

Molecular design and synthesis of copolymers with large photoinduced birefringence

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Abstract

In order to achieve both large photoinduced birefringence (Δn_{PI}) and good long-term stability, we designed and synthesized four series of side-chain-type copolymers consisting of a photoresponsive azo moiety and a long π -conjugated moiety. Chemical and physical characterization, such as the estimation of Δn_{PI} and its dependence on the copolymerization ratio of the two functional moieties, have been compared. Consequently, fairly large value (observed highest value was 0.244) and superior stability of Δn_{PI} have been achieved in a copolymer consisting of the 2-[4-(4-cyanophenylazo)phenoxy]ethyl moiety and the 2-[2-methyl-4-(4-phenylazophenylazo)phenoxy]ethyl moiety at a 50:50 molar ratio (PCDY50). Furthermore, an unusual dependence of Δn_{PI} on the copolymerization ratio has been found in some copolymer series. The dependence has been phenomenologically explained by assuming the formation of a supramolecular assembly between the different moieties, that might induce molecular cooperative photo-alignment resulting in a large macroscopic Δn_{PI} . In addition, durability of the copolymer with respect to Δn_{PI} has been examined using PCDY50. As a result, it was confirmed that the recording and erasing process could be repeated more than 10^5 times at certain optical conditions.

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1. Introduction

Very recently, a new optical disk with high capacity (~ 25 GB) has been commercialized under the name of “Blu-Ray” disk. A competitive technology, called “HD-DVD”, has also been independently developed at the same time. These new optical data storage technologies allow us to record a large amount of data of digital TV broadcasts over 2 h long. However, even such new technology is insufficient to store professional-quality movies or TV broadcasts. Moreover, since these new technologies are still based on the pit recording method, there is the physical problem of the diffraction limit. Namely, the recording density of the optical disk based on pit recording technology cannot exceed ~ 1 [Tb/in.²]. In order to overcome this limitation, a novel archi-

ture for the recording technique is required. One of the most promising techniques is to use the optical near-field and another is holographic recording.

The holographic recording technology has been intensively studied so far. As a result, a high-performance medium for write-once usage has been developed and suitable materials [1] that can satisfy many severe criteria required for practical application, such as high dynamic range, high photosensitivity, volume (or thickness) invariability, preservation stability, optical clarity, processability, and good mechanical strength, have been presented. On the other hand, materials for rewritable application are still at the initial stage [2–5].

Under these circumstances, we have developed new azobenzene copolymers that exhibit large birefringence and good long-term stability of recorded data by utilizing the photoinduced birefringence property of azobenzenes, which originates from the photoinduced molecular reorientation phenomenon, for rewritable holographic recording. As is very

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well known, the principal axis of anisotropic azo molecules aligns perpendicularly to the electric field of the incident beam when we irradiate the azo film with a linearly polarized beam. In particular, azobenzene with side-chain-type polymers are promising materials regarding this phenomenon, because of 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 birefringence value, response time, long-term stability (archival life) and durability, is still required regarding conventional azobenzene materials before they can be used in practical applications.

In this study, we undertook to improve the value of photoinduced birefringence and long-term stability by introducing another moiety with large intrinsic molecular birefringence into the polymer. For instance, we expected the additional moieties in the copolymer, which is in a random state at the initial stage (before light irradiation), realign together with the molecular reorientation of the photoresponsive azo moiety upon linearly polarized beam excitation. Herein, our concept of molecular design and synthesis have been described, and the photoinduced birefringence properties of the newly developed azobenzene copolymers and their durability to repeated recording and erasing have been reported in order to discuss their potential for rewritable data storage application.

2. Materials and methods

In this study, a 2-[4-(4-cyanophenylazo)phenoxy]ethyl moiety and a 2-[4-(2-cyanopyridine-5-ylazo)phenoxy]ethyl moiety were introduced as triggers of photoalignment. Their response to photo-excitation is satisfactorily fast since they have an electron donor ($-\text{CH}_2-\text{CH}_2-\text{O}-$) group and acceptor ($-\text{CN}$) group at both ends of the aromatic rings. In addition, highly anisotropic moieties with a long π -electron conjugation, i.e., the 2-[2-methyl-4-(4-phenylazophenylazo)phenoxy]ethyl moiety, 2-[4-(4-trifluoromethylphenylethynyl)phenoxy]ethyl moiety, and 2-[4-(4-(4-trifluoromethylphenylethynyl)phenylethynyl)phenoxy]ethyl moiety, were employed to increase the birefringence and the alignment stability of the system. Through their combination, the four copolymers shown in Fig. 1 have been synthesized and investigated as to their optical properties.

