Synthesis of Polymers Having Tetraphenyldiaminobiphenyl Units for a Host Polymer of Photorefractive Composite

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Received February 17, 1997. Revised Manuscript Received July 25, 1997[⊗]

Acrylate type of monomer having tetraphenyldiaminobiphenyl (TPD) unit was prepared and was homo- and copolymerized with *n*-butyl acrylate using AIBN as an initiator. Electrochemical property of synthesized polymers was evaluated with cyclic voltammetry. All polymers exhibited the irreversible oxidation peak at 1.1 V in the initial cycle due to the oxidative coupling of TPD unit and two pairs of reversible oxidation and reduction peaks were observed in the subsequent cycles. Drift mobilities of synthesized polymers were in the range of 10^{-5} cm^2/V s at applied field of 1.6×10^5 V/cm and were 100 times higher than that of PVK. Photorefractivity of polymers doped with 4-(*N*,*N*-diethylamino)-β-nitrostyrene (nonlinear chromophore) and fullerene (C_{60}, charge generator) was investigated with two-beam coupling (2BC) technique. A 100-μm thick composite film showed gains of 9 and 40 cm^{-1} at an external electric fields of 50 and 70 V/μm, respectively. The phase shift between the index grating and interference pattern was 43° at an external electric field of 50 V/μm.

Introduction

Charge- (hole or electron) transport compounds have been widely used in many fields, including electrophotography, organic electroluminescent devices, and so on. They also play an important role in photorefractive (PR) materials, which attract much interests in recent years because of the potential application in holographic optical data storage and real time imaging process.[1]

To generate PR effect, materials require photocarrier generation, charge transport over macroscopic distances, and the charge trapping mechanism together with a linear electrooptic (EO) response,[2] although, a new mechanism using orientational enhancement effect (OEE) is proposed.[3] To fulfill these requirements, PR materials usually possess photoconductive and EO-active properties. Many PR polymers have been reported since the required functionalities are easily provided by the addition of specific molecules into polymeric systems, and they can be classified into two groups: (1) fully functionalized polymers[4−11] that possess all the components required chemically linked to the polymer chain, and (2) host−guest systems[12−27] that consist of photoconducting polymers doped with EO-active chromophore or EO polymers doped with charge-transporting agents. The first reported PR polymeric

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

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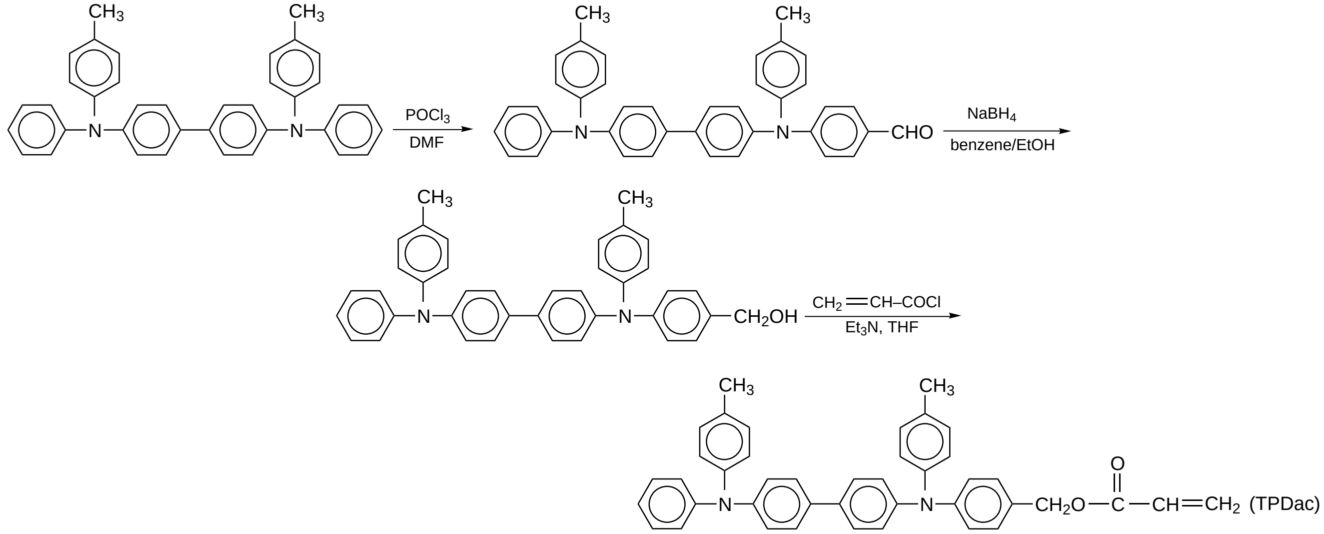
S0897-4756(97)00094-X CCC: $14.00

Scheme 1. Preparation of TPD-Containing Monomers



material was an EO polymer doped with a hole-transport agent.[12] In the case of host−guest systems, photoconducting polymers doped with EO-active chromophore provided better PR properties such as net coupling gains, diffraction efficiencies, and response time.[13−27]

As a photoconducting polymer, poly(9-vinyl carbazole) (PVK) has been exclusively used.[13−26] However, the drift mobility in PVK is 5×10^{-7} cm^2/V s at an electric field of 2×10^5 V/cm[27,28] and is lower than that of the materials molecularly doped with triphenylamine derivatives,[29−31] among which the most attractive one is *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD).[31] It is interesting to synthesize the polymers having TPD units and to use them as host polymer for PR composite. Since it is not completely understood what determines the PR performance, it is important to investigate the effect of drift mobility on PR properties. Silence et al. reported that the response of PR material is limited by the total charge generation and not by drift mobility.[32] They used a polysilane derivative as a high mobility host. The charge-transport mechanism of polysilane is not well understood,[33] while that of TPD has been well studied and is believed to be a hopping process.[28,31]

In this study, charge-transport polymers containing TPD units in side chains were prepared, and characteristics of synthesized polymers were investigated including their electrochemical properties and drift mobility. A PR device consisting of the prepared polymer, a low molecular weight EO active chromophore (DEANST), which has fairly high first hyperpolarizability (2.2×10^{-28} esu),[13] and a charge generator was fabricated. The PR properties were measured by the two-beam coupling method. It is shown that the synthesized polymers are promising candidates for a high-mobility host polymer of photorefractive composites.

