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# Synthesis and characterization of polytriphenylamine based graft polymers for photorefractive application

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#### 1. Introduction

Organic photorefractive (PR) materials have been intensively investigated in recent years because of potential applications to holographic optical data storage and real-time image processes and several advantages such as higher nonlinearity, low dielectric constant, and structural flexibility as described in several review/ feature articles [1-5]. Although it is reported more recently that multifunctional copolymers containing carbazole and dicyanomethylene-dihydrofuran units show outstanding PR performance such as fast buildup and erasure times of a few tens of milliseconds, large refractive index modulation (over  $10^{-2}$ ) and two-beam coupling gain (above 350 cm<sup>-1</sup>) [6], generally hostguest systems with low glass transition temperatures  $(T_g)$ , which consist of photoconducting polymers doped with an electrooptically (EO) active chromophore and a small amount of charge generator or photosensitizer, have shown excellent PR properties such as high diffraction efficiency, large net gain [7–13], and fast response [14,15]. This suggests that the high mobility of EO active chromophore for the orientation plays an important role for the high performance of PR composites.

In addition to a conventional poly(*N*-vinylcarbazole) (PVK), triphenylamine (TPA)-based polymers such as polyacrylate [11–14] and polyether [16] have also attracted much attention as host

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#### ABSTRACT

Novel graft copolymers, PTPA-g-PEAs containing poly(triphenylamine) (PTPA) backbone and poly(ethyl acrylate) (PEA) branches were synthesized by the oxidative coupling polymerization of triarylamine monomers followed by grafting of ethyl acrylate via an atom transfer radical polymerization (ATRP). Photorefractive (PR) composites based on the graft copolymers showed good static PR properties and fast response time under moderate conditions. The highest diffraction efficiency (19.7% at 45 V/µm) was observed with the composite containing the graft polymer with 18 mol% of graft density and 27 wt% of PTPA. And the fastest response (8 ms at 50 V/µm) was achieved when PTPA content was 68 wt%. © 2012 Elsevier Ltd. All rights reserved.

polymers due to their efficient hole transporting ability, and high photo-charge generation efficiency. As we reported previously, various polymers containing TPA moiety in their main chains have been prepared via an addition [17,18] or addition—condensation [19,20] reaction using nucleophilic nature of phenyl group. We also reported that 4-alkyltriphenylamine can be polymerized via the chemical oxidative coupling reaction using ferric chloride as an oxidant to afford poly(4-alkyltriphenylamime)s (PTPAs) [21,22], and that poly(4-butyltriphenylamine) showed much higher photoconductivity compared with PVK [22].

Although highly photoconductive PTPAs are promising candidates for a PR host material as mentioned above, no attempts to apply PTPAs to PR materials have been made as far as we know. Generally PR host materials should show high miscibility with EO chromophores, and plasticizers if the original polymers possess high  $T_g$  [7,11–13]. Because of high  $T_g$  nature of PTPAs [22], it is necessary to utilize a plasticizer for the facile reorientation of EO chromophore. However, our preliminary studies revealed that PTPAs show poor miscibility with a plasticizer as well as with an EO chromophore, leading to phase separation in PR composite films. It is considered that this fact results in no application of PTPAs to PR materials so far.

In order to increase the compatibility of EO chromophore and lower  $T_g$  of the resulting composites, we here designed graft copolymers consisting of PTPA main chain and polar poly(ethyl acrylate) (PEA) side chains. This is the first attempt to apply graft copolymers to PR materials. In general, block copolymers and graft copolymers could provide microphase-separated morphologies





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such as spheres, cylinders, and lamela, dependent on the graft density or the chemical composition [23–25]. In our previous study, it is indicated that phase separated PR materials based on block copolymers consisting of photoconductive and EO active blocks show higher PR properties (105 cm<sup>-1</sup> of gain coefficient at 45 V/µm) compared the corresponding statistical random copolymer (15 cm<sup>-1</sup> at 45 V/µm) [26]. Therefore, in our graft copolymer systems with microphase separated structure, additional enhancement of PR performance is anticipated. In the polar and flexible PEA rich phase, high compatibility with EO chromophore, and its sufficient mobility for the smooth orientation through internal space charge field are expected, which is important for sufficient static PR performance and fast response. In addition, photoconductive PTPA chain is expected to form such a distinctive domain in phase separated systems, and the problem of dark current in low  $T_{g}$  materials can be solved without sacrificing the orientational mobility of dopants.

In this paper, it is reported that novel graft copolymers consisting of PTPA main chain and PEA side chain were successfully prepared via oxidative copolymerization of TPA derivatives, followed by grafting PEA chains via atom transfer radical polymerization (ATRP) and were applied to PR host polymers. PR properties of the composites containing the synthesized graft copolymer, an EO chromophore (4-*N*,*N*-diethylamino- $\beta$ , $\beta$ -dicyanostyrene, DEADCST [27]) and a photosensitizer (2,4,7-trinitro-9-fluorenone, TNF) were investigated, and relationships between the PR properties and the characteristics of graft polymer were discussed. DEADCST is a general EO chromophore, showing moderate dipole moment (7.8 D in chloroform [28]), and higher ionization potential (5.7 eV) [29] than PTPAs (5.3 eV) [22,30]. Because of the higher ionization potential, DEADCST cannot serve as a hole-trap [5]. The relationship between the PR properties and the characteristics of graft polymers is discussed.

