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Synthesis and Characterization of Photorefractive Polymer Containing Electron Transport Material

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An acrylate type monomer was prepared by the reaction of 2-hydroxyethyl acrylate with 9-oxo-9*H*-thioxanthene-3-carboxylic acid 10,10-dioxide and was polymerized using AIBN as an initiator and *N*,*N*-dimethylformamide as a solvent to yield a polymer containing a thioxanthene unit (P-THEA). The resulting polymer had a number-average molecular weight of 18 000 and a glass-transition temperature of 113 °C. Photorefractive (PR) composites consisting of P-THEA as an electron-transporting component, 4-*N*,*N*-diethylamino-*E*-*β*-nitrostyrene (DEANST) as a nonlinear optical chromophore, and butyl 9-oxo-9H-thioxanthene-3-carboxylate 10,10-dioxide (TH-^{n}Bu) as a plasticizer were prepared. These composites had an absorption coefficient of 11−33 cm^{-1} at 633 nm and glass-transition temperature of 32−42 °C. A PR device with a thickness of 100 μm was fabricated by sandwiching the PR composite between two ITO coated glasses. The electric field and DEANST concentration dependencies of the gain coefficients and diffraction efficiency were investigated by two-beam coupling and four-wave mixing methods. The electron-transporting nature of PR composite was confirmed by the comparison of the sign of coupling coefficient with that of a PVK-based composite.

Introduction

Photorefractivity was originally observed in inorganic crystals, which show a photoconductivity and a linear electrooptic response simultaneously.[1] Photocharges generated in a photorefractive (PR) material by a spatially modulated light migrate through drift and/or diffusion processes and eventually are trapped. The resulting internal space-charge field modulates the material's refractive index via the linear electrooptic (EO) effect (also known as the Pockels effect). Organic PR materials have also been investigated intensively this decade, due to their low dielectric constants, large optical nonlinearity, and structural flexibility compared to inorganic PR materials.[2] High PR performance, such as high diffraction efficiency, large coupling gain, and fast response, has been observed for host−guest systems with low glass transition temperature (T_g) consisting of a photoconducting polymer, an EO chromophore, and a small amount of a photosensitizer.[3] To lower the T_g, a plasticizer has sometimes been utilized. In these composite materials, large index modulation is believed to come primarily from orientational photorefractivity that is related to the polarizability anisotropy of the dopant chromophore.[3−5]

As a photoconducting host polymer, a hole-transport polymer, especially poly(vinyl carbazole) (PVK), has been exclusively used. Despite the extensive efforts to avoid the crystallization of EO molecules or to extended the durability of PR device,[6,7] crystallization or aggregation of EO chromophores is an inherent problem that limits the lifetime of PR devices.

In contrast to hole-transporting materials, a relatively small number of studies have been conducted for electron-transporting materials.[8] The materials that have been under investigation are mainly molecularly doped systems consisting of inert polymers and electron-transporting molecules such as fluorenone,[9,10] thiopyran,[11] and thioxanthene[12] derivatives. We developed electron-transporting polymer containing fluorenone[13] or thioxanthene[14] derivatives, which had the drift

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mobility of 3.5×10^{-6} and 7.0×10^{-7} cm^2/V s at 6.4×10^5 V/cm, respectively. These values are higher than those observed for molecularly doped systems because of the higher concentration of electron-transporting units. Furthermore, these polymers show excellent morphological stability compared with molecularly doped systems.

In this paper, we applied the electron-transporting polymer having a thioxanthene unit to a host polymer of a photorefractive composite. As far as we know, this is the first report of the utilization of electron-transporting polymer in this field. It is demonstrated that an electrical interaction between a thioxanthene unit and EO chromophore existed and that the stability of the composite increased compared with the conventional composite based on PVK, even though the concentration of EO chromophore was fairly high. Photorefractivity was investigated in relation to the amount of EO chromophore.

Experimental Section

Synthesis. All reagents were obtained commercially and were used without further purification otherwise noted.

