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Optical properties of poly(disilanyleneoligothienylene)s and their doping characteristics

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Optical absorption spectra, photoluminescence (PL), Stokes shift, and electroluminescence (EL) in poly(disilanyleneoligothienylene)s have been found to be dependent on the length of oligothienylene units. The color of EL changes from green to red with increasing length of oligothienylene from three to seven thiophene rings. Their stability is much higher than polysilanylene and increases with increasing length of oligothienylene and by C_{60} doping. Photoconductivity is strongly enhanced and PL is remarkably quenched upon C_{60} doping, which were discussed by the photo-induced electron transfer between aromatic units in these polymers and C_{60} . © 1999 American Institute of Physics. [S0021-8979(99)01501-7]

I. INTRODUCTION

Conducting polymers with highly extended π -electron systems in their main chains have attracted much interest from both fundamental and practical viewpoints, because of their novel physical phenomena and various new functional applications, such as insulator-metal transition upon doping, batteries,^{1,2} electrochromism,³ electroluminescent (EL) devices.^{4,5} Recently, we reported on quenching of photoluminescence (PL) and enhancement of photoconductivity (PC) of conducting polymer upon C_{60} doping.⁶

On the other hand, polysilanes, which are considered to be one-dimensional systems due to the delocalization of σ orbitals along the Si backbone, have also attracted much attention, because of their various interesting phenomena such as doping effects,⁷ thermochromism,⁸ photoconductive response with large hole mobility and large nonlinear optical effects. We have also reported that PL was quenched upon C_{60} doping in polysilanes with aromatic moieties in the side chain.⁹ Detection of electroluminescence in polysilanes was also reported on.^{10,11}

Therefore, polymers containing silanylene and π -conjugated electron systems in their main chain are interesting from both scientific and practical points of view. Recently, we reported the unique properties of poly(disilanyleneoligothienylene)s (PDSiOP), the backbone main chain structures of which consist of disilanylene and oligophenylene units. Optical, electrical, electrochemical, C_{60} doping and lasing properties of PDSiOP have been discussed.¹²⁻¹⁴

In this article, we report the novel optical and electrical properties such as photoluminescence and electrolumines-

cence in poly(disilanyleneoligothienylene)s (PDSiOT) depending strongly on the length of oligothienylenes.

II. EXPERIMENT

PDSiOT, the molecular structures of which are shown in Fig. 1, were synthesized by the method already reported.¹⁵ That is, for example, PDSiOT with pentathienylene, poly(disilanylene-pentathienylene), was prepared by crosscondensation of the di-Grignard reagent produced from 1,2-bis(5'-bromo-2,2'-bithien-5-yl)tetraethyl-disilane with 2,5-dibromothiophene in the presence of the Ni(II) catalyst. These polymers thus obtained are soluble in common organic solvents such as chloroform and tetrahydrofuran, but the solubility decreased markedly with increasing the number of thienylene rings per disilanylene unit.

Thin films of these polymers were formed on quartz plates and ITO (In-Sn-oxide)-coated glass plates with a sheet resistance of $10 \Omega/\square$ by a spin coating method for measurements. Absorption and PL were measured utilizing spectrophotometer Hitachi 330 and spectrophotometer Hitachi F-2000, respectively. EL devices with the structures of MgIn/PDSiOT/ITO were fabricated by vacuum deposition of MgIn onto thin polymers films on ITO. EL measurements were also carried out by the method already reported.¹⁰⁻¹² Photoconductivity and their doping effects were also studied

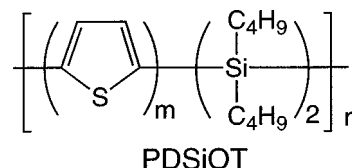


FIG. 1. Molecular structures of PDSiOT.

