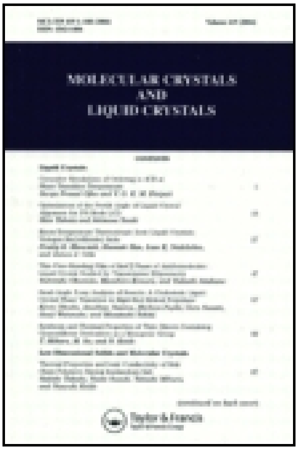

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Synthesis and Optical Characterization of Photoresponsive Polyester Blend Filmsfor Holographic Data Storage

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Synthesis and Optical Characterization of Photoresponsive Polyester Blend Films for Holographic Data Storage

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Two types of new photoresponsive polyester containing 4-cyanoazobenzene (CNAz) and 4-[4-(phenylazo)phenylazo]-o-cresol (DY7) moiety have been synthesized and their optical properties of the two polymer blend were evaluated. The polymers were synthesized from the reaction between azobenzene modified epoxy resin and isophthaloyl chloride. Thin films with good optical quality of each azobenzene modified epoxy resin, its polymer and its polymer blend were obtained by spin coating. The photoinduced birefringence (Δn) measurement was performed with excitation beams of 405 nm, 458 nm, and 488 nm. As a result, with increasing the DY7 content, the Δn was increased due to large intrinsic birefringence of DY7 that originates from extended π-conjugation and highly anisotropic structure of the moiety.

Keywords: blending effect; molecular cooperative motion; molecular reorientation; photoinduced birefringence; photoresponsive polyester

INTRODUCTION

Azobenzene polymers have been extensively investigated for optical device applications because of their peculiar photoresponsive properties by light irradiation [1–4]. In particular, azobenzene polymers are most promising candidate for rewritable holographic memory applications [5,6].

Recently, we reported the side chain type azobenzene copolymer for holographic material, which shows fairly large photoinduced birefringence (Δn) value caused by molecular cooperative motion of two different side-chains in the copolymer (PCDY50) [7–9]. In connection with our previous work, we tried a new approach for further development

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of holographic data storage media, i.e., we employed the same two photoresponsive moieties that was used in the PCDY50 into newly developed azobenzene modified epoxy resins with middle molecular weight and polymerized. The cooperative molecular motion of the photoresponsive chromophores observed in the PCDY50 was expected to be brought about in the blend system consists of two azobenzene modified epoxy resins as well.

The epoxy resin, 2,2′-bis-(4-glycidyloxyphenyl)propane, generally possess excellent properties such as good solubility in common organic solvent, good adhesion to substrates, good film formation and high reactivity with amine, hydroxy, and carboxylic acid. In this paper, new possibility of two polyester bearing 4-cyanoazobenzene moiety (CNAz) and 4-[4-(phenylazo)phenylazo]-*o*-cresol (DY7) moiety for holographic material will be described. In addition, the Δn properties of azobenzene modified epoxy resin, its polymer, doping system, and its polymer blend will be described in this paper.

EXPERIMENTAL

Chemicals

2,2′-Bis-(4-glycidyloxyphenyl)propane (bisphenol-A type epoxy resin) and triphenylphosphine (TPP), isophthaloyl chloride were purchased from Tokyo Kasei. 4-[4-(Phenylazo)phenylazo]-*o*-cresol (DY7) was purchased from Aldrich.

Measurements

The chemical structure was confirmed by ^{1}H NMR in $CDCl_3$ (JEOL, 600 MHz) and FT-IR spectroscopy (Thermo Nicolet 8700). The UV absorption measurement was performed by UV/VIS spectrophotometer (Hitachi UV 4100 s). The glass transition temperature was measured by differential scanning calorimeter (DSC) at a heating rate 10°C/min under nitrogen gas. (TA Instrument DSC Q100).