9-Oxo-9*H*-thioxanthene-3-butyloxycarbonyl-10,10-dioxide (TH-^{n}Bu). Into a 200 mL three-necked flask fitted with a mechanical stirrer and a condenser were added 10.0 g (0.035 mol) of 9-oxo-9*H*-thioxanthen-3-carboxylic acid 10,10-dioxide (Aldrich) dissolved in 125 mL of *N*,*N*-dimethylformamide (DMF), 3.50 g (0.042 mol) of sodium hydrogen carbonate, and 5.70 g (0.042 mol) of 1-bromobutane. After stirring at 45 °C for 2 h, the reaction mixture was poured into 500 mL of water and the precipitate was collected by filtration. The precipitate was washed with distilled water and a small amount of cold methanol, successively. The residue was purified by column chromatography (silica gel, chloroform) to yield 9.12 g (0.026 mol, 74%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.78 (d, 1H, $J = 1.0$ Hz, Ar$-$H), 8.38 (d, 2H, $J = 1.0$ Hz, $2 \times$ Ar$-$H), 8.33 (dd, 1H, $J = 7.5, 1.0$ Hz, Ar$-$H), 8.18 (1H, dd, $J = 7.5, 1.0$ Hz), 7.89 (dt, 1H, $J = 7.5, 1.0$ Hz, Ar$-$H), 7.80 (dt, $J = 7.5, 1.0$ Hz, Ar$-$H), 4.42 (t, 2H, $J = 7.0$ Hz, $-$OCH_2-), 1.81 (m, 2H, $-$OCH$_2$CH_2-), 1.50 (m, 2H, $-$OCH$_2$CH$_2$CH_2-), 1.01 (t, 3H, $J = 7.0$ Hz, CH_3).

2-Acryloyloxyethyl-9-oxo-9*H*-thioxanthene-3-carboxylate 10,10-Dioxide (THEA). To a 1000 mL three-necked flask fitted with a mechanical stirrer and a condenser were added 30.0 g (0.104 mol) of 9-oxo-9*H*-thioxanthene-3-carboxylic acid 10,10-dioxide, 54.4 mL (0.520 mol) of 2-hydroxylethyl acrylate, and 500 mL of dry tetrahydrofuran (THF) under nitrogen atmosphere. To the reaction mixture were added 1.26 g (0.0104 mol) of 4-*N*,*N*-dimethylaminopyridine and 23.6 g (0.114 mol) of *N*,*N*′-dicyclohexylcarbodiimide. The reaction mixture was stirred at room temperature for 24 h. After the addition of 5 mL of distilled water and filtration of the resulting dicyclohexylurea, the concentrated solution was poured into 1000 mL of water and white powder was precipitated. The chloroform solution of the white powder was washed with 0.1 N hydrogen chloride solution, 15% aqueous sodium hydrogen carbonate and water, successively. After the evaporation of the chloroform, the residual powder was purified by recrystallization (THF/methanol 1/2) to yield 23.2 g (0.060 mol, 58%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.79 (s, 1H, Ar$-$H), 8.39 (m, 2H, $2 \times$ Ar$-$H), 8.33 (dd, 1H, $J = 8.0, 1.5$ Hz, Ar$-$H), 8.19 (dd, 1H, $J = 8.0, 1.5$ Hz, Ar$-$H), 7.89 (dt, 1H, $J = 7.5, 1.5$ Hz, Ar$-$H), 7.80 (dt, 1H, $J = 7.5, 1.5$ Hz, Ar$-$H), 6.45 (dd, 1H, $J = 17.0, 1.5$ Hz, CH$=$CH_2), 6.17 (dd, 1H, $J = 17.0, 10.5$ Hz, C$H$$=CH_2$), 5.87 (dd, $J = 10.5, 1.5$ Hz, CH$=$CH_2), 4.66 (m, 2H, CH$_2$$=$CHCOOC$H_2CH_2$O), 4.55 (m, 2H, CH$_2$$=$CHCOOCH$_2CH_2$O); ^{13}C NMR (125 MHz, CDCl$_3$) δ 177.9, 165.7, 163.6, 141.5, 141.1, 135.4, 134.9, 133.7, 133.5, 133.3, 131.4, 130.6, 129.5, 129.3, 127.9, 125.0, 123.6, 63.9, 61.8.

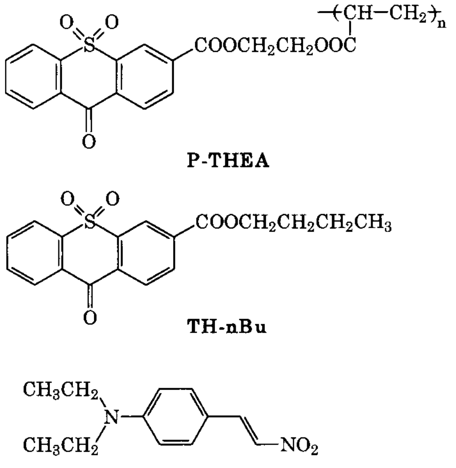

Figure 1. Chemical structures used for PR composites.

