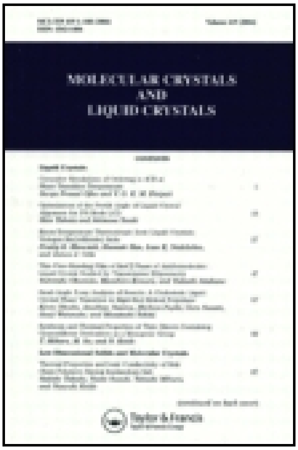

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Large Photo-Induced Birefringence in Azobenzene Copolymer

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Large Photo-Induced Birefringence in Azobenzene Copolymer

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In order to develop the photoresponsible materials for holographic memory, we report an amorphous azobenzene copolymer having large photo-induced birefringence (Δn) and having good thermal stability. We have achieved large photo-induced Δn value of 0.244 in the amorphous film containing azobenzene chromophore at the specific composition ratio. Any relaxation has not been observed even after turn off the writing beam. This large Δn value is attributed to the effective molecular cooperative motion between two chromophores and highly anisotropic molecular structure. Also, the good thermal stability was originated from a rigid rod-like *structure of long π-conjugated copolymer segment. From the result, our copolymer can be applied as a new class of material for high performance holographic memory application.*

Keywords: azobenzene copolymer; molecular re-orientation; photo-induced birefringence; photo-isomerization

INTRODUCTION

Azobenzene containing polymers for optical device applications has been widely and extensively investigated in the past decade such as non-linear optical device [1], optical storage [2], photo-induced surface relief (PSR) [3–5] and so on. In addition, azobenzene compounds or its polymers are most useful materials for rewritable holographic memory applications [6,7].

To improve optical performance of holographic memory, large photo-induced birefringence (Δn) property is strongly required. Of course, it is well known that a large Δn can be achieved by increase

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the π-electron conjugation length of the chromophore. However, in polymeric system, photo-induced Δn could not easily obtain a large value because it must be considered to increase the order parameter of the chromophores in the bulk that is affected by many physical factors such as dipole moment of the chromophores, miscibility, dye functionalization, chain entanglement, glass transition temperature and so on. Even more, optical quality or surface condition of the film is also important factor for this purpose.

In this paper, we describe the synthesis of a new type of photo-responsible material, poly{4-[2-(methacryloyloxy)ethyloxy-4′-cyanoazobenzene]-*co*-4-[[2-(methacryloyloxy)ethyloxy]-2-methyl-4-(phenylazo)] azobenzene}: PCDY50, and its photo-induced birefringence property will be describe.

EXPERIMENTAL

Chemicals

2,2′-Azobisisobutyronitrile (AIBN, from Wako Pure Chemicals) was recrystallized from methanol. 4-cyanoaniline, 2-bromoethanol, methacryloyl chloride purchased from Tokyo Kasei and were used without further purification. Phenol and disperse yellow-7 (DY7) were purchased from Aldrich and were used without further purification. Tetrahydrofuran (THF) was used dehydration grade from Aldrich.

Measurements

The chemical structure and composition confirmed by ^{1}H-NMR in $CDCl_3$ (Jeol, 600 MHz) and elementary analysis. The UV absorption measurement was performed by UV/Vis. spectrophotometer (Hitachi UV-4100s). The molecular weight of the copolymer was estimated in THF by using gel permeation chromatography (Waters Model 150 C, GPC) equipped with an RI detector with flow rate 1.2 ml/min. Thermal analysis was measured by differential scanning calorimeter at a heating rate 5°C/min under nitrogen gas. (Seiko Instrument DSC 6100.)

Synthesis of Azobenzene Compound

1.1. 4-Hydroxy-4′-Cyanoazobenzene

Following synthesis was done according to conventional azo coupling method [8,9]. In a 500 ml of 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∼5°C, 2.5 g of $NaNO_2$ (36 mmol) in

75 ml water was slowly added to the former solution. This solution was added slowly at 0 ~ 5°C to a coupling part of phenol (2.8 g, 30 mmol) in 10% NaOH solution and the pH adjusted to 8 ~ 9 with concentrated NaOH solution. After stirring for 6 h, the precipitate was collected and washed with distilled water. The crude product was recrystallized in ethanol/water mixture. Orange crystal powder was filtered and vacuum dried (yield = 75%). ^{1}H-NMR, δ (ppm): 7.05 (d, 2 H), 7.78 (d, 2 H), 7.95 (m, 4 H).

