

Effect of Molecular Aggregation on the Photo-Induced Anisotropy in Amorphous Polymethacrylate Bearing an Aminonitroazobenzene Moiety

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We investigated H-type molecular aggregation in a simply spin-coated amorphous homopolymer film of polymethacrylate containing push-pull azobenzene moieties. It was found that the aggregate formation was strongly influenced by thermal treatment and that the aggregate created in the polymer film could be easily disrupted by irradiation of a linearly polarized light. In the first writing cycle of aggregated polymer film, photo-induced birefringence showed a steep increase to the highest value followed by a gradual decrease to the certain asymptotic value under longer irradiation of a linearly polarized light. This unique behavior could be attributed to the cooperative motion and the disruption of the aggregated molecules under continuous irradiation of light.

Keywords : Molecular aggregation. Linearly polarized light. Photo-induced birefringence.

Introduction

Polymers containing azobenzene moieties have drawn much attention in the field of optical data storage, nonlinear optics, and holographic applications.¹⁻⁷ A number of researchers have investigated the photo-induced anisotropy originating from the *trans-cis-trans* photoisomerization and molecular rearrangement under irradiation of a linearly polarized light.³⁻⁷

In order to achieve the maximum photo-induced birefringence, the concentration of azobenzene in polymers should be as high as possible, which inevitably causes the molecular aggregation in the solid state. Molecular aggregation is a well-known phenomenon as mainly observed in Langmuir-Blodgett (LB) or self-assembled films, which gives rise to spectral change (hypsochromic or bathochromic shift) due to parallel (H-aggregate) or inclined (J-aggregate) dipole-dipole arrangement.^{4,8-14} Recently, Labarthe *et al.* reported molecular aggregation in the series of liquid crystalline polymer films and photo-induced birefringence of samples which were treated under different annealing conditions.⁶

In this study, we investigated the molecular aggregation behavior in an amorphous homopolymer containing a high concentration of a polar aminonitroazobenzene moiety under thermal treatment and light irradiation. The polymer adopted for this work is a high molecular weight ($\bar{M}_n \sim 11,400$) amorphous homopolymer of 2-methyl-acrylic acid 6-{methyl-[4-(4-nitro-phenylazo)-phenyl]-amino}-hexyl ester, which was also included as a liquid crystalline polymer in the molecular aggregation study of Labarthe *et al.*⁶ Our present work, that was carried out simultaneously and independently from the latter work, aims at reporting several different and additional observations related to the molecular aggregation in the amorphous polymer film. Our observations are summarized as follows. We did not observe any liquid crystallinity in the polymer film probably due to the different molecular weight

or film thickness from those of Labarthe *et al.*⁶ The concentration of aggregation was easily controlled by heating the polymer film followed by cooling with the different rate. In case of heating and quenching, the aggregation was excluded and there remained isolated free azo molecules in the polymer film. On the other hand, in case of heating and slow cooling, the aggregation was developed extremely to a higher concentration. The aggregate created in the polymer film could be easily disrupted by irradiation of a linearly polarized light, which suggests a promising application to the optical data storage. The effect of aggregation on the photo-induced birefringence by irradiation of linearly a polarized light was also studied in this work.

Experimental Section

Monomer and Polymer Synthesis.¹⁵ Monomer and polymer were synthesized according to the literature method.¹⁵ 2-methyl-acrylic acid 6-{methyl-[4-(4-nitro-phenylazo)-phenyl]-amino}-hexyl ester was prepared by esterification between methacryloyl chloride and azo chromophore, 6-{methyl-[4-(4-nitro-phenylazo)-phenyl]-amino}-hexan-1-ol. The azo chromophore was synthesized via diazotization and coupling reaction between 6-(methyl-phenyl-amino)-hexan-1-ol and 4-nitroaniline. Homopolymerization of 2-methyl-acrylic acid 6-{methyl-[4-(4-nitro-phenylazo)-phenyl]-amino}-hexyl ester was carried out in freshly dried NMP with a trace amount of AIBN at 60 °C. The polymerization was terminated by pouring the reaction mixture into methanol. Red polymer (PDR6H) was collected and purified by several reprecipitations from 1,1,2,2-tetrachloroethane into methanol until there was no monomer left in the product. It was dried in vacuum at 90 °C for 48 h. The yield was about 70%. The glass transition temperature of PDR6H was measured to be 90 °C.