Experimental Section

Synthesis. All reagents were bought from Tokyo Kasei Co. and were used without further purification otherwise noted. The synthesis scheme of a monomer containing TPD unit is shown in Scheme 1.

***N*,*N*′-Diphenyl-*N*,*N*′-bis(4-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD).** TPD was synthesized by a modified Ullmann condensation.[33] A 500-mL three-neck flask fitted with a mechanical stirrer and a condenser was charged with 20 g (59.5mmol) of *N*,*N*′-diphenyl-[1,1′-biphenyl]-4,4′-diamine, 311 g (1430mmol) of 4-indotoluene, 36.5 g (246mmol) of anhydrous potassium carbonate, 30.4 g (160mmol) of copper-(I) iodide, and 5.55 g (21mmol) of 18-crown-6. The reaction mixture was heated at 200 °C for 24 h. After cooling and the addition of 200 mL of toluene, the reaction mixture was filtered. After the evaporation of solvent and unreacted iodotoluene, crude product was obtained and was purified by using column chromatography (silica gel, toluene:hexane = 50:50), yield 20 g (65%), mp 163−166 °C. ^{1}H NMR (CDCl$_3$) δ from TMS: 2.25 [s, 6H, −(CH$_3$)$_2$], 6.97−7.42 [m, 26H, aromatic protons].

***N*-(4-Formylphenyl)-*N*′-phenyl-*N*,*N*′-bis(4-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD-CHO).** TPD was formylated by the Vilsmeier reaction.[35] To a 100-mL three-neck flask equipped with a nitrogen inlet, a dropping funnel, a magnetic stirrer, and a condenser was added 10 mL of dry *N*,*N*-dimethylformamide (DMF) under nitrogen atmosphere. Phosphorus oxychloride (5.94 g, 38.7mmol) was added dropwise at 0 °C. After 2.5 h of stirring at 0 °C, 20 g (38.7 mmol) of TPD and 50 mL of dry DMF was added and stirred for 6 h at 80 °C. After cooling, the reaction mixture was poured over 200 g of water−ice mixture containing 15 g of sodium acetate. Precipitated solid was washed with water twice and dried. The unreacted TPD and diformylated product were removed by column chromatography (silica gel, toluene:hexane = 67:33 → 100:0). The TPD−CHO was obtained as yellow powder, yield 9.18 g (43%), mp 96−99 °C. ^{1}H NMR (CDCl$_3$) δ from TMS: 2.32[s, 6H, −(CH$_3$)$_2$], 6.97−7.69 [m, 26H, aromatic protons], 9.79 [s, 1H, −CHO].

***N*-(4-Hydroxymethylphenyl)-*N*′-phenyl-*N*,*N*′-bis(4-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD−CH$_2$OH).** To a 200-mL three-neck flask equipped with a nitrogen inlet and a magnetic stirrer were added 11.7 g (21.5 mmol) of TPD−CHO and 160 mL of the mixture of benzene and ethanol (1:1)

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Table 1. Polymerization Conditions and Characteristics of TPD Containing Polymer[a]

	TPDac (mol %)		TPD in polymer (wt %)	$M_n/10^4$	$M_w/10^4$	M_w/M_n	T_g (°C)	λ_{max} (nm)
	in feed	in polymer						
PTPDac	100	100	85.8	2.3	8.5	3.7	150.3	310, 351
PTPDac−BA1	43.9	39.1	68.6	2.3	9.1	4.0	105.5	315, 354
PTPDac−BA2	39.1	35.5	64.6	2.2	8.6	3.9	87.0	313, 354
PTPDac−BA3	29.4	23.1	57.6	4.4	12.9	3.0	65.5	313, 354
PTPDac−BA3	29.4	23.1	57.6	4.4	12.9	3.0	65.5	313, 354

[a] Polymerization conditions: [TPDac + BA] = 1 M, [AIBN] = 0.01 M, in benzene, 60 °C, 24 h.

under nitrogen atmosphere. After dissolution of TPD−CHO, 1.02 g (26.9 mmol) of sodium borohydride was added to the reaction mixture. After stirring for 2 h at ambient temperature, solvent was removed by evaporation and residual solid was washed with water to remove inorganic salts. A benzene solution of crude product was poured into hexane, and a light yellow powder was obtained, yield 9.97 g (85%), mp 93−96 °C. ^{1}H NMR ($CDCl_3$) δ from TMS: 1.60 [s, 1H, −(OH)], 2.32[s, 6H, $-(CH_3)_2$], 4.61 [s, 2H, $-CH_2-$], 6.93−7.45 [m, 26H, aromatic protons].

