

# Photoinduced cooperative molecular reorientation on azobenzene side-chain-type copolymers

Takashi Fukuda<sup>a,\*</sup>, Jun Young Kim<sup>a</sup>, Daisuke Barada<sup>a,b</sup>, Kiyoshi Yase<sup>a</sup>

<sup>a</sup> Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST),  
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

<sup>b</sup> Institute of Applied Physics, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan

Available online 24 July 2006

## Abstract

In order to improve the value of photoinduced birefringence and the long-term stability of azobenzene copolymer, two series of azobenzene side-chain-type copolymers consisting of two repeating units, one bearing cyanoazobenzene (or cyanoazopyridine) and the other bearing a long  $\pi$ -conjugated chromophore (bisazobenzene), have been synthesized and compared with respect to their photoinduced birefringence characteristics. Consequently, a fairly large value (observed highest value was 0.244) and superior stability (initial relaxation value was less than 0.2%) of photoinduced birefringence have been achieved. Furthermore, unusual behavior of the photoinduced birefringence depending on the copolymerization ratio of the two chromophores has been found, i.e., a sharp peak of the photoinduced birefringence has been observed at a copolymerization ratio of around 50:50 mol%. This phenomenon could be attributed to mutual promotion of the photoinduced molecular reorientation process, that is cooperative molecular motion, taking place at a specific stoichiometric composition ratio of the two chromophores.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Photoinduced cooperative motion; Molecular reorientation; Azobenzene copolymer; Photoinduced birefringence; Holographic data storage

## 1. Introduction

In recent years, the demand for an innovative data storage system with huge capacity has been increasing. Of course the existing systems, such as hard disk drive (HDD) and digital versatile disc (DVD), are still developing very rapidly, however, it is pointed out that there is a practical limit of about 1 [Tb/in.<sup>2</sup>] for the recording density. In order to overcome this limitation, a novel architecture for recording is required. One of the most promising techniques is to use the optical near-field and another is holographic recording.

Photo-crosslinkable polymeric materials have been widely examined for write-once holographic recording media [1,2]. On the other hand, rewritable holographic recording media are still being developed and photochromic azobenzene materials are considered to be possible candidates for this purpose [3–6], because we can utilize the photoinduced birefringence property of azobenzenes for the rewritable holographic recording

that is enabled by the photoinduced molecular reorientation phenomenon, as is illustrated in Fig. 1.

Assuming that an amorphous azobenzene film is irradiated by a linearly polarized beam, molecules are subjected to the *trans*–*cis* photoisomerization process but the *cis*-form of azobenzenes substituted by donor and acceptor terminal groups is unstable and easily relaxes back to the *trans*-form. During this process, the molecular directions of the relaxed *trans* molecules need not coincide with those of the original state. Then, if we continue the beam excitation, *trans*–*cis*–*trans* isomerization cycles are iterated continuously. However, the molecules that lie in a direction perpendicular to the electric field of the incident excitation beam do not absorb the light because they do not have any transition dipole moment in the polarization direction of incoming light. As a result, the molecules that align perpendicular to the electric field of the incident beam are excluded from the photoisomerization cycles, thus the population of such azobenzene molecules increases with irradiation time. This whole process is called photoinduced molecular reorientation (or photoalignment) of azobenzenes, and it generates macroscopic birefringence in the bulk (photoinduced birefringence). In particular, azobenzene-attached side-chain-type polymers are promising materials to show this phenomenon due to

\* Corresponding author. Tel.: +81 29 861 6280; fax: +81 29 861 6280.  
E-mail address: [t-fukuda@aist.go.jp](mailto:t-fukuda@aist.go.jp) (T. Fukuda).

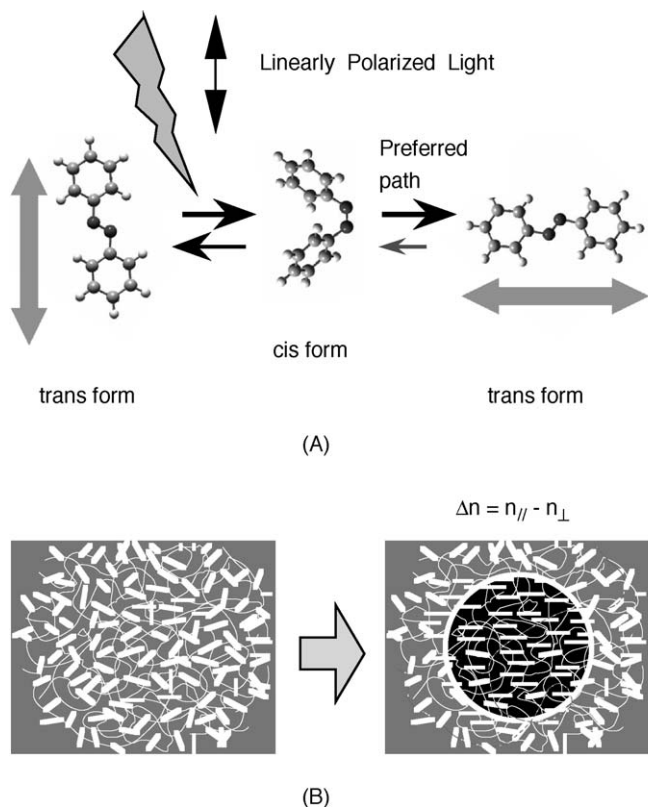


Fig. 1. Schematic illustrations of (A) photoinduced molecular reorientation in azobenzenes and of (B) photoinduced birefringence.

their optical properties, chemical and physical stability and processability.