Synthesis of 4-Hydroxy-4′-cyanoazobenzene (CNAz)

The synthetic procedure was previously described [8]. ^{1}H NMR, δ (ppm) : 7.05 (d, 2H), 7.78 (d, 2H), 7.95 (m, 4H).

4-cyanoazobenzene Modified Epoxy Resin (EBACN)

In a 100 ml of three neck round-bottom flask equipped with a condenser, 0.89 g of *CNAz* (4 mmol), 0.68 g of EB (2 mmol), 26 mg of TPP

(0.1 mmol) were dissolved in 15 ml of 1,4-dioxane under dry nitrogen atmosphere and stirred for 24 h at 100°C. The resulting solution cooled down to room temperature and extracted 300 ml of $CHCl_3$with 300 ml of K_2CO_3 aqueous solution. Then organic layer washed with 500 ml of distilled water until the washing solution became neutral. After extract procedure, the organic chloroform layer dried with $MgSO_4$ for 6 hr then filtered off. The chloroform removed by rotary evaporator under reduced pressure. After vacuum dry for 72 h, the orange-red solid obtained (yield = 76%). ^{1}H NMR, δ (ppm) : 1.64 (s, 6H), 3.95 (m, 2H), 4.17 (d, 8H), 6.81 (d, 4H), 7.05 (d, 4H), 7.12 (d, 4H), 7.78 (d, 4H), 7.95 (m, 8H). FT-IR (KBr, cm^{-1}): 3500 (OH stretching), 3115 ~ 3014 (CH of aromatic), 2976 ~ 2835 (CH_3 of aliphatic), 2227 (CN cyano stretching), 1600 (C=C of aromatic), 1571 (N=N of aromatic azo), 850 (CH of aromatic).

DY-7 Modified Epoxy Resin (EBADY7)

In a 100 ml of three neck round-bottom flask equipped with a condenser, 1.44 g of DY-7 (4 mmol), 0.68 g of EB (2 mmol), 26 mg of TPP (0.1 mmol) were dissolved in 15 ml of 1,4-dioxane under dry nitrogen atmosphere and stirred for 24 h at 100°C. The resulting solution cooled down to room temperature and extracted 300 ml of $CHCl_3$ with 300 ml of K_2CO_3 aqueous solution. Then organic layer washed with 500 ml of distilled water until the washing solution became neutral. After extract procedure, the organic chloroform layer dried with $MgSO_4$ for 6 h then filtered off. The chloroform removed by rotary evaporator under reduced pressure. After vacuum dry for 72 h, the dark-brown solid obtained (yield = 77%). ^{1}H-NMR, δ (ppm) : 1.64 (s, 6H), 2.31 (s, 6H), 3.95 (m, 2H), 4.17 (d, 8H), 6.81 (d, 4H), 6.96 (d, 2H), 7.12 (d, 4H), 7.50 ~ 7.55 (m, 6H), 7.82 (s, 2H), 7.84 (d, 2H), 7.96 (d, 4H), 8.02 ~ 8.07 (m, 8H). FT-IR (KBr, cm^{-1}): 3500 (OH stretching), 3117 ~ 3013 (CH of aromatic), 2973 ~ 2910 (CH_3 of aliphatic), 1606 (C=C of aromatic), 1578 (N=N of aromatic azo), 850 (CH of aromatic).

Polymerization of EBACN (pEBACN)

In a 100 ml of three neck round-bottom flask equipped with a condenser, 0.98 g of EBACN (1.25 mmol) was dissolved in 15 ml of THF and 1.5 ml of TEA. The reaction solution was kept at 0 ~ 5°C under dry nitrogen atmosphere. A dissolved solution of isophthaloyl chloride (0.25 g, 1.25 mmol) was added slowly to the reaction solution and then stirred for 24 h at 60°C under a dry nitrogen atmosphere. Then, reaction solution was poured into methanol. The precipitate was collected and vacuum dried for 48 h (yield = 65%). FT-IR (KBr, cm^{-1}): 3115 ~ 3014 (CH of aromatic), 2976 ~ 2835 (CH_3 of aliphatic), 2227 (CN cyano stretching), 1721 (C=O of ester stretching), 1600 (C=C of aromatic), 1571 (N=N of aromatic azo), 850 (CH of aromatic).