#### 2. Experimental

#### 2.1. Materials

2-(4-Bromophenyl)ethanol, tert-butyldimethylchlorosilane, 2,4,7-trinitro-9-fluoren- one (TNF), and 1-bromo-4-butylbenzene were obtained commercially from Tokyo Chemical Industry Co. (Japan). 1-Bromo-4-[2-(tert-butyldimethylsilyloxy) ethyl]benzene (1) was synthesized according to the literature [31]. Palladium (II) acetate was obtained from Sigma-Aldrich Co. Tri-tert-butylphosphine was obtained from Hokko Chemical Industry Co. (Japan). Other chemicals were obtained commercially from Wako Chemical Co. (Japan) and were used without further purification except otherwise noted. 4-Butyltriphenylamine (BTPA) was synthesized by C-N coupling reaction of diphenylamine with 1-bromo-4butylbenzene as described in Ref. [22]. Xylene and chloroform were purified by distillation from calcium hydride. 4-N,N-Diethylamino- $\beta$ , $\beta$ -dicyanostyrene (DEADCST) was synthesized according to the literature [27].

## *2.2.* Synthesis of 4-[2-(tert-butyldimethylsilyloxy)ethyl] triphenylamine (**2**)

To a 500-mL three-necked flask equipped with a magnetic stirrer, a condenser and a nitrogen inlet were added **1** (36.20 g, 0.11 mol), diphenylamine (21.40 g, 0.12 mol), palladium (II) acetate (0.0335 g, 0.14 mmol), and *t*-BuONa (13.20 g, 0.13 mol). After the addition of xylene (140 mL) and 0.1 M P(*t*-Bu)<sub>3</sub> xylene solution (1.0 mL, 0.10 mmol), the mixture was stirred at 120 °C for 6 h under nitrogen atmosphere. After cooling down to 80 °C, 100 mL of water was added to the reaction mixture. The organic layer was washed

with water and concentrated by evaporation, followed by purification using column chromatography (silica gel, toluene). The white solid was obtained (43.8 g, 95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.29–7.00 (14H, m, **-Ar**), 3.85 (2H, t, *J* = 6.9 Hz, -O-CH<sub>2</sub>-), 2.82 (2H, t, *J* = 6.9 Hz, Ar-CH<sub>2</sub>-), 0.92 (9H, s, -Si-*t*-Bu), 0.04 (6H, s, -Si-**Me**<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  148.00, 145.93, 134.06, 130.05, 129.10, 124.63, 123.73, 122.31 (**-Ar**), 64.55 (-O-CH<sub>2</sub>-), 38.95 (Ar-CH<sub>2</sub>-), 25.94 (Si-C-Me<sub>3</sub>), 18.36 (-Si-C-Me<sub>3</sub>), -5.38 (-Si-Me<sub>2</sub>). Anal. Calcd for C<sub>26</sub>H<sub>33</sub>NOSi: C, 77.37; H, 8.24; N, 3.47. Found: C, 77.51; H, 8.27; N, 3.35.

#### 2.3. Synthesis of 4-(2-hydroxyethyl)triphenylamine (3)

To a 1000-mL flask equipped with a magnetic stirrer were added **2** (43.82 g, 0.10 mol) and 580 mL of THF, H<sub>2</sub>O, and acetic acid mixture solution (THF/H<sub>2</sub>O/AcOH = 20/20/60 vol%). After stirring at room temperature for 4 days, 100 mL of diethyl ether was added to the reaction mixture. The ethereal layer was washed with water and concentrated by evaporation followed by purification using column chromatography (silica gel, chloroform). The white solid was obtained (23.1 g, 74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.26–6.97 (14H, m, – **Ar**), 3.86 (2H, t, *J* = 6.6 Hz, –C**H**<sub>2</sub>-OH), 2.83 (2H, t, *J* = 6.6 Hz, Ar–C**H**<sub>2</sub>-), 1.49 (1H, s, –O**H**). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  147.87, 146.32, 132.75, 129.80, 129.17, 124.48, 123.98, 122.56 (–**Ar**), 63.66 (–**C**H<sub>2</sub>–OH), 38.55 (–Ar–**C**H<sub>2</sub>–). Anal. Calcd for C<sub>20</sub>H<sub>19</sub>NO: C, 83.01; H, 6.62; N, 4.84. Found: C, 83.32; H, 6.71; N, 4.83.