Polymer (P-THEA). A glass ampule was charged with 3.0 g (7.8 mmol) of THEA, 12.8 mg (7.8×10^{-2} mmol) of 2,2′-azobis(isobutyronitrile), and 7.8 mL of DMF in a dry nitrogen atmosphere and sealed. DMF was purified by distillation under reduced pressure. After polymerization at 70 °C for 24 h, the reaction mixture was poured into a large amount of acetone. The recovered polymer was purified by reprecipitation of a chloroform solution into methanol, followed by drying in vacuo.

Measurements. NMR spectra were recorded at 50 °C with a JEOL α-500 spectrometer operating at 500 MHz for ^{1}H and at 125 MHz for ^{13}C. UV spectra were obtained with a JASCO V-500 UV/VIS/NIR spectrometer. The molecular weights of synthesized polymers were estimated by gel permeation chromatography using a column packed with styrene$-$divinylbenzene gel beads. Chloroform was used as an eluent and the molecular weight was calibrated using polystyrene standards (Shodex). The glass transition temperature (T_g) was determined from a differential scanning calorimetry (DSC) chart that was recorded by a SEIKO Instruments DSC 220 under nitrogen at heating rate of 10 °C /min.

PR Sample Preparation and Measurements. All the chemical structures of materials used for PR composites are shown in Figure 1. PR devices were fabricated as follows. The mixture of P-THEA, TH-^{n}Bu, and 4-*N*,*N*-diethylamino-*E*-β-nitrostyrene (DEANST), which was prepared according to the literature,[15] was dissolved in 1,2-dichloroethane. The solution was filtered through a 0.5 μm filter and then heated to 40 °C for solvent evaporation until a highly viscous solution was obtained. The resulting solution was dripped on indium tin oxide (ITO, 30 Ω/□) covered glass substrate. After the evaporation of solvent, sample was heated with a hot plate at about 60 °C at which temperature the composite was softened. The composite was sandwiched with another ITO covered glass. The sample thickness was controlled to be approximately 100 μm with the use of a Teflon spacer.

The photorefractive properties of the P-THEA/DEANST/TH-^{n}Bu composites were studied by the two-beam coupling (2BC) and four-wave mixing (FWM) techniques. Holographic grating was written using coherent beams from an NEC GLS-5410 He$-$Ne laser operating at 633 nm. All experiment were carried out at room temperature(22 ± 2 °C). The detailed experimental geometry for the 2BC and FWM experiment is shown in Figure 2. In 2BC experiments, the incoming laser beam (*p*-polarized) was split into two writing beams (beams 1 and 2) with equal intensity (130 mW/cm^2). The two writing beams with an angle of 20° were directed onto the sample, which was tilted at an angle of 50° with respect to the bisector of the two writing beams to achieve a nonzero projection of the EO coefficients. The transmitted beam intensities were monitored with photodiodes (Hamamatsu Photonics, S2281). In the FWM experi-

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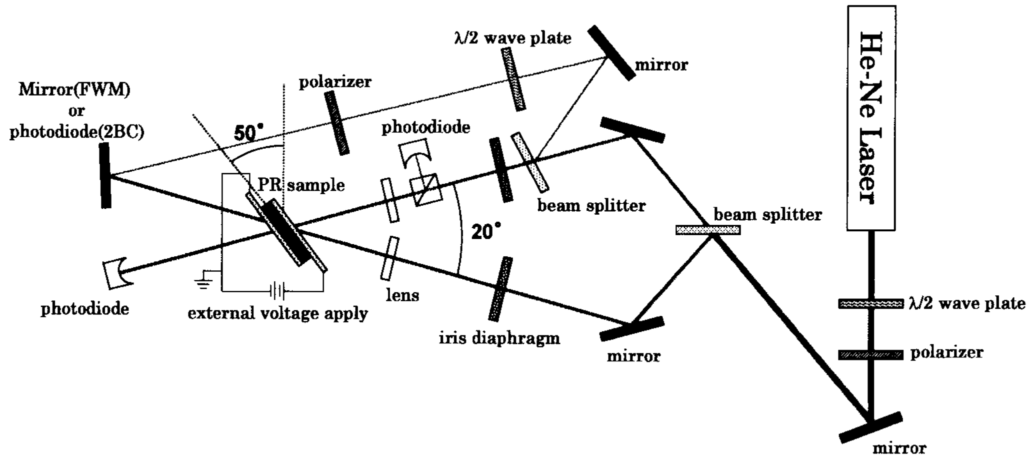