Accordingly, though the azobenzenes are very promising materials for rewritable holographic recording media, further improvement of the performance, such as the birefringence value, response time, long-term stability (archival life) and durability, is still required for conventional azobenzene materials before they can be used in practical applications. Under these circumstances, we have tried to improve the value of photoinduced birefringence and long-term stability by designing a new azobenzene copolymer. The photoinduced birefringence can be improved in two ways. One is to enlarge the intrinsic molecular birefringence of the azobenzene moiety and the other is to increase the order parameter of the birefringent moiety. To attain long archival life, the glass transition temperature and liquid crystallinity of the material are key factors that should be carefully designed and adjusted. Thus, we have synthesized new azobenzene copolymers that consist of cyanoazobenzene (or cyanoazopyridine) and long  $\pi$ -conjugated side chain (bisazobenzene), i.e., poly{2-[4-(4-cyanophenylazo)phenoxy]ethyl methacrylate-co-2-[2-methyl-4-(4-phenylazophenylazo)phenoxy]ethyl methacrylate} (PCDY) and poly{2-[4-(2-cyano-pyridine-5-ylazo)phenoxy]ethyl methacrylate-co-2-[2-methyl-4-(4-phenylazophenylazo)phenoxy]ethyl methacrylate} (PPDY), in order to improve the optical performance [7–9]. The former segment is introduced as a photoalignment trigger with good optical response and the latter provides large birefringence, a high order parameter and good stability of the aligned state.

As one can easily imagine, since the optical performances also depend on the copolymerization ratio, a series of copolymers with different copolymerization ratios have been synthesized and compared with respect to their photoinduced birefringence property.

## 2. Materials and methods

### 2.1. Chemicals

2,2'-Azobisisobutyronitrile (AIBN, from Wako Pure Chemicals) was recrystallized from methanol. 4-Cyanoaniline, 5-amino-2-cyano pyridine, 2-(ethylamino)ethanol and 2-bromoethanol were purchased from Tokyo Kasei, and used without further purification. Phenol and 4-[4-(phenylazo)phenylazo]-*o*-cresol were purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) of dehydration grade was purchased also from Aldrich.

### 2.2. Chemical characterization

The chemical structure and composition were confirmed by  $^1\text{H}$  NMR in  $\text{CDCl}_3$  (JEOL, 600 MHz) and elementary analysis. The UV absorption measurement was performed using a UV-vis spectrophotometer (Hitachi U-4100). The molecular weight of each copolymer was estimated in THF by gel permeation chromatography (Waters Model 150-C, GPC) equipped with an RI detector at a flow rate of 1.2 ml/min. The columns (TOSOH, TSKgel GMH-M) were calibrated with polystyrene standards. Thermal analyses were performed using a differential scanning calorimeter (TA Instrument Q100, DSC). Conventional DSC and modulated DSC measurements were performed at a heating rate of  $10^\circ\text{C}/\text{min}$ , and at a heating rate of  $2^\circ\text{C}/\text{min}$ , a modulation amplitude of  $\pm 2^\circ\text{C}$  and a modulation period of 60 s, respectively, under nitrogen gas.

### 2.3. Synthesis of azo compounds

#### 2.3.1. 4-(4-Cyanophenylazo)phenol (**1a**)

In a 500 ml round-bottom flask, 4.25 g of 4-cyanoaniline (36 mmol) was dissolved in 150 ml of 2 M HCl solution. While stirring the solution at  $0\text{--}5^\circ\text{C}$ , 2.5 g of  $\text{NaNO}_2$  (36 mmol) in 75 ml of water was slowly added to the former solution. During the addition of  $\text{NaNO}_2$  the reaction temperature was kept below  $5^\circ\text{C}$  in order to stabilize diazonium ions. This solution was added slowly at  $0\text{--}5^\circ\text{C}$  to a coupling part of phenol (2.8 g, 30 mmol) in 10% NaOH solution and the pH was adjusted to 8–9 with concentrated NaOH solution. Then this reaction solution was stirred at room temperature for 6 h. The precipitate was collected by filtration, washed with 500 ml of distilled water three times, and this crude product was recrystallized in a mixture of 200 ml EtOH and 300 ml water. The resulting orange crystalline solid was filtered and vacuum dried (yield = 75%).

#### 2.3.2. 2-[4-(4-Cyanophenylazo)phenoxy]ethanol (**1b**)

In a 500 ml three-neck round-bottom flask equipped with a condenser, 2.23 g of (**1a**) (10 mmol), 2.5 g of 2-bromoethanol

(20 mmol), and 2.76 g of potassium carbonate (20 mmol) were dissolved in 100 ml of acetone and refluxed for 72 h. The resulting solution was cooled to room temperature. The solvent was removed by evaporation under reduced pressure. The solid residue was extracted with 200 ml of chloroform and 200 ml of saturated potassium carbonate aqueous solution followed by extraction again with 200 ml of chloroform and 200 ml of sodium chloride aqueous solution. Then the organic layer was washed with 300 ml of distilled water more than three times until the washing became neutral. After the extraction procedure, 200 ml of the organic chloroform layer was dried with 5 g of  $MgSO_4$  for 6 h then filtered off. The chloroform was removed by evaporation under reduced pressure. The crude product was recrystallized in 200 ml of EtOH overnight. An orange–yellow precipitate was obtained (yield = 80%).