Polymerization of EBADY7 (pEBADY7)

In a 100 ml of three neck round-bottom flask equipped with a condenser, 1.95 g of EBADY7 (2 mmol) was dissolved in 20 ml of tetrahydrofuran (THF) and 2 ml of triethylamine (TEA). The reaction solution was kept at 0 ~ 5°C under dry nitrogen atmosphere. A dissolved solution of isophthaloyl chloride (0.4 g, 2 mmol) was added slowly to the reaction solution and then stirred for 24 h at 60°C under a dry nitrogen atmosphere. Then, reaction solution was poured into methanol. The precipitate was collected and vacuum dried for 48 h (yield = 63%). The synthetic routes are shown in Figure 1. FT-IR (KBr, cm^{-1}): 3117 ~ 3013 (CH of aromatic), 2973 ~ 2910 (CH_3 of aliphatic), 1737 (C=O of ester stretching), 1606 (C=C of aromatic), 1578 (N=N of aromatic azo), 850(CH of aromatic).

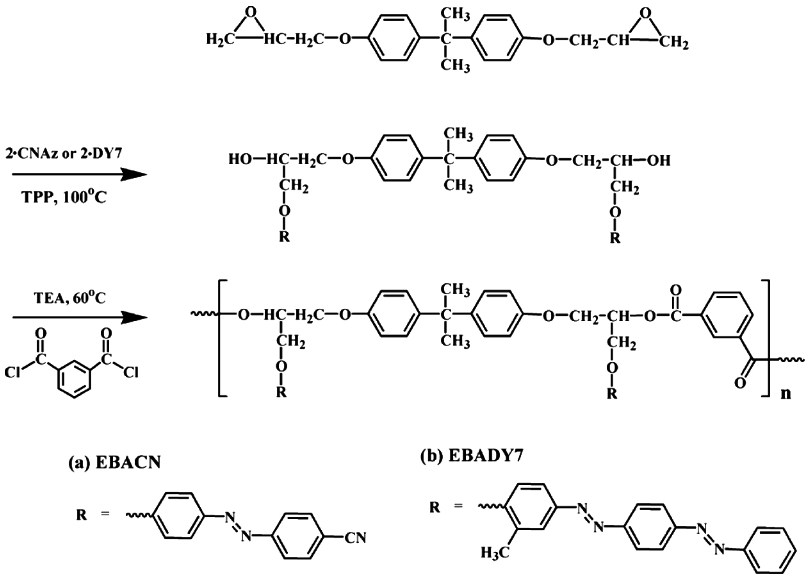

FIGURE 1 Synthetic routes of photoresponsive polyester. (a) EBACN and (b) EBADY7.

Film Preparation and Optical Characteristics

Polymer was dissolved in 1:1 mixture of tetrahydrofuran/chloroform at a concentration of 5 wt%. Then polymer solution was spin coated onto glass substrate at 700 rpm for 30 sec, providing a optically clear film (approx. thickness = 1.0 μm) by measured surface profiler (Kosaka Lab. Ltd., Surfcorder SE1700α). Measurement of photoinduced birefringence (Δn) was performed by the optical system reported previously [7]. The film was irradiated by a linear polarized Ar^+ ion laser beam (Coherent, $\lambda = 405$, 458, and 488 nm, irradiance = 1 W/cm^2). The birefringence was probed simultaneously with a He-Ne ($\lambda = 633$ nm) laser using a polarimeter (Thorlabs Co., PA410) and calibrated by film thickness.

