Characterization of Pseudo Photorefractive Materials Based on Polyacrylate Containing 9-Oxo-9*H*-thioxanthene-10,10-dioxide Moiety

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Pseudo photorefractive effect was observed in composites based on polyacrylate containing 9-oxo-9*H*-thioxanthene-10,10-dioxide (TH) moiety doped with 4-(*N,N*-diethylamino)- β -nitrostyrene (DEANST), and in copolymers with both moieties without an external electric field. Lowering glass transition temperature of the composites by the addition of a low molecular weight plasticizer decreased the gain coefficients, and afforded unstable index grating. Due to the fact that the addition of stronger electron donating carbazole derivative also made the gain coefficient lower, charge transfer interaction between TH and DEANST plays an important role to establish the grating. Compared with the composite systems, the corresponding copolymers required the longer time to reach the saturated gain coefficient, indicating that the mass transfer of the electro-optically active moiety was essential to create the phase-shifted index grating with the interference pattern.

Keywords: Photorefractivity, Zero-electric field, 9-Oxo-thiothanthene-10,10-dioxide, Glass transition temperature

1. Introduction

Photorefractive (PR) phenomenon in an organic material was originally reported in 1990 [1]. Since then, a variety of organic PR materials have been intensively investigated including multi-functional polymers [2-8], composites consisting of a hole or an electron transporting polymer doped with an electro-optically active (EO) chromophore [9-13], multi-functional molecular glasses [14-21], because PR devices can be utilized in holographic optical data storages, and real time data processing. Among various classes of PR materials, the composites (host/guest systems) and multi-functional molecular glasses have attracted much attention due to their higher performance including higher diffraction efficiencies, and larger two beam coupling (2BC) gains as well as faster response.

For most of reported PR materials, a high external field is necessary to give rise to a PR effect via photocarrier generation, and drift/diffusion of carriers to build up the space-charge

field. This is one of the disadvantages of organic PR materials from the view point of practical applications. There have been several reports about pseudo PR effects without an external electric field [22-25]. Azo-dye doped silica glasses prepared via the sol-gel process followed by the heat induced densification with and without corona poling, showed 444 and 188 cm⁻¹ of gain coefficient in the absence of the external electric field, respectively [22]. Zhang et al. reported that carbazole based polyphosphazenes with azo-dye moieties exhibited large coupling gains [24,25]. Our group also reported that an amorphous film of asymmetric succinate containing electron accepting 9-oxo-9*H*-thioxanthene-10,10-dioxide and electron donating 4-amino- β -nitrostyrene moieties showed an asymmetric energy transfer (coupling gain; 42 cm⁻¹) without an external electric field [26]. An asymmetric energy transfer in a 2BC experiment, which is originated from the phase shift between the interference pattern of coherent beams and the

spatial modulation of resulting refractive index discriminates PR effect from other phenomena creating gratings of refractive index such as photoisomerization, and photochromism. Hitherto the exact mechanism has not been elucidated for the asymmetric energy transfer observed in above mentioned material systems similar to common PR active materials.

In this study, we report pseudo PR effect for composites based on polyacrylate containing 9-oxo-9*H*-thioxanthene-10,10-dioxide moiety (PTHA) and *N,N*-diethylamino- β -nitrostyrene, (DEANST), and copolymers containing both moieties. PTHA was originally reported by Sato et al. as an electron transporting polymer [27], and was utilized as a usual PR-host polymer [13]. The composites, PTHA / DEANST with low glass transition temperature (T_g) exhibited PR effect without a photosensitizer due to the charge transfer interaction electron accepting PTHA and electron donating DEANST. Compared with PR composites based on hole transporting poly(*N*-vinyl carbazole), PTHA / DEANST composites showed much higher response rate on the similar conditions. In 2BC experiments, the opposite sign of the phase shift was observed to confirm that the space charge field was established via electron transporting process. From the preliminary experiments, it is found that the composites with relatively high glass transition temperature show pseudo PR effect without an external electric field. The relationship between the properties of the composites like the glass

Fig. 1. Chemical structures of compounds used in this study.

transition temperature and the pseudo photorefractivity is discussed.