***N*-(4-Acryloyloxymethylphenyl)-*N*′-phenyl-*N*,*N*′-bis(4-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPDac).** To a 100-mL three-neck flask fitted with nitrogen inlet, magnetic stirrer, and dropping funnel, 8.82 g (16.2 mmol) of $TPD-CH_2-OH$, 2.04 g (20.2mmol) of triethylamine and 40 mL of dry tetrahydrofuran (THF) was added under nitrogen atmosphere, and the solution was cooled to 0 °C. The mixture of 1.83 g (20.2 mmol) of distilled acryloyl chloride and 15 mL of THF was added dropwise. After 2 h of stirring, the reaction vessel was allowed to warm to room temperature, and stirring was continued for additional 10 h to complete the reaction. Precipitated salt was removed by filtration. After evaporation of THF, residual solid was washed with distilled water and purified by column chromatography (silica gel; benzene:hexane = 67:33 → 100:0), yield 4.94 g (51.1%), mp 69−71 °C. ^{1}H NMR ($CDCl_3$) δ from TMS: 2.28 [s, 6H, $-(CH_3)_2$], 5.18 [s, 2H, $-CH_2-$], 5.82, 6.43 [J = 11.5Hz, 17.5 Hz, d, 2H, $CH_2{=}CH-$], 6.19 [J = 10 Hz, m, 1H, $CH_2{=}CH-$], 6.99−7.44 [m, 26H, aromatic protons].

Polymerization. Homo- and copolymerization of TPDac with *n*-butyl acrylate (BA) were carried out in a glass ampule under a dry nitrogen atmosphere at 60 °C for 24 h. 2,2′-Azobis(isobutyronitrile) was used as an initiator and benzene as a solvent. BA and benzene were purified by distillation before use. Polymerization conditions were summarized in Table 1. Reaction mixture was poured into a large amount of acetone. Recovered polymers were purified 2−3 times by reprecipitation of benzene solution into acetone, followed by drying in vacuo.

Measurements. NMR measurements were conducted at 50 °C with JEOL α-500 spectrometer operating at 500 MHz for ^{1}H, and at 125 MHz for ^{13}C. UV spectra were obtained in THF solutions using a JASCO V-500 UV/vis/NIR spectrophotometer. The molecular weight of synthesized polymers were estimated by gel permeation chromatography using a column packed with styrene−divinylbenzene gel beads. THF was used as an eluant and the molecular weight was calibrated using polystyrene standards (Shodex). Glass transition temperatures (T_g) were determined from differential scanning calorimetry (DSC) chart which was recorded by SEIKO Instruments DCS 220 under nitrogen at heating rate of 10 °C/min. Redox potentials were measured with cyclic voltammetry in a one-compartment cell with a polarization unit (TOHO PS-06). The measurements were conducted for the cast film on Platinum working electrode in dry acetonitrile containing tetrabutylammonium perchlorate (0.1 M) as an electrolyte under nitrogen atmosphere. Platinum spiral was used as a counter electrode, and Ag/AgCl as a reference electrode.

Samples for drift mobility measurements were prepared as follows. Titanyl phthalocyanine (TiOPc) was spin coated from organic solvent onto the aluminum vapor deposited on the slide glass, then dried at 90 °C for 30 min. The 1,2-dichloroethane solution (typically 0.25 g/mL) of polymer or polymer and 4-*N*,*N*-diethylamino-β-nitrostyrene (DEANST), which was prepared according to the literature,[36] was filtered through a 5 μm filter. The polymer solution was spread on TiOPc layer using wire bar or spin coater. The films were allowed to dry for several hours at room temperature and then dried at 90 °C for 1 h to remove residual solvent. Semitransparent gold electrode was prepared on the film surface by vacuum deposition at a pressure of (3−7) × 10^{-5} Pa. Film thicknesses were determined by a profilometer (DEKTAK II, Solan). Drift mobility was measured with a conventional time-of-flight method[36] at room temperature using a xenon flash lamp (Hamamatsu photonics, L2359), and digitizing oscilloscope (GOULD, DSO 630).

PR Sample Preparation and Measurements. The photorefractive property of the PTPDac−BA2/DEANST/C_{60} composite was studied by the two-beam coupling technique, and phase shift between the photorefractive index grating and the interference pattern was determined by moving the grating using a piezoelectric transducer. Sample was prepared as follows: 85 mg of polymer and 15 mg of DEANST was dissolved in 2.0 mL of toluene containing fullerene (C_{60}, 1.0 mg/10 mL). The filtered solution was heated to 100 °C for solvent evaporation until a highly viscous solution was obtained. The resulting solution was dripped onto indium tin oxide (ITO)-covered glass substrate. After the evaporation of residual solvent, sample was heated with hot plate at ca. 100 °C at which the composite softened. The composite was sandwiched with another ITO-covered glass. The sample thickness was controlled to be approximately 100 μm with the use of Teflon spacer. Holographic gratings were written using two p-polarized, mutually coherent beams from an NEC GLS-5410 He−Ne laser operating at 633 nm. Transmitted beam intensities were monitored with photodiodes (Hamamatsu Photonics, S2281).

Results and Discussion

Synthesis and Characterization. An acrylate type of monomer containing TPD moiety (TPDac) was synthesized in four steps. Figure 1 shows ^{1}H NMR spectra of TPDac. Protons of methyl and benzyl methylene groups resonate at 2.28 and 5.18 ppm, respectively. Three types of acrylic protons appear at 5.82, 6.19, and 6.43 ppm. Signals at 6.99−7.44 ppm can be assigned to aromatic protons. The number of carbon types in ^{13}C NMR spectrum was 30, which is consistent with the monomer. The synthesized TPDac was confirmed to have the expected structure. TPDac was homopolymerized or copolymerized with BA using AIBN initiator. Figure 2 shows ^{1}H NMR spectra of homopolymer (PTPDac) and copolymer (PTPDac−BA2). Each signal can be assigned to the protons in the expected structure. The chemical compositions of copolymers were determined from the ^{1}H NMR relative peak intensities of benzyl protons at 4.9 ppm in TPDac unit and those of methyl protons at 0.9 ppm in BA unit. The weight

