Synthesis and Characterization of a New Photoconducting Poly(siloxane) Having Pendant Diphenylhydrazone for Photorefractive Applications

Sang Ho Lee, Woong Sang Jahng, and Ki Hong Park*

Optoelectronic Materials Research Center, Korea Institute of Science and Technology, P. O. BOX 131, Cheongryang, Seoul 136-791, Korea

Nakjoong Kim and Won-Jae Joo

Department of Chemistry, Hanyang University, Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea

Dong Hoon Choi

College of Environment & Applied Chemistry, Kyunghee University, Younginn, Kyungki-do 449-701, Korea

Abstract: A new photoconducting polymer, diphenyl hydrazone-substituted polysiloxane, was successfully synthesized by the hydrosilylation method and characterized by FT-IR, ^{1}H-NMR, and ^{29}Si-NMR spectroscopy. The glass transition temperature (T_g) of the polysiloxane having pendant diphenyl hydrazone was ca. 62 °C, which enabled a component of a low-T_g photorefractive material to be prepared without the addition of any plasticizers. This polysiloxane, with 1 wt% of C_{60} dopant, showed a high photoconductivity (2.8×10^{-12} S/cm at 70 V/μm) at 633 nm, which is necessary for fast build-up of the space-charge field. A photorefractive composite was prepared by adding a nonlinear optical chromophore, 2-{3-[2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenylidene} malononitrile, into the photoconducting polysiloxane together with C_{60}. This composite shows a large orientation birefringence ($\Delta n = 2.6 \times 10^{-3}$ at 50 V/μm) and a high diffraction efficiency of 81% at an electric field of 40 V/μm.

Keywords: photorefractive, diphenyl hydrazone, polysiloxane, photoconducting, hydrosilylation.

Introduction

The photorefractive effect was first reported with LiNbO$_3$ crystal more than 35 years ago.[1] A variety of potentially important applications have been proposed using inorganic crystals, including high-density optical data storage, image processing, phase conjugation, beam fanning limiter, and optical correlator.[2] However, because of difficulties in crystal growth and sample preparation, inorganic crystals have been limited for mass production. For last decade, extensive studies have been carried out on organic photorefractive materials to overcome some of problems associated with inorganic materials. Photorefractive organic materials have many advantages of lower dielectric constants, lower cost, and easier processing than inorganic materials.

Among many organic photorefractive materials reported to date, polymeric host-guest system has been extensively investigated because of their excellent photorefractive prop-

erties, compositional flexibility and easy fabrication method.[3,4] The charge-transporting polymers such as poly(vinyl carbazole) or poly(siloxane carbazole), doped with nonlinear optical chromophores have been generally adopted due to their excellent photorefractive performance. The large refractive index modulations, up to $\Delta n = 10^{-2}$, and fast response times, down to 1 ms, have been reported with this polymeric system.[5-8]

Carbazole-substituted polysiloxane (**PSX-Cz**) is one of the most well-known photoconducting polymers for photorefractive systems.[9] The glass transition temperature (T_g) of these **PSX-Cz** composites could be lowered to room temperature simply by adding a NLO chromophore. It was notable that the photorefractive properties could be improved by using a low T_g polysiloxane because this system did not contain inactive molecules such as a plasticizer.[10]

In this study, a new photoconducting poly(siloxane) with pendent 4-(*N,N*-diethylamino)benzaldehyde diphenylhydrazone (**DEH**) was synthesized by a hydrosilylation reaction. The **DEH**-doped polymer has been reported as a good candidate with excellent hole-mobility and photorefractivity.[11-13]

*e-mail: khopark@kist.re.kr

The problem of phase separation, however, can be induced in the case of polymers doped with both **DEH** and nonlinear optical chromophores. Therefore, in order to circumvent this problem, we synthesized a polysiloxane with **DEH** as a side chain. The photorefractive composite was prepared by doping a nonlinear optical chromophore and a photosensitizer into the new photoconducting polysiloxane. We characterized the photorefractive performance of the composite by use of the DC photocurrent measurement, a transmission ellipsometry method, and a degenerate four wave mixing technique.

Experimental

Materials. 4-Fluorobenzaldehyde, 1,1-diphenylhydrazine hydrochloride, sodium acetate trihydrate, poly(methylhydrosiloxane), Aliquat®336, hydrogen hexachloro-platinate(IV) hydrate, anhydrous toluene, and buckminsterfullerene (C_{60}) were purchased from the Aldrich and were used without further purification.

