Visible Light Photoconduction of Poly(disilanyleneoligothienylene)s and Doping Effect of C_{60}

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ABSTRACT: The photoconductive properties of poly(disilanyleneoligothienylene)s [PDS(Th)$_m$; $m = 2-4$], which have a disilanylene group and an oligothienylene unit in a polymer backbone, and fullerene (C_{60}) doping effects were investigated. It was found that these polymers are photoconductive and have photocarrier generation maxima in accordance with their optical absorption spectra. The polymer PDS(Th)$_4$ was photoconducting when irradiated in the visible light and the quantum efficiency for photocarrier generation was 2% at 480 nm ($E = 6 \times 10^5$ V cm^{-1}). The hole-drift mobility was measured and ranged between 1.1×10^{-4} cm^2 V^{-1} s^{-1} at 2×10^5 V cm^{-1} and 2.1×10^{-4} cm^2 V^{-1} s^{-1} at 6×10^5 V cm^{-1} at room temperature. As far as we know, this is the first observation of photocarrier generation in the visible region in silicon-based polymers. Furthermore, C_{60} doping enhanced the photoconductivity quantum efficiency effectively to 85% at 470 nm ($E = 3 \times 10^5$ V cm^{-1}) by a photoinduced charge transfer mechanism.

Introduction

Over the last several years, there has been growing interest in the synthesis and properties of silicon-containing polymers such as polysilanes and polymers with the regular alternating arrangement of an Si−Si bond and π-electron system in a main chain. These polymers can be used as photoresists, conducting and photoconducting materials, and ceramic precursors.[1] Furthermore, polysilanes show high hole-drift mobilities on the order of 10^{-4} cm V^{-1} s^{-1},[2] and hence application of these polymers for the hole-transport layers in photocopiers and laser beam printers has been extensively studied.[3,4]

On the other hand, the photocarrier generation efficiency of polysilanes is low upon direct irradiation. It has been reported to be about 1% for poly(methylphenylsilane) (PMPS) in the ultraviolet region at high electric fields.[2] However, Wang *et al.*[5] and Kepler *et al.*[6] have reported that the photocarrier generation efficiency of PMPS was significantly increased by doping with fullerene (C_{60}). We have recently shown that the photoluminescence of polysilanes with the aromatic side groups bonded directly to the backbone is strongly quenched upon C_{60} doping and the effectiveness of photoinduced charge transfer between the main chain of the polysilanes and C_{60} depends highly on the nature of the aromatic side groups.[7] Unfortunately, in this system high photocarrier generation efficiency is limited to the UV region, and therefore, it is inconvenient to use this system as the photocarrier generation layer for visible light irradiation.

Recently, Malliaras *et al.*[8] and Ishikawa *et al.*[9,10] have reported the synthesis of the polymers with a regular alternating arrangement of a silylene or disilanylene unit and an oligothienylene unit in the polymer backbone, whose absorption and luminescence are in the visible region.

In this paper, we report the photoconductivity in the visible light region of poly[(disilanylene)oligo(2,5-thienylene)]s [PDS(Th)$_m$; $m = 2-4$] that have a regular alternating arrangement of a disilanylene unit and an oligothienylene unit. We also report that the photoconductivities of the polymers are greatly enhanced by C_{60} doping.

Experimental Section

Synthesis of Poly[disilanyleneoligo(2,5-thienylene)]s, PDS(Th)$_m$ ($m = 2-4$). Poly[disilanylenebi(2,5-thienylene)], PDS(Th)$_2$, was synthesized by the dehalogenative coupling reaction of 1,2-bis(bromothienyl)disilanes with magnesium in the presence of a catalytic amount of dichloro[bis(diphenylphosphino)ethane]nickel(II), while PDS(Th)$_3$ and PDS(Th)$_4$ were prepared by the Ni(II)-catalyzed Grignard cross coupling of 1,2-bis(5-bromothien-2-yl)-1,1,2,2-tetraethyldisilane with 2,5-dibromothiophene and 5,5′-dibromo-2,2′-bithiophene, respectively. Preparation of these monomers and polymers was already reported in the previous literature.[10]