¹H-NMR (CDCl₃) δ (ppm) 1.65-0.88 (5H, CH₃C-, -CH₂-

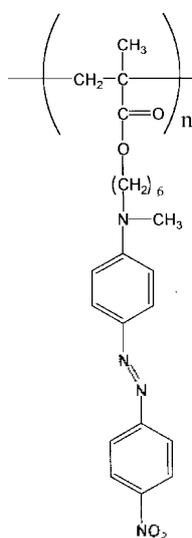
in the main chain: 8H, $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}-$), 3.00 (3H, $\text{CH}_3\text{N}-$), 3.34 (2H, $-\text{CH}_2\text{N}-$), 3.90 (2H, $-\text{CH}_2\text{O}-$), 6.64 (2H, aromatic, ortho to $-\text{N}$), 7.84 (2H, aromatic, meta to $-\text{NO}_2$), 8.26 (2H, aromatic, ortho to $-\text{NO}_2$).

Characterization. $^1\text{H-NMR}$ spectra were recorded with a Jeol JNM-LA300 spectrometer. Differential scanning calorimetry (DSC) measurement was performed on a PERKIN-ELMER DSC 7 with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) was conducted with a Du Pont TGA analyzer (Model 2950) at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The molecular weight was determined with gel permeation chromatograph (GPC) (Waters model 440). UV-visible absorption spectra were recorded using a Hewlett Packard UV-Vis. spectrophotometer (PDA type, $\lambda = 190\text{--}1100\text{ nm}$).

Film Fabrication. Polymer films were prepared by spin-coating from 1,1,2,2-tetrachloroethane solution onto slide glass and dried in vacuum at $100\text{ }^\circ\text{C}$ for 48 h. The film thickness was precisely measured by a surface profilometer (Alpha step 200) to calculate the absolute value of birefringence. Typical film thickness of PDR6H films ranged from 80 to 150 nm.

Results and Discussion

Synthesis and Characterization. The monomer and polymer were successfully synthesized according to the literature procedure.¹⁵ The chemical structure of synthesized polymer PDR6H is shown in Scheme 1. The structures of monomer and polymer were confirmed by the spectral analysis with NMR. The number average molecular weight was about 11,400 (degree of polymerization ~ 27 , $\overline{M}_w/\overline{M}_n \sim 1.42$). The obtained polymer was well soluble in 1,1,2,2-tetrachloroethane, although it showed poor solubility in common organic solvents such as chloroform, methylene chloride and tetrahydrofuran. In the TGA thermogram, 10 % weight loss was only observed on heating the polymer up to $300\text{ }^\circ\text{C}$.



Scheme 1. Structure of PDR6H.

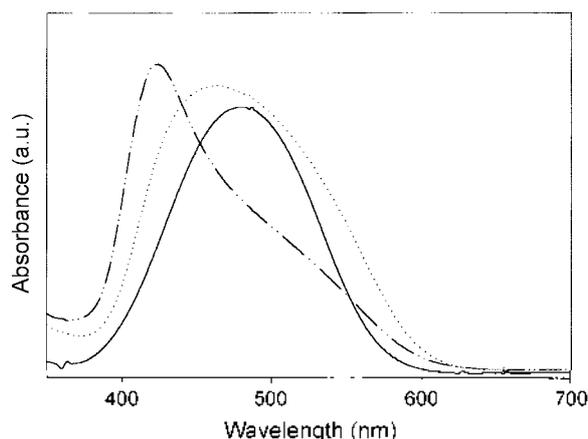
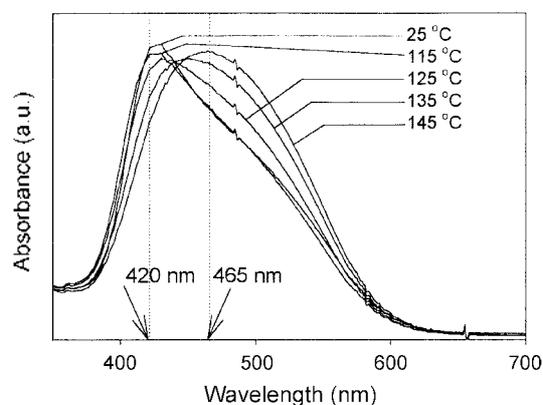


Figure 1. UV-visible absorption spectra of PDR6H: (a) dilute solution in THF (solid); (b) the sample 1 (dash-dot-dot); (c) the sample 2 (dotted).