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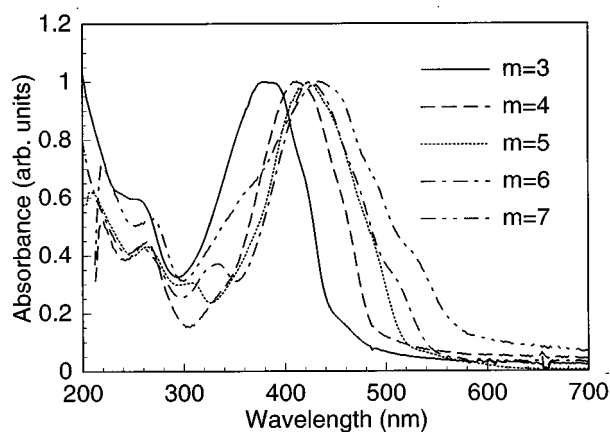


FIG. 2. Absorption spectra of PDSiOT as a function of oligothiophylene length.

by the method already reported.^{9,13,14} Steady-state PC was measured by irradiation of the sample with Xe arc lamp light passed through a monochromator.

Electrochemical measurement such as cyclic voltammetry and *in situ* spectral change upon electrochemical doping were carried out with three electrodes system containing working electrode with sample, a platinum counter electrode and a silver reference electrode in the electrolyte solution of tetrabutylammonium tetrafluoroborate (TBABF₄)/propylenecarbonate (PC) utilizing the Hokuto Denko HB-105 function generator and the HA-105 potentiostat.

III. RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of PDSiOT with various lengths of thiophylene rings. As evident from these figures, the absorption edge shifts to longer wavelength with increasing the number of thiophylene rings in the main chain. From the analysis of the absorption spectral edge corresponding to highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap of PDSiOT, using the relationship of $(h\nu \times \alpha)^2$ vs $h\nu$ (α : absorption coefficient) under the assumption of direct transition, the band-gap energies of PDSiOT were evaluated as 2.2–2.8 eV depending on the number of thiophylene length.

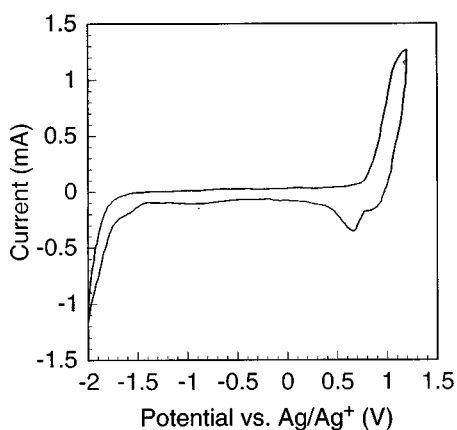


FIG. 3. Typical cyclic voltammogram of PDSiOT ($m=7$).

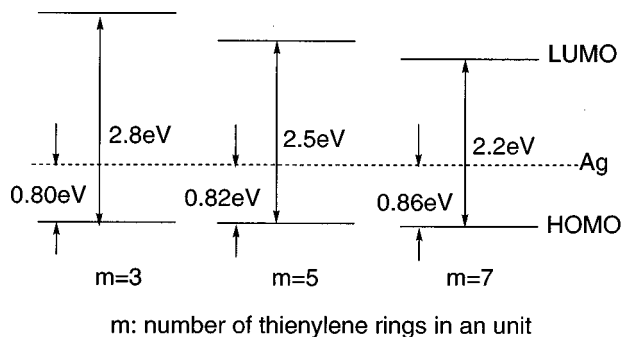


FIG. 4. Energy band diagram of PDSiOT.

Figure 3 shows the typical cyclic voltammogram of PDSiOT ($m=7$) in TBABF₄/PC. The top of valence band (HOMO) was determined from the observed threshold potential of the electrochemical oxidation in the cyclic voltammogram. The electronic energy schemes in these polymers evaluated utilizing the absorption edges and the threshold in cyclic voltammogram are indicated in Fig. 4. As evident in this figure, the bottom of conduction band (LUMO) of PDSiOT becomes lower in energy with increasing length of thienylenes. On the other hand, lowering of HOMO with the length of thiophylene is much less.

Corresponding to these red shifts of the band gap, the PL peaks also exhibit redshifts with increasing the number of thiophylene rings as shown in Fig. 5. Figure 6 shows the dependence of the band gap and the energy of the PL peak on the number of thiophylene rings. It should be mentioned that the PL intensity decreases with increasing the number of thiophylene rings. The Stokes shift of PL peak from the absorption edge was also dependent on the number of thiophylene rings, as shown in Fig. 7. That is, the Stokes shift decreases with increasing the number of thiophylene rings. The Stokes shift in polythiophene film¹⁶ is small in comparison with PDSiOT as also evident in Fig. 7. These results suggest that the optical properties of PDSiOT in the visible range are determined by the oligothiophylene moieties in the main chain.