For example, PDS(Th)$_4$ was prepared by the following procedure: A mixture of 49 mg (2.00 mmol) of magnesium and 0.496 g (1.00 mmol) of 1,2-bis(5-bromothien-2-yl)-1,1,2,2-tetraethyldisilane in 3 mL of dry THF was stirred in a Pyrex tube (15 mm × 150 mm) at room temperature, and the mixture was heated to reflux about 3 h until all magnesium was consumed. To the resulting di-Grignard reagent was added 0.324 g (1.00 mmol) of 5,5′-dibromo-2,2′-bithiophene and 11 mg (2 mol %) of dichloro[bis(diphenylphosphino)ethane]nickel(II), and then the glass tube was degassed under reduced pressure and sealed. The mixture was heated at 150 °C for 80 h, and then the reaction mixture was hydrolyzed and filtered. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layer and extracts were dried over anhydrous magnesium

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Scheme 1

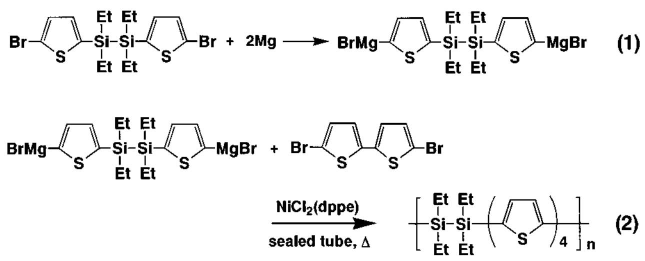

Table 1. Yields, Molecular Weights Measured by GPC, and Absorption λ_{max} in THF Solution of PDS(Th)$_m$

m	yields (%)	M_w	M_w/M_n	λ_{max} (nm)
2	81	51 000	3.4	343
3	78	47 000	3.4	389
4	97	34 000	2.4	415

sulfate. After the solvent was evaporated, the residue was reprecipitated from ethanol-chloroform to give poly[tetraethyldisilanylenequater(2,5-thienylene)], PDS(Th)$_4$, in 97% yield as an orange-red solid (Scheme 1). The yields, molecular weights, and the absorption maxima (λ_{max}) in THF solution of the polymers, which were used in the present study, are shown in Table 1. The molecular weights and molecular weight distributions were determined by GPC and are relative to polystyrene standards.

Measurements of Photoconductivity, Photocurrent, Hole-Drift Mobility, Ionization Potential, and Absorption Spectra. The samples used for the photoconductivity measurements were composed of indium tin oxide (ITO)/PDS(Th)$_m$ (m = 2−4)/Au sandwich-type cell. Polymer films (2−4 μm) were prepared by spin-coating of a toluene solution of PDS(Th)$_m$ on a transparent ITO-coated quartz plate. A counter Au electrode (20 nm) was deposited on the polymer film by vacuum evaporation under 1×10^{-3} Pa at a deposition rate of 0.1 nm/s. In the case of C_{60}-doped samples, C_{60} was prepared by arc discharge using graphite as an electrode provided by Materials and Electrochemical Research (99.9% grade), and C_{60}-doped films were prepared by the spin-coating of a toluene solution involving the appropriate weight ratio of PDS(Th)$_m$ and C_{60}.

The cell was placed in an optical cryostat (Technolo Kogyo Co. Ltd., CN-3) evacuated to 10^{-1} Pa. Steady state photocurrent measurements were carried out using an electrometer with an applied voltage between the Au and ITO electrodes. Monochromatic light from a 300-W Xe lamp through a monochromator was used as a light source for irradiation. The light intensity was monitored by a silicon photodiode (Hamamatsu Photonics, S1337-66BQ).

A sandwich-type cell composed of ITO/PDS(Th)$_4$/Au was used for the drift mobility measurements. A toluene solution of PDS(Th)$_4$ was cast on an ITO-coated quartz plate, and dried at 50 °C *in vacuo*. A semitransparent Au electrode was added by vacuum deposition on the surface of PDS(Th)$_4$ to form a sandwich-type cell. The thickness of the film was determined by a surface roughness meter. The hole-drift mobility measurements were carried out *in vacuo* by the usual time-of-flight (TOF) technique using a nitrogen-gas-laser pulse (337 nm, pulse duration 3 ns; power 100 μJ).