Figure 2. Experimental setup for 2BC and FWM: laser wavelength, 633 nm; tilt angle, 50°; two writing beams angle, 20°; beam intensity of writing and reading, 130 and 0.8 mW/cm^2, respectively. All measurements were carried out in room temperature (18−22 °C).

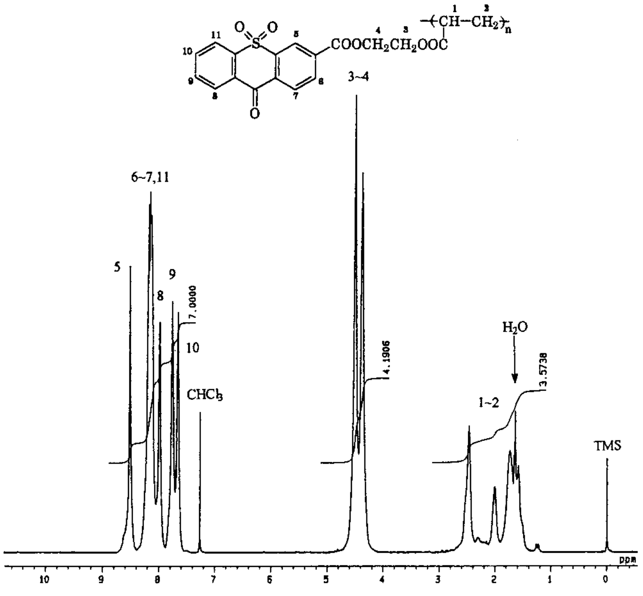

Figure 3. ^{1}H NMR spectrum of P-THEA in CDCl$_3$ at 50 °C and 500 MHz.

ments, two *s*-polarized beams of equal intensity (130 mW/cm^2) wrote a grating, which was probed by a much weaker *p*-polarized beam (0.8 mW/cm^2) counter-propagating to one of the writing beams, as shown in Figure 2.

Results and Discussion

Characterization of Polymer and PR Composite. Synthesized acrylate, THEA, was radically polymerized using AIBN as an initiator to obtain an electron-transporting polymer. Figure 3 shows the ^{1}H NMR spectrum of P-THEA, where all the signals were assigned to the protons in the expected structure. The number- and weight-average molecular weights of P-THEA were 17 900 and 47 000, respectively. P-THEA shows the glass transition at 113 °C.

Table 1. Absorption Coefficients and T_g of the P-THEA/DEANST/TH-^{n}Bu Composites

no.	P-THEA (wt %)	DEANST (wt %)	TH-^{n}Bu (wt %)	α (cm^{-1})	T_g (°C)
1	100	0	0	0	113
2	90	0	10	0	70
3	90	10	0	12	63
4	80	0	20	0	43
5	80	20	0	22	47
6	70	0	30	0	25
7	70	30	0	33	42
8	70	20	10	24	38
9	70	10	20	11	32

Table 1 shows the absorption coefficients and T_g of the P-THEA/DEANST/TH-^{n}Bu composites with 100 μm thickness. The absorption coefficient of the composite at 633 nm increased with the concentration of DEANST molecules. For comparison, the composites consisting of poly(methyl methacrylate) and DEANST were also prepared. Because of the tail of the absorption of DEANST, these composites with 100 μm thickness show the absorption coefficients of 1.0 and 1.3 cm^{-1} for those containing 20 and 30 wt % of DEATST, respectively. These values are much smaller than those observed in P-THEA/DEANST/TH-^{n}Bu. P-THEA and TH-^{n}Bu are completely transparent at this wavelength. These results indicate that the electrical interaction exists between P-THEA and/or TH-^{n}Bu and DEANST. The thioxanthene moiety has electron-withdrawing groups and can play the role of electron acceptor. On the other hand, the DEANST molecule is considered to have an electron-donating nature because of the existence of the electron-donating diethylamino group. Therefore, it is considered that a charge-transfer interaction between DEANST molecules and thioxanthene units exists in the composites. It is expected that this interaction increases the solubility of EO chromophore in the electron-transporting polymer and the morphological stability of a composite. Our PR materials would have the ability of charge generation without adding the charge generator or photosensitizer due to the absorption by the charge-transfer complex. It was also found that absorption coefficients were not affected, even if a part of the P-THEA was replaced with TH-^{n}Bu.