### 2.3.3. 2-[4-(4-Cyanophenylazo)phenoxy]ethyl methacrylate (**1c**)

In a 100 ml round-bottom flask, 0.7 g of (**1b**) (2.62 mmol) and 0.53 g of triethylamine (5.24 mmol) were dissolved in 30 ml of dichloromethane. The solution was kept at 0–5 °C under a dry nitrogen atmosphere. A solution of methacryloyl chloride (0.57 g, 5.24 mmol in 2 ml  $CH_2Cl_2$ ) was added slowly to the above mixture. The reaction mixture was stirred at 0–5 °C for 2 h and then stirred at room temperature for 24 h. The TEA/HCl salt was filtered off and the solvent removed by evaporation under reduced pressure. The solid residue was extracted with 100 ml of chloroform and 100 ml of saturated potassium carbonate aqueous solution, and was extracted again with 200 ml of chloroform and 200 ml of sodium chloride aqueous solution. Then organic layer was washed with 200 ml of distilled water more than three times until the washing became neutral. After the extraction procedure, 200 ml of the organic chloroform layer was dried with 5 g of  $MgSO_4$  for 6 h then filtered off. The chloroform was removed by evaporation under reduced pressure. The crude product was recrystallized in 300 ml of *n*-hexane overnight. An orange–yellow powder was obtained (yield = 85%). Elem. Anal. Calcd. for  $C_{19}H_{17}N_3O_3$ : C 68.05%, H 5.11%, N 12.53%. Found: C 67.88%, H 5.07%, N 12.37% (average of three measurements). The chemical structure and  $^1H$  NMR result are shown in Fig. 2(A).

### 2.3.4. 2-[4-(2-Cyanopyridine-5-ylazo)phenoxy]ethyl methacrylate (**2**)

This compound was synthesized using the same procedure as described for (**1a**), (**1b**) and (**1c**). The following yield of the purified product was obtained. Red powder (yield = 86%), Elem. Anal. Calcd. for  $C_{18}H_{16}N_4O_3$ : C 64.28%, H 4.79%, N 16.66%. Found: C 64.20%, H 4.78%, N 16.52% (average of three measurements). The chemical structure and  $^1H$  NMR result are shown in Fig. 2(B).

### 2.3.5. 2-[2-methyl-4-(4-phenylazophenylazo)phenoxy]ethyl methacrylate (**3**)

This compound was synthesized using the same procedure as described for (**1b**) and (**1c**), but slightly modified. The following yield of the purified product was obtained. Brownish-red powder

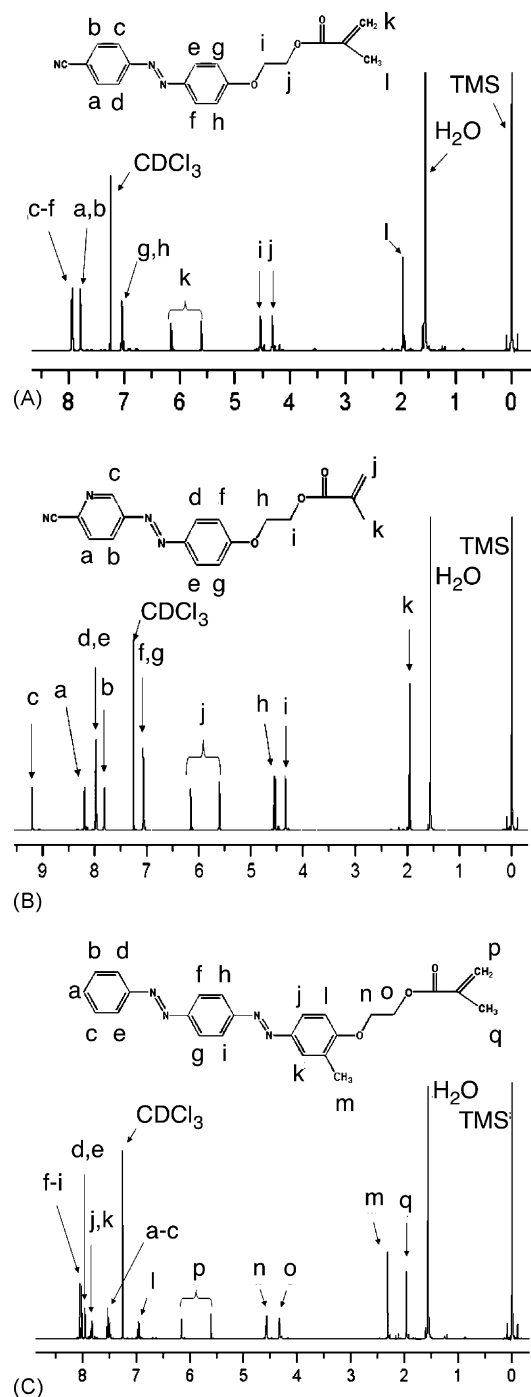


Fig. 2.  $^1H$  NMR analysis of synthesized azo compounds. (A), (B) and (C) are for 2-[4-(4-cyanophenylazo)phenoxy]ethyl methacrylate, 2-[4-(2-cyanopyridine-5-ylazo)phenoxy]ethyl methacrylate and 2-[2-methyl-4-(4-phenylazophenylazo)phenoxy]ethyl methacrylate, respectively.