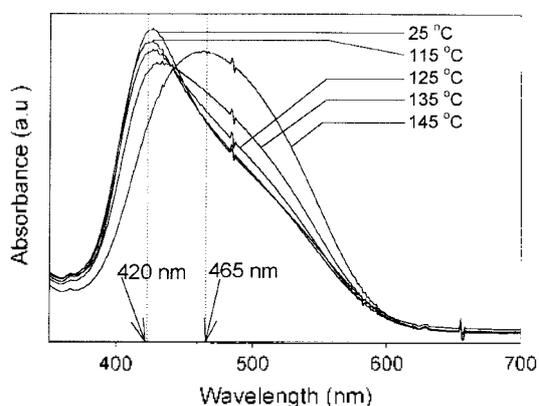
Film Property. The spin-coated and dried film was heated to $150\text{ }^\circ\text{C}$ and cooled down to room temperature (Sample 1). Sample 2 was also prepared by heating the dried film to $150\text{ }^\circ\text{C}$ and quenching to room temperature. The UV-Visible absorption spectra of solution and film of the polymer are shown in Figure 1. The absorption spectrum of the sample 1 is much more blue-shifted ($\lambda_{\text{max}} = 420\text{ nm}$) and the shape of spectrum is highly skewed than that of solution ($\lambda_{\text{max}} = 480\text{ nm}$). This behavior is well consistent with the result of Labarthe's study.⁶ Such a blue-shifted absorption of molecular aggregates is theoretically explained with molecular exciton theory proposed by Kasha.⁸ H-type molecular aggregation, an assembly with chromophores arranged in such a way so that their dipoles are parallel to each other, has mainly been found in Langmuir-Blodgett or self-assembled films.¹²⁻¹⁴ The possible reason of this H-type aggregation in spin-coated PDR6H film can be accounted that the synthesized polymer has a very high concentration of push-pull azobenzene molecules which are decoupled from polymer backbone through a long alkyl spacer group (6-methylene). The left-skewed shape of spectrum means that two kinds of $\pi \rightarrow \pi^*$ electronic transitions can be expected in this polymer film. One is the transition in H-aggregated chromophores ($\lambda_{\text{max}} \sim 420\text{ nm}$) and the other in isolated chromophores ($\lambda_{\text{max}} \sim 465\text{ nm}$). λ_{max} of the film was strongly influenced by the concentration of H-aggregated chromophores. We prepared the sample 1 by heating the sample to $150\text{ }^\circ\text{C}$ and cooling it to room temperature. During the slow cooling process, aggregation could be developed, that causes shift of λ_{max} that appears at 420 nm. On the other hand, in the case of the sample 2, aggregated structure was almost disrupted by heating and the isolated molecules were frozen by quenching ($\lambda_{\text{max}} \sim 465\text{ nm}$). It was demonstrated, therefore, that the extent of aggregation could be controlled by thermal treatment and the cooling rate. In cases of heating and quenching, the structure of isolated dye chromophores is dominant in the film state because of disruption of aggregate ($\lambda_{\text{max}} \sim 465\text{ nm}$, the sample 2). On the other hand, in case of heating and slow cooling, the extent of aggregates could be maxi-

mized ($\lambda_{\max} \sim 420$ nm, the sample 1) with the change of the cooling rate. Shortly, the concentration of aggregate in the polymer film was well controlled by cooling rate. This process of induction and disruption of aggregates was observed to be quite reversible.

Temperature Effect on Aggregate Formation. To investigate the formation of molecular aggregate in the PDR6H film, UV-Visible absorption spectra at various temperatures during heating and cooling cycles were recorded. The rate of heating and cooling was about 30 °C/min. UV-Visible absorption spectra shown in Figure 2 were recorded after storing the sample for 10 min to reach thermal equilibrium at the desired temperature. In the heating cycle of the sample 1, no significant change was observed until the temperature reached to 115 °C. This means that H-aggregate in PDR6H film is thermally stable to this temperature. UV-Visible absorption spectrum showed drastic change from 115 to 145 °C (absorbance at λ_{\max} became larger and λ_{\max} was red-shifted). This is, no doubt, due to the disruption of aggregate by heating the sample. The aggregated structure was re-developed during slow cooling as shown in Figure 2(b). The resulting absorption spectrum at room temperature (25 °C) is much the same as that of the sample 1 in Figure 1(b) because cooling condition was controlled in a similar fashion. Such a reversible thermochromism of the polymer film was not investigated in



(a) heating



(b) cooling

Figure 2. Absorption spectra of PDR6H at various temperatures: (a) heating cycle and (b) subsequent cooling cycle of the sample 1.

the same polymer in Labarthe's study.⁶

The Effect of Aggregation on the Optical Anisotropy. Figure 3 shows the experimental setup for investigating the change of absorption spectrum during irradiation of a linearly polarized light. The sample 1 was irradiated by a linearly polarized light ($\lambda = 532$ nm, 80 mW/cm²) and the spectral change is shown in Figure 4. It is seen that the absorbance at 420 nm decreased and that at 465 nm increased, which indicates that the disruption of the molecular aggregates occurred by irradiation of light through the *trans-cis-trans* photoisomerization and rearrangement of azobenzene moieties. We could observe the photochromic behavior clearly in this process. This distinct spectral change by irradiation might be utilized as a principle of the optical data storage, since the H-aggregated structure is thermally stable to 115 °C but highly sensitive to a linearly polarized light.