#### 2.4. Synthesis of 2-[4-(diphenylamino)phenyl]ethyl 2bromopropionate (TPA-I)

To a 500-mL three-neck flask equipped with a magnetic stirrer and a nitrogen inlet were added 3 (23.09 g, 80 mmol), 2bromopropionic acid (16.70 g, 90 mmol), N,N'-dicyclohexylcarbodiimide (DCC) (18.50 g, 90 mmol), DMAP (0.030 g, 4.0 mmol) and 400 mL of THF. The reaction mixture was stirred at room temperature under N<sub>2</sub> atmosphere. After the filtration, the solution was washed with water and concentrated by evaporation, followed by purification using column chromatography (silica gel, toluene). The white solid was obtained (30.0 g, yield 89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.24–6.95 (14H, m, –**Ar**), 4.41–4.30 (3H, m, OOC–C**H**–Br,  $-CH_2-O-CO$ ), 2.92 (2H, t, J = 7.1 Hz, Ar $-CH_2-$ ), 1.79 (3H, d, J = 6.9 Hz,  $-CH_3$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  170.00 (-COO-), 147.71, 146.39, 131.48, 129.70, 129.10, 124.27, 123.90, 122.51 (-Ar), 66.26 (O-CH<sub>2</sub>-), 40.01 (-CH-), 34.10 (Ar-CH<sub>2</sub>-), 21.58 (CH<sub>3</sub>-). Anal. Calcd for C<sub>23</sub>H<sub>22</sub>BrNO<sub>2</sub>: C, 65.10; H, 5.23; N, 3.30. Found: C, 65.20; H, 5.36; N, 3.21.

## 2.5. General procedure for synthesis of poly(triphenylamine) macroinitiator (PTPA-I)

To a two-necked 500-mL flask equipped with a magnetic stirrer were added a total of 50 mmol of TPA-I and BTPA (the feed ratios are listed on Table 1.), and 200 mL of distilled CHCl<sub>3</sub> under nitrogen atmosphere. After heating to 40 °C, FeCl<sub>3</sub> (32.6 g, 0.20 mol) was added to the mixture in three portions (0 h: 0.10 mol, after 1 h: 0.05 mol, after 3 h: 0.05 mol) and the mixture was stirred at 40 °C for 6 h under nitrogen atmosphere. The reaction mixture was poured into methanol to recover the product followed by washing with methanol several times. Collected powder was dissolved in THF to remove the insoluble part by filtration. The filtrate was concentrated and reprecipitated with acetone containing small amount of aqueous ammonia. The product was filtered and dried in vacuo. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.47–7.09 (m, –**Ar**), 4.41–4.33 (m, OOC–C**H**–Br, –C**H**<sub>2</sub>–O–CO), 2.95 (t, *J* = 6.6 Hz, Ar–C**H**<sub>2</sub>–), 2.58

Table 1	
Oxidative coupling copolymerization of TPA-I with BTPA	a

Run	TPA-I feed in	content (mol%) in n polymer <sup>e</sup>	$M_{\rm n}({\rm gmol}^{-1})(PDI)^{\rm f}$	$T_{\mathrm{g}}  (^{\circ}\mathrm{C})^{\mathrm{g}}$	Yield (%)
I-1	69	68	4000 (3.0)	165	56
I-2	41	39	6000 (2.4)	169	68
I-3 <sup>b</sup>	40	41	5200 (1.9)	154	63
I-4 <sup>c</sup>	22	20	5200 (2.0)	113	63
I-5 <sup>d</sup>	21	18	2400 (1.6)	142	39

<sup>a</sup> Polymerization of monomers (a total of 50 mmol of TPA-I and BTPA) was carried out using 4 equiv. of FeCl<sub>3</sub> in 200 mL of chloroform at 40  $^{\circ}$ C for 6 h.

<sup>b</sup> Polymerized in a tenth scale.

<sup>c</sup> Polymerized in a half scale.

<sup>d</sup> FeCl<sub>3</sub> was added all at once.

e Estimated from <sup>1</sup>H NMR data.

<sup>f</sup> Determined by GPC using polystyrene standards.

<sup>g</sup> Determined by DSC at a heating rate of 10 °C/min under nitrogen.

(t, *J* = 7.3 Hz, Ar–CH<sub>2</sub>–), 1.81 (d, *J* = 7.0 Hz, –CH<sub>3</sub>), 1.66–1.55 (m, Ar– CH<sub>2</sub>–CH<sub>2</sub>–), 1.42–1.32 (m, CH<sub>3</sub>–CH<sub>2</sub>–), 0.94 (t, *J* = 7.2 Hz, –CH<sub>3</sub>).