(yield = 85%), Elem. Anal. Calcd. for  $C_{25}H_{24}N_4O_3$ : C 70.08%, H 5.65%, N 13.08%. Found: C 69.84%, H 5.50%, N 12.86% (average of three measurements). The chemical structure and  $^1H$  NMR result are shown in Fig. 2(C).

## 2.4. Radical copolymerizations

Random copolymers were obtained via the following procedures. The monomer solutions were degassed by a freeze and

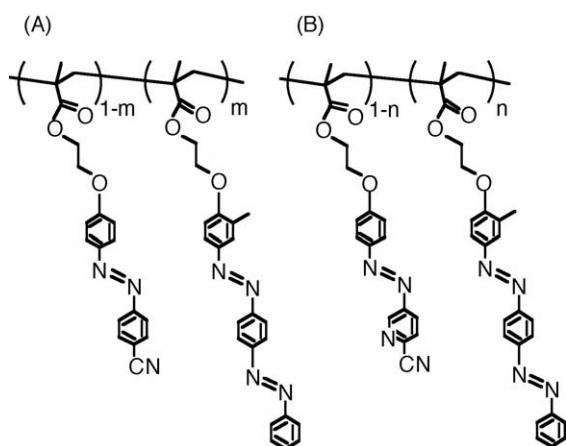


Fig. 3. Chemical structures of (A) PCDY (poly(1c)–(3)) and (B) PPDY (poly(2)–(3)) copolymers. Expressions of PCDY## and PPDY## represent the copolymers bearing ## mol% of 2-[2-methyl-4-(4-phenylazophenylazo)phenoxy]ethyl moiety, i.e., the numbers of ## correspond to the copolymerization ratio that are denoted in this figure as  $m$  and  $n$ , respectively.

thaw process performed three times. Then, radical copolymerizations of poly(1c)–(3) and poly(2)–(3) (Fig. 3) were carried out in each ampoule, in which THF and AIBN were also added as a solvent and a radical initiator, respectively, at 60 °C for 24 h. The monomer feeding ratios were varied from 1:0 to 0:1. Then, the resultant solution was poured into methanol. The precipitate was filtered and vacuum dried for 48 h (yield = 90%). From the preliminary examination through UV–vis. absorption measurement, we believe that the feeding ratio of the monomers coincides well with the actual copolymerization ratio.

### 2.5. Film preparation

All copolymers were dissolved in dichloromethane at a concentration of 5% in weight. Films about 0.8  $\mu\text{m}$  thick were obtained on glass substrates by spin coating at 700 rpm for 30 s. The film thickness was measured using a surface profiler (Kosaka, Surfcoorder SE1700 $\alpha$ ). From our preliminary experiments, it was found that the optical quality of the film strongly affects the absolute value of the photoinduced birefringence. Therefore, we have paid great attention to the spin coating procedure in order to obtain clear, homogeneous, smooth, non-scattering, high-quality thin films. The sample solution was filtered through a membrane with 0.2  $\mu\text{m}$   $\varnothing$  pores, the substrate temperature was maintained at approximately 25 °C, and the atmospheric gas was exchanged for dried nitrogen in order to eliminate moisture.

### 2.6. Photoinduced birefringence measurement

The optical configuration for the measurement of photoinduced birefringence ( $\Delta n_{\text{PI}}$ ) is shown in Fig. 4. Ar<sup>+</sup> (Coherent,  $\lambda = 488$  nm, beam diameter = 3 mm and irradiance = 1 W/cm<sup>2</sup>) and He–Ne (Melles Griot,  $\lambda = 633$  nm, beam diameter = 1 mm and power = 3 mW) lasers were employed as the excitation and probe beams, respectively. The two beams were collinear and incident normally on the sample film. The polarization condi-

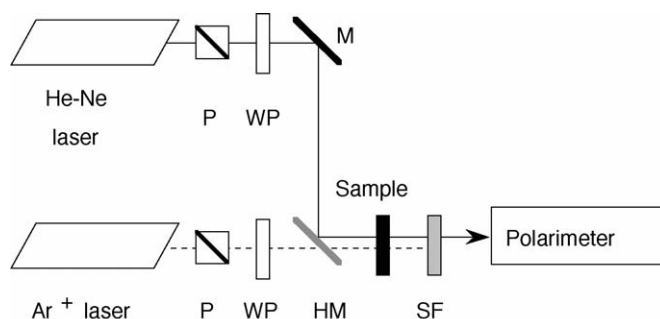


Fig. 4. The optical set-up for photoinduced birefringence measurement.

tions of both incident beams were controlled to be linear using a polarizer and a half-wave plate, and the direction of the He–Ne beam was set to be vertical and that of the Ar<sup>+</sup> beam was set to be  $-45^\circ$  with respect to the He–Ne beam. The change in the polarization condition of the transmitted beam was monitored by measuring Stokes' parameters with a polarimeter (Thorlabs, PA510). The photoinduced birefringence value was estimated by the observed Stokes' parameters and the film thickness.