To investigate the effect of aggregation on photo-induced birefringence, the sample 1 and 2 were prepared. The optic setup for studying the photo-induced birefringence was illustrated in Figure 5. The transmission was recorded using 632.8 nm laser as a probe beam. Linearly polarized light ($\lambda = 532$ nm, 80 mW/cm²) was irradiated on the surface of

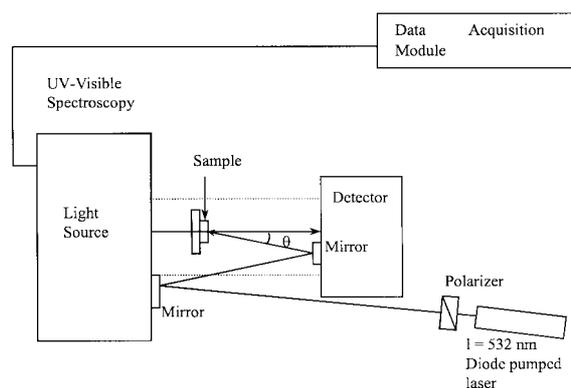


Figure 3. Schematic diagram of optic set-up for investigating the change of absorption spectra of film during irradiation of a linearly polarized light. : $\theta = 20^\circ$.

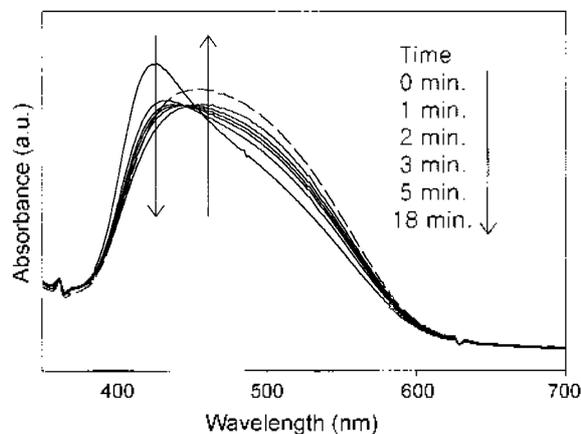


Figure 4. Spectral change of the sample 1 on exposure to 532 nm laser at some time intervals: 532 nm laser was on for 0, 1, 2, 3, 5, 18 mins (solid) and 5 mins after 532 nm laser was off (dash).

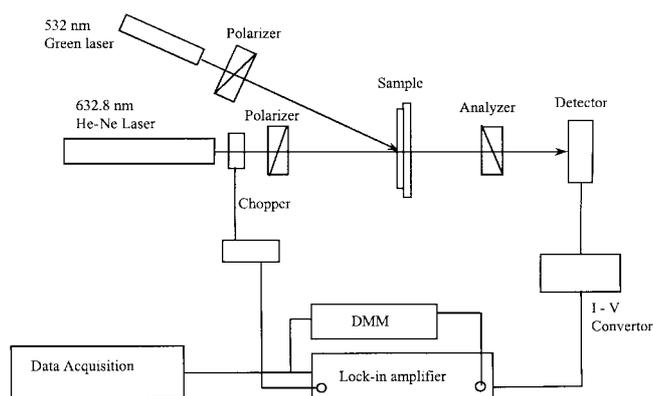


Figure 5. Schematic diagram of optic set-up for investigating photo-induced birefringence of film.

the thin film with a polarization angle 45° with respect to that of probe beam.