#### 2.6. General procedure for synthesis of polytriphenylamine-graftpoly(ethyl acrylate) (PTPA-g-PEA)

Macroinitiator PTPA-I (2.00 g), anisol (40 mL) and a stirring bar were placed into 200-mL round-bottom flask and then stirred at room temperature until the polymer totally dissolved. A stated amount of ethyl acrylate, CuBr, and *N*,*N*,*N''*,*N''*-penta- methyl-diethylenetriamine were added to the flask which then was placed into an oil bath at 90 °C. After cooling to room temperature, the solution was filtered with Al<sub>2</sub>O<sub>3</sub> plug in order to remove the catalyst. The concentrated solution was precipitated with methanol (or cold methanol). After reprecipitation, filtrated product was dried in vacuo. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.41–7.15 (m), 4.18–3.98 (br m), 2.92–2.89 (br m), 2.59–2.56 (br m), 2.31–2.27 (br m), 1.92–1.84 (br m), 1.66–1.63 (br m), 1.41–1.36 (br m), 1.22–1.16 (br m), 0.95 (t, *J* = 7.1 Hz).

#### 2.7. Characterizations

Molecular weight and polydispersity (PD) were estimated by gel permeation chromatography (GPC) equipped with JASCO 880-PU pump, a column packed with styrene-divinylbenzene gel beads, and a JASCO UV-970 detector. Chloroform was used as an eluent, and the molecular weight was calibrated using polystyrene standerds. <sup>1</sup>H NMR spectra were recorded at room temperature with a JEOL JNM-ECA500 spectrometer (<sup>1</sup>H: 500 MHz, <sup>13</sup>C: 125 MHz). UV spectra were obtained with a JASCO V-670 UV/VIS/NIR spectrometer. The *T<sub>g</sub>* was determined from differential scanning calorimetry (DSC) thermograms recorded with a Rigaku Thermo Plus DSC8230 in the temperature range from -50 to 200 °C under nitrogen flow.

The photoconductivity in the graft copolymers doped with 1 wt % of TNF was evaluated by measuring the voltage drop by a 1 M $\Omega$  resistor resulting from the photocurrent ( $I_{ph}$ ) through the film which was fabricated on indium tin oxide (ITO, 30  $\Omega$ ) covered glass substrate and was deposited with gold electrode [32]. Film thickness was determined by a profilometer (DektakII, Solan). A He–Ne laser with an intensity of 120 mW/cm<sup>2</sup> was used as a light source. The photoconductive sensitivity (*S*) is calculated according to

$$S = \frac{I_{\rm ph}L}{I_0AV} \tag{1}$$

where L is the film thickness,  $I_0$  is the irradiated laser power density, A is the irradiated area, V is the applied voltage.

#### 2.8. PR sample preparation and measurements

Photorefractive (PR) devices were prepared as follows; PTPA-*g*-PEA, DEADCST, and TNF were dissolved in THF or CH<sub>2</sub>Cl<sub>2</sub> (PTPA-*g*-PEA/DEADCST/TNF = 90/9/1 wt%). The solution was filtered through a 0.5 µm filter, concentrated to around one-third the original volume and dropped on indium tin oxide (ITO, 30  $\Omega$ ) covered glass. After the evaporation of the solvent, the sample was



Scheme 1. Synthetic route of PTPA-g-PEA.



Fig. 1. <sup>1</sup>H NMR spectrum of PTPA-I (I-1 in Table 1) measured in CDCl<sub>3</sub>.

heated on a hot plate and the surface was covered with another ITO glass to form a thin film sandwiched by two transparent electrodes. The sample thickness was approximately 100  $\mu m$  which was determined by the Teflon spacer used.

The PR properties were studied by the two-beam coupling (2BC) and four-wave mixing (FWM) techniques using the experimental setup described elsewhere [26]. A holographic grating was written using coherent beams from an NEC GLS-5410 He-Ne laser operated at 633 nm. All experiments were carried out at room temperature. In the 2BC experiments, the incoming laser beam (p-polarized) was split into two writing beams with the same intensity (130 mW/ cm<sup>2</sup>). The two writing beams at 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 experiments, two s-polarized beams of equal intensity  $(130 \text{ mW/cm}^2)$  were used to write a grating, which was probed by a much weaker p-polarized beam (0.8 mW/cm<sup>2</sup>) counterpropagating to one of the writing beams.

#### 3. Results and discussion

#### 3.1. Synthesis of monomers and macroinitiator

All the synthetic routes are shown in Scheme 1. Two triphenylamine (TPA) monomers were successfully synthesized in

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moderate total yields (TPA-I: 56.7%, BTPA: 94.4%). An initiating unit, 2-bromopropionyl group, for ATRP was introduced to TPA-I so that ethyl acrylate can be propagated as a graft chain.

Macroinitiators (PTPA-Is) with different TPA-I and BTPA compositions were synthesized utilizing oxidative coupling with FeCl<sub>3</sub> as an oxidant. <sup>1</sup>H NMR spectrum of PTPA-I is shown in Fig. 1. From the spectrum, it can be clearly seen that the signals appear at 1.8 (CHBrCH<sub>3</sub>) and 4.3 ppm (CHBrCH<sub>3</sub> and CH<sub>2</sub>OCO) confirming the ATRP initiating groups on the backbone of PTPA-I. Table 1 summarizes the polymerization conditions and characteristics of PTPA-I. Compositions of TPA-I were calculated by the integral ratio (0.94 ppm for CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> vs. 4.41–4.33 ppm for CHBrCH<sub>3</sub> and CH<sub>2</sub>OCO) in <sup>1</sup>H NMR spectrum and the results showed that the polymer compositions are roughly the same as the initial TPA-I feed ratios (Table 1). The number-average molecular weight ( $M_n$ ) and  $T_g$  of PTPA-I are about 2400–6000 (PDI = 2.0–3.0) and 113–169 °C, respectively (Table 1).