## 3. Results and discussion

The chemical and optical properties of the PCDY and PPDY series have been measured and compared. The molecular weight of each copolymer ranged from  $8.0 \times 10^3$  to  $2.4 \times 10^4$ . Conventional DSC data for the PCDY copolymers (Fig. 2(A)) are shown in Fig. 5. Two (or three) endothermic peaks in each curve (except PCDY0: homopolymer of 2-[4-(4-cyanophenylazo)phenoxy]ethyl methacrylate) can be assigned to phase transitions from the glass to the nematic and successively to the isotropic state (some include a transition from the glass to the smectic phase before the transition to the nematic phase). The transition temperatures varied depending on the copolymerization ratio. On the other hand, the glass transition temperatures ( $T_g$ ) were observed to be in almost the same range of 105–115 °C all through PCDY33 to PCDY80. In PCDY20, since the endothermic peak located at around 115 °C overlapped the glass transition, a temperature-modulated DSC measurement was performed and its  $T_g$  was found to be 97 °C. Consequently, it could be confirmed that the glass transition temperature of each PCDY was not strongly dependent on the composition ratio in a moderate copolymerization range. Similarly, in PPDY copolymers (Fig. 2(B)), the tendency was almost the same. The  $T_g$  of each PPDY copolymer was in the range from 110 to 125 °C all through PPDY33 to PPDY80, which are slightly higher than those of PCDYs.

Fig. 6 shows UV–vis absorption spectra of the PCDY50 and PPDY50 copolymer thin films. The PCDY50 and PPDY50 films exhibited absorption maxima at 370 and 373 nm, respectively. These are results of a convolution of the absorption bands of 2-[4-(4-cyanophenylazo)phenoxy]ethyl methacrylate ( $\lambda_{\text{max}} = 360$  nm and  $\lambda_{\text{cut-off}} = 550$  nm) or 2-[4-(2-cyanopyridine-5-ylazo)phenoxy]ethyl methacrylate ( $\lambda_{\text{max}} = 370$  nm and  $\lambda_{\text{cut-off}} = 550$  nm) and 2-[2-methyl-4-(4-phenylazophenylazo)phenoxy]ethyl methacrylate ( $\lambda_{\text{max}} = 384$  nm and  $\lambda_{\text{cut-off}} =$

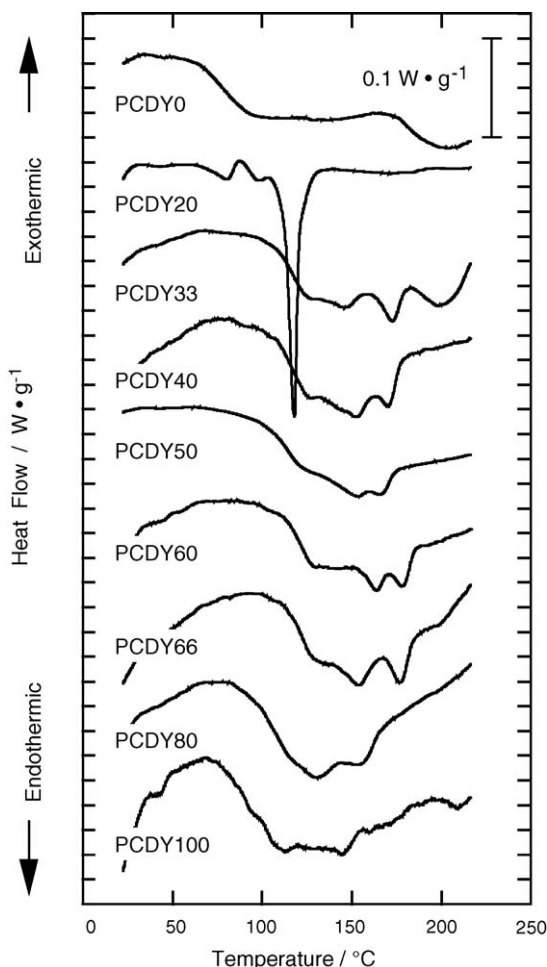


Fig. 5. DSC data for each PCDY copolymer.

570 nm). In both films, although the optical densities at 488 nm (pump beam wavelength) are not so high, the molecular reorientation could be induced and photoinduced birefringence could be observed satisfactorily.

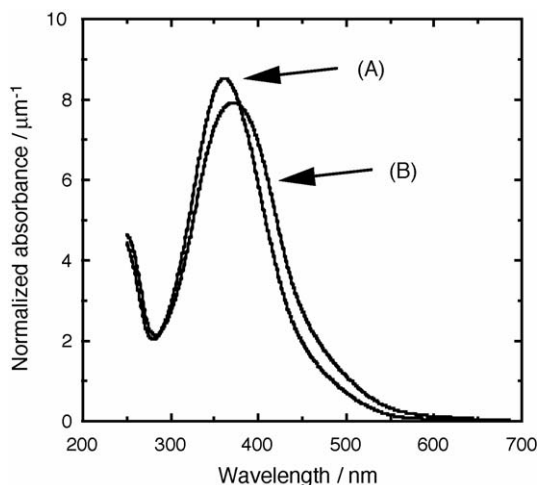


Fig. 6. Absorption spectra of (A) PCDY50 and (B) PPDY50 copolymer thin films.