1.2. 4-(2-Hydroxyethyloxy)-4′-Cyanoazobenzene

In a 500 ml of three neck round-bottom flask equipped with a condenser, 2.23 g of *4-hydroxy-4′-cyanoazobenzene* (10 mmol), 2.5 g of 2-bromoethanol (20 mmol), 2.76 g of potassium carbonate (20 mmol) were dissolved in 100 ml acetone and refluxed for 72 h. The resulting solution cooled down to room temperature and extracted with chloroform. The crude product was recrystallized in ethanol for overnight. The orange-yellow precipitate was obtained (yield = 80%). ^{1}H-NMR, δ (ppm): 4.34 (t, 2 H), 4.58 (t, 2 H), 7.05 (d, 2 H), 7.78 (d, 2 H), 7.95 (m, 4 H).

1.3. 4-[2-(Methacryloyloxy)Ethyloxy]-4′-Cyanoazobenzene: (CyAz)

In a 100 ml of round-bottom flask, 0.7 g of *4-(2-hydroxyethyloxy)-4′-cyanoazobenzene* (2.62 mmol) and 0.53 g of triethylamine (5.24 mmol), were dissolved in 30 ml of THF. The solution was kept at 0 ~ 5°C under dry nitrogen atmosphere. A solution of methacryloyl chloride (0.57 g, 5.24 mmol) was added slowly to the above mixture. The reaction mixture was stirred for 24 h. Then resulting solution was filtered-off and the solvent removed by evaporation under reduced pressure. The solid residue extracted with chloroform and washed with potassium carbonate aqueous solution for three times. The crude product was recrystallized in 300 ml of *n*-hexane for overnight. The orange-yellow color powder was obtained (yield = 85%). The chemical structure and composition were confirmed by elementary analysis and ^{1}H-NMR.

Elem. Anal. Calcd. for $C_{19}H_{17}N_3$; C 68.05%, H 5.11%, N 12.53%. Found; C 67.08% H 5.01% N 12.48%. ^{1}H-NMR, δ (ppm): 1.97 (s, 3 H), 4.34 (t, 2 H), 4.58 (t, 2 H), 5.61 (d, 1 H), 6.16 (d, 1 H), 7.05 (d, 2 H), 7.78 (d, 2 H), 7.95 (m, 4 H).

2.1. 4-(2-Hydroxyethyloxy)-2-Methyl-4′-(Phenylazo) Azobenzene

In a 300 ml of three neck round-bottom flask equipped with a condenser, 1 g of DY7 (3.16 mmol), 0.79 g of 2-bromoethanol (6.32 mmol), 0.87 g of potassium carbonate (6.32 mmol) were dissolved in 50 ml acetone and refluxed (50°C) for 72 h. The resulting solution cooled down to room temperature and extracted with chloroform. The crude product was recrystallized in ethanol for overnight. The brownish-red color powder was obtained (yield = 85%). ^{1}H-NMR, δ (ppm): 2.31 (s, 3 H), 4.34 (t, 2 H), 4.58 (t, 2 H), 6.96 (d, 1 H), 7.50$\sim$7.55 (m, 3 H), 7.82 (s, 1 H), 7.84 (d, 1 H), 7.96 (d, 2 H), 8.02$\sim$8.07 (m, 4 H).

2.2. 4-[2-(Methacryloyloxy)Ethyloxy-2-Methyl-4′-(Phenylazo)] Azobenzene: (DY7)

The synthesis of this compound was done according to above described for CyAz. The following yield of the purified product was obtained: brownish-red color powder (yield = 85%). Elem. Anal. Calcd. for $C_{25}H_{24}N_4$; C 70.08%, H 5.65%, N 13.08%. Found; C 69.51% H 5.54% N 12.84%, ^{1}H-NMR, δ (ppm): 1.97 (s, 3 H), 2.31 (s, 3 H), 4.34 (t, 2 H), 4.58 (t, 2 H), 5.61 (d, 1 H), 6.16 (d, 1 H), 6.96 (d, 1 H), 7.50$\sim$7.55 (m, 3 H), 7.82 (s, 1 H), 7.84 (d, 1 H), 7.96 (d, 2 H), 8.02$\sim$8.07 (m, 4 H). The synthetic routes of all azobenzene compounds are shown in Figure 1.

Radical Copolymerization

The monomer solution was degassed by freeze and thaw process for several times. Then, radical copolymerization of PCDY50 was carried out with 1:1 feed ratio in THF at 60°C for 24 h and 3 wt% of AIBN was used as a radical initiator. Then, the resultant solution was poured into methanol. The precipitate was filtered and vacuum dried for 48 h (yield = 90%). The chemical structure of copolymer is shown in Figure 2.