Synthesis of 4-[allyl(methyl)amino]benzaldehyde (1). In a 250 mL three-necked flask equipped with a magnetic stirrer and a reflux condenser, 10 g (0.141 mol) of *N*-methyl-allylamine, 100 mL of *N,N*-dimethylformamide (DMF), 10 g of potassium carbonate, and 4 drops of Aliquat®336 were added and stirred at 55 °C. 4-Fluorobenzaldehyde (17.45 g / 0.141 mol) was dropped slowly into the mixture. This mixture was reacted at a reflux for 7 days. The reaction mixture was poured into cold water. The product was extracted with methylene chloride, and the organic layer was dried over anhydrous magnesium sulfate, filtered, and then was evaporated the solvent. This product was purified by column chromatography on silica gel (eluent, ethyl acetate : hexane = 1 : 8). The product was obtained as yellow viscous oil (10.46 g, 41% yield): ^{1}H-NMR (CDCl$_3$); δ(ppm) 9.8~9.6 (1H, s), 7.8~7.6(2H, d), 6.8~6.6 (2H, d), 5.8 (1H, m), 5.2~5.0 (2H, q), 4.0 (2H, s), 3.0 (3H, s).

Synthesis of 4-[allyl(methyl)amino]benzaldehyde 1,1-diphenylhydrazone (2). Into a flask 100 mL of ethanol, 10 g of 4-[allyl(methyl)amino]benzaldehyde (57.07 mmol) was added with stirring at room temperature. The mixture of 1,1-diphenylhydrazine hydrochloride 15.11 g (68.48 mmol) and sodium acetate trihydrate 11.65 g (85.60 mmol) in ethanol was slowly dropped into the above solution and maintained at room temperature. The mixture was reacted for 5 hrs and then cooled at room temperature. Residual solvent was evaporated under reduced pressure. This mixture was extracted with methylene chloride, and the organic layer was dried with anhydrous sodium sulfate. The product was purified by column chromatography on silica gel (eluent, ethyl acetate : hexane = 1 : 4). The product was obtained as yellow viscous oil (18.69 g, 96% yield): ^{1}H-NMR (CDCl$_3$); δ (ppm) 7.8~6.8 (Ar 14H, 1H, m), 5.8 (1H, m), 5.2~5.1 (2H, t), 4.0 (2H, d), 3.0 (3H, s).

Synthesis of Poly[4-(diphenyl-hydrazonomethyl)-phenyl]-[3-(methoxy-dimethyl-silanyl)-propyl]-methyl-amine (PSX-Hz). A dried 100 mL of two-necked flask was equipped with a magnetic stirrer and a reflux condenser under argon. Into this flask, 4-[allyl(methyl)amino]-benzaldehyde 1,1-diphenylhydrazone (6 g, 17.57 mmol) and 40 mL of toluene were added and purged with argon. The portion of poly (methylhydrosiloxane) (1.06 g, 17.57 mmol) was dissolved with anhydrous toluene and added to the flask with several drops of hydrogen hexachloro-platinate (IV) hydrate under argon atmosphere. The solution was heated at 150 °C for 5 hrs, and then poured into methanol. The precipitate was filtered, dried, and purified three times by reprecipitation from methanol to give 4.92 g (82% yield) of a desired product as pale yellow solid: ^{1}H-NMR(CDCl$_3$); δ (ppm) 7.4~7.2 (ArH, 6H, m), 7.2~7.0 (ArH, 6H, -HC=N-, 1H, m), 6.6~6.4 (ArH, 2H, m), 3.2~3.0 (-CH$_2$-, 2H, m), 2.8~2.6 (CH$_3$-, 3H, m), 1.6 ~1.4 (-CH$_2$-, 2H, m), 0.5~0.3 (CH$_2$-, 2H, m), 0.2~0 (-CH$_3$, 3H, m).