Ionization potentials were measured by an atmospheric photoelectron emission analyzer (Rikenkeiki, AC-1). For optical measurements, thin films (0.1−0.3 μm) were prepared by spin-coating a toluene solution of the polymer on a quartz plate and then dried *in vacuo*. Absorption and photoluminescence spectra were obtained using a Hitachi U-3210 spectrometer and a Hitachi 850 fluorescence spectrophotometer.

Results and Discussion

Photoconductivity of Poly(disilanyleneoligothienylene)s. Absorption spectra of the PDS(Th)$_m$ (m = 2−4) as cast films are shown in Figure 1. The absorption maxima of the polymers shift to a longer wavelength as the number of the thienylene rings increases. As reported previously,[10] the absorption of these polymers corresponds to that of the α,ω-bis(disilanyl)-substituted oligothiophenes, in which only small red shifts are observed comparing the ordinary oligo(2,5-thiophenes). This suggests that π-electrons on the oligothienyl moieties are hardly delocalized through the polymer chain. Therefore, the absorptions may be assigned as a π−π* interband transition of the oligothienyl moieties.

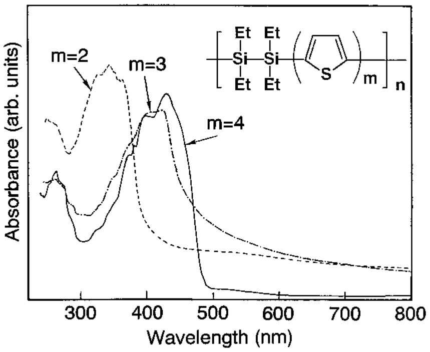

Figure 1. Absorption spectra of PDS(Th)$_m$ (m = 2−4) as cast films.

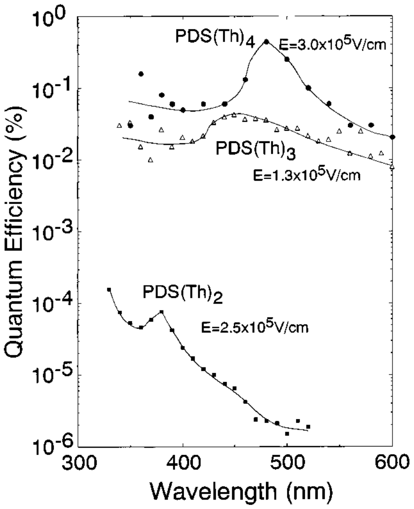

Figure 2. Wavelength dependence of the photocurrent quantum efficiency of PDS(Th)$_m$ (m = 2−4) under the irradiation of monochromatic light through an ITO electrode under an applied voltage.

The wavelength dependence of the photocurrent quantum efficiency of PDS(Th)$_m$ (m = 2−4) is shown in Figure 2. Comparing the photocurrent quantum efficiency curves with their absorption spectra, the position of each maximum peak for the photocurrent quantum efficiencies appears at 30−40 nm longer wavelength than that of the respective absorption maximum. These peaks correspond to the absorption edge of the polymers. This means that almost all incident light would be absorbed in the vicinity of the illuminated surface of the films in the region of the absorption bands of the polymers. The generated excitons must be quenched because the density of the excitons in this area is probably very high. Consequently, the peaks of the photocurrent quantum efficiency appear at the edge of the absorptions, which establish the bulk excitation in the whole film.

Interestingly, the photocurrent quantum efficiency of both PDS(Th)$_3$ and PDS(Th)$_4$ is determined to be on the order of 10^{-1}% to 10^{-2}% at an electric field of about 10^5

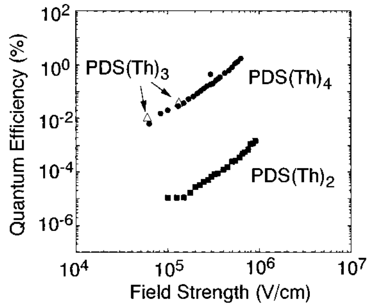

Figure 3. Field dependence of the photocurrent quantum efficiency of PDS(Th)$_m$ (m = 2−4) under the irradiation of monochromatic light of their quantum efficiency peak wavelength (λ = 380, 450, and 480 nm each).