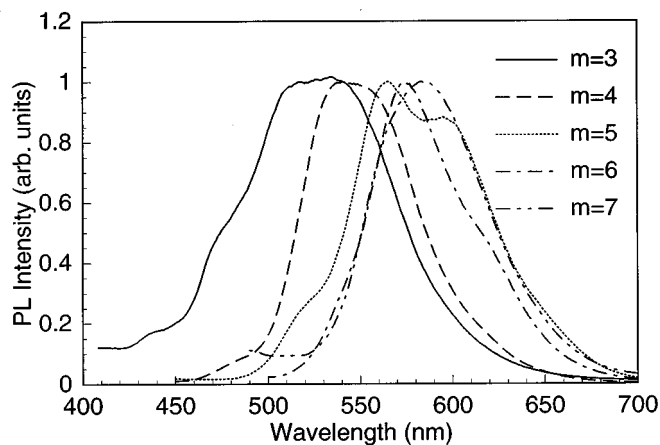


FIG. 5. Photoluminescence spectra of PDSiOT as a function of oligothiophylene length.

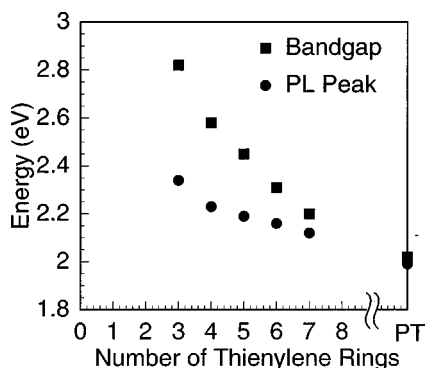


FIG. 6. Dependence of the bandgap and the energy of the PL peak on the number of thiophene rings. PT in this figure indicates polythiophene which includes large number of thiophene rings.

The film of oligothiophene formed by spin coating is not good enough quality for optical study. Therefore, the optical property of oligothiophene in solution was compared with those of PDSiOT in solution. Figure 8 shows the absorption and PL spectra of both oligothiophene and PDSiOT containing the same oligothiophene in its structure. It should be noted that the absorption edge and the wavelength of PL peak are different from those of PDSiOT with the same oligothiophene in its structure. It should also be mentioned that the Stokes shift in PDSiOT was larger than that of the same oligothiophene. This suggests that the Si atoms sandwiching oligothiophene influences on the electronic states of oligothiophenes and the relaxation of the main chain upon excitation.

Figure 9 indicates the absorption spectral change in PDSiOT ($m=6$) upon electrochemical doping. As evident in this figure, upon doping, absorption peaks evolve in the spectral range longer in wavelength than the absorption edge, that is, in the energy range of the forbidden gap, which can be interpreted by the formation of polaronic state as the case of most conjugated polymers such as polythiophene. These spectral change upon doping supports the interpretation that the optical property of these polymers are determined by the oligothiophene units in the main chain.

It should also be mentioned that strong EL was also demonstrated utilizing these polymers as emitting layer in the EL device with a structure of MgIn PDSiOT/ITO. As

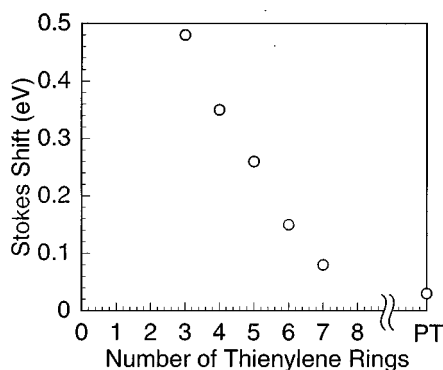


FIG. 7. Dependence of Stokes shift of PL peak from the absorption edge on the number of thiophene rings. PT in this figure indicates polythiophene.