#### 3.2. Graft copolymers

Graft polymerizations were conducted using PTPA-Is with various compositions as macroinitiators. Graft copolymer (PTPA-*g*-PEA) was prepared by grafting PEA via ATRP from the initiating sites on the backbone of PTPA-I. The polymerization conditions and characteristics of PTPA-g-PEA are listed in Table 2. Fig. 2 shows <sup>1</sup>H NMR spectrum of PTPA-*g*-PEA (G-4). New signals appeared in the region from 1.3 to 2.3 ppm compared with the spectrum of

			-				
Run	PTPA-I	EA/PTPA-I feed ratio <sup>c</sup>	Time (h)	Grafted PEA $M_n  (\text{gmol}^{-1})^d$	$T_{\rm g}~(^{\circ}{\rm C})^{\rm e}$	PTPA ratio (wt%) <sup>d</sup> (GD (mol%)) <sup>d</sup>	Yield (%)
G-1	I-1	10	21	870	-6	39 (68)	49
G-2	I-1	5	20	450	-4	56 (68)	69
G-3	I-1	3	20	270	25, 120	68 (68)	68
G-4	I-3	30	20	1800	-14	33 (39)	41
G-5 <sup>b</sup>	I-2	34	24	1300	-9	40 (41)	30
G-6	I-3	5	20	260	21, 139	78 (39)	50
G-7	I-5	100	12	4800	-17	27 (18)	36
G-8	I-4	35	21	1900	-15	46 (20)	29
G-9	I-4	25	12	800	55, 98	67 (20)	35

<sup>a</sup> Polymerization was carried out in anisole in the presence of CuBr and PMDETA with a mole ratio of [Initiator]<sub>0</sub>/[CuBr]<sub>0</sub>/[PMDETA]<sub>0</sub> = 1/1/1.2.

<sup>b</sup> Polymerized in a tenth scale.

<sup>c</sup> Feed ratio of ethyl acrylate (EA) to ATRP initiating units of PTPA-I.

<sup>d</sup> Calculated from <sup>1</sup>H NMR.

<sup>e</sup> Determined by DSC at a heating rate of 10 °C/min under nitrogen.



Fig. 2. <sup>1</sup>H NMR spectrum of PTPA-g-PEA (G-4 in Table 2) measured in CDCl<sub>3</sub>.

macroinitiator, which are attributed to grafted PEA units. Since PEA homopolymer is soluble in methanol, and can be removed from the product in the purification process, it was confirmed that the PEA chains were successfully grafted onto the PTPA main chain. The degree of polymerization of PEA side chains was determined by the intensity ratio of the signals at 3.98–4.18 to those at 2.82–2.92 ppm in <sup>1</sup>H NMR spectrum of PTPA-*g*-PEA. Weight ratio of PTPA moieties was calculated using the following equation;

$$PTPA wt\% = \frac{nM_{TPA-I} + mM_{BTPA}}{nM_{TPA-I} + mM_{BTPA} + nM_{n(PEA)}}$$
(2)

where *n* and *m* are the unit numbers of TPA-I and BTPA in PTPA-*g*-PEA,  $M_{\text{TPA-I}}$  and  $M_{\text{BTPA}}$  are molecular mass of TPA-I and BTPA units, and  $M_{n(\text{PEA})}$  is the number-average molecular weight of grafted PEA, respectively.

The thermal behaviors of PTPA-g-PEA were investigated by DSC, and complicated results were obtained as reported in the literature [33]. DSC thermograms are shown in Fig. 3, and Table 2 shows  $T_g$  of each polymer. When the PTPA content is lower than 60 wt%, one glass transition was observed near  $T_g$  of PEA, suggesting that glass transition is predominantly governed by PEA side chain regardless of the graft density. Similar phenomenon was also observed in polythiophene derivatives containing polystyrene side arms [34]. Whereas PTPA-g-PEAs with higher PTPA content (G-3, G-6, and G-9) show two distinct glass transitions, indicating that two domains exist, one PTPA rich and the other PEA rich phases. For G-9, two  $T_g$  values seem to be more a averaged, which is resulted from the cooperative contribution of both PTPA backbone and PEA side arms. It is considered that the relatively low graft density nature of G-9

prohibits the phase separation observed in G-3 and G-6. These results suggested that PTPA-g-PEAs can provide different micro-domains by their compositions.