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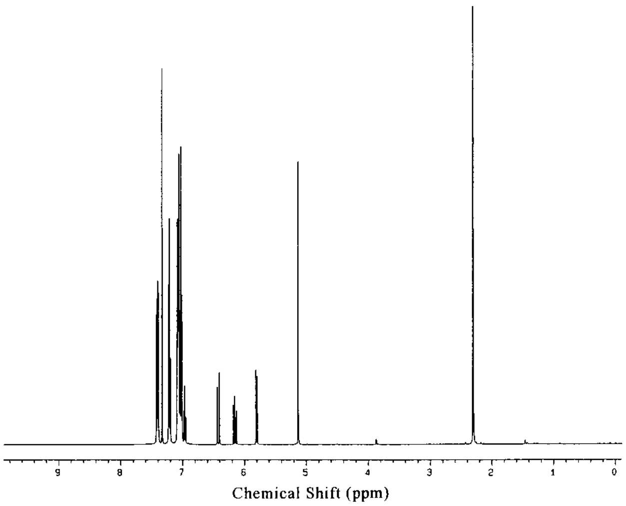

Figure 1. ^{1}H NMR spectrum of TPDac monomer measured in $CDCl_3$, at 50 °C.

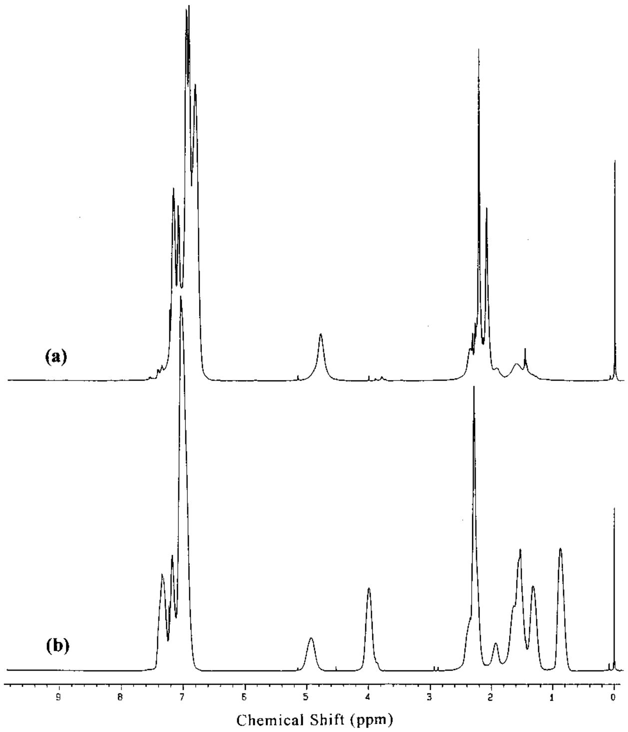

Figure 2. ^{1}H NMR spectra of PTPDac (a) and PTPDac−BA2(b) measured in $CDCl_3$, at 50 °C.

percentages of TPD moiety were calculated from chemical compositions. Table 1 shows the polymerization conditions and the characteristics of synthesized polymers. All the polymer prepared had the number average molecular weight over 2.0×10^4 and were soluble in a variety of organic solvents such as benzene, toluene, THF, chloroform, and 1,2-dichloroethane.

The polymers had two UV absorptions at ca. 310 and ca. 350 nm, mainly due to the absorption of TPD unit. The UV spectra of the polymers are almost identical with those of TPDac and TPD. It is considered that the incorporation of TPD units in polymer chain has a negligible effect on the electronic state of TPD unit.

The high PR performance such as high diffraction efficiency and large net gain has been fulfilled with an orientational enhancement effect[22−26,38] when a low T_g composite was utilized. The plasticizer has been often doped in order to lower the T_g of a composite.[22,24]

Table 2. Redox Potential of Synthesized Polymers[a]

	$E_{pa1,2}$ (V)	$E_{pc1,2}$ (V)
PTPDac	0.90, 0.95	0.84, 0.92
PTPD−BA1	0.86, 0.95	0.84, 0.93
PTPD−BA2	0.85, 0.94	0.82, 0.92
PTPD−BA3	0.85, 0.95	0.83, 0.92
TPD	0.77, 0.92	0.72, 0.85

[a] Pt working and counter electrode. Ag/AgCl reference electrode. 0.1 M $(n\text{-Bu})_4NClO_4$ in acetonitrile.

However, phase separation or aggregation of plasticizer makes the optical properties worse or limits the stability or durability of composites. It is important to control T_g of a host polymer by copolymerizing it with a flexible monomer, in attempt to avoid the use of a plasticizer, and minimize the phase separation. Since poly(*n*-butyl acrylate) has low T_g of −54 °C,[39] BA was used as comonomer in order to lower T_g of the polymer.

DSC studies revealed that PTPDac exhibits a glass transition at ca. 150 °C, and the glass transition temperature of copolymers decreases as the BA mole fraction increases as expected. No other thermal process such as the melting of a side chain was found in the temperature range investigated (−50 to 180 °C) indicating that the prepared polymers are amorphous. The copolymer containing 65 mol % of BA unit (PTPDac−BA2) had a T_g of 87 °C, and the T_g decreased to 30 °C by doping it with 15 wt % of DEANST, as described below.