2. Experimental

2.1. Materials

Figure 1 shows the chemical structures of compounds used in this study. Acrylate monomer (THA) and its homopolymer (PHTA) were synthesized as described in previous papers [13, 26]. GPC analysis revealed that number average

Scheme 1. Synthetic root for FAA monomer and P(THA-*co*-NVAA).

Table 1. Preparation conditions and characteristics of copolymers.

P(THA- <i>co</i> -FAA)	Composition in mole (THA /FAA)		Yield ^c (%)	$M_n^d/10^3$	M_w/M_n^d	P(THA- <i>co</i> - -NVAA)	Yield ^c (%)	Weight ratio (THA /NVAA)
	feed ^a	polymer ^b						
S1 ^b	70/30	72/28	79.9	13.5	6.0	C1	71.6	78/22
S2 ^b	80/20	81/19	71.8	8.5	6.0	C2	77.6	86/14
S3 ^b	90/10	90/10	75.5	11.4	5.9	C3	82.0	93/7

^a Totally 10 mmol of monomers in DMF (8 mL). ^b Determined by ¹H-NMR. ^c For P(THA-*co*-FAA).

^d Determined by GPC. ^e For P(THA-*co*-NVAA).

molecular weight and polydispersity index of PTHA were 1.2×10^4 and 3.6, respectively. TH-Bu as a plasticizer [13], electron donating materials, DEANST [10] and 2,7-dimethoxy-9*H*-carbazole (DMCz) [28] were synthesized according to the literatures. All chemicals were commercially available and used as received.

2.2. 2-(*N*-4-Formylphenyl-*N*-methylamino)ethyl acrylate (FAA)

FAA, compound **5** was synthesized as described in Scheme 1. Starting material **1** [2-(*N*-methyl-*N*-phenylamino)ethanol] was converted to acetate, compound **2**, by the reaction with acetic anhydride followed by formylation with a Vilsmeier reagent prepared from phosphoryl chloride and *N,N*-dimethylformamide (DMF) to obtain compound **3**. Deprotection followed by a column chromatography (silica / ethyl acetate : chloroform 1:3) afforded compound **4**. Final step for FAA synthesis was as follows.

A 200-mL three-necked flask equipped with a magnetic stirrer, a condenser, a dropping funnel, and a nitrogen inlet was charged with 5.0 g (28 mmol) of compound **4**, 3.1 g (30 mmol) of triethylamine and 50 mL of tetrahydrofuran (THF) and the solution was cooled to 0 °C. The mixture of 4.0 g (44 mmol) of acryloyl chloride and 10 mL of THF was added dropwise. After 1 h stirring, the reaction vessel was allowed to warm to room temperature, and stirring was continued for 10 h. The reaction mixture was poured into water, and extracted with chloroform. The extract was washed with a dilute sodium bicarbonate solution. After the solvent evaporation, the residual solid was purified by a column chromatography (silica gel, ethyl acetate / chloroform=1/3). Product was obtained as a viscous liquid (yield; 4.3 g, 66%). ¹H-NMR (CDCl₃) δ from TMS: 9.70 (s, 1H, CHO), 7.68 (d, *J*=8.9 Hz, 2H, Ar), 6.74 (d, 1H, *J*=8.9 Hz, 2H, Ar), 6.35 (dd, *J*=17.0, 1.5 Hz, 1H, -CH=CH₂), 6.04 (dd, *J*=17.0, 10.5 Hz, 1H, -CH=CH₂), 5.90 (dd, *J*=10.5, 1.5 Hz, 1H, -CH=CH₂), 4.38 (t, *J*=5.2 Hz, 2H,

CH₂=CHCOOCH₂CH₂N-), 3.74 (CH₂=CHCOO-CH₂CH₂N-), 3.07 (s, 3H, N-CH₃).