#### 3.3. Two-beam coupling (2BC) and photoconductivity

To verify the photorefractivity in composites, 2BC experiments were performed on the sample films with a thickness of 100  $\mu$ m. All the devices were uniform and transparent films except for high PTPA content polymers (G-3, G-6) which afforded turbid films resulting from the crystallization of dopant. Although PBTPA shows almost no compatibility with DEADCST, the introduction of high polar and soft grafted PEA chain significantly improved compatibility of the chromophore in the composite. The high optical quality of the PR devices was maintained even after one month of sample preparation at room temperature.

Asymmetric energy transfer was observed for devices based on PTPA-g-PEAs in 2BC experiments. The 2BC gain coefficient  $\Gamma$  was calculated using the following equation;

$$\Gamma = \frac{1}{L} \ln \left( \frac{\gamma \beta}{\beta + 1 - \gamma} \right) \tag{3}$$

where *L* is the optical path,  $\beta$  the intensity ratio of the two incident beams, and  $\gamma = I/I_0$  the beam coupling ratio where *I* and  $I_0$  are the detected signal intensities with and without the pumping beam, respectively. The applied field dependence of gain coefficients (*T*) measured for devices D-1 and D-2 based on the same graft density (68 mol%, see Table 3) of PTPA-g-PEAs are shown in Fig. 4 (left). The coupling gains for both devices monotonically increased with the



Fig. 3. DSC thermograms for synthesized graft copolymers: graft density is approximately 68% (a), 40% (b), and 20% c). The chemical composition of each polymer is listed on Table 2.

Table 3

Run	Polymer	PTPA ratio (wt%) (GD (mol%))	$T_{\rm g}~(^{\circ}{ m C})^{\rm a}$	$\alpha (\mathrm{cm}^{-1})^{\mathrm{b}}$	$\Gamma (\mathrm{cm}^{-1})^{\mathrm{c}}$	$\eta \; (\%)^{\mathrm{d}}$	τ (ms) <sup>e</sup>
D-1	G-1	39 (68)	-6	24	76 (35) <sup>f</sup>	10.8	33 (30) <sup>f</sup>
D-2	G-2	56 (68)	-4	28	30	1.6	28
D-3	G-4	33 (39)	-14	14	42	17.8	35
D-4	G-5	40 (41)	-9	24	66	0.3	14
D-5	G-7	27 (18)	-17	7	21	19.7	63
D-6	G-8	46 (20)	-15	9	24	5.2	15
D-7	G-9	67 (20)	98	19	18	2.8	8(50) <sup>f</sup>

Photorefractive properties for the devices based on PTPA-g-PEA.

<sup>a</sup> Glass transition temperatures of PTPA-g-PEAs.

<sup>b</sup> Absorption coefficients at 633 nm determined by UV spectra.

<sup>c</sup> Gain coefficient at 55 V/µm determined by 2BC.

 $^d\,$  Diffraction efficiency at 45 V/µm determined by FWM.

 $^{e}$  Response time constant at 40 V/ $\mu$ m.

<sup>f</sup> The values in parentheses represent the applied electric field (V/ $\mu$ m).

applied electric field. The values of gain coefficient ( $\Gamma$ ) at 55 V/µm are listed in Table 3 for all devices examined. PR devices with low PTPA ratios tend to show high coupling gains. Graft density is also a significant factor affecting on coupling gains. The denser grafting of PEA side chains becomes, the higher  $\Gamma$  of the PR composite is obtained.

Absorption coefficients ( $\alpha$ ) were determined in UV–vis spectra of the PR composite films with a 100 µm thickness from absorption tails resulting from charge transfer (CT) interaction between PTPA chain and TNF. These PR composites have the absorption coefficients from 7 to 28 cm<sup>-1</sup> at 633 nm (Table 3). The values of absorption coefficient increase as the graft density as well as PTPA ratio of polymer increase in spite of the same sensitizer content. It is speculated that the absorption coefficient was dependent on the local inhomogeneity in the composite. Fig. 5 shows the illustration of the graft density dependence of the local structures in the composite (e.g. D-1 and D-6). For high graft density, PTPA main chain is almost isolated in the PEA, and PTPA moiety is uniformly located. In such a structure, TNF molecules are easily accessible to PTPA chains, and interact with them to generate CT complexes, which consequently provide a high absorption coefficient. On the other hand, PTPA chains can aggregate to some extent in the case of low graft density, although only one  $T_g$  was observed as discussed above. The PTPA rich domains in the composite become relatively larger than that in the composite with high graft density assuming that TNF molecules are mainly located in a PEA rich phase. Thus the possibility for PTPA chain to encounter dopants decreases resulting in a low absorption coefficient.

This morphologic difference influenced on the coupling gain because the complex between PTPA and TNF is a site to generate charges which related with photoconductivity as described below. Consequently, the device using PTPA-g-PEA with high graft density, D-1 (using G-1 as a host), shows the highest gain value. From the practical point of view for optical amplification, gain coefficients ( $\Gamma$ ) must exceed the absorption loss of a photorefractive sample ( $\Gamma - \alpha > 0$ ). For all the samples the net gain was obtained.