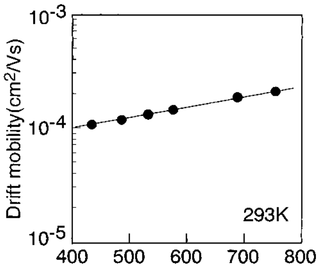

Figure 4. Field dependence of the hole-drift mobilities in PDS(Th)$_4$ at room temperature.

V cm^{-1}, while that of PDS(Th)$_2$ is measured to be on the order of 10^{-5}%, which is smaller by 2 or 3 orders of magnitude. Furthermore, the difference between polymers PDS(Th)$_{3,4}$ and PDS(Th)$_2$ is clearly shown in the electric field dependence of their photocurrent quantum efficiencies (Figure 3). These results may be ascribed to their different electronic structures. Tanaka *et al.* have reported the electronic structure of simplified poly(disilanyleneoligothienylene)s [SiH$_2$SiH$_2$(Th)$_m$]$_n$ with m = 1−5. Their results show that the value of the π−π* band gap decreases as the number of thiophene rings (m) increases, whereas that of the σ−σ* band gap does not change significantly.[11] As a result, the band gap of the π−π* becomes smaller than that of the σ−σ*, when the m is larger than 3. Therefore, photocarrier generation from the polymers having the increased π-conjugation would be expected to be high. We suppose that in the case of PDS(Th)$_3$ and PDS(Th)$_4$, the π-conjugation length is enough to generate photocarriers effectively, but in the case of PDS(Th)$_2$, both π-conjugation and σ-conjugation length are not enough.

PDS(Th)$_3$ and PDS(Th)$_4$ are indeed photoconducting in the visible light region, however, their quantum efficiency is only 2.0% at high electric field ($E = 6 \times 10^5$ V cm^{-1}).

Hole-Drift Mobility. Figure 4 shows the field dependence of the hole-drift mobility of PDS(Th)$_4$ at room temperature (293 K). As can be seen in Figure 4, the logarithm of the mobility depends on the square root of the field strength, and the mobility varies from 1.1×10^{-4} cm^2 V^{-1} s^{-1} at 2×10^5 V cm^{-1} to 2.1×10^{-4} cm^2 V^{-1} s^{-1} at 6×10^5 V cm^{-1}.

These results are of considerable interest because these values are on the same order as the hole-drift mobility of polysilanes previously reported.[2] To our knowledge, this is the highest mobility in σ−π-conjugated polymers reported so far. The carrier mobility of polythiophene and alkylpolythiophenes are reported to be on the order of 10^{-5}−10^{-4} cm^2 V^{-1} s^{-1}.[12,13] On the other hand, Garnier *et al.*[14,15] reported the hole mobilities of some oligothiophenes as thin film field-effect transistors, and sexithiophene has the highest mobility (2×10^{-3} cm^2 V^{-1} s^{-1}) among them. Recently, Dodabalapur *et al.*[16] reported a higher mobility, $(1-3) \times 10^{-2}$ cm^2 V^{-1} s^{-1} in the same construction using sexithiophene. However, quaterthiophene and alkyl-substituted quaterthiophene showed a lower hole mobility (2×10^{-7} and 5×10^{-5} cm^2 V^{-1} s^{-1}, respectively) than those of the polythiophene and alkylpolythiophene.[14] Comparing these results with the high drift mobility of PDS(Th)$_4$, it seems likely that some effect of σ−π-conjugation between the oligothiophenes and the Si−Si unit or some π-conjugation interaction between oligothiophene units is present in our system.