Sample Preparation. The photorefractive composite was prepared by doping an electro-optic chromophore and C_{60} into the photoconducting polymer matrix, **PSX-Hz**. The mixture consisting of **PSX-Hz** : **DB-IP-DC**: C_{60} in a ratio of 69 : 30 : 1(wt%) was dissolved in dichloromethane. The solution was filtered through a 0.2 μm filter and casted on an indium tin oxide (ITO)-patterned glass plate, dried for 12 hrs at ambient temperature and subsequently heated in an oven at 90 °C for 24 hrs to remove the residual solvent. Then the composite was softened by placing it on a hot plate at 100 °C and then covered with the upper ITO coated glass. The thickness of about 100 μm could be controlled using Teflon spacers between two ITO glass plates.

Characterization and Measurement

^{1}H-NMR and ^{29}Si-NMR spectra were taken by Varian Gemini NMR Spectroscopy 300 MHz. FT-IR spectra were obtained on a Perkin Elmer spectrum GX FT-IR Spectrophotometer. The glass transition temperatures (T_g) were determined with a differential scanning calorimeter (DSC), Perkin-Elmer Pyris 1 series, at a heating rate of 10 °C/min under nitrogen atmosphere.

The DC photocurrent measurement was performed on about 100 μm-thick polymeric composite film sandwiched between ITO electrodes at a temperature of T_g. The illuminating beam from He-Ne laser (633 nm) was expanded into the diameter of 6 mm and its intensity was 13 mW/cm^2.

The electro-optical property of the polymeric composite was characterized by the transmission ellipsometric measurement at various electric fields.[14] The sample tilted by +45 ° and -45 ° in air was placed between the polarizer and the analyzer. The birefringence (Δn) of the sample was determined from the transmittance of the reading beam passing through crossed polarizers upon applied electric field.

Diffraction efficiency(η) was measured by a degenerate

four-wave mixing method. The experiment was performed near the T_g (27 °C) of the polymeric composite. Two coherent laser beams from He-Ne laser were irradiated on the sample in tilted geometry with the incident angle of 30° and 60° with respect to sample normal. Both of writing beams were s-polarized and had the equal intensity of 60 mW/cm². A p-polarized counter-propagating beam was used to read out the recorded photorefractive grating. Attenuated reading beam with the intensity of 0.1 mW/cm² was used. The internal diffraction efficiency (η_{max}) of photorefractive material was determined from equation $\eta_{int} = I_{R,diffracted}/(I_{R,diffracted} + I_{R,transmitted})$.[6]

Result and Discussion

Synthesis. The chemical structures of the compounds used in this work are shown in Figure 1. The optically anisotropic chromophore, 2-{3-[(E)-2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenyliden} malononitrile (**DB-IP-DC**) was synthesized by a previously described method.[15]

The synthetic pathway of photoconducting polysiloxane is outlined in Scheme I. Photoconducting compound **2** was prepared by a condensation reaction of compound **1** with 1,1-diphenyl hydrazine hydrochloride. The chemical structures of compounds **1** and **2** were confirmed by FT-IR and ¹H-NMR spectroscopy. In an IR spectrum of compound **2** (Figure 2(c)), the C=O stretching band at 1720 cm⁻¹ was evidently disappeared after the condensation. The chemical shifts of vinyl protons of compound **2** could be identified at 5.15 and 5.80 ppm of ¹H-NMR spectrum in Figure 3.

A photoconducting polymer, diphenyl hydrazone-substituted poly(siloxane) (**PSX-Hz**), was obtained by a hydrosilylation of poly(methylhydrosiloxane) with compound **2**. Hydrosilylation has been known as a very convenient method for the synthesis of various silicon-containing polymer.[16] Hydrogen