RESULTS AND DISCUSSION

The reaction between epoxy resin, 2,2′-bis-(4-glycidyloxyphenyl)propane, and azobenzene compounds (CNAz and DY7 each) occurs in two stages. Firstly, TPP act as the catalyst to react epoxide ring. Then, hydroxy group of azobenzene compound reacts with epoxide group, yielding another hydroxy group in epoxy resin. Resulting compound formed film by spin coating, although its molecular weight was not so high, since the azobenzene modified epoxy resin, EBACN and EBADY7, shows good adhesion to glass substrate as well as clear film formation with 0.55 μm thickness.

Azobenzene diol, EBACN and EBADY7, were polymerized with dichloride monomer (isophthaloyl chloride) in presence of TEA as HCl by-product acceptor. These photoresponsive pEBACN and pEBADY7 also show clear film formation property. pEBACN and pEBADY7 showed the glass transition temperatures (T_g) of 78 and 110°C, respectively. The T_g of pEBADY7 was higher than the T_g of pEBACN due to the bulky pendant structure of DY7 moiety.

Figure 2 shows UV/VIS spectra of the CNAz and the DY7 as a function of various concentrations. The CNAz and the DY7 exhibited maximum absorption bands (λ_{max}) of 360 nm and 384 nm, respectively. The red-shifted λ_{max} of DY7 with respect to that of the CNAz chromophore is attributed to an extended π-conjugation of the DY7 chromophore. As shown in Figure 2, an optical density and absorption coefficiency of DY7 are relatively higher than CNAz chromophore at 488 nm. When irradiated with excitation beam, however, photoisomerization could be occurred satisfactorily in both cases.

Figure 3 shows the four selected Δn behaviors of blend film of pEBACN and pEBADY7 at (a) 1:0, (b) 2:1, (c) 1:4, and (d) 0:1 ratio from

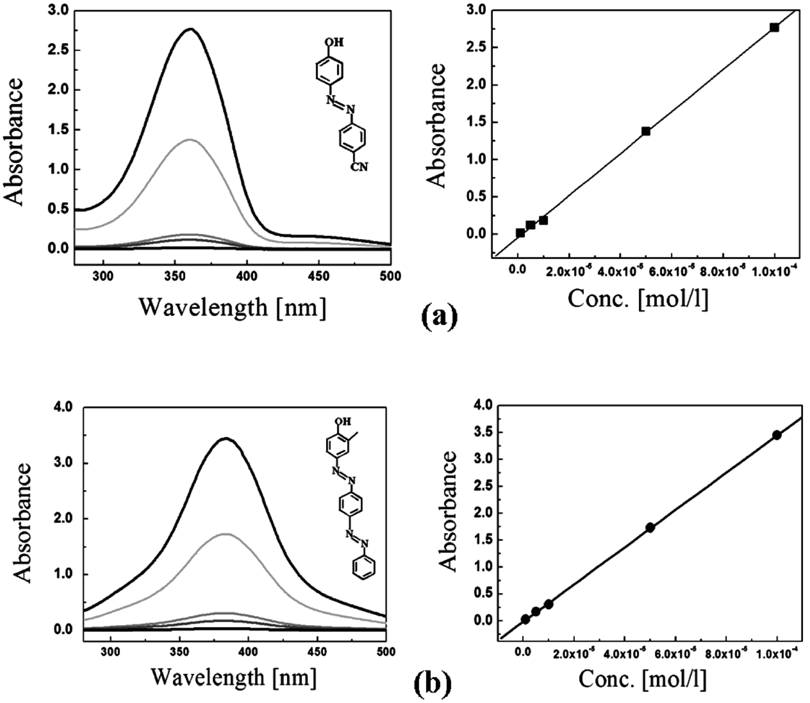

FIGURE 2 UV/Vis absorption spectra of azobenzene compounds with various concentrations dissolved in chloroform. (a) CNAz and (b) DY7.

a whole mixing ratio. These four films show the fast response time, less than 5 sec, calculated from the elapsed time that was required from 10 to 90% of the initial increase of the Δn value. The fast response of the blend film indicated that the optically triggered unidirectional aligned state of the chromophores could be induced immediately under the beam excitation. From the viewpoint of practical application, it is desirable to improve optical performance for holographic memory applications.

