I (°C)	Temp II (°C)	Slope I (E_{a1}/R)	Slope II (E_{a2}/R)
PMMA/10 wt% DR1	0.24	0.040	45	70	2.368	12.938
Copolymer I	0.35	0.045	87	110	1.388	15.632
Copolymer II	0.20	0.042	91	120	1.205	19.394
Copolymer III	0.31	0.071	59	75	1.154	23.797
Copolymer IV	0.16	0.075	57	82	0.449	32.424

*Temperature I: The temperature at inflection point. Temperature II: The temperature at which induced birefringence vanished totally. Slope I: The slope in the low temperature range (T<Temp I, T'). Slope II: The slope in the high temperature range (Temp II>T>Temp I, T') isomerized and reoriented, the mesogenic molecule was moved cooperatively.[10] The azobenzene molecules are surrounded by bulkier groups than methylmethacrylate, which become more hindered geometrically. Therefore, the activation energy to induce the side chain motion becomes smaller than that of CP I and CP II. The birefringence vanished around 75-80 °C that is higher than T_g (~57 °C) of CP III. This can be explained that the strong interaction between two monomers shifts the temperature at which induced birefringence disappeared totally. Although the contribution of main chain motion affects the disruption of reorientation of azobenzene molecules, the small degree of local orientation of azobenzene unit sustained for longer period. We reported why this copolymer shows the slow rate of growth and decay of birefringence at room temperature although the glass transition temperature was observed around 57 °C.[16]

Two polar azobenzene units were tethered in one repeating unit of CP IV so that the dipolar interaction imposes some more hindrance to polymer segment. Stronger interaction between the monomers can be expected to restrict the molecular side chain motion to isotropic state. Induced birefringence disappeared around 75-80 °C. This temperature is far higher than T_g (~37 °C) of CP IV. This implies that the stronger interaction provides the better temporal stability of induced birefringence. Larger shift of the temperature at which the birefringence vanished is observed, compared with that in CP III. According to the cooperative motion of mesogenic unit, it is more difficult to induce the side chain mobility under a same history of temperature. Therefore, the slope (E_{a1}/R) in the low temperature range is the lowest among five polymeric systems. Two copolymers bearing a mesogenic monomer showed unique properties compared to those of copolymer I and II. When the side chains are interactive mutually, activation energy to disrupt the optical anisotropy becomes smaller than those of the others. Once the reorientation was proceeded, dipole in each side chain tends to stabilize in an antiparallel way. Resulting from that phenomenon, it is more difficult to randomize the molecular ordering. This was proved by the relationship between ln (Δn) and 1000/T, shown in Figure 10.

Shortly, we found that the photoinduced birefringence decays as the sample temperature increased. Around the onset temperature that glass transition behavior appears, birefringence starts to fall down to minimum level. Temperature dependence of stability of photoinduced birefringence led us to figure out how much thermal energy are needed to disrupt the optical anisotropy during exposure to the excitation light and what structural factors govern the stability of photoinduced birefringence respectively.

Conclusion

We synthesized four different types of copolymer bearing an aminonitroazobenzene chromophore in the side chain. Aminonitroazobenzene was synthesized to tether it to the side chain copolymers through the flexible methylene spacers. All copolymers contain amnonitroazobenzene molecules in the side chain. Optical anisotropy can be induced under exposure to a linearly polarized light at 532 nm. The relationship between the birefringence and the sample temperature was provided to understand the temporal stability at various temperatures. The stability of photoinduced birefringence was affected by various structural factors in copolymers. The hydrogen bond between the side chains, dipolar interaction of azobenzene molecules, Van der Waals interaction, and cooperative motion of environmental molecules in the vicinity of azobenzene molecules are found to be important factors to affect the rate of relaxation and the stability of birefringence.

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