hexachloro-platinate(IV) hydrate was used as a catalyst and anhydrous toluene as a solvent. The hydrosilylation was monitored by a residual Si-H stretching intensity that came a convenient window of the FT-IR spectrum (Figure 2). The Si-H peak of **PSX-Hz** at 2160 cm⁻¹ was completely disappeared after hydrosilylation for 48 hrs. Moreover, absorption peaks of **DEH** were newly appeared as shown in Figure 2(b). As shown in ¹H-NMR spectrum of Figure 3(b), Si-H peak at 4.6 ppm of **PSX-Hz** was almost disappeared by hydrosilylation in ¹H-NMR spectra. Also, as shown in ²⁹Si-NMR spectra (Figure 4), original poly(methyl hydrosiloxane) had two coupled signals at -32.7 and -36.7 ppm due to -O-
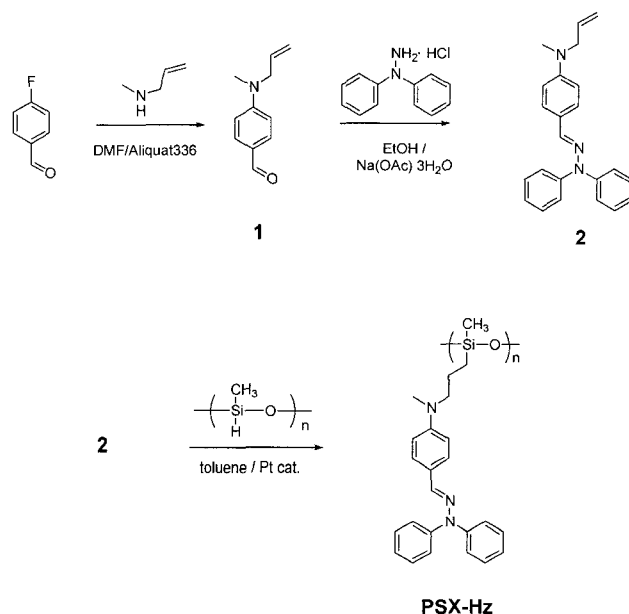
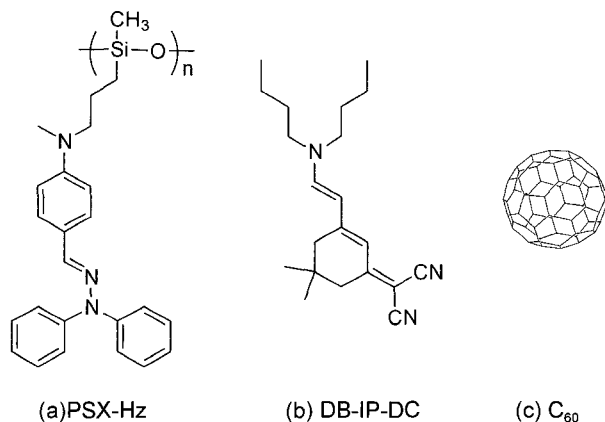**Scheme I.** Synthesis of a photoconducting polymer.

Figure 1. Chemical structures of components of photorefractive composite : (a) polysiloxane, **PSX-Hz**; (b) optically anisotropic chromophore, 2-{3-[2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenyliden}malononitrile (**DB-IP-DC**); (c) sensitizer, buckminsterfullerene (**C₆₀**).
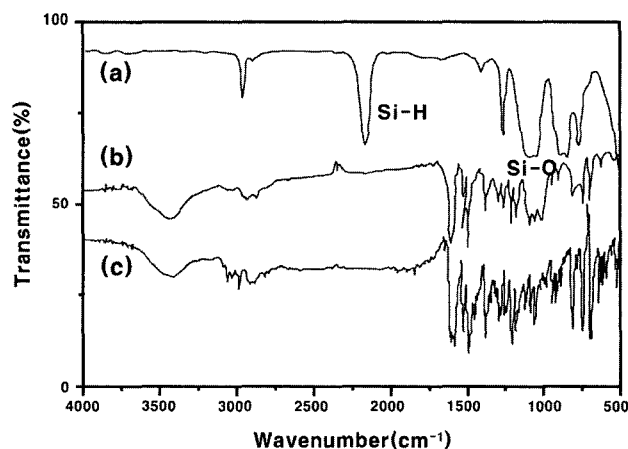
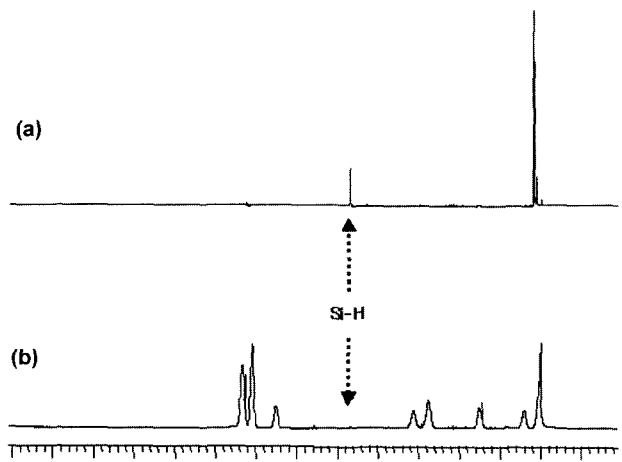**Figure 2.** FT-IR spectra; (a) Poly(methylhydrosiloxane), (b) PSX-Hz, and (c) compound 2.