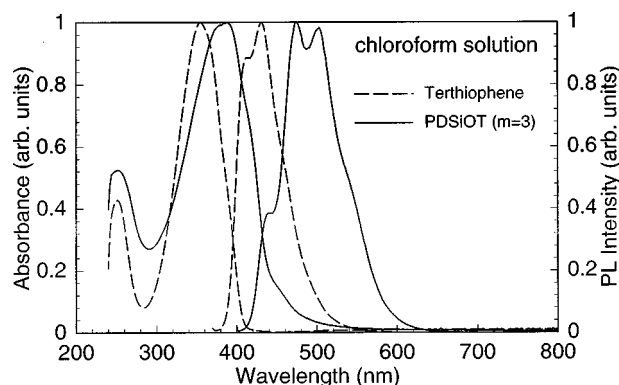


FIG. 8. Absorption and PL spectra of both oligothiophene and PDSiOT containing the same oligothiophene in its structure.

evident in Fig. 10, green EL was realized with PDSiOT ($m=3$) with terthiophene and the emission peak shifted with increasing the number of thiophene rings. PDSiOT with sixthiophene exhibited EL of red in color as also evident in Fig. 10. These facts also clearly indicate that the optical properties are mostly determined by the length of oligothiophenes.

The stability of these polymers and their emission characteristics are much higher than that of simple polysilanylbenzenes. It should also be mentioned that the stability of these polymers increases with increasing the length of oligothiophene. This may be explained by stabilization of short Si-Si bonds with side alkyl chains and by sandwiching between aromatic molecular units. The absorption of short wavelength light by aromatic units such as oligothiophenes may also result in the increase of stability.

The absorption spectrum of PDSiOT did not change markedly upon C_{60} doping, which suggests that C_{60} is not an effective dopant for PDSiOT in the ground state. However, the stability was still enhanced upon introduction of C_{60} in these polymers. The increased stability to light irradiation upon C_{60} doping suggests that the photoexcited species were killed by C_{60} , resulting in the suppression of photoinduced degradation.

The effects of C_{60} doping in PDSiOT under dark conditions are small. However, optical properties are influenced

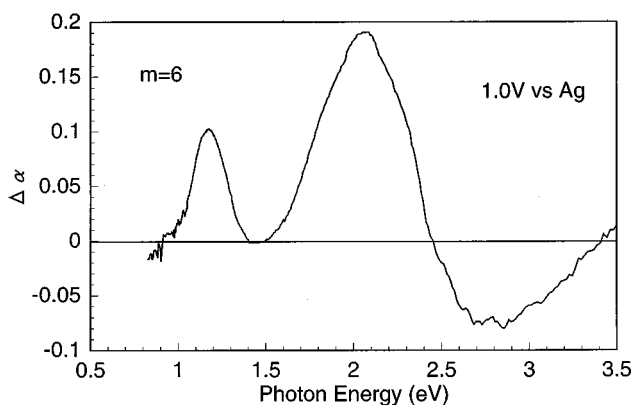


FIG. 9. Change of the absorption spectrum of PDSiOT ($m=6$) taken *in situ* during electrochemical *p*-type doping.

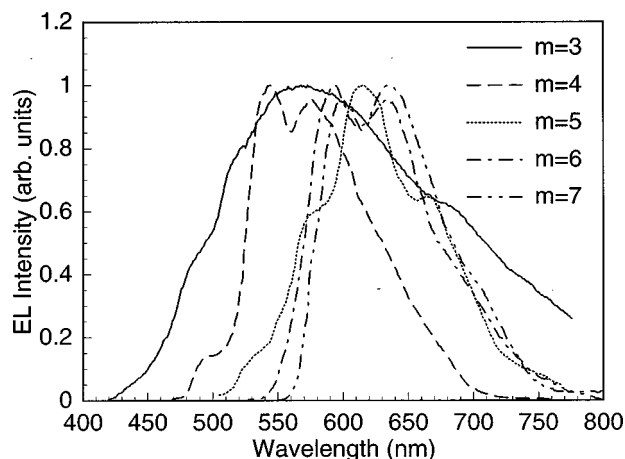


FIG. 10. Electroluminescence spectra of PDSiOT as