2.3. Copolymer of THA with FAA [P(THA-*co*-FAA)](S1-S3)

Copolymerization of THA with FAA (totally 10 mmol of monomers with different ratio) were carried out in a glass ampule under a dry nitrogen atmosphere at 70 °C for 24 h using 2,2'-azobis(isobutyronitrile) (1 wt% of monomers), and 8 mL of DMF as an initiator and a solvent, respectively. The reaction mixture was poured into a large amount of methanol. Recovered polymers were purified 2-3 times by a reprecipitation of chloroform solution into hot ethanol, followed by drying in vacuo. Polymerization conditions and characteristics of resulting copolymers are summarized in Table 1.

2.4. Conversion of P(THA-*co*-FAA) to P(THA-*co*-NVAA) (C1-C3)

Into a 50-mL three-necked flask equipped with a magnetic stirrer, a condenser and a nitrogen inlet were added 0.87 g of P(THA-*co*-FAA), 5.0 mL of chloroform, 10 mL of nitromethane, and 0.17 g of ammonium acetate. The reaction mixture was refluxed at 80 °C for 15 h, and then was poured into ethanol to recover the product as a red powder.

2.5. Measurements

NMR spectra were recorded at 50 °C with JEOL α -500 spectrometer operating at 500 MHz for ¹H and 125 MHz for ¹³C. Absorption coefficients at 633 nm were determined for PR devices using a JASCO V-570 UV/VIS/NIR spectrophotometer. The molecular weights of synthesized polymers were estimated by gel permeation chromatography using a column packed with styrene-divinylbenzene gel beads [29]. Chloroform was used as an eluent and the molecular weight was calibrated using polystyrene standards (Shodex). Glass transition temperature (*T*_g) was determined from a differential scanning

Fig. 2. ^1H -NMR spectra of P(THA-*co*-FAA) (S1) (a) and P(THA-*co*-NVAA) (C1) (b) measured in CDCl_3 at 50°C and 500 MHz.

calorimetry (DSC) chart recorded by Rigaku Thermo plus DSC 8230 under nitrogen at heating rate of $10^\circ\text{C}/\text{min}$.

2.6. PR measurement

PR devices were prepared as follows: the composite or the copolymer was dissolved in 1,2-dichloroethane at ca. 10 wt%. The solution was filtered through a $0.5\ \mu\text{m}$ filter, concentrated to around the one-third volume and dropped on a glass slide or an indium tin oxide (ITO, $30\ \Omega$) covered glass. After the evaporation of the solvent, the sample was heated with hot plate at about 60°C and the surface was covered with another glass to form a thin film sandwiched by two transparent electrodes. The sample thickness was given by approximately $100\ \mu\text{m}$ a Teflon spacer use.

The PR properties were studied by the two-beam coupling (2BC) and four-wave mixing (FWM) techniques using experimental setup described elsewhere [13]. Holographic grating was written using coherent beams from an NEC GLS-5410 He-Ne laser operating at 633 nm. All experiments were carried out at room temperature ($22 \pm 2^\circ\text{C}$). In 2BC experiments, the incoming laser beam (p-polarized) was split into two writing beams with the same intensity ($110\ \text{mW}/\text{cm}^2$). The two writing beams with an angle of 20° were directed onto the

sample, which was normal to the bisector of the two writing beams. The transmitted beam intensities were monitored with photodiodes (Hamamatsu Photonics, S2281). In FWM experiments, two s-polarized beams of equal intensity ($110\ \text{mW}/\text{cm}^2$) wrote a grating, which was probed by a much weaker p-polarized beam ($0.8\ \text{mW}/\text{cm}^2$) counter-propagating to one of the writing beams.