2.1. Synthesis of azo monomers

2.1.1. 2-[4-(4-Cyanophenylazo)phenoxy]ethyl methacrylate (**1**)

2-[4-(4-Cyanophenylazo)phenoxy]ethyl methacrylate (**1**) was obtained by esterification of 2-[4-(4-cyanophenylazo)phenoxy]ethanol (**1a**) with methacryloyl chloride. **1a** was obtained through the Williamson reaction of 4-(4-cyanophenylazo)phenol (**1b**) with 2-bromoethanol. **1b** was obtained by conventional azo coupling of 4-cyanoaniline with phenol. Details of the synthesis have been reported previously

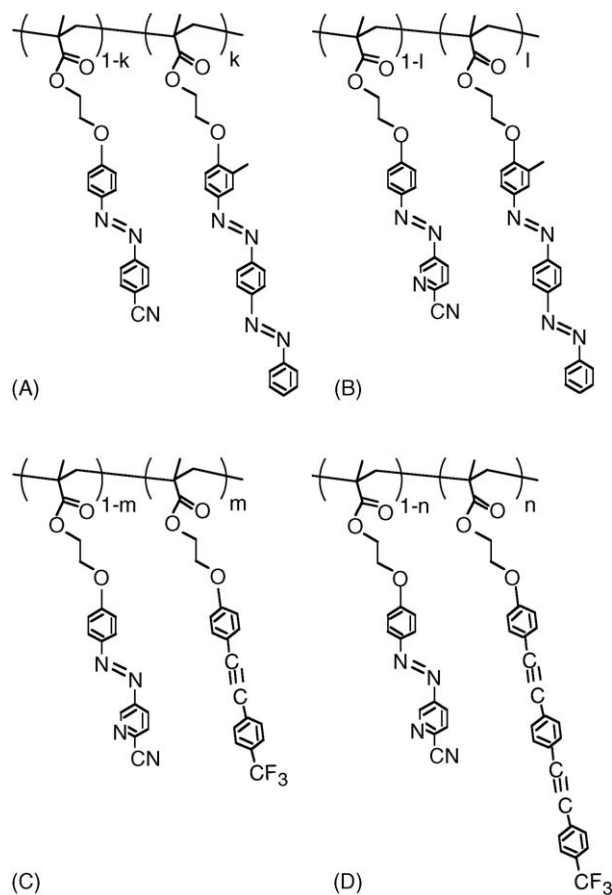


Fig. 1. Chemical structures of four copolymers: (A) PCDY, (B) PPDY, (C) PPMT, and (D) PPBT.

[6,7]. (Yield = 85%) ^1H NMR in CDCl_3 , δ (ppm): 1.97 (s, 3H), 4.34 (t, 2H), 4.58 (t, 2H), 5.61 (d, 1H), 6.16 (d, 1H), 7.05 (d, 2H), 7.78 (d, 2H), 7.95 (m, 4H).

2.1.2. 2-[4-(2-Cyanopyridine-5-ylazo)phenoxy]ethyl methacrylate (**2**)

Starting from 5-amino-2-cyanopyridine, 2-[4-(2-cyanopyridine-5-ylazo)phenoxy]ethyl methacrylate (**2**) was synthesized following the same procedure as described above. (Yield = 85%) ^1H NMR in CDCl_3 , δ (ppm): 1.97 (s, 3H), 4.34 (t, 2H), 4.58 (t, 2H), 5.61 (d, 1H), 6.16 (d, 1H), 7.05 (d, 2H), 7.82 (d, 1H), 7.98 (d, 2H), 8.19 (d, 1H), 9.2 (s, 1H).

2.2. Synthesis of birefringent monomers

2.2.1. 2-[2-Methyl-4-(4-phenylazophenylazo)phenoxy]ethyl methacrylate (**3**)

2-[2-Methyl-4-(4-phenylazophenylazo)phenoxy]ethyl methacrylate (**3**) was obtained by esterification of 2-[2-methyl-4-(4-phenylazophenylazo)phenoxy]ethanol with methacryloyl chloride. (Yield = 81%) ^1H NMR in CDCl_3 , δ (ppm): 1.97 (s, 3H), 2.31 (s, 3H), 4.34 (t, 2H), 4.58 (t, 2H), 5.61 (d, 1H), 6.16 (d, 1H), 6.96 (d, 1H), 7.50–7.55 (m, 3H), 7.82 (s, 1H), 7.84 (d, 1H), 7.96 (d, 2H), 8.02–8.07 (m, 4H).