Figure 3. ¹H-NMR spectra of (a) poly(methylhydrosiloxane) and (b) diphenyl hydrazone-substituted poly(siloxane).
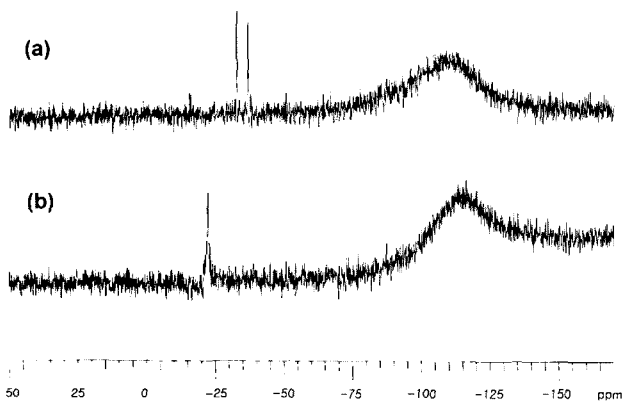

Figure 4. ²⁹Si-NMR spectra of the (a) poly(methylhydrosiloxane) before hydrosilylation and (b) diphenyl hydrazone-substituted poly(siloxane) after hydrosilylation.

Si(H)(CH₃)-O-group.[17] After hydrosilylation, ²⁹Si chemical shift of **PSX-Hz** deriving from O-Si(R)(CH₃)-O- group was given by a single signal at 22.3 ppm.[17]

The polymer solution was poured into a vigorously stirred methanol to isolate the polymer solid. The polymer was purified by three reprecipitation from methanol. Particularly for the removal of catalyst, we treated with ion-exchange resin (Amberlite® IRC-718). The **PSX-Hz** could be successfully synthesized in a high yield (82%) and the weight-average molecular weight of polymer, determined by gel permeation chromatography, was 25,700 and polydispersity was 2.61. According to the DSC thermograms in Figure 5, the glass transition temperature was about 62 °C at the second heating. **PSX-Hz** was fairly soluble in common solvents such as tetra-hydrofuran, chloroform, acetone and *N,N*-dimethylform-amide.
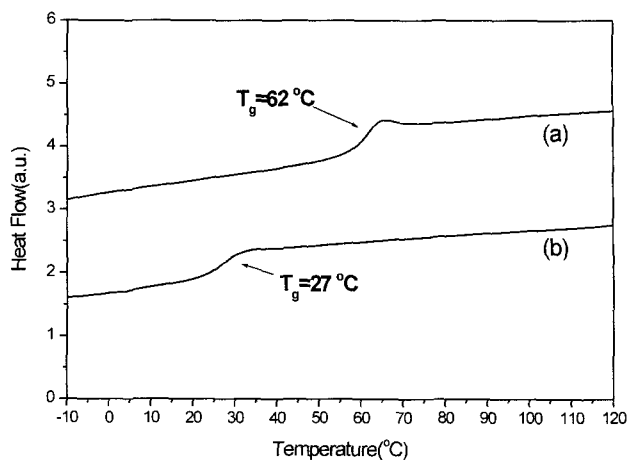

Figure 5. DSC thermogram ; (a) **PSX-Hz** and (b) **PSX-Hz**: **DB-IP-DC**: **C₆₀** composite.

Photoconductivity of PSX-Hz Composite. The photore-fractive composite sample consisted of 69 wt% of **PSX-Hz** (a photoconductor), 30 wt% of **DB-IP-DC** (a NLO chromo-phore) and 1 wt% of **C₆₀** (photosensitizer) and did not show any phase separation or crystallization at room temperature for over a year. The glass transition temperature of the com-posite was around 27 °C determined by DSC (Figure 5). The photoconductivity, σ_{ph}, is governed by the photocharge gen-eration efficiency and the charge mobility, and is described by

$$\sigma_{ph} = n\mu = (\phi\alpha I\tau_{eff}/h\nu)\,\mu \qquad (1)$$

where n is the number of charge density of the mobile holes produced at light intensity I, ϕ the quantum efficiency of photo-charge generation, α the absorption coefficient at frequency ν, h Plank constant and μ the hole mobility.