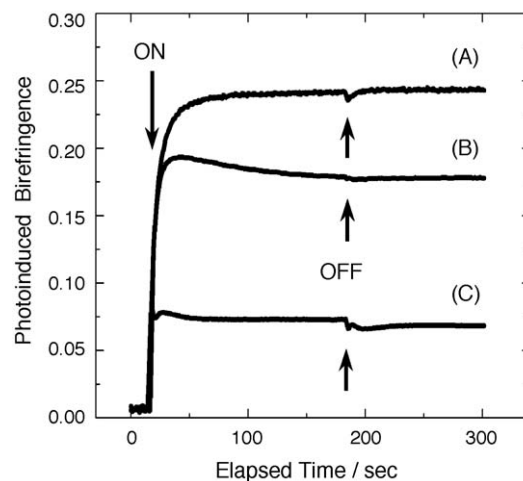


Fig. 7. Photoinduced birefringence dynamics of (A) PCDY50 and (B) PPDY50.

Fig. 7 shows the dynamics of photoinduced birefringence ( $\Delta n_{PI}$ ) as a function of light irradiation time. Fig. 7(C) shows that of a 50:50 copolymer consisting of 2- $\{2$ -ethyl- $[4$ -(4-nitrophenylazo)phenyl]amino $\}$ ethyl methacrylate and methylmethacrylate (PMD50) as a reference, which is a typical azobenzene side-chain copolymer often reported. As a result, it was found that PCDY50 (Fig. 7(A)) and PPDY50 (B) exhibit quite large photoinduced birefringence. The absolute values for PCDY50 and PPDY50 were 0.244 and 0.172, respectively. These values are 3.5 and 2.5 times larger than that of PMD50. Response times of PCDY50 and PPDY50 were 24 and 7 s, respectively. These values are not inferior to those of other conventional azobenzene polymers. (The response time was evaluated as the time required for the  $\Delta n_{PI}$  value to increase from 10 to 90% of a steady value.) Furthermore, it should be emphasized that there was obvious relaxation after the termination of the excitation beam (the absolute value was 0.2% at most). This stability of the photoinduced birefringence was considered to be brought about by the highly anisotropic molecular shape of the bisazobenzene moiety, which hinders free molecular rotation in the longitudinal direction, and by an appropriate molecular interaction between the two azo moieties making up the polymer side chains. This result indicates promising characteristics for practical application. In contrast, quick relaxation of the  $\Delta n_{PI}$  value by approximately 10% and a subsequent continuous slow decay were observed ( $-1\%$  within 100 s in addition) for PMD50.

In the same manner as described above,  $\Delta n_{PI}$  measurements were performed on all PCDY and PPDY copolymers. Consequently, unique results were obtained, as shown in Fig. 8(A). In both copolymer series, a sharp peak was observed for the  $\Delta n_{PI}$  value at around the 50 mol% of bisazobenzene composition ratio. If we assume that order parameters of the side chains in the copolymers are constant or varied in proportion to the composition ratio, this observation cannot be explained at all. Here,  $\Delta n_{PI}$  was assumed to be expressed as a linear combination of two terms that consist of the 2-[2-methyl-4-(4-phenylazophenylazo)phenoxy]ethyl methacrylate composition ratio ( $\phi$ ), the intrinsic molecular birefringence ( $\Delta n_1$  and  $\Delta n_2$ )

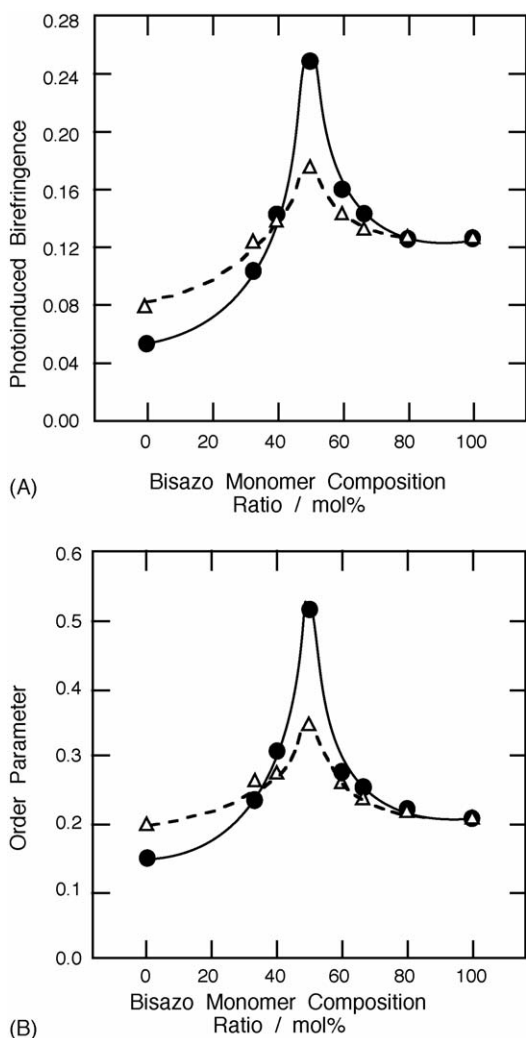


Fig. 8. (A) Dependence of the photoinduced birefringence on the copolymerization ratio. Horizontal axis indicates the composition ratio of 2-[2-methyl-4-(4-phenylazophenylazo)phenoxy]ethyl methacrylate monomer in the copolymer. Black circles and open triangles are the data for PCDYs and PPDYs, respectively. (B) A graph of the converted photoinduced birefringence value into the order parameter as a function of copolymerization ratio.

and an order parameter ( $S$ ):  $\Delta n_{\text{total}} = \{\phi \Delta n_1 + (1 - \phi) \Delta n_2\} S$ , where  $\Delta n_1$  and  $\Delta n_2$  for the chromophores contained in the compound **1(c)** (or **2**) and **3** are 0.35 (or 0.40) and 0.60, respectively.