2.2.2. 2-[4-(4-Trifluoromethylphenylethynyl)phenoxy]ethyl methacrylate (**4**)

2-[4-(4-Trifluoromethylphenylethynyl)phenoxy]ethyl methacrylate (**4**) was synthesized by esterification of 2-[4-(4-trifluoromethylphenylethynyl)phenoxy]ethanol (**4a**) with methacryloyl chloride with the yield of 65%. **4a** was obtained through the Williamson reaction of 4-(4-trifluoromethylphenylethynyl)phenol (**4b**) with 2-bromoethanol (Yield=73%). **4b** was obtained by Sonogashira coupling of 4-ethynyl-trifluorotoluene and 4-iodophenol (Yield=93%). More details will be reported elsewhere. $^1\text{H NMR}$ in CDCl_3 , δ (ppm): 1.96 (s, 3H), 4.26 (t, 2H), 4.51 (t, 2H), 5.60 (d, 1H), 6.15 (d, 1H), 6.91 (d, 2H), 7.48 (d, 2H), 7.59 (m, 4H).

2.2.3. 2-{4-[4-(4-Trifluoromethylphenylethynyl)phenylethynyl]phenoxy}ethyl methacrylate (**5**)

2-{4-[4-(4-Trifluoromethylphenylethynyl)phenylethynyl]phenoxy}ethyl methacrylate (**5**) was synthesized by methacrylation of 2-[4-[4-(4-trifluoromethylphenylethynyl)phenylethynyl]phenoxy]ethanol (**5a**) with the yield of 52%. **5a** was obtained through the Williamson reaction of 4-[4-(4-trifluoromethylphenylethynyl)phenylethynyl]phenol (**5b**) with 2-bromoethanol (Yield=47%). **5b** was obtained by repeating Sonogashira coupling twice using 4-ethynyl-trifluorotoluene, 1-bromo-4-iodobenzene and 4-ethynylphenol. More details will be reported elsewhere. $^1\text{H NMR}$ in CDCl_3 , δ (ppm): 1.96 (s, 3H), 4.26 (t, 2H), 4.51 (t, 2H), 5.60 (d, 1H), 6.15 (d, 1H), 6.73 (d, 2H), 7.47–7.52 (m, 6H), 7.61 (m, 4H).

2.3. Radical copolymerization

The two selected monomers were dissolved into THF and degassed by a freeze and thaw process performed three times. Then, radical copolymerization was carried out in an ampoule, in which AIBN was also added as a radical initiator, 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 dried in a vacuum for 48 h. Copolymers were obtained at a typical yield of around 90%. As a result, four kinds of copolymers were synthesized for this study, i.e., poly(1-co-3) (PCDY), poly(2-co-3) (PPDY), poly(2-co-4) (PPMT), and poly(2-co-5) (PPBT).

2.4. Chemical characterization

The chemical structure and composition ratio were confirmed by $^1\text{H NMR}$ in CDCl_3 (JEOL, 600 MHz). The molecular weight of each copolymer was estimated in THF by gel permeation chromatography (Waters Model 150-C, GPC) at a flow rate of 1.2 ml/min. Thermal analyses were performed by differential scanning calorimeter (TA Instrument Q100, DSC). Conventional DSC measurements were carried out at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen gas atmosphere. Modulated DSC measurements were also performed at a heating rate of $2^\circ\text{C}/\text{min}$, modulation amplitude of $\pm 2^\circ\text{C}$ and modulation period of 60 s under nitrogen gas atmosphere.