The electric field dependence on photocurrent is shown in Figure 6. The conductivity value under illumination was an order of magnitude larger than those in dark. The photocon-ductivity of **PSX-Hz** composite was estimated to be 2.8×10^{-12} S/cm at applied electric field of 70 V/μm, which was one order of magnitude larger than that in the case of carbazole-based poly(siloxane) composites.[15] This remarkably high photoconductivity was attributed to the superior hole trans-porting ability of **DEH** compared to carbazole.

Electro-optic Effect. Field-induced birefringence of the photorefractive polymer composite was characterized by a transmission ellipsometric method under various applied electric fields. As shown in Figure 7, birefringence (Δn) of the composite containing 30 wt% of **DB-IP-DC** chromophore was quadratically increased with the applied electric fields. The composite showed an excellent anisotropic behavior of $\Delta n = 2.6 \times 10^{-3}$ at 50 V/μm, which is sufficient large for the preparation of the efficient photorefractive materials.[21] The
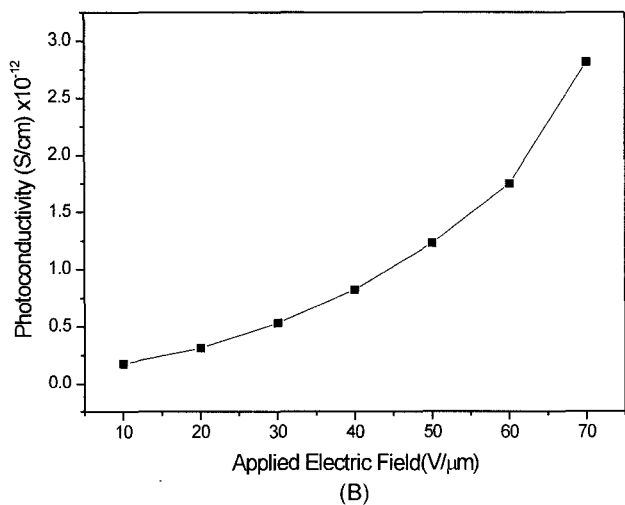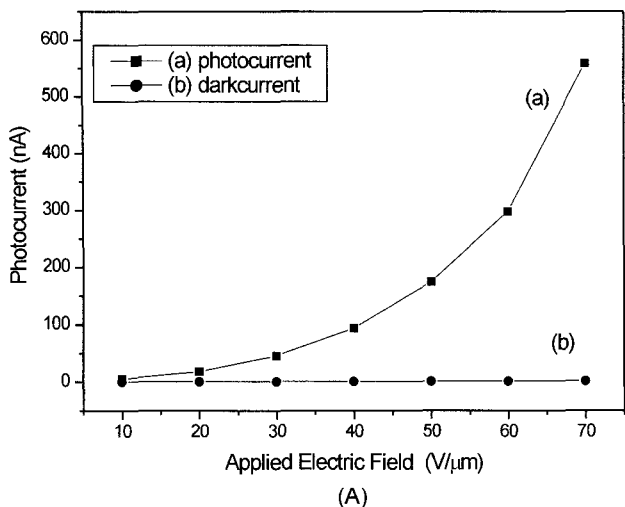
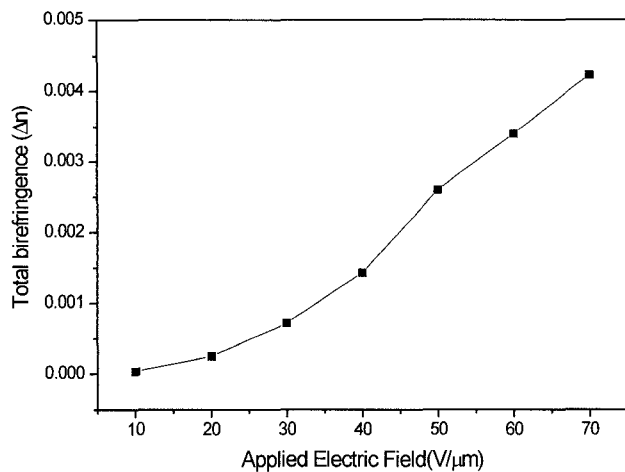**Figure 6.** Photocurrent and darkcurrent (A) and photoconductivity(B) of **PSX-Hz:DB-IP-DC:C$_{60}$** composite.