As shown in Table 1, the T_g values of the composites were dependent on the content of the both small molecules, i.e., DEANST and TH-^{n}Bu. Therefore, the addition of TH-^{n}Bu made it possible to obtain PR composites with different DEANST contents and almost the same T_g. In the following section, we used composites **7** to **9** for PR device fabrication. EO chromophore could be aligned by an applied electric field at room temperature, since the glass-transition temperature of

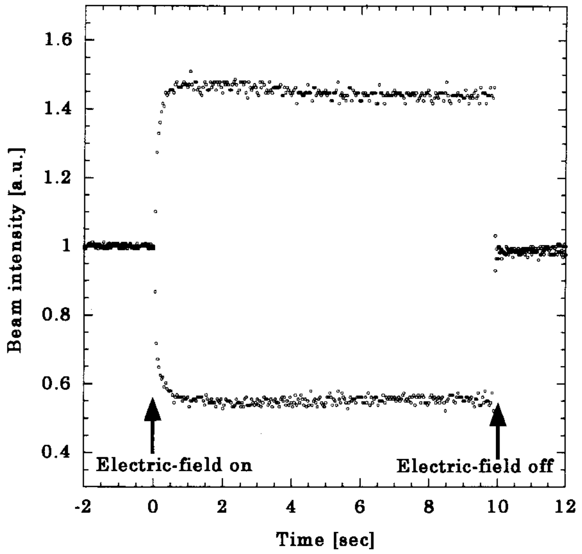

Figure 4. Asymmetric energy transfer observed for P-THEA/DEANST = 70/30 composite in a 2BC experiment; dc external electric field of 50 V/μm was applied at 0 s and was off at 10 s.

these composites ranged 32−42 °C. Therefore, no poling was performed before the measurements. These composites have good optical quality, and the crystallization or phase separation of DEANST or TH-^{n}Bu was not observed after fabrication.

Photorefractivity. Two-Beam Coupling. To verify the photorefractivity of the composites, a 2BC experiment was performed by switching on and off the applied electric field. Because of the low T_g of the composites, the EO chromophore (DEANST) can be easily oriented by the applied electric field. Figure 4 shows an asymmetric energy transfer of P-THEA/DEANST = 70/30 in a 2BC experiment at 50 V/μm. When the electric field was applied, a clear asymmetric energy transfer between the two beams was observed. One beam gained the energy, while the other lost. When the direction of the electric field was changed, the direction of the energy transfer was reversed. The asymmetric energy transfer was observed for all the composites, which clearly indicated their photorefractive nature.

To calculate the 2BC gain coefficient of the composites, the subsequent 2BC experiments were performed by chopping one of the two incident beams and monitoring the transmitted intensity of the second beam with a photodiode. The 2BC-gain coefficient Γ was calculated from the following equation,[16]

$$\Gamma = (1/L)\ \ln\ [\gamma\beta/(\beta + 1 - \gamma)]$$

where L is the optical path, β is the intensity ratio of the two incident beams, and γ is beam coupling ratio.

Figure 5 shows the electric field dependence of the gain coefficients measured for the three composites of P-THEA/DEANST/TH-^{n}Bu. It is indicated that the gain coefficient increased with the applied electric field for all the composites and it also increased with the DEANST content at a given electric field. From the point of view of the practical optical amplification, gain coefficients (Γ) must exceed the absorption loss (α) of a photorefractive sample. For the samples of the P-THEA/DEANST = 70/30 and P-THEA/DEANST/TH-^{n}Bu = 70/20/10, the net gain coefficients (Γ − α) was observed over 35 and 60 V/μm, respectively.