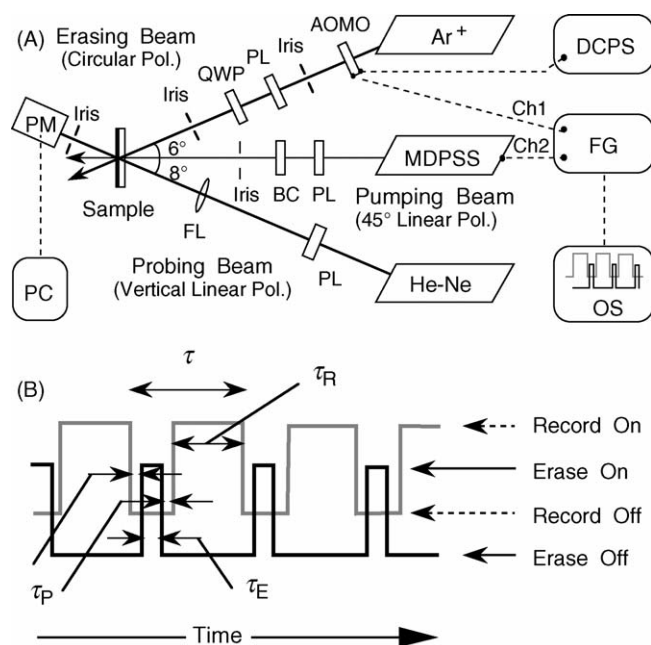


Fig. 2. (A) Schematic drawing of an optical system for sample durability evaluation. (MDPSS, AOMO, PL, QWP, BC, FL, PM, DCPS, FG, OS, and PC are a modulated diode pump solid-state laser of 405 nm, an acousto-optic modulator, a polarizer, quarter wave plate, Berek compensator, focusing lens, polarimeter, dc power supply, function generator, oscilloscope, and computer, respectively.) (B) A timing diagram of recording and erasing beam exposure.

2.5. Film preparation

All copolymers were dissolved in dichloromethane at a concentration of 5% in weight, and the solutions were filtered through a membrane with $0.2\ \mu\text{m}$ \varnothing pores. Then, homogeneous and clear films about $1\ \mu\text{m}$ thick were obtained on a glass substrate by spin coating at approximately 25°C under dried nitrogen flow.

2.6. Optical characterizations

Photoinduced birefringence (Δn_{PI}) was evaluated using a pump-probe optical configuration. Ar^+ ($\lambda = 488\ \text{nm}$, beam diameter = 3 mm and irradiance = $1\ \text{W}/\text{cm}^2$) and He-Ne ($\lambda = 633\ \text{nm}$, beam diameter = 1 mm and power = 3 mW) lasers were employed as the pump and probe beams, respectively. Two beams were collinear and incident normally on the sample film. The polarization conditions of both incident beams were controlled to be linear using a polarizer and half-wave plate. The direction of the He-Ne beam was set to be vertical and that of the Ar^+ beam was set to be -45° with respect to the He-Ne beam. The photoinduced birefringence was determined by measuring the change in the polarization condition of the transmitted He-Ne beam.

In addition to the single process of photoinduced birefringence measurement, the sequential recording and erasing process was reported to evaluate the durability of the sample films. The optical setup for the durability test is illustrated in Fig. 2. A diode-pumped solid-state (DPSS) laser ($\lambda = 405\ \text{nm}$, beam diameter = $2\ \text{mm} \times 3\ \text{mm}$ and irradiance = $0.4\ \text{W}/\text{cm}^2$), Ar^+ laser ($\lambda = 488\ \text{nm}$, beam diameter = 3 mm and irradi-

Table 1
Summary of DSC characterization

Sample	T_g	Notes
PCDY series	100–115 °C ($0.2 \leq k \leq 1$) ~80 °C ($0 \leq k < 0.2$)	A few endothermic peaks that can be assigned to phase transition of liquid crystalline state (nematic and smectic) were observed
PPDY series	100–125 °C	Three or four endothermic peaks that can be assigned to phase transition of liquid crystalline state (nematic and smectic) were observed
PPMT series	80–90 °C	No obvious endothermic peaks were observed other than a inflection point due to glass transition
PPBT series	160–170 °C	Inflection points due to glass transition were not conspicuous for all. An endothermic peak was observed at around 170–190 °C

ance = 1.2 W/cm²), and He–Ne laser ($\lambda = 633$ nm, beam diameter = 1 mm and power = 3 mW) were employed as the recording, erasing and probing beams, respectively. (The wavelengths of the recording and erasing beams are not limited to 405 and 488 nm. We can choose any other wavelength from 400 to 500 nm that corresponds to the π – π^* absorption band of the material. Beam intensity was selected from a range without any risk of photo-bleaching.) The polarization conditions of recording, erasing and probing beams were controlled to linear at +45° with respect to the vertical line, circular and vertically linear, respectively. The recording beam was incident normal to the sample from the back (substrate side), and the erasing and probing beams were incident to the sample at small angles of 6° and 8°, respectively. As shown in Fig. 2(B), recording and erasing beams were alternately irradiated on the films repeatedly.

3. Results and discussion

The molecular weight of the obtained copolymers were estimated to be 8.0×10^3 – 2.4×10^4 . Glass transition temperatures of all copolymers are summarized in Table 1.

Photoinduced birefringence (Δn_{PI}) measurements were performed on all copolymers. As shown in Fig. 3, the results were unique and interesting. Namely, a sharp peak was observed for Δn_{PI} of PCDY and PPDY when the composition ratio of compound 1 or 2 was at around 50 mol%, whereas there was no obvious peak for Δn_{PI} of PPMT and PPBT. The former feature indicates that the polymer side chains contained in compounds 1 (or 2) and 3 mutually promote their photoinduced molecular reorientations mutually and that this effect can be maximized when their composition ratio is balanced. Although the detailed mechanism of this unusual behavior is not clear at this moment, it is certain that such orientational enhancement was achieved via appropriate molecular interaction between compounds 1 (or 2) and 3. One possible explanation is the formation of supramolecular assembly between different moieties, which induces molecular cooperative motion [8–10].