birefringence (Δn) originates from the alignment of chromophores with noncentrosymmetric structures under poling field. In the case of low T_g photorefractive material, the modulation of refractive index (Δn) is known to arise predominantly from reorientation of the optically nonlinear chromophore under the spatially modulated space-charge field.[4] The large orientational birefringence of the polymeric composite is due to a large dipole moment of the **DB-IP-DC** chromophore as well as a high polarizability anisotropy of chromophore associated with the effective conjugation.[15] Be reminded that this measurement provides the useful information in the evaluation of the chromophore.

Diffraction Efficiency of the PSX-Hz Composite. The photorefractive property of polymeric **HSX-Hz**: **DB-IP-DC**: **C$_{60}$** composite was evaluated by diffraction efficiency, which was measured by a degenerate four wave mixing method. Figure 8 shows the electric field dependence on the steady-state diffraction efficiency. According to Kogelniks coupled-wave theory, the diffraction efficiency (η) can be approximated by the following Eq. (2) and (3). It showed an oscillatory behavior.[9, 18]

$$\eta = \sin^2[C_{DFWM} \cdot \Delta n] \tag{2}$$

$$C_{DFWM} = \frac{\pi \cdot d}{\lambda_0 \cos[(a_1 + a_2)/2]} \tag{3}$$

where Δn is the photorefractive index modulation, λ_0 is the wavelength, α_1 and α_2 are internal angles of two laser beams, and d is sample thickness. The maximum diffraction efficiency (η_{max}) of 100 μm-thick film was 81% at 40 V/μm. This is a fairly high diffraction efficiency compared to the other composite.[19] One of main reasons for high efficiency might be the easiness of orientation of EO chromophore because of a low glass transition temperature and structural flexibility of this polysiloxane backbone.[20] Besides, the ori-
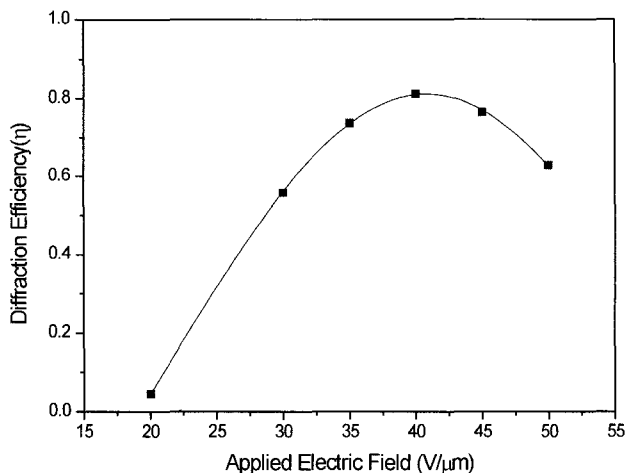

Figure 7. Electric field induced birefringence of the composite, **PSX-Hz**: **DB-IP-DC**: **C$_{60}$**, at various applied electric field.

Figure 8. Steady-state diffraction efficiency depending on electric field of **PSX-Hz**: **DB-IP-DC**: **C$_{60}$** composite.

entational birefringence ($\Delta n \cong 2.6 \times 10^{-3}$) of the composite led to the high diffraction efficiency at a moderate electric field of 50 V/μm.

Conclusions

Diphenyl hydrazone-substituted polysiloxane (**PSX-Hz**) as a photoconducting matrix was successfully synthesized by a hydrosilylation method with a platinum catalyst. The glass transition temperature of **PSX-Hz** was observed to be about 62 °C. The photorefractive **PSX-Hz** composite containing 30 wt% of **DB-IP-DC** chromophore and 1 wt% of **C$_{60}$** did not show any phase separation or crystallization at room temperature for over a year. The photoconductivity of polysiloxane composite was determined to be 2.8×10^{-12} S/cm at the applied electric field of 70 V/μm. The birefringence (Δn) of the composite was 2.6×10^{-3} at 50 V/μm, implying a good orientational arrangement of NLO chromophores. The diffraction efficiency was as high as 81% at an applied field of 40 V/μm, which implied that this **PSX-Hz** based material, could be a good candidate for photorefractive application.

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