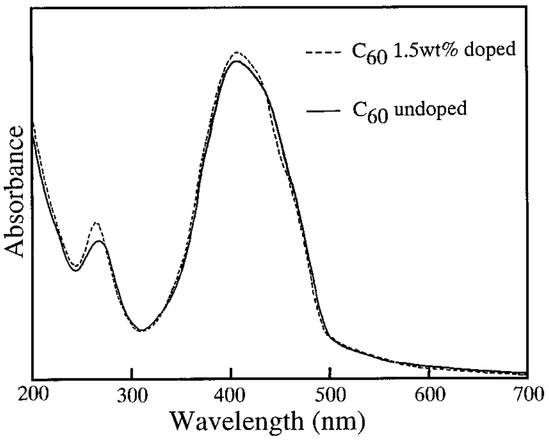

Figure 5. Absorption spectra of PDS(Th)$_4$ and PDS(Th)$_4$/C$_{60}$.

Effect of C$_{60}$ Doping. An increase in photocarrier generation of poly(methylphenylsilane) (PMPS) by fullerene (C$_{60}$) doping has been previously reported by Wang *et al.*[5] In this case, no change is observed in its absorption spectra, but the photoluminescence is effectively quenched.[7] In order to increase the photocarrier generation efficiency of the present polymer in the visible light region, we examined the effect of the C$_{60}$ doping.

First, we prepared a film of PDS(Th)$_4$ doped with 1.5 wt % of C$_{60}$ on a quartz plate and measured the changes in the absorption and photoluminescence spectra. No change was observed in the absorption spectra as shown in Figure 5, indicating that no charge transfer occurs in the dark. The photoluminescence spectra of PDS(Th)$_4$ and C$_{60}$-doped PDS(Th)$_4$, which were illuminated with 400 nm light are shown in Figure 6. The photoluminescence of PDS(Th)$_4$ at about 530 nm was strongly quenched by addition of a small amount of C$_{60}$, similar to the case of PMPS. The ionization potential of PDS(Th)$_4$ measured by a low-energy photoelectron emission analyzer was found to be 5.5 eV, and the bandgap of PDS(Th)$_4$ was estimated to be 2.6 eV from its absorption spectrum. On the basis of these results, the energy diagram of PDS(Th)$_4$ and C$_{60}$ is shown in Figure 7. As for PMPS, the valence band (VB) of PDS(Th)$_4$ is located 0.2 eV lower than the LUMO of C$_{60}$; consequently, direct charge transfer probably does not occur. However, on exposure to light whose energy exceeds the bandgap, an electron may be transferred from the excited state of PDS(Th)$_4$ to C$_{60}$. Therefore, the photocarrier generation efficiency would be expected to be increased with fullerene doping.

The photocurrent quantum efficiencies of undoped PDS(Th)$_4$ and PDS(Th)$_4$ doped with 1.5 wt % C$_{60}$ versus wavelength are shown in Figure 8. The photocurrent quantum efficiency of the doped sample is greatly

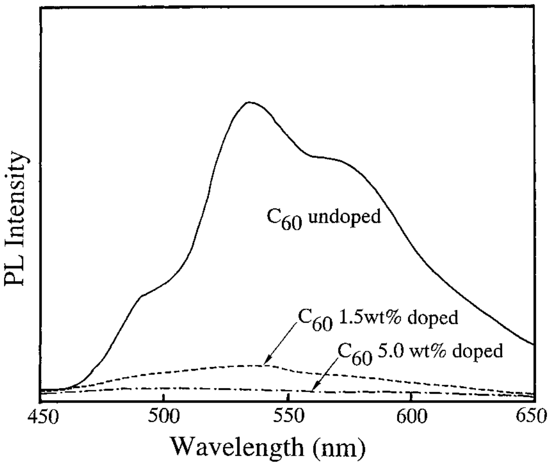

Figure 6. Photoluminescence spectra of PDS(Th)$_4$ and PDS(Th)$_4$/C$_{60}$.

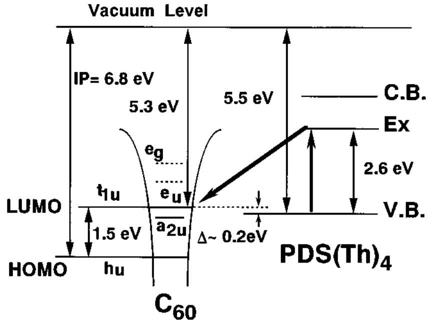

Figure 7. Energy diagram of PDS(Th)$_4$ and C$_{60}$.