The dipole moment of the moieties are 5.70, 7.59 and 1.65 Dedye for compounds 1–3, respectively. (The dipole moment values were calculated by MOPAC with the PM5 parameter.) Therefore, it is possible that the affinity between compounds 3 and 1 in greater than that between compounds 3 and 2 since the difference in dipole moments is relatively small. Therefore, a more conspicuous peaking effect could be observed in PCDY (poly(1-co-3)). However, the dipolar balance is not necessarily

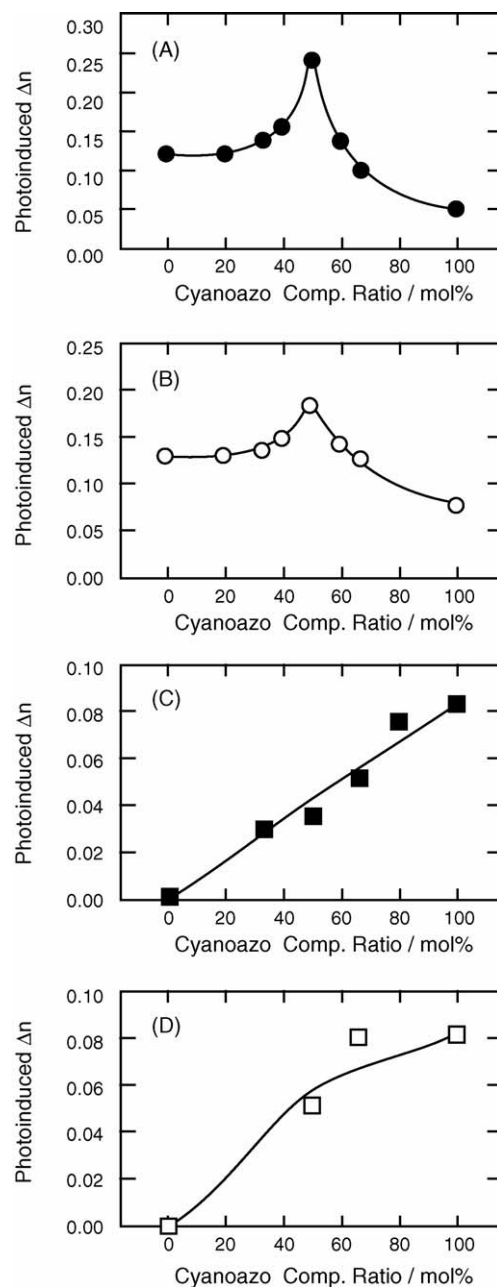


Fig. 3. Dependence of photoinduced birefringence on the composition ratio of cyano azo compounds. (Solid lines are freehand drawings.)

an essential aspect for orientational enhancement, since such a peaking effect was not observed in PPMT (poly(2-co-4)) and PPBT (poly(2-co-5)). The dipole moments of compounds **4** and **5** are 6.14 and 6.43 Debye, respectively. Thus, the differences in dipole moments in PPMT and PPBT are much smaller than that in PCDY or in PPDY. Nevertheless, no obvious peaks could be observed for PPMT and PPBT. This means that the polymer side chains in compounds **2** and **4** (or **5**) do not mutually promote their photoinduced molecular reorientations and only compound **2** responds to the irradiated beam. One of the reasons for this result can be attributed to a miscibility problem between compounds **2** and **4** (or **5**) due to their molecular structures and related electronic properties. This point should be clarified via further research in order to find an effective strategy for designing high-performance molecules.

In order to discuss the dependence of the peaking tendency on the composition ratio more quantitatively, we here assume that a molecular pair of different moieties (AB) is more stable than a pair of the same moieties (AA or BB). (A and B each stand for a functional moiety in the copolymer.) Then, possible numbers of a state (Z) at a certain temperature can be expressed as being proportional to

$$Z \propto \exp \left[-\frac{N_{AB}W_{AB} + N_{AA}W_{AA} + N_{BB}W_{BB}}{k_B T} \right]. \quad (1)$$