3. Results and discussion

3.1. Synthesis of P(THA-*co*-NVAA)

As a preliminary experiment, the copolymerization of THA with the corresponding acrylate monomer, 2-(*N*-4- β -nitrovinylphenyl-*N*-methylamino)ethyl acrylate (NVAA) was carried out to obtain the target copolymers in a similar way described in Section 1. No polymeric products were obtained probably due to the degradative chain transfer to nitrovinyl group [30]. As the alternative, post functionalization was adopted to prepare the target copolymers.

As the first step, the copolymerization of THA with FAA was conducted to obtain precursor copolymer [P(THA-*co*-FAA)]. The copolymers with different chemical compositions were successfully obtained, and the characteristics of resulting copolymers were listed in Table 1. As reported in the literature [31], benzaldehyde moiety does not impede the conventional polymerization. The values of M_w/M_n are, however, larger than that of homopolymer, suggesting the possibility of the extraction of aldehyde hydrogen leading to the branched structure in the copolymers. Then, Knoevenagel condensation was carried out to convert the formyl group to the nitrovinyl group.

As shown in Fig. 2, it was found that the formyl group was completely converted to the nitrovinyl group via a Knoevenagel condensation. Characteristics of copolymers are shown in Table 1.

3.2. Two-beam coupling

Table 2 lists the characteristics of the PTHA based composites and copolymers including the absorption coefficient (α), and the glass transition temperature (T_g) accompanied with the coupling gain representing pseudo photorefractivity. In 2BC experiments, the coupling gain coefficients were calculated using the following equation (1),

$$\Gamma = (\cos \theta / L) [\ln(\gamma_0 \xi) - \ln(\xi + 1 - \gamma_0)] \quad (1)$$

Table 2. Characteristics of pseudo PR materials.

	weight ratio	α^c (cm^{-1})	T_g^d ($^{\circ}\text{C}$)	Γ^e (cm^{-1})
D1 ^a	90/10/0/0	20	60.0	75.0
D2 ^a	80/20/0/0	33	50.2	61.0
D3 ^a	70/30/0/0	42	38.0	0
D4 ^a	80/10/10/0	21	46.8	76.0
D5 ^a	70/10/20/0	21	40.3	72.0
D6 ^a	60/10/30/0	21	36.0	45.7
D7 ^a	50/10/40/0	26	26.7	0
D8 ^a	90/8/0/2	25	63.0	48.0
D9 ^a	90/5/0/5	20	66.5	20.5
D10 ^a	90/2/0/8	15	69.5	0
C1 ^b	78/22	24	100.3	120
C2 ^b	86/14	11	114.2	54.5
C3 ^b	93/7	6.3	119.5	3.3

^a PTHA / DEANST / TH-Bu / DMCz. ^b THA / NVAA.^c Absorption coefficient at 633 nm. ^d Glass transition temperature. ^e Maximum coupling gain coefficient.

where L is the sample thickness, ξ is the ratio of the two beam intensities, $\gamma_0 = I / I_0$ is the beam coupling ratio where I_0 is the intensity without the pump beam, and I is the intensity with pump beam on, and θ is the incident angle of beam inside the sample.

Although the composites with 10 and 20 wt% of DEANST showed the relatively higher gain coefficient compared with the molecular glass without an external electric field [26], that of 30 wt% of DEANST exhibited no asymmetric energy transfer. This composite showed “normal” photorefractivity with an external electric field ($\Gamma = 64 \text{ cm}^{-1}$ at $50 \text{ V}/\mu\text{m}$ [13]). As previously reported, the charge transfer interaction exists between PTHA and DEANST. The absorption coefficient of the composite (D1-D3 in Table 2) increased with the content of DEANST. On the contrary, the 2BC gain coefficient decreased as the increase of DEANST content accompanied with the decrease of T_g . We assumed that T_g plays an important role to exhibit pseudo PR properties at zero electric field. Although it is generally recognized that the materials with T_g around room temperature show high diffraction efficiency, large coupling gain, and fast response, higher T_g is essential in this case. To verify the assumption, we investigated the effect of T_g on the coupling gain using the composites with the same DEANST content and different T_g (D1, D4-D7), where PTHA was partially replaced by the low molecular weight TH-Bu (Fig. 1). As shown in Table 2, these composites have almost the same absorption coefficient (α), and T_g was decreased with the TH-Bu content. It seems that Γ was

Fig. 3. Time dependence of coupling gain coefficient for PR composites with different glass transition temperature (D1, D4, D5, D6) without external electric field.