According to the above assumption, the order parameters for the optically aligned state in each copolymer were calculated. The results are shown in Fig. 8(B). From this figure, several important aspects can be understood. (1) A significant peak was observed at a copolymerization ratio of around 50 mol%. This tendency was common in both copolymer systems, though the sharpness of the peaks differ somewhat. (2) The highest value of the estimated order parameter for photoinduced molecular alignment was over 0.5 for the PCDY copolymer. This value is comparable to that of a typical nematic liquid crystal despite this polymer being a randomly oriented amorphous solid before light exposure. (3) The order parameters for the extreme examples, where the bisazo monomer composition ratio is 0 or 100 mol%, were almost the same ( $S \sim 0.2$ ).

It should be emphasized that the observed highly aligned state was achieved at the copolymerization ratio of around 50 mol%. Although there is no other direct experimental evidence so far, this result implies that the two azo moieties mutually promote their photoalignment process and the efficiency of the process becomes maximum when the two azo moieties exist in equal proportion in the system. A hypothesis for the cooperative molecular reorientation in azobenzene copolymer has been already suggested by Natansohn and Rochon [10]. However, such a dramatic enhancement of  $\Delta n_{\text{PI}}$  as observed in our study has not been previously reported. We infer that one of the most important factors in inducing an efficient cooperative molecular motion is the affinity between the two chromophores in the copolymer.

To provide supplementary information, we measured the photoinduced birefringence for the 50:50 mol% mixture of PCDY0 (or PPDY0) and PCDY100. However, the chromophore concentrations in these mixed samples were equal to that of PCDY50 or PPDY50; the  $\Delta n_{\text{PI}}$  values were just 0.135 and 0.100 for the PCDY0/PCDY100 and PPDY0/PCDY100 mixtures, respectively. The observed values were limited to the mean  $\Delta n_{\text{PI}}$  values of the two homopolymers in the mixture. From this result, it is concluded that one of the essential requirements to bring about the cooperative molecular reorientation is that the two chromophores should be arranged in the same polymer main chain but not as a simple mixture. This might be explained from the viewpoint of the correlation length between the chromophores. In contrast to this observation, Ubukata et al. [11] reported that photoinduced surface relief grating (SRG) formation could be enhanced in a mixture of azobenzene side-chain copolymer and low-molecular-weight nematic liquid crystal (4'-penty-4-cyanobiphenyl: 5CB). They reported that the photofabrication efficiency of the SRG was maximized when the azobenzene moiety and 5CB are mixed at a 1:2 molar ratio, and concluded that molecules of the azobenzene and the liquid crystal form a supramolecular assembly that exhibits molecular cooperative motion. The difference from our experiment on a mixed system is that they employed a low-molecular-weight material as a counter-chromophore. It can be inferred that their system allows the formation of a specific supramolecular assembly more easily than our polymer blend system. Nevertheless, the importance of the molecular interaction between the two chromophores is common in both cases, and we believe that the unique enhancement of the  $\Delta n_{\text{PI}}$  values in our copolymer systems can also be explained from a similar viewpoint as illustrated in Fig. 9.

The two azo chromophores in the copolymer are randomly oriented at the initial stage (before light irradiation). When the linearly polarized light irradiation begins, each side chain is subjected to continuous *trans*–*cis*–*trans* photoisomerization cycles and photo-plasticization of the bulk is induced. Then the side chains tend to realign perpendicularly to the direction of the electric field of the linearly polarized light. However, not only this kind of individual optical response of each moiety but also cooperative molecular motion can be expected via an appropriate molecular affinity. Thus, the side chains align with each other more efficiently, resulting in large macroscopic  $\Delta n_{\text{PI}}$ .

Of course, this kind of molecular cooperative motion does not necessarily occur in all azobenzene copolymer systems. We