Charge transport in organic materials is believed to be governed by the hopping process involving redox reaction of charge-transport molecules. Cyclic voltammetry (CV) is a preliminary characterization technique to determine the redox properties of organic and polymeric materials.[40] Figure 3 shows typical cyclic voltammograms of PTPDac−BA2 copolymer recorded at scanning rate of 150 mV s^{-1}. The first redox cycle exhibited a large oxidation wave with a maximum electropotential at 1.10 V and two small reduction waves at 0.79 and ca. 0.9 V (Figure 3a). The oxidation current at 1.10 V disappeared in the second cycle, indicating that the initial oxidation process at 1.1 V was not reversible. The two pairs of oxidation−reduction peaks were observed after the irreversible oxidation peak disappeared as shown in Figure 3b. All the polymers exhibited similar redox behavior. The peak potentials of reversible redox waves for each polymer are listed in Table 2, together with those of TPD. Redox potentials were almost independent of the chemical compositions of copolymers and were slightly higher than those of TPD.

Similar irreversible oxidation peaks were observed in molecular triarylamine[41,42] and in polymeric systems.[40,43] Compton et al. have shown oxidative coupling in a polymeric system and proposed the mechanism of an irreversible coupling to form a bis(benzidine) moiety, which then undergoes a reversible oxidation.[40] The

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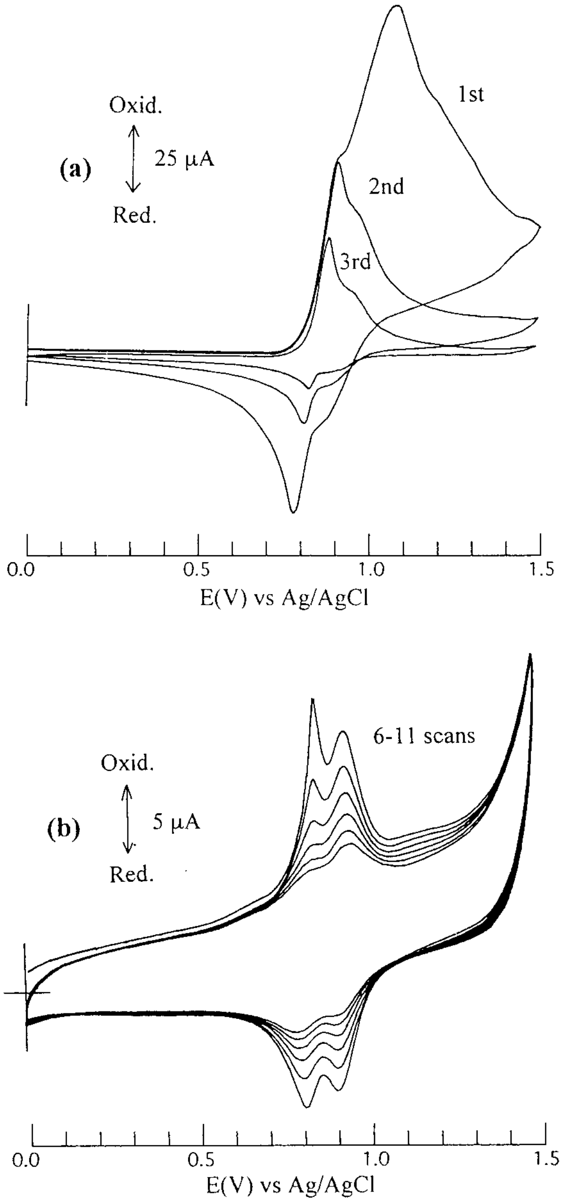

Figure 3. Cyclic voltammograms of PTPDac−BA2. (a) 1−3 scans, (b) 6−11 scans in 0.1 M (n-Bu)$_4$NClO$_4$ in acetonitrile, scanning rate 150 mV/s.

irreversible oxidation in our systems is, therefore, considered to be due to a partial oxidative coupling in the TPD unit in the side chain.

Drift Mobility. In organic PR materials, the response time of diffraction efficiency and gain depends on the rate of growth of space-charge field (E_{sc}).[2] For the establishment of E_{sc}, mainly three processes are involved, i.e., charge generation, the transport of generated charges, and the trapping. Therefore, drift mobility is one of the important rate-determining factors in the establishment of E_{sc}. Zhang et al. reported that the electric-field dependence of the grating writing rates has the same slope as that of the photoconductivity when they are plotted on a semilog scale.[44] We investigated the drift mobility of synthesized polymers and the DEANST-doped composites in order to establish the relationships between the drift mobility and PR parameters.

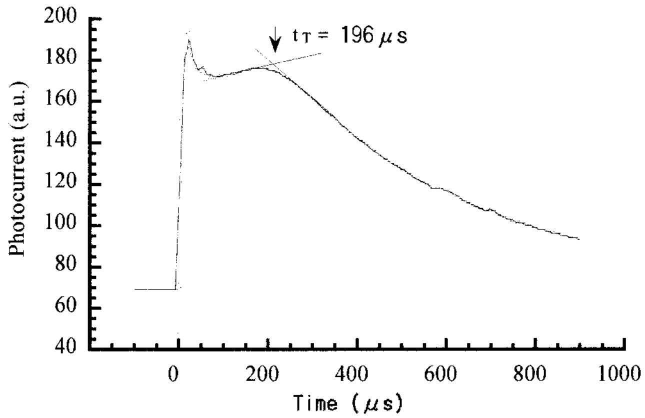

Figure 4. Photocurrent transient signal of TOF experiment for PTPDac−BA3: thickness 11 μm, temperature 293 K, applied voltage 220 V.