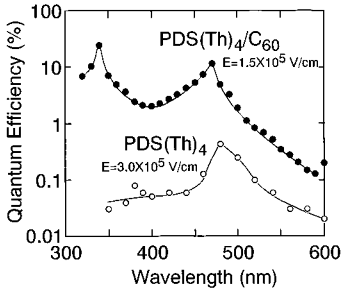

Figure 8. Wavelength dependence of the photocurrent quantum efficiency of PDS(Th)$_4$ and PDS(Th)$_4$/C$_{60}$ under the irradiation of monochromatic light through an ITO electrode under an applied voltage.

enhanced, compared with that of the undoped one. In fact, the photocurrent quantum efficiency of undoped PDS(Th)$_4$ was only 0.5% (E = 3 × 10^5 V cm^{-1}) upon irradiation at 480 nm. The photocurrent quantum efficiency of the C$_{60}$-doped PDS(Th)$_4$, however, increased to 11.5% (E = 1.5 × 10^5 V cm^{-1}) upon irradiation at 470 nm.

Figure 9 shows the field dependence of the photocurrent quantum efficiency of PDS(Th)$_4$ and PDS(Th)$_4$ doped with C$_{60}$. The quantum efficiency of the doped sample increases with the field strength and reaches a maximum value of 85% at a field of 3 × 10^5 V cm^{-1}. This efficiency is similar to that of Y−titanylphthalocyanine, which exhibits the highest sensitivity for an organic material.[17]

This enhancement of the photoconductivity caused by C$_{60}$ doping may be ascribed to the photoinduced electron transfer. Sariciftci *et al.* reported this type of photoinduced electron transfer from a conducting polymer to fullerene,[18] and they also reported the similar photoinduced electron transfer in oligothiophene/C$_{60}$ composite films.[19] We have recently reported that while the photoinduced electron transfer from polysilanes with alkyl substituents to C$_{60}$ does not occur, the electron transfer from polysilanes with the aromatic side groups (e.g., PMPS) to C$_{60}$ is effective.[7] Yoshino *et al.* have also reported that the photoconduction of poly(3-alkylthiophene) is remarkably enhanced upon C$_{60}$ doping.[20] Therefore, we believe that the photoinduced electron transfer occurs between π-orbitals of the thienylene rings and those of C$_{60}$.

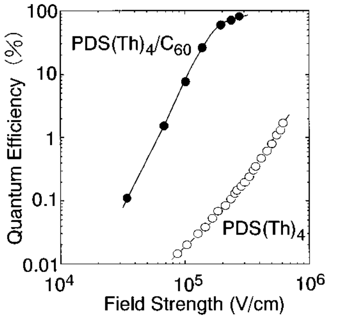

Figure 9. Field dependence of photocurrent quantum efficiency of PDS(Th)$_4$/C$_{60}$ under the irradiation of monochromatic light (λ = 470 nm), compared with that of PDS(Th)$_4$ under the 480 nm light.

Conclusion

The photoconductive properties of poly(disilanyleneoligothienylene)s [PDS(Th)$_m$, m = 2−4] with or without C$_{60}$ doping have been investigated. PDS(Th)$_4$ showed the photoconduction at 480 nm, providing the first example of visible photoconduction in silicon-based polymers, and its hole-drift mobility was on the order of 10^{-4} cm^2 V^{-1} s^{-1} at room temperature. The photocurrent quantum efficiency for PDS(Th)$_4$ was increased to 85% by C$_{60}$ doping (E = 3 × 10^5 V cm^{-1}, 470 nm), and this doping effect may be explained by the photoinduced charge transfer mechanism. These results suggest that C$_{60}$-doped poly(disilanyleneoligothienylene)s may be very useful photoconductor materials for electrophotography. Further studies on the hole-drift mobility and photocurrent stability of these polymers are progressing and will be reported elsewhere.

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