Here, N_{AA} , N_{BB} and N_{AB} are the numbers, and W_{AA} , W_{BB} and W_{AB} are the stabilization energies for AA, BB and AB pairs, respectively. For further simplification, we consider that W_{AA} , W_{BB} and W_{AB} can be expressed as $-W$, $-W$ and $-kW$, respectively. (W and k are positive values and k is greater than 1) If we denote the composition ratio of component A as x ,

$$N_{AB} = C_0 x, \quad N_{AA} = 0, \quad N_{BB} = C_0 \frac{1-2x}{2},$$

$$\text{for } 0 \leq x \leq \frac{1}{2}$$

$$N_{AB} = C_0(1-x), \quad N_{AA} = C_0 \frac{2x-1}{2}, \quad N_{BB} = 0,$$

$$\text{for } \frac{1}{2} \leq x \leq 1.$$

Then we obtain

$$Z \propto f(x) = \exp \left[\left\{ xk + \frac{1-2x}{2} \right\} \frac{C_0 W}{k_B T} \right], \quad \text{for } 0 \leq x \leq \frac{1}{2} \quad (2)$$

$$Z \propto f(x) = \exp \left[\left\{ (1-x)k + \frac{2x-1}{2} \right\} \frac{C_0 W}{k_B T} \right],$$

$$\text{for } \frac{1}{2} \leq x \leq 1. \quad (3)$$

Thus, Δn_{PI} can be expressed as a function of the composition ratio x

$$\Delta n_{PI} = C \{ \Delta n_{x=0} + (\Delta n_{x=1} - \Delta n_{x=0}) x \} \int \frac{f(x)}{f(x)} dx, \quad (4)$$

where C is a constant factor.

Table 2
Summary of fitting parameters

	Sample	k	$C_0 W / k_B T$
(A)	PCDY	1.44	7.37
(B)	PPDY	1.31	4.11
(C)	PPMT	1.16	2.60
(D)	PPBT	1.26	2.62

Using Eq. (4), each datum was fitted by the least-squares method. Fitting parameters of the relative stabilization coefficient (k) and the stabilization energy (W) are listed in Table 2.

As was expected, it was found that the stabilization coefficients (k) and the stabilization energies (W) for PCDY and PPDY

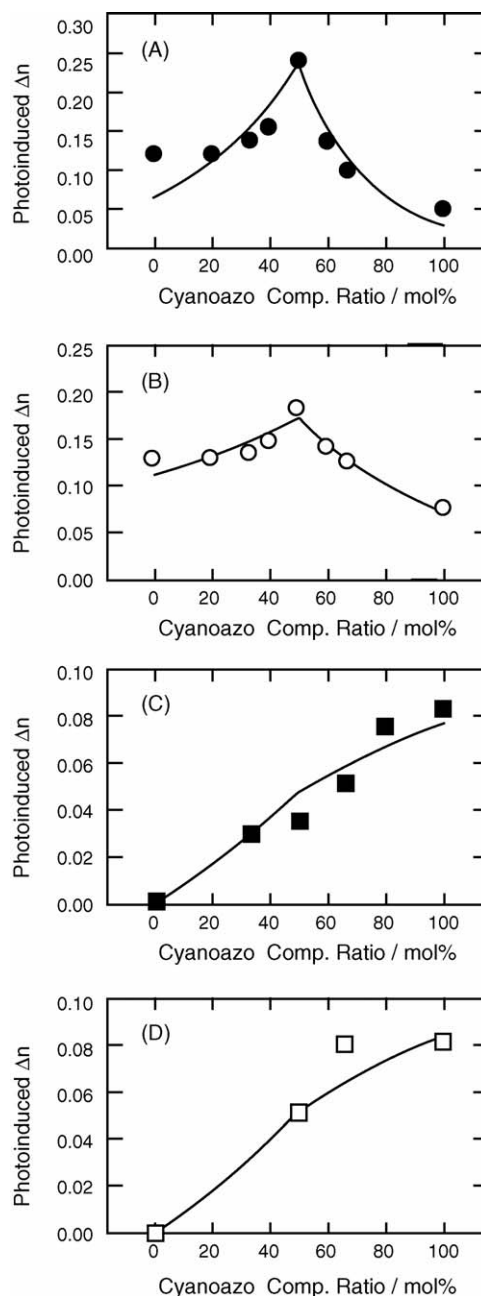


Fig. 4. Experimental data and fitting curve for the dependence of photoinduced birefringence on the composition ratio.