Fig. 4. Time dependence of coupling gain coefficient for PR composites (D1, D2) and copolymers (C1, C2) without external electric field.

dependent on the T_g , as we assume. For D7 with T_g of 26.7°C , no asymmetrical energy transfer was observed.

Figure 3 shows the time dependence of coupling gain for each composite. With the decrease of T_g (D4 and D5), the required time to reach maximum value (response time) seems to be shortened. However, the gain coefficient decreased after the maximum value indicative of the instability of the established index grating. It is found that high T_g is essential not only for the pseudo photorefractivity without an external electric field, but for the stable index grating.

It is assumed that CT interaction between PTHA and DEANST makes it possible to absorb the light resulting in the formation of index grating. We

investigated the effect of the addition of another electron donor, DMCz (Fig. 1) on the 2BC gain coefficient to confirm the assumption. As shown in Table 2 (D1, D8-10), the addition of DMCz decreased the Γ value. DMCz, stronger electron donor exhibited CT interaction with PTHA, but did not afford the index grating probably due to the smaller dipole moment and weaker birefringent nature compared with DEANST. It is predicted that the origin of index grating is the photo-alignment of DEANST resulting from photoisomerization [32], and the following the diffusive mass transfer.

Figure 4 shows the time dependence of coupling gain for the comparison of copolymers and composites (C1, C2, D1, and D2). The copolymer C3 showed only 3.3 cm^{-1} , although the content of NVA moiety was comparable to the DEANST content in D1. According to the lower absorption coefficients in C3, it is considered that the formation of CT complex was impeded due to the lack of translational or rotational freedom of NVA moiety. Although C2 showed the lower absorption coefficient compared with D2, similar Γ values were obtained for C2 and D2. It is noteworthy that more stable index grating was formed in C2 indicating that the relaxation process is suppressed in C2 because of the higher T_g and restriction of mobility of NVA unit. The highest Γ was obtained in C1, and the resulting index grating seemed stable. However, compared with D1, the longer writing time was required for the saturation for C1, indicating that the photo-alignment of NVA moiety and the following the diffusive mass transfer is important for the establishment of index grating phase-shifted with the interference pattern.

3.3. Four wave mixing

Figure 5 shows the time dependence of diffraction efficiency for D1 and C2. The diffraction efficiency presented here was determined by the ratio of the intensity of diffracted signal to that of incident reading beam. Higher diffraction efficiency (28.8%) was observed in D1. In contrast to 2BC experiments, the formation of phase-shifted index grating is not necessary for the holographic diffraction. The higher response observed for D1 was attributed to more facile photo-alignment of DEANST moiety compared with C1. Since the stability of index grating formed in C1 was verified by 2BC result, it is considered that the decrease of diffraction efficiency after 120 min was due to the overmodulation of the index grating [9,33].

Fig. 5. Time dependence of diffraction efficiency for PR composite (D1) and copolymer (C1).

4. Conclusion

Pseudo photorefractivity was investigated for the composites based on polyacrylate containing 9-oxo-9*H*-thioxanthene-10,10-dioxide (TH) moiety and 4-(*N,N*-diethylamino)- β -nitrostyrene (DEANST). The addition of TH analogue with low molecular weight, electron donating carbazole derivative as the third components revealed that the higher glass transition temperature and the charge transfer interaction between the polymer and DEANST play important roles in the establishment of stable index grating resulting from the photo-alignment, and the diffusive mass transfer. The copolymers consisting of both moieties also exhibited pseudo photorefractivity. Higher glass transition temperature of the copolymers made the resulting index grating more stable.

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