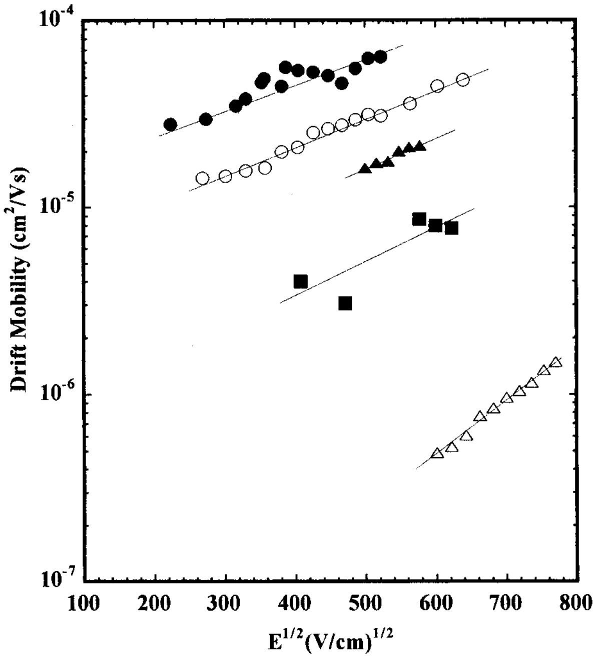

Figure 5. Field dependence of drift mobility. (●) PTPDac−BA2, (○) PTPDac−BA3, (▲) PTPDac−BA2 doped with 10 wt % of DEANST, (■) PTPDac−BA2 doped with 15 wt % of DEANST, (△) PVK.

The homopolymer (PTPDac) and the copolymer with 68.6 wt % of TPD content (PTPDac−BA1) were too brittle to provide high-quality thin films with ca. 10 μm thickness for TOF measurements as some cracks appeared in the films during solvent evaporation. Other two polymers and a copolymer doped with 10 or 15 wt % of DEANST afforded films with good optical quality.

Figure 4 shows an example of the photocurrent transient curve recorded in one of the above samples. As indicated by the arrow in Figure 4, well-defined transit times (t_T) were observed in all samples examined. The charge mobility μ is calculated according to

$$\mu = L^2/t_T V$$

where L is the sample thickness and V the applied voltage. Drift mobility data are plotted semilogarithmically against the square root of applied field E (V/L) as shown in Figure 5. Almost linear relationships were obtained for all samples. This type of dependence is

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[44] Zhang, Y.; Ghosal, S.; Casstevens, M. K.; Burzynski, R. *J. Appl. Phys.* **1996**, *79*, 8920.

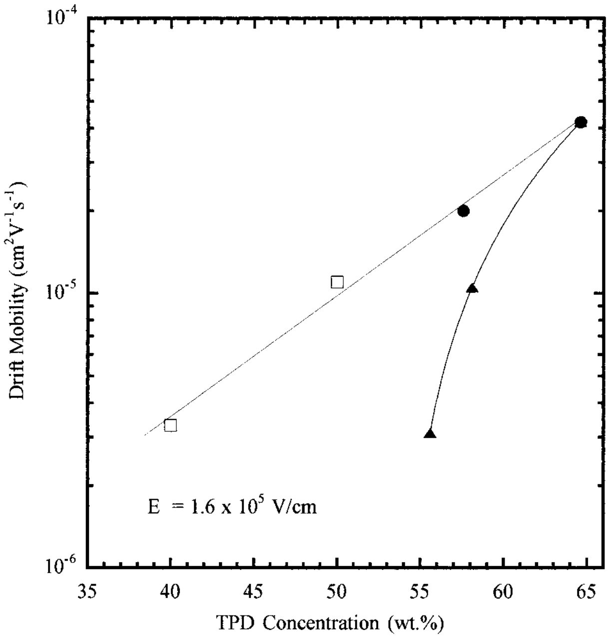

Figure 6. Relationship between TPD concentration and drift mobility: (●) PTPDac–BA copolymer, (▲) PTPDac–BA2 doped with DEANST, (□) TPD in polycarbonate (in ref 30).

frequently observed in molecularly doped polymers[29,30] although no fully reasonable explanation exists. The charge mobility of PVK was also measured by the same method. The PVK had the mobility in the range of 10^{-7} order at applied electric field, which was almost equal to the reported values.[27,28] Therefore, the synthesized polymers show about 100 times higher mobility than that of PVK.

Figure 6 shows the relationships between the concentration of TPD unit and logarithm of drift mobility at an electric field of 1.6 × 10^5 V/cm. Stolka et al. reported the mobility of the TPD-doped polycarbonate with different TPD content,[31] and their data are also plotted in Figure 6. A linear relationship is obtained in this concentration range of TPD. As expected, the mobility increased with the increase of TPD unit. The composite containing DEANST showed lower drift mobility than that expected from the TPD concentration. This finding is consistent with the results of Vannikov[45] and Young,[46] who reported that the presence of polar molecules decreases the drift mobility. Silence reported the opposite behavior for the polysilane doped with coumarin-153, which showed 10–20 times higher mobility than that of undoped one.[32] The mobility of PVK doped with 15 wt % of DEANST was so small that no transit time was observed. The drift mobility of TPD polymer decreased to ca. 1/10 by doping 15 wt % of DEANST. If the same relation holds for PVK, the mobility of doped PVK is expected to be in the range of 10^{-8} cm^2 V^{-1} s^{-1}.

Photorefractivity. PR device consisting of PTPDac–BA2/DEANST/C_{60} (84.9/14.9/0.2 wt %) was fabricated. As a comparison, PVK/DEANST/ECZ/C_{60} (54.8/15/30/0.2 wt %) was also fabricated. PR material with PTPD had good optical quality and did not provide crystallization or phase separation of DEANST even after 3 months of fabrication and measurement. While one with PVK showed crystallization of DEANST after a few weeks of measurement. The absorption coefficients (α) of PTPDac–BA2/DEANST/C_{60} and PVK/DEANST/ECZ/C_{60} films were 6.5 and 3.1 cm^{-1} at 633 nm, respectively. The glass transition temperature of the PTPD and PVK composites were 30 and −18 °C, respectively. This low glass transition temperature indicates that the second-order NLO chromophore, DEANST can be fairly easily oriented by the application of a dc electric field. Therefore, no poling was performed before 2BC measurements.