Fig. 6 shows the electric field dependencies of the photoconductive sensitivity in PTPA-g-PEA graft copolymers (G-1, G-4, and G-7). For all copolymers examined (G-1, G-4, and G-7), the sensitivity increased with the applied electric field. For each sample, the photoconductive sensitivity was at least an order of magnitude higher than that of reported PVK-based systems at a given applied electric field [6]. Notice that the values in these samples were comparable to that of bis-triarylamine side-chain polymer based systems ( $0.2-1.5 \times 10^{-9}$  cm/ $\Omega$ W at 40 V/µm) [3], although TPA unit contents in our polymer are lower than that of side-chain polymer. This fact could be attributed to the more effective conjugation of the polymeric triarylamine main chains [22].

Photoconductivity is also dependent on the graft density or the micro morphology of graft copolymer. By comparison of sensitivities for the samples, G-1, G-4 and G-7 (relatively lower PTPA content with different graft density), G-1 with the highest graft density showed the highest sensitivity. It seems that the accessibility of TNF molecules to PTPA backbone mainly governs the photoconductive sensitivity since these polymers possess similar PTPA contents. Since photoconductivity is affected by a variety of factors such as drift mobility, trap density and so on, further studies are necessary to elucidate the process in heterogenous samples presented here.

#### 3.4. Four wave mixing (FWM)

The electric field dependencies of the steady-state diffraction efficiency ( $\eta$ ) for the devices were investigated, and the values of  $\eta$  at 45 V/µm are listed in Table 3. The diffraction efficiency was



Fig. 4. Electric field dependencies of the gain coefficients (left) and the diffraction efficiencies (right) using PTPA-g-PEA with the same graft density.



**Fig. 5.** Schematic illustrations of (a); the structures of PTPA-g-PEAs with the similar PTPA ratio, (b); plausible morphology in the composite, and (c); the accessibility of dopants (TNF).

determined by the ratio of the intensity of diffracted signal to that of incident reading beam. PR devices with low PTPA contents show high diffraction efficiencies. In the devices containing high PEA contents, it is possible that EO chromophore maintains high mobility to respond the incident beams. Fig. 4 (right) shows electric field dependencies of diffraction efficiency for D-1 and D-2, which are similar to those of gain coefficient. As shown in Table 3, there is inconsistency between  $\Gamma$  and  $\eta$ . The highest  $\Gamma$  and  $\eta$  were observed in D-1 and D-5, respectively. This is probably due to the difference of absorption coefficient. Since  $\eta$  values are determined from the ratio of the intensity of the diffracted beam to that of the incident reading beam, the diffraction efficiency is underestimated for the devices with high absorption.



**Fig. 6.** Electric field dependencies of the photoconductive sensitivity (PC) in PTPA-g-PEA graft copolymers (G-1, G-4, and G-7) sensitized with 1 wt% of TNF at wavelength of 633 nm.



Fig. 7. Electric field dependence on the response times in D-7 and a build-up transient at 50 V/ $\mu$ m (inset).

#### 3.5. Response time

To determine response time ( $\tau$ ), time-resolved FWM experiments were performed. This parameter is very important for real applications such as dynamic holography and real-data processing. The response time of PR grating formation was measured as followed. One writing beam and the reading beam were illuminated on the sample and an electric field was applied. After 60 s, the second writing beam was illuminated on the sample. The inset in Fig. 7 shows an example of a buildup transient for the device denoted as D-7 and curve fitting using the following equation [1];

$$\eta(t) = \eta^0 [1 - \exp(-t/\tau)]^2$$
(4)

where  $\eta^0$  is the steady-state diffraction efficiency.

Fig. 7 shows electric field dependence of  $\tau$  estimated for sample D-7. Table 3 lists response time constants at 40 V/µm for each device. PR composites showed response times of the order of 10 ms. The composites with higher PTPA contents generally afforded faster responses, and the shortest response time was observed when the PTPA contents was 67 wt% with the graft density of 20 mol% (D-7). Moon et al. reported that the PR composites based on the polymer containing dicarbazole moiety in the main chain showed high PR performance [12]. However the response time was ca. 1 s at 50 V/µm. In general, it is well-known that the response time is related with the photoconductivity of the material. As discussed above, it is considered that relatively fast response is attributed to high photoconductive nature of PTPA main chain.

#### 4. Conclusions

Here we have prepared novel graft polymers containing a poly(triphenylamine) (PTPA) backbone and poly(ethyl acrylate) (PEA) branches by the combination of oxidative coupling polymerization and ATRP techniques. PR composites based on these polymers show good static PR properties and fast response times under moderate conditions. In 2BC experiment, the higher is the graft density, the higher gain coefficient is obtained. In FWM experiment, with the increase of PEA content, diffraction efficiency increased and the highest diffraction efficiency (19.7% at 45 V/ $\mu$ m) was observed for PTPA-*g*-PEA (graft density: 18 mol%, PTPA ratio: 27 wt%) composite. PTPA-*g*-PEA (graft density: 20 mol%, PTPA ratio: 68 wt%) composite showed response time of 8 ms at an applied field of 50 V/ $\mu$ m. It is also found that local morphology of the composite plays an important role to determine the PR performance. In spite of fast response, there is a room to improve gain coefficient and diffraction efficiency in the composite based on graft copolymers presented here. Optimization of the composite parameters, such as the type and the content of a chromophore and a sensitizer, and the composite morphology is still ongoing.