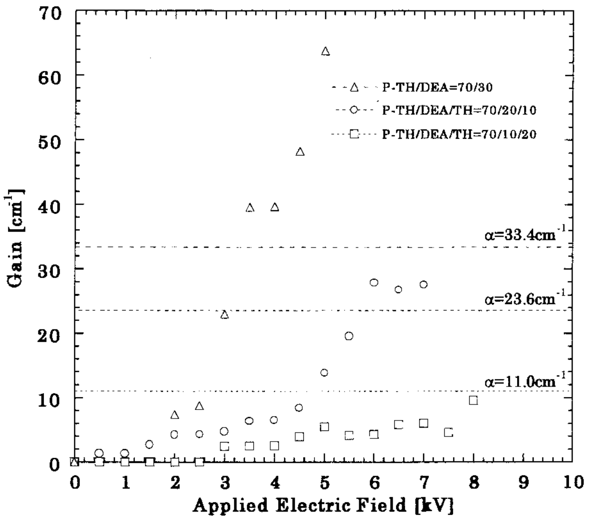

Figure 5. Electric field dependence of the gain coefficients: triangle, P-THEA/DEANST = 70/30; circle, P-THEA/DEANST/TH-^{n}Bu = 70/20/10; square, P-THEA/DEANST/TH-^{n}Bu = 70/10/20.

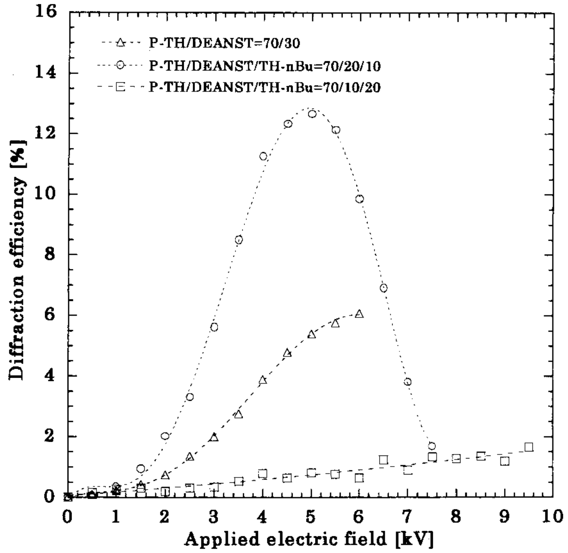

Figure 6. Electric field dependence of the diffraction efficiency. Symbols are the same as those in Figure 5.

Four-Wave Mixing. Figure 6 shows the electric field dependencies of the steady-state diffraction efficiency. The diffraction efficiencies increased with the applied electric field and reached a maximum for P-THEA/DEANST/TH-^{n}Bu = 70/30/0 and 70/20/10, 60 and 50 V/μm, respectively. Diffraction efficiency increased in the order P-THEA/DEANST/TH-^{n}Bu 70/20/10 > 70/30/0 > 70/10/20. The diffraction efficiency presented in Figure 6 was determined by the ratio of the intensity of diffracted signal to that of incident reading beam. Since our PR composites show fairly high optical absorption, as shown in Table 1, the intensity of diffracted signal as well as that of the incident beam were depressed. Therefore, the diffraction efficiency was underestimated. For example, in the case of the sample of P-THEA/DEANST = 70/30, the transmitted beam intensity was decreased to only about 30% of incident

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Table 2. Properties of the Photorefractive Composite Materials at 50 V/μm

composite	ratio (wt %)	T_g (°C)	α (cm^{-1})	η (%)	τ (s)	Γ (cm^{-1})	$\Gamma - \alpha$ (cm^{-1})
P-THEA/DEANST	70/30	42	33	5.4	0.22	64	31
P-THEA/DEANST/TH-^{n}Bu	70/20/10	38	24	12.7	0.41	14	−10
P-THEA/DEANST/TH-^{n}Bu	70/10/20	32	11	0.8	0.27	6	−5
PVK/DEANST/ECZ/C$_{60}$	65/30/5/0.2	38	8	10.0	2.8	31	24
PVK/DEANST/ECZ/C$_{60}$	70/20/10/0.2	35	9	3.2	1.4	19	10