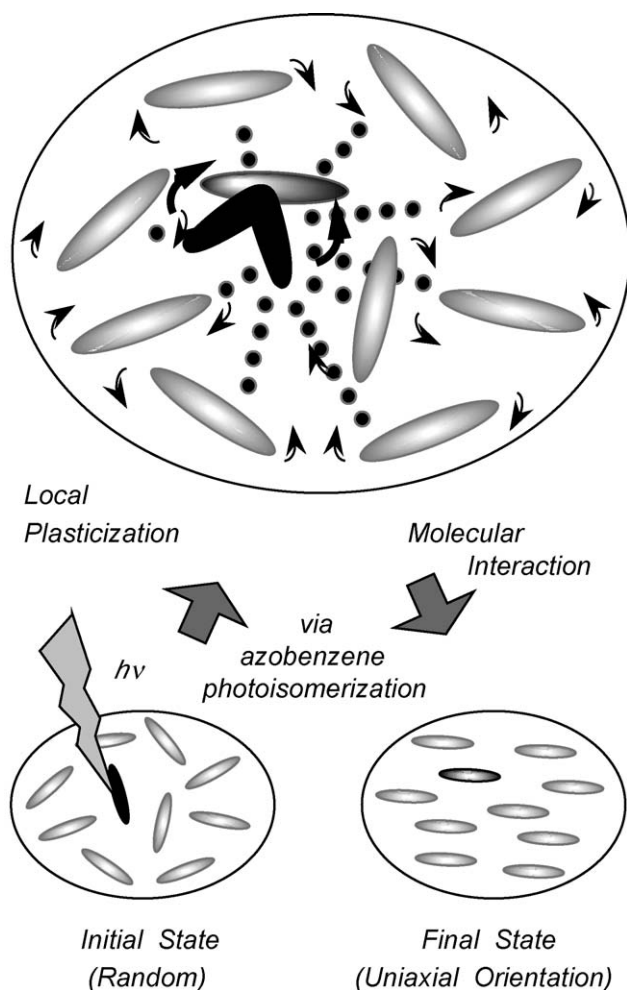


Fig. 9. Schematic illustrations of photoinduced cooperative molecular reorientation.

have already investigated other azobenzene side-chain-type copolymers, for example, a copolymer consisting of both azobenzene and bistolan (2-{4-[4-(4-trifluoromethyl)phenylethynyl]phenylethynyl]phenoxy}ethyl) moieties. However, the unusual  $\Delta n_{PI}$  dependence on composition ratio reported in this paper was not observed and the absolute values of  $\Delta n_{PI}$  were very low (less than 0.08). This result emphasizes the importance of the affinity between the two chromophores in bringing about the photoinduced molecular cooperative reorientation. Moreover, not only the  $\Delta n_{PI}$  value, but many other requirements must be satisfied to enable practical application, such as solubility in solvents, chemical and physical stability, processability and optical quality of films. From this point of view, our PCDY50 and PPDY50 are materials that can meet all of the requirements

listed above. More quantitatively, for example, the solubility of the copolymer in chloroform is higher than 200 g/L at 20 °C and the typical haze value of the spin-coated film is less than 0.5. Therefore, these materials are considered to be promising ingeniously designed candidates for rewritable holographic memory application.

#### 4. Conclusion

In this study, two azobenzene side-chain-type copolymer series have been synthesized and investigated as to their photoinduced birefringence ( $\Delta n_{PI}$ ) characteristics. As a result, a fairly large value of  $\Delta n_{PI}$  (0.244 for the PCDY50 and 0.172 for the PPDY50) and a superior stability of  $\Delta n_{PI}$  have been achieved, as was expected. Furthermore, it was found that the order parameters of optically aligned side chains could be enhanced specifically at a stoichiometric condition of around 50:50 for two chromophores. The maximum value of the photo-triggered order parameter was over 0.5 for PCDY50. This is quite a high value in amorphous random copolymers. We successfully introduced an additional monomer (2-[2-methyl-4-(4-phenylazophenylazo)phenoxy]ethyl methacrylate) that possesses a highly anisotropic shape, a long  $\pi$ -conjugated electronic structure and good affinity to another chromophore. Starting from the present observations, further investigation of the mechanism of photoinduced molecular cooperative reorientation is anticipated for a real application of azobenzene materials as a rewritable holographic data storage medium.

#### References

- [1] H.J. Coufal, D. Psaltis, G.T. Sincerbox (Eds.), *Holographic Data Storage*, Springer Series in Optical Sciences, vol. 76, Springer-Verlag, Berlin Heidelberg, New York, 2000.
- [2] W.L. Wilson, K.R. Curtis, K. Anderson, M.C. Tackitt, A.J. Hill, M. Pane, C. Stanhope, T. Earhart, W. Loechel, C. Bergman, K. Wolfgang, C. Shuman, G. Hertrich, K. Pharris, K. Malang, B. Riley, M. Ayres, *SPIE Proc.* 5216 (2003) 178–191.
- [3] A. Natansohn, P. Rochon, J. Gosselin, S. Xie, *Macromolecules* 25 (1992) 2268.
- [4] S.J. Zilker, T. Bieringer, D. Haarer, R.S. Stein, J.W. Egmond, S.G. Kostromine, *Adv. Mater.* 10 (1998) 855.
- [5] P.S. Ramanujam, S. Hvilsted, F. Ujhelyi, P. Koppa, E. Loerincz, G. Erdei, G. Szarvas, *Synth. Met.* 124 (2001) 145.
- [6] Y. Sabi, M. Yamamoto, H. Watanabe, T. Bieringer, D. Haarer, R. Hagen, S.G. Kostromine, H. Berneth, *Jpn. J. Appl. Phys.* 40 (2001) 1613.
- [7] J.Y. Kim, T. Fukuda, *Jpn. J. Appl. Phys.* 45 (2006) 456.
- [8] J.Y. Kim, T. Fukuda, *Mol. Cryst. Liq. Cryst.* 446 (2006) 71.
- [9] H. Sumimura, T. Fukuda, J.Y. Kim, D. Barada, M. Itoh, T. Yatagai, *Jpn. J. Appl. Phys.* 45 (2006) 451.
- [10] A. Natansohn, P. Rochon, *ACS Symp. Ser.* 672 (1997) 236.
- [11] T. Ubukata, T. Seki, K. Ichimura, *Adv. Mater.* 12 (2000) 1675.