#### References

- [1] Moerner WE, Silence SM. Chem Rev 1994;94:127-55.
- [2] Ostroverkhova O, Moerner WE. Chem Rev 2004;104:3267-314.
- [3] Thomas J, Norwood RA, Peyghambarian N. J Mater Chem 2009;19:7476–89.
   [4] Thomas J, Christenson CW, Blanche P-A, Yamamoto M, Norwood RA, Peyghambarian N. Chem Mater 2011;23:416–29.
- [5] Köber S, Salvador M, Meerholz K. Adv Mater 2011;23:4725–63.
- [6] Gallego-Gómez F, Álvarez-Santos JC, Rodríguez-Redondo JL, Font-Sanchis E, Villalvilla JM, Sastre-Santos Á, et al. J Mater Chem 2012;22:12220–8.
- [7] MeerholzK,VolodinBL,KippelenB,PeyghambarianN.Nature1994;371:497–500.
- [8] Chun H, Moon IK, Shin DH, Kim N. Chem Mater 2001;13:2813-7.
- [9] Moon IK, Choi CS, Kim N. Polymer 2007;48:3461–7.
- [10] Moon IK, Choi CS, Kim N. J Photochem Photobio A Chem 2009;202:57–62.
- [11] Tay S, Blanche P-A, Voorakaranam R, Tunc AV, Lin W, Rokutanda, et al. Nature 2008;451:694–8.
- [12] Thomas J, Hernandez CF, Yamamoto M, Camack K, Matsumoto K, Walker GA, et al. Adv Mater 2004;16:2032–6.
- [13] Blanche P-A, Bablumian A, Voorakaranam R, Christenson C, Lin W, Gu T, et al. Nature 2010;468:80–3.

- [14] Ogino K, Nomura T, Shichi T, Park SH, Sato H, Aoyama T, et al. Chem Mater 1997;9:2768–75.
- [15] Hofmann U, Schreiber A, Haarer D, Zilker SJ, Bacher A, Bradley DDC, et al. Chem Phys Lett 1999;311:41–6.
- [16] Ostrauskaite J, Karickal HR, Leopold A, Haarer D, Thelakkat DM. J Mater Chem 2002;12:58-64.
- [17] Wang X, Chen Z, Ogino K, Sato H, Miyata S, Tan H. Polym J 2000;32:778-83.[18] Wang X, Nakao M, Ogino K, Sato H, Tan H. Macromol Chem Phys 2001;202:
- 117–25.
- [19] Son J-M, Nakao M, Ogino K, Sato H. Macromol Chem Phys 1999;200:65-70.[20] Son I-M, Mori T. Ogino K, Sato H. Macromolecules 1999;32:4849-54.
- [20] Son J-M, Mon T, Ogno K, Sato H. Macroniolecules 1999,52.4649–54. [21] Ogino K, Kanegae A, Yamaguchi R, Sato H, Kurjata J. Macromol Rapid Commun
- 1999;20:103–6.
- [22] Takahashi C, Moriya S, Fugono N, Lee HC, Sato H. Synth Met 2002;129:123-8.
- [23] Olvera de la Cruz M, Sanchez IC. Macromolecules 1986;19:2501-8.
- [24] Eisenbach CD, Heinemann T. Macromolecules 1995;28:4815-21.
- [25] Miyata T, Takagi T, Uragami T. Macromolecules 1996;29:7787-94.
- [26] Ogino K, Goma T, Kagayama D, Sato H, Yonezawa N. J Photopolym Sci Technol 2006;19:419–24.
- [27] Díaz-García MA, Wright D, Casperson JD, Smith B, Glazer E, Moerner WE, et al. Chem Mater 1999;11:1784–91.
- [28] Ogino K, Park S-H, Sato H. Appl Phys Lett 1999;74:3936-8.
- [29] Jeong J-M, Abe K, Sato H, Pretula J, Kaluzynski K, Ogino K. Synth Met 2003; 139:11–9.
- [30] Tan Y, Gu Z, Tsuchiya K, Ogino K. Polymer 2012;53:1444-52.
- [31] Cao Z, Tsuchiya K, Ogino K. Chem Lett 2012;41:1541-3.
- [32] Park S-H, Ogino K, Sato H. Polym Adv Technol 2000;11:349–58.
- [33] HongSC,PakulaT,MatyjaszewskiK.MacromolChemPhys2001;202:3392-402.
- [34] Shen J, Tsuchiya K, Ogino K. J Polym Sci Part A Polym Chem 2008;46:1003–13.