A conventional experimental setup for 2BC was adopted.[3] Two writing beams with equal intensities of 250 mW/cm^2 were intersected in the sample at incident angles of 38.2° and 60.8° (in air with respect to the film normal), respectively, and with a sample tilt angle of 50°. Figure 7 shows the results of two successive experiments under the applied field of 70 V/μm. In the first experiment, beam 2 was switched on at time $t = 2$

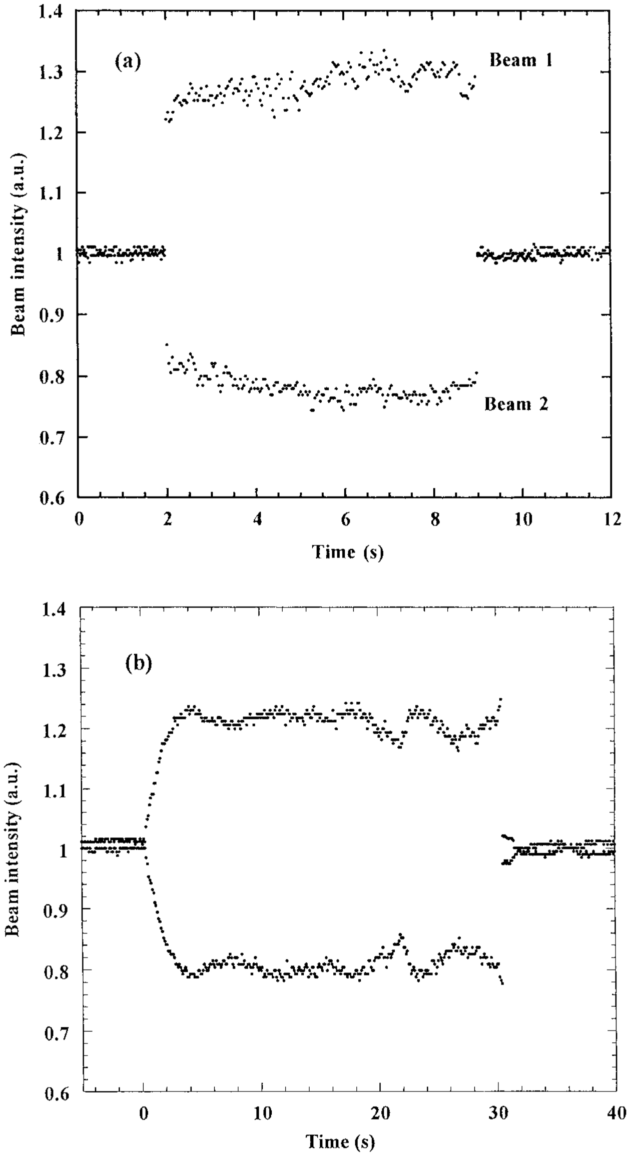

Figure 7. Asymmetric two-beam coupling in PTPDac–BA2/DEANST/C_{60} (a), PVK/DEANST/C_{60} (b). Applied electric field (a) 70 V/μm, (b) 50 V/μm, beam 1 increased in intensity as beam 2 is turned on at $t = 2$ s and blocked at $t = 9$ s, and beam 2 decreased an approximately equal amount as beam 1 is turned on at $t = 2$ s and blocked at $t = 9$ s.

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(45) Vannikov, A. V.; Kryukov, A. Yu.; Tryurin, A. G.; Zhuravleva, T. S. *Phys. Status Solidi A* **1989**, *115*, K47.

(46) Young, R. H.; Fitzgerald, J. J. *J. Chem. Phys.* **1995**, *102*, 6290.

s and switched off at $t = 9$ s, while the intensity of beam 1 was monitored. In the second experiment, the intensity of beam 2 was monitored as beam 1 was switched on at $t = 2$ s and switched off at $t = 9$ s. As shown in Figure 7, asymmetric energy transfer from one beam to the other beam occurred in our materials. The two-beam coupling gain is calculated using

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

where L is the sample thickness, ξ is the ratio of the beam intensities, $\gamma_0 = I/I_0$ is the beam coupling ratio, where I_0 is the detected signal intensity without the pumping beam and I is the intensity with pump beam on, and θ is the incident angle of the beam inside the sample. The gain of PTPDac−BA2 was found to be 9 cm^{-1} at 50 V/μm and 40 cm^{-1} at 70 V/μm, giving a net gain coefficient of 2.5 and 33.5 cm^{-1}, respectively. On the other hand, the device using PVK had a gain of 38 cm^{-1} at 50 V/μm, and net gain of 34.9 cm^{-1}. The net gain of PVK was larger than PTPD. It was found that the gain was not affected by the drift mobility.

The response time was calculated from the change of beam intensity of 2BC experiment by fitting the following exponential curve:

$$E_{sc} = E_{sc}^{\circ}[1 - \exp(-t/\tau)]$$

where E_{sc}° is the saturation value of the space charge field and τ is the characteristic growth time or response time. Figure 8 shows the fitting curve of 2BC experiment. The device using PTPDac−BA2 had response times of 8.5 and 7.5 ms at 50 and 70 V/μm, respectively. On the other hand, PVK/DEANST/ECZ/C_{60} had a response time of 1.1 s at 50 V/μm, which is almost the same as that of PVK/EPNA/ECZ/C_{60} (54.9:30:15:0.1 wt %) system, i.e., on the order of 1 s.[47] Thus, it can be said that the charge mobility has great effect on the response time.