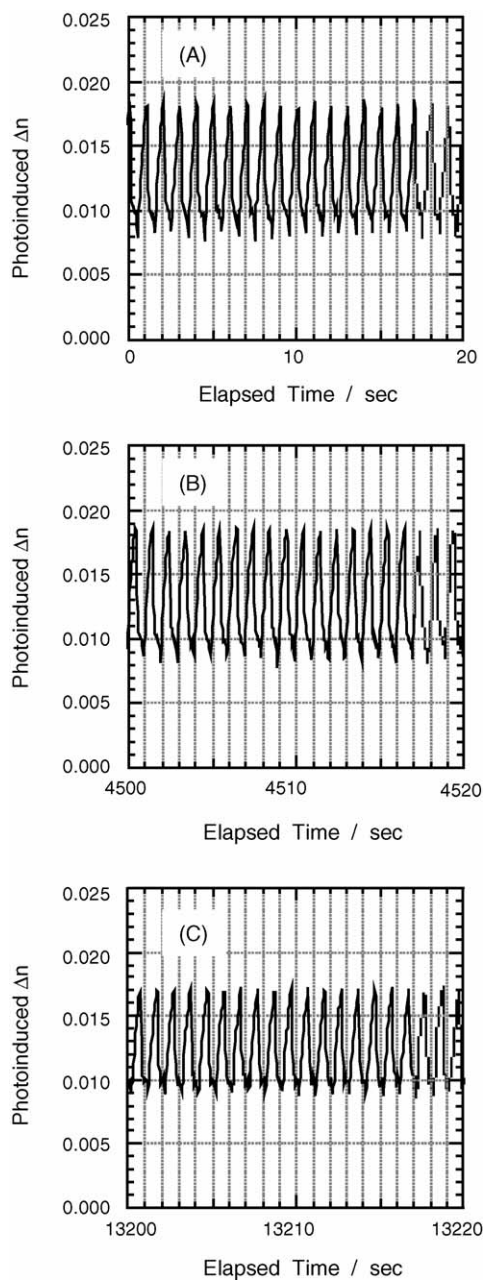


Fig. 5. Photoinduced birefringence on sequential recording and erasing operated at 1 Hz repetition rate. (A) The initial stage of the measurement (0–50 cycles), (B) 1.25 h after (4500–4550 cycles), and (C) 3.67 h after (13200–13250 cycles), respectively.

were larger than those for PPMT and PPBT. The fact that k values for PPMT and PPBT are close to unity means that there is no special affinity between compounds **2** and **4** (or **5**). This is consistent with the previous discussion. Using these parameters, the peaking characteristics are reproduced in Fig. 4(A) and (B).

Next, a durability test for repeated recording and erasing has been performed on PCDY50, which exhibited the highest Δn_{PI} in this study. (Under the experimental conditions in this study, it took about 45 s until the increment of the photoinduced birefringence was saturated.) Figs. 5 and 6 show the results for different repetition periods (τ). Duty ratios of recording and erasing times were adjusted to $\tau_R = 0.50\tau$, $\tau_E = 0.40\tau$, and $\tau_P = 0.05\tau$.

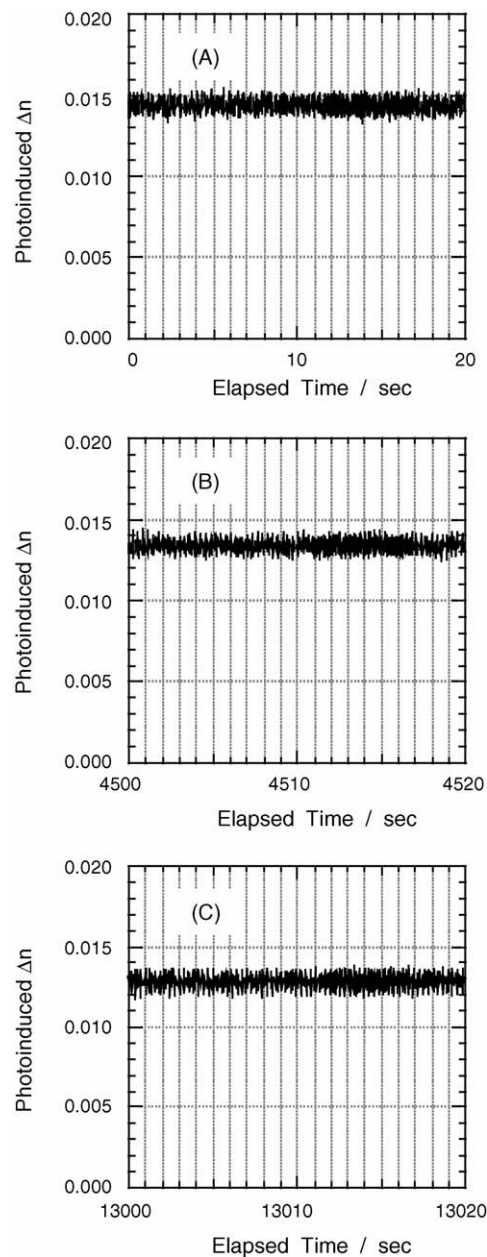


Fig. 6. Photoinduced birefringence on sequential recording and erasing operated at 10 Hz repetition rate. (A) The initial stage of the measurement (0–500 cycles), (B) 1.25 h after (4500–4550 cycles), and (C) 3.67 h after (13000–13050 cycles), respectively.