On the other hand, the absolute Δn values of above blend ratio were not large enough as was expected. Namely, the values were (a) 2.3×10^{-2}, (b) 4.3×10^{-2}, (c) 5.2×10^{-2}, and (d) 6.3×10^{-2}, respectively, that was determined by the subtraction of the initial value of Δn from the value at 300 sec. As a result, the observed Δn value was increased as the pEBADY7 ratio increased. In addition, a relaxation behavior after turn off the excitation beam was also similar, i.e., the relaxation was reduced with increasing the pEBADY7 ratio. This

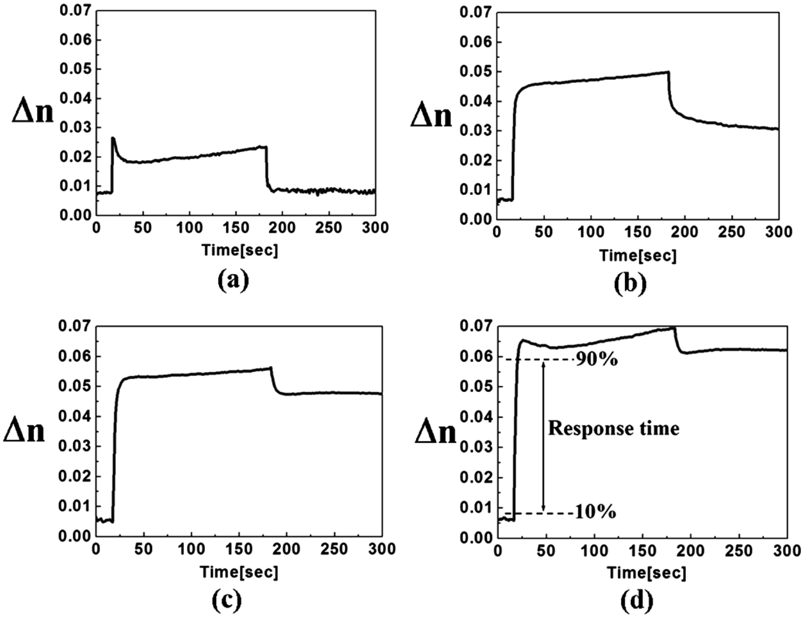

FIGURE 3 Photoinduced Δn of blend films with various mixing ratio. The excitation begins at 15 sec and is terminated at 180 sec. (a) pEBACN 100%, (b) pEBADY7 33%, (c) pEBADY7 80% and (d) pEBADY7 100%.

might be explained that the pEBADY7 could act as stabilizer for the reorientated state of photoresponsive moieties in the system.

In contrast to the pEBADY7 polymer film, the Δn values of EBADY7 monomer was 1.6×10^{-2}. This Δn value was smaller than that of the pEBADY7 polymer. However, the Δn was immediately relaxed to random state. From the comparison with the data of pEBADY7, the difference can be explained that the molecular weight of EBADY7 was not high enough to hinder the thermal agitation, even more the chromophore could easily move because there is no chain-entanglement like a polymer chain. In case of the EBADY7 doped system, that was mixed into poly(methylmethacrylate) matrix at the concentration of 10 wt%, the Δn values of 6.0×10^{-3} was observed when irradiated excitation beam. After turn off the excitation beam, the Δn was reduced only 28%. Consequently, polymer matrix could stabilize the reoriented state of a chromophore even in the doping system.