Film Preparation and Optical Characteristics

PCDY50 was dissolved in dichloromethane at a concentration of 5% in weight. Then polymer solution was spin coated onto glass substrate at 700 rpm for 30 second, providing the clear smooth (d = 0.8 μm) by measured surface profiler (Kosaka Lab. Ltd., Surfcorder SE1700α). Measurement of photo-induced (Δn) was performed by the optical system illustrated in Figure 3. PCDY50 film was irradiated by a linear polarized Ar$^+$ ion laser beam (Spectra-physics, $\lambda = 488$ nm, irradiance = 1 W/cm^2). The birefringence was probed simultaneously with a He-Ne ($\lambda = 633$ nm) laser by using polarimeter (Thorlabs Co., PA410) and calibrated by film thickness. In addition, the photo-induced surface relief (PSR) structure inscribed on the PCDY50 thin

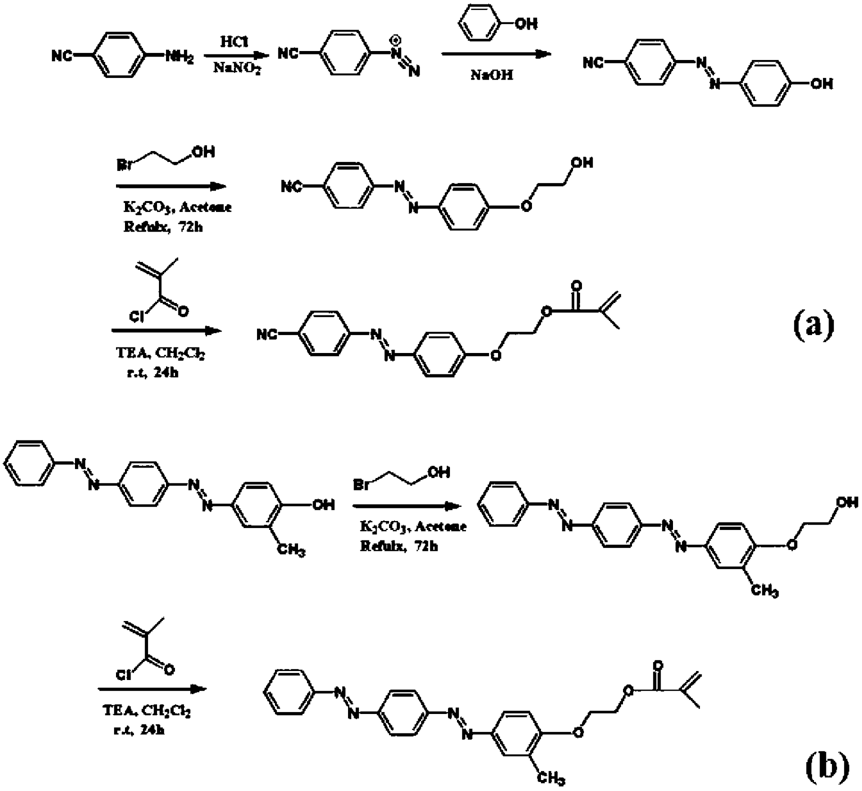

FIGURE 1 Synthetic routes of azobenzene compounds. (a) CyAz, (b) DY7.

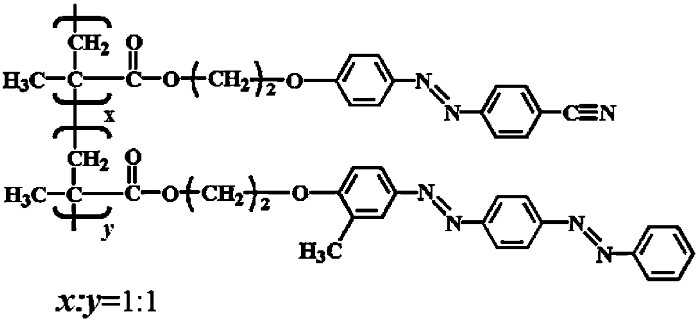

FIGURE 2 The chemical structure of PCDY50.