Another experiment to verify photorefractivity is the measurement of the phase shift between the photorefractive index grating and the interference pattern. This phase shift gives rise to an asymmetric energy transfer in 2BC coupling. It is possible to evaluate this phase shift by moving the grating providing that the movement of grating is carried out in much shorter time than the lifetime of grating. In Figure 9, the transmitted intensities of the two beams are plotted against the displacement of the grating (50 V/μm). Theoretical fitting[48] of these data gave the phase shift of 43°, which indicates that an asymmetrical energy transfer results from the PR effect.

Our investigation of photorefractivity in the composite based on a TPD-containing polymer is in progress. Detailed PR results including electrooptic and photoconductivity data will appear in subsequent papers.

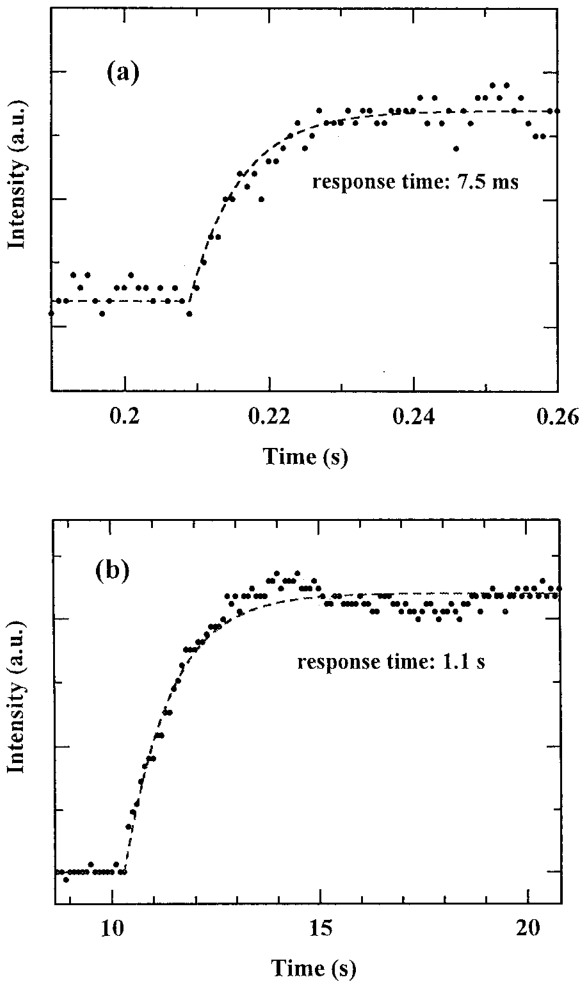

Figure 8. The fitting curves of 2BC experiments. (a) PTPDac−BA2/DEANST/C_{60} ($E = 70$ V/μm), (b) PVK/DEANST/ECZ/C_{60} ($E = 50$ V/μm).

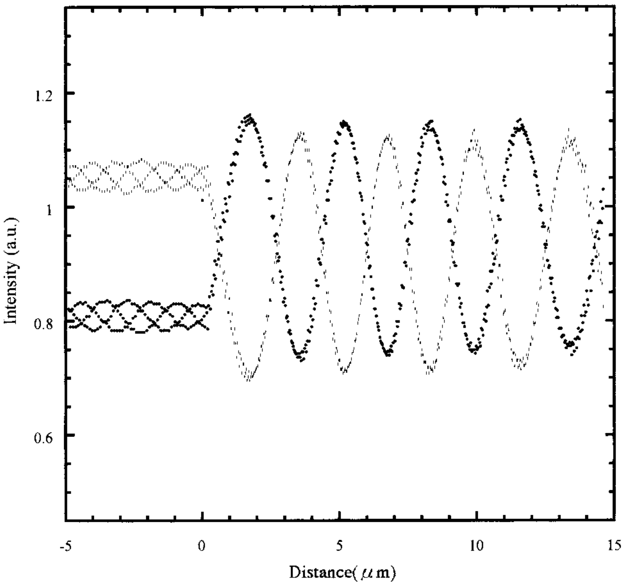

Figure 9. Transmitted power of two coupling beams when the sample was translated at 49.3 μm/s. Applied electric field 50 V/μm.

Conclusions

An acrylate type of monomer having a tetraphenyldiaminobiphenyl (TPD) unit was prepared and was homo- and copolymerized with n-butyl acrylate using AIBN as an initiator. The glass transition temperature could be controlled by the chemical composition of the copolymers. Cyclic voltammetry data showed that the redox property of polymers was the same as that of TPD. Drift mobilities of synthesized polymers were in the

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(47) Bolink, H. J.; Krasnikov, V. V.; Malliaras, G. G.; Hadziioannou, G. *J. Phys. Chem.* **1996**, *100*, 16356.

(48) Walsh, C. A.; Moerner, W. E. *J. Opt. Soc. Am. B* **1992**, *9*, 1642.

range of 10^{-5} cm^2/V s at applied field of 1.6×10^5 V/cm and were 100 times higher than that of PVK. The composites doped with DEANST, a second-order nonlinear optical active compound, showed lower drift mobility than the value expected from TPD concentration. Photorefractivity of polymers doped with DEANST and fullerene as a charge generator was investigated with the 2BC technique. The 2BC gain of the composite was 9 and 40 cm^{-1} in a 100-μm-thick-film at an external electric field of 50 and 70 V/μm, respectively. The response time of the PR device containing TPD was about 8 ms, while that of the PR device consisting of PVK was in the order of 1 s. The phase shift between the index grating and the interference pattern was 43° at an external electric field of 50 V/μm. It is found that the synthesized polymers are promising candidates as a host polymer with high drift mobility for photorefractive composites.

Acknowledgment. Financial support of this work from a Grant-in-Aid for Scientific Research (No. 08236213) by the Ministry of Education, Science, and Culture, Japan is gratefully acknowledged.

CM970094K