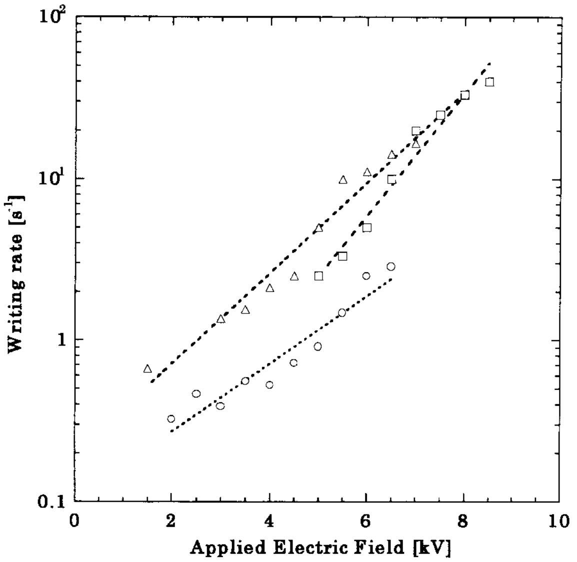

Figure 7. Electric field dependence of the writing rate at 130 mW/cm^2 writing intensity. Symbols are the same as those in Figure 5.

beam, due to the absorption. It is well-known that the diffracted signal measured by FWM experiment is caused not only by PR grating but also by the other grating-like absorption grating. This fact also explains the different results obtained by 2BC and FWM measurements.

To determine response time, time-resolved FWM experiments were performed. The response time (τ) was calculated using the following equation[17]

$$\eta(t) = \eta^0[1 - \exp(-t/\tau)]^2$$

where η^0 is the steady-state diffraction efficiency.

Figure 7 shows the electric field dependencies of the writing rate. P-THEA/DEANST = 70/30 and P-THEA/DEANST/TH-^{n}Bu = 70/10/20 showed almost the same response times, which were faster than those observed for P-THEA/DEANST/TH-^{n}Bu = 70/20/10. These results can be explained at least qualitatively by the standard single-charge-carrier model for PR grating formation.[18] In this model, the time constant τ is proportional to the material's dielectric time constant τ_{di}, given by following equations

$$\tau = A\tau_{di}$$

$$\tau_{di} = \epsilon/4\pi e\mu N_0$$

if the recombination time is much shorter than the dielectric relaxation time. In this equation, A is a proportional constant, μ is the photocharge mobility, e is the elementary charge, ϵ is the dielectric constant of the PR material, and N_0 is the number density of the charge carriers.

As the DEANST concentration increased, the number density of the charge-transfer complex also increased, leading to the increase of the absorption coefficient or the number of the carriers, while the concentration of thioxanthene moiety (both of P-THEA and TH-^{n}Bu) decreased, resulting in the decrease of the electron drift mobility. Moreover, it is well-known that the presence of polar molecules, DEANST in this study, suppresses the drift mobility of materials.[19–21] These facts account for the rather complex DEANST concentration dependence on the response time. In P-THEA/ DEANST = 70/30 composite, the most important rate-determining factor may be the electron mobility, while charge generation occurs easily. With the decrease of DEANST, the step of photocharge generation may become significant to determine the response time. However, the trap density may also be dependent on the concentration of EO chromophore, as reported.[22] Because no specific measurements were conducted to determine which factor (photocharge generation, migration, trapping, reorientation of chromophore) is limiting the response rate, it is not possible to explain our results quantitatively.

Comparison. There are some reports for the photorefractivity of composites using PVK as a photoconducting host and DEANST as an EO chromophore.[23,24] Since PR characteristics are strongly dependent on the experimental conditions, such as the intensity and wavelength of the writing laser beam, the sample thickness, and measurement geometry, PR properties of PVK/DEANST/ECZ/C$_{60}$ composites were also determined for a precise comparison, where ECZ representing *N*-ethylcarbazole played the role of a plasticizer and C$_{60}$ of a photosensitizer. These composites contained 20 or 30 wt % of DEANST, which allowed the precise comparison of PVK-based composites with P-THEA-based ones presented here. Table 2 lists the characteristics of PR composites examined. Larger absorption coefficients observed in our composites are attributed to the existence of a charge-transfer complex as mentioned above. It was found that the diffraction efficiencies and gain coefficients of our composites were comparable with those of the PVK-based one. It is noteworthy that our composites showed much higher response rate than PVK-based composites. Recently PVK-based composites showing a higher response rate (50 ms at 50 V/μm) were