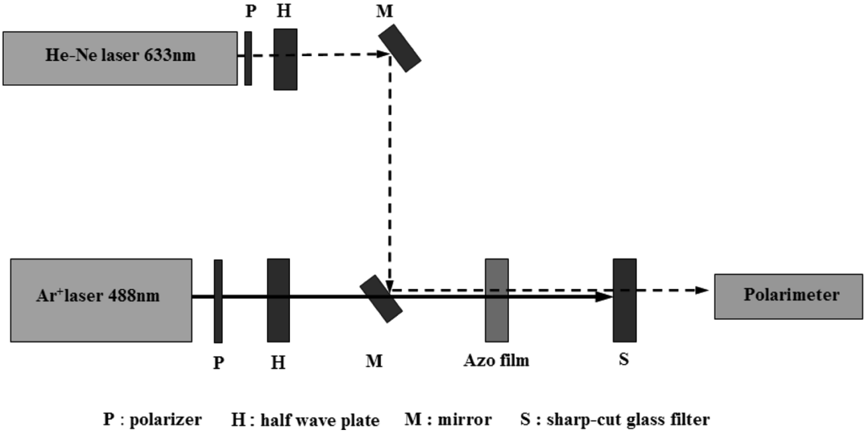

FIGURE 3 A schematic illustration of the optical set-up for measuring Δn value.

film by the optical setup previously reported [3]. Circular polarized Ar^+ ion laser beam of 488 nm at irradiance of 100 mW/cm^2 was employed as a light source. In order to evaluate diffraction efficiency, the first-order diffraction of He-Ne (633 nm) laser beam was monitored by using photodiode equipped lock-in-amplifier.

RESULTS AND DISCUSSION

The PCDY50 was synthesized and its optical property was characterized. The glass transition temperature (T_g) and the molecular weight of this copolymer were 130°C and 8×10^3, respectively. The DY7 moiety has been chosen because it has weak dipole moment and long π-conjugated structure. It was considered to promote large Δn property. Also, this kind of molecular design could be expected to give excellent thermal stability due to the rigid *rod-like* structure that restrains molecular movement effectively. Figure 4 shows UV/Vis. spectra of PCDY50. The maximum absorption band is shown at 370 nm. It is overlapped from the two absorption bands of CyAz ($\lambda_{max} = 360$ nm) and of DY7 moiety ($\lambda_{max} = 384$ nm), respectively. Although the optical density at 488 nm (pump beam) is relatively very low, the molecular re-orientation occurred and photo-induced Δn could be observed satisfactorily.

The PCDY50 shows good solubility in common organic solvent. We used dichloromethane for spin coating and obtained optically fine film (0.8 μm thickness) that can be used the Δn measurement and the PSR

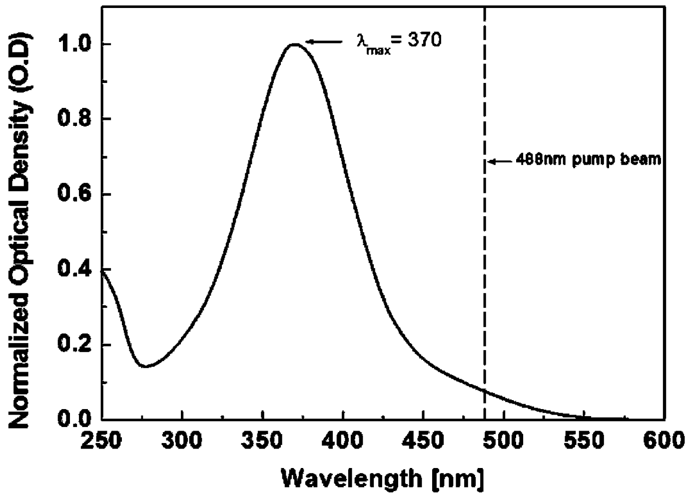

FIGURE 4 UV/Vis. absorption spectrum of PCDY50 (Conc. 3.3×10^{-6} M in $CHCl_3$, O.D at 488 nm = 0.077).

fabrication. It was figured out that the optical quality of the film was strongly affects to the absolute value of Δn. Figure 5 shows dynamics of photo-induced Δn as a function of light irradiation time. From this