Fig. 5 shows the result for 0.50 s irradiation of a 405 nm linearly polarized beam (recording process) with successive 0.40 s irradiation of a 488 nm circularly polarized beam (erasing process). Under these conditions, though photoinduced birefringence was not erased completely and the absolute value of photoinduced birefringence was relatively low ($\Delta n_{\text{record}} = 0.0183$), a clear contrast between the recording and erasing states was observed: $\Delta n_{\text{record}}/\Delta n_{\text{erase}} = 0.0183/0.0081 = 2.26$ at the initial stage (Fig. 5(A)), $\Delta n_{\text{record}}/\Delta n_{\text{erase}} = 0.0173/0.0082 = 2.11$ at around 4.5×10^3 cycles (Fig. 5(B)) and $\Delta n_{\text{record}}/\Delta n_{\text{erase}} = 0.0168/0.0082 = 2.05$ at around 1.32×10^4 cycles (Fig. 5(C)). The reductions of contrast was less than 10%

of the initial value even after 1.33×10^4 cycles under these conditions.

Then, the repetition period was reduced to 0.1 s, namely, 50 ms irradiation of a 405 nm linearly polarized beam (recording process) and successive 40 ms irradiation of a 488 nm circularly polarized beam (erasing process). The result is shown in Fig. 6. Under these conditions, some contrast between the recording and erasing states was observed: $\Delta n_{\text{record}}/\Delta n_{\text{erase}} = 0.0154/0.0135 = 1.14$ at the initial stage (Fig. 6(A)), $\Delta n_{\text{record}}/\Delta n_{\text{erase}} = 0.0146/0.0118 = 1.24$ at around 4.50×10^4 cycles (Fig. 6(B)) and $\Delta n_{\text{record}}/\Delta n_{\text{erase}} = 0.0136/0.0116 = 1.17$ at around 1.30×10^5 cycles (Fig. 6(C)). As a result, it was found that the contrast was not changed at all even after 1.31×10^5 cycles under these conditions. Although the absolute value of photoinduced birefringence and the contrast obtained under these conditions were relatively low, it was confirmed that the recording and erasing process could be repeated for more than 10^5 cycles, which is one of the targeted numbers for rewritable recording.

4. Conclusion

We have developed new photoresponsive copolymers consisting of an azo moiety and a high-birefringence moiety as side chains and investigated their photoinduced birefringence (Δn_{PI}) characteristics. As a result, a unique dependence of Δn_{PI} on the copolymerization ratio was found for PCDY and PPDY copolymers, which contain the 2-[2-methyl-4-(4-phenylazophenylazo)phenoxy]ethyl moiety and the 2-[4-(4-cyanophenylazo)phenoxy]ethyl (or 2-[4-(2-cyanopyridine-5-ylazo)phenoxy]ethyl) moiety. The highest values of Δn_{PI} for PCDY and PPDY were achieved with the copolymerization ratio of 50:50. The values of Δn_{PI} were 0.244 and 0.172, respectively, under 488 nm beam excitation at 1 W/cm^2 . These high values of Δn_{PI} in amorphous random copolymers might be brought about by cooperative molecular reorientation of the two

functional moieties. Moreover, PCDY50 and PPDY50 are also superior in their solubility for solvents, chemical and physical stability, processability and optical quality of films. Furthermore, considerable durability (more than 10^5 repetitions of recording and erasing cycles) has been confirmed for PCDY50. Therefore, these copolymers are considered to be promising candidates for application to rewritable holographic memory.

In contrast to the above, no apparent enhancement of Δn_{PI} was observed and the observed Δn_{PI} was not sufficiently high for PPMT and PPBT. This difference might be attributed to the poor compatibility between the 2-[4-(2-cyanopyridine-5-ylazo)phenoxy]ethyl moiety and the 2-[4-(4-trifluoromethylphenylethynyl)phenoxy]ethyl (or 2-[4-(4-trifluoromethylphenylethynyl)phenoxy]ethyl) moiety. However, the dominant factor governing intermolecular affinity between different functional moieties is not clear at this moment. Systematic study on this point is anticipated in the further development of rewritable holographic data storage media.

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