In the recent work of Labarhet, the photo-induced birefringence of three samples prepared under different heat treatment was already investigated.⁶ It was reported that the samples showed different values of photo-induced birefringence according to the annealing temperature. Our sample 2 showed conventional rising and decaying behaviors of photo-induced birefringence. Birefringence showed high rate of growth in early stage and approached slowly to the asymptotic maximum value as usual (Figure 6(b)). The sample 2 with a high concentration of free isolated azo molecules seems to follow the general process of photo-induced birefringence (angular hole burning and angular redistribution). Trans molecules with transition dipole moment parallel with the electric field of the pump light are photoselectively excited and convert to the cis state. Molecules rotate from the initial direction of excitation during conversion to the cis state and the back *cis-trans* isomerization. On the other hand, in the case of the sample 1, it is characteristically observed that the photo-induced birefringence showed an initial steep increase to the maximum value followed by a gradual decrease to the asymptotic value (Figure 6(a)). This peculiar phenomenon was not dealt in the Labarhet study.⁶ It should also be noted from Figure 6 that the structure with a higher concentration of aggregate shows higher value of birefringence. Hore *et al.* studying the temperature dependence of photo-induced anisotropy of azo polymers emphasized that rotational diffusion of side chain azo chromophore disordered the orientation of chromophore.¹⁶ Blanche *et al.* studying photo-induced orientation of azo chromophore in various matrices reported that in azo polymer with high rotational diffusion rate, anisotropy is very small during pumping and disappeared immediately when the pump beam is turned off.¹⁷ Brown *et al.* studying dipolar interaction of azobenzene side groups in copolymers concluded that dipolar interaction between the intramolecular azo groups reduces the mobility of the side chain but enhances the orientational stability.⁷ Therefore thermal diffusional rotation of azo chromophores seems to prevent the orientational stability of azo group and causes the birefringence to decrease. Azobenzene chromophores in

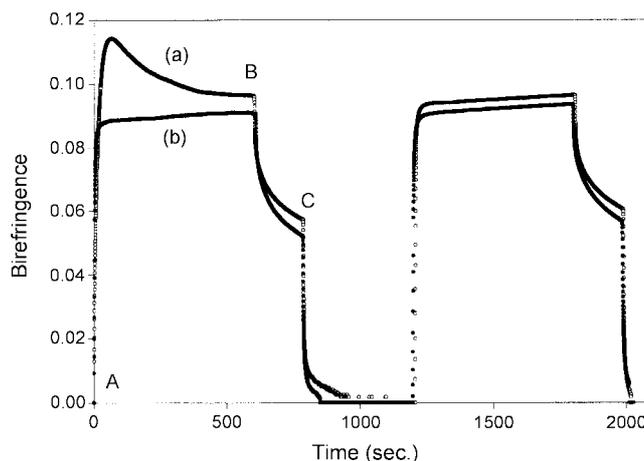


Figure 6. Growth and relaxation curves of birefringence: (a) the sample 1 (upper curve) and (b) the sample 2 (lower curve). At point A, the linearly polarized laser (pump beam) is turned on; at point B, the pump beam is turned off; at point C, the circularly polarized laser (erasing beam) is turned on.

the aggregates are bound by intermolecular and intramolecular dipolar interaction and closely neighbored each other and it results in diminishing the diffusional rotation effect. Therefore, the strongly coupled chromophores in the aggregates is likely to induce a higher birefringence than the free chromophores in the polymer matrix during irradiation of the linearly polarized pump beam. In the initial stage of irradiation, the linearly polarized light excited the chromophores in the aggregates parallel to the pump polarization direction predominantly. And the chromophores in the aggregates whose long molecular axes are perpendicular to the pump polarization direction are intact during irradiation. Hence, the reoriented dipoles and the dipoles in the aggregate perpendicular to the pump polarization direction cause quite high birefringence in the initial stage of irradiation. For the first few minutes, the birefringence of the sample 1 became higher than that of the sample 2 due to the cooperative motion of aggregated molecules. However, further irradiation of light induced disruption of almost all aggregates, which reduced the maximum value of birefringence to the certain value asymptotically. The value is a little higher than that of sample 2 because small portion of aggregates remained under irradiation of a linearly polarized light. In erasing process of birefringence by a circularly polarized light, the sample 1 showed lower erasing rate than the sample 2. That was also attributed to the disruption of remaining aggregates after irradiation of a linearly polarized light. But in the second and subsequent cycles, the growth shapes of the sample 1 became very similar with those of the sample 2 because most of the aggregates were already disrupted in the first cycle of light irradiation.

Conclusion

H-type molecular aggregation of push-pull azobenzene dyes in a spin-coated polymer film was investigated. It was found

that the extent of aggregate could be controlled by thermal treatment and irradiation of a linearly polarized excitation light. We could prepare the sample with a desired concentration of aggregate under the control of cooling rate. Irradiation of a linearly polarized light resulted in disruption of aggregates and creation of isolated free azo molecules. In the first rising cycle of photo-induced birefringence, the birefringence value of the sample 1 was higher than that of the sample 2 in the first few minutes but gradually decreased to the certain value asymptotically under further irradiation of a linearly polarized light.

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