Figure 4 shows the Δn dependence on blending ratio of pEBADY7 and pEBACN observed with the excitation beams of (a) 405 nm, (b) 458 nm, and (c) 488 nm, respectively. The tendencies of Δn variation

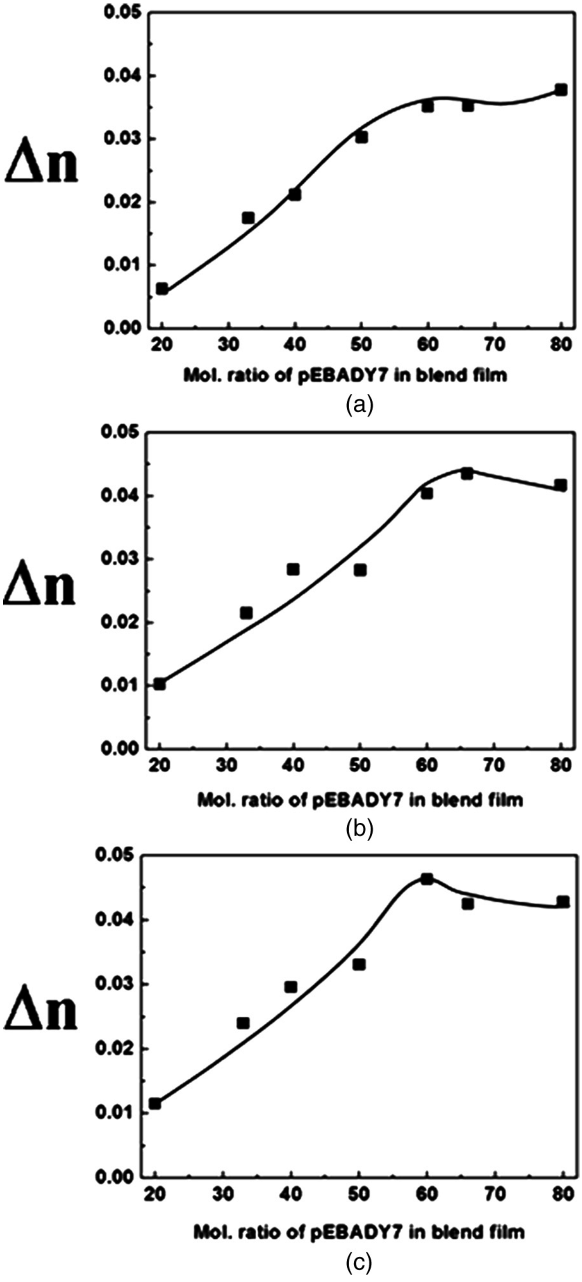

FIGURE 4 Blending ratio dependence of photoinduced birefringence irradiated by three excitation beams. (a) 405 nm, (b) 458 nm, and (c) 488 nm, respectively.

on the blending ratio for different wavelength excitation were similar in general. However, it was found that 458 nm excitation can induce the highest Δn value than the other wavelength at least in our experiment.

As shown in the figure, the Δn value increased with increase of the pEBADY7 content on the whole mixing ratio. However, there observed a broad peak at around 60 mol% of pEBADY7 concentration though the feature was not so obvious comparing to our PCDY50 copolymer previous reported [8,9]. However, the observed nonlinear response can be explained as the molecular cooperative motion has been brought about at an appropriate blending ratio. This tendency is agree with our previous result on the PCDY50. One of the possible reasons is that the effect of cooperative motion has not occurred effectively in the polymer blend of pEBADY7. It could be attributed to the miscibility problem of two polyesters and to the difference in microscopic arrangement of two photoresponsive moieties in the blend system.

CONCLUSIONS

New photoresponsive polyester containing CNAz and DY7 moiety have been synthesized and their photoinduced birefringence (Δn) were evaluated such as the Δn properties of azobenzene modified epoxy resin, doping system, its polymer, and its polymer blend. The pEBADY7 was effective to stabilize the reoriented state of chromophores in blend with pEBACN. In addition, it was shown that fast response behavior which can be used practical application for holographic memory.

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