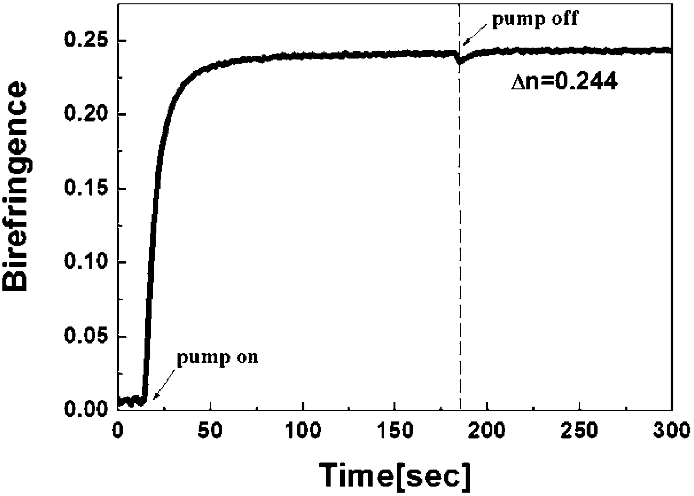

FIGURE 5 The dynamics of photo-induced Δn of PCDY50. The excitation starts at 15 sec, and terminated at 180 sec.

experiment, it was confirmed that the response time of 24.42 sec and a large photo-induced birefringence value of 0.244 were achieved with the PCDY50 amorphous film.

This result might be explained from a viewpoint of molecular cooperative motion between two azobenzene chromophores in the copolymer. In order to confirm this molecular cooperative motion, we have synthesized many copolymers with different composition ratio and compared these optical characteristics. From this examination, we found that the photo-induced Δn values varied in the range of 0.05 ~ 0.244. It depended on the composition ratio in copolymer. The largest value of the Δn was observed at around the 1:1 composition ratio. This feature implies that molecular cooperative motion resulting highly ordered condition could be achieved in the copolymer consists of specific composition ratio. Similar characteristics in cooperative motion of chromophores have been reported in liquid crystalline system [10]. Although our polymer is not liquid crystalline, it has rigid *rod-like* moiety (DY7 unit) so that the chromophore might bring a *liquid crystalline-like* circumstances in local area. We believe that could assist the molecular cooperative motion in the polymer bulk. This feature is also helpful for a good stability of aligned state of the molecules.

One more reason that we could obtain very large photo-induced Δn value in PCDY50 might be attributed to the photochromic nature of

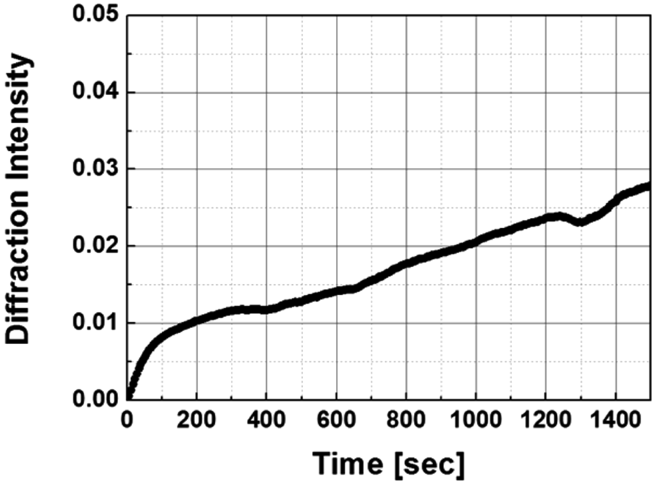

FIGURE 6 Real time monitoring of diffraction efficiency during PSR formation.

both chromophores. Each segment of PCDY50 has azobenzene moieties so that each segment is able to response and to re-orient along the perpendicular direction with respect to the linearly polarized excitation beam. Therefore, *pseudo-liquid crystalline* nature was essential property for bring out maximum Δn value of PCDY50. Also, the individual optical response was important factor to achieve very large photo-induced Δn.

In addition, from the structural viewpoint of DY7 moiety, weak push-pull chromophore structure and highly anisotropic structure provide good stability and large Δn value.

Figure 6 shows a PSR formation ability of PCDY50. The first-order diffraction efficiency was monitored by 633 nm He-Ne laser during the PSR inscription process performed by 488 nm Ar^+ laser beam. The PSR formation characteristic is closely related to the efficiency and the response of photoisomerization in each azo moiety. As the result, the diffraction efficiency was increased almost proportional to the irradiation time.

CONCLUSION

A new type of azobenzene copolymer that is potentially useful for holographic memory application was synthesized and evaluated in terms of optical characteristics. We achieved a large photo-induced birefringence value ($\Delta n = 0.244$) with newly synthesized PCDY50. In this experiment, we can summarize two factors were essential to achieve large photo-induced Δn value and orientational stability: i) structural steric effect originated from a long π-conjugated rigid *rod-like* azobenzene moiety (DY7 unit), and ii) effective molecular cooperative motion in specific composition ratio (CyAz:DY7 = 1:1 in copolymer) between two choromophores. These results are useful for the further material design toward holographic memory development.

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