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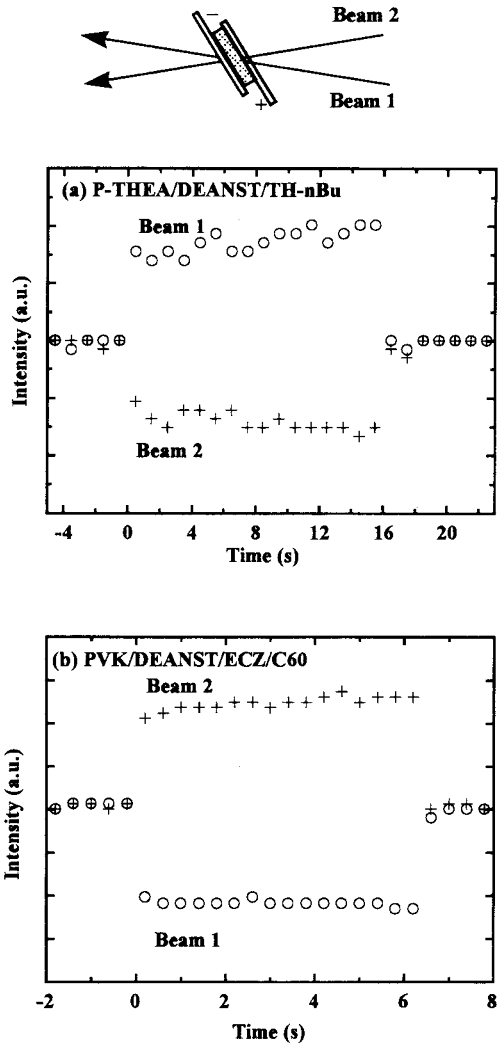

Figure 8. Asymmetric two-beam coupling in P-THEA/DEANST/TH-^{n}Bu = 70/20/10 (a) and PVK/DEANST/ECZ/C60 = 69.8/20/10/0.2 (b): (○) beam 1; (+) beam 2; schematic experimental setup, shown above graphs; applied electric field, (a) 65 V/μm and (b) 30 V/μm. One of the beams (1 or 2) was turned on at 0 s, and the intensity of the other beam was monitored.

reported.[25] However, the response rate was determined at higher writing intensity (1 W/cm^2) than in this study (130 mW/cm^2).

Because of the electron-donating nature of the DEANST molecule, there remains the possibility that hole transport occurs through the amine functionality of the chromophore in our composites. A clear signature of electron transport would be the opposite sign of phase shift between the space-charge field and the light distribution in an electron-transporting material compared with a hole-transporting material. To verify the electron-transporting nature of our composites, a coupling direction was also compared with PVK-based materials. As shown in Figure 8, the different coupling direction was observed between P-THEA-based and PVK-based materials. In the experimental geometry shown in Figure 8, in the former composite beam 1 exhibited the energy gain and beam 2 the loss. On the other hand, in the latter, beam 2 showed the energy gain and beam 1 the loss. These results represent the electron-transporting nature for the space-charge field build-up.

A significant difference was observed between the durability of PR devices, especially in the composites containing 30 wt % of DEANST. PR composites using P-THEA had good optical quality and did not provide the crystallization or phase separation of DEANST, even after 3 months of fabrication and measurements, while PVK-based composite that containing 30 wt % of DEANST showed crystallization of DEANST after 1 week of measurements. It is considered that a specific interaction between the DEANST and thioxanthene unit increased the solubility of DEANST and the stability of the molecularly dispersed systems.

Conclusions

Electron-transporting polymer having a thioxanthene unit in the side chain was applied to a host polymer of photorefractive composites. The composites consisting of a host polymer, DEANST as a NLO chromophore, and a low molecular weight thioxanthene derivative as a plasticizer were fabricated. UV measurements indicated that DEANST molecules form a charge-transfer complex with the thioxanthene moiety causing a photocarrier generation without any photosensitizer. 2BC experiments verified the photorefractivity of our composites. With the increase of DENAST content, the 2BC gain coefficient increased. P-THEA/DEANST = 70/30 composite showed the highest gain coefficient of 64 cm^{-1} at 50 V/μm. On the other hand, in FWM experiment the highest diffraction efficiency was observed for P-THEA/DEANST/TH-^{n}Bu = 70/20/10. The electron-transporting nature of our PR composites was verified by the 2BC experiments, where an different coupling direction was observed for P-THEA-based and PVK-based materials. The latter is believed to show the hole-transporting nature. This paper is the first report concerning the photorefractivity of composites using the electron-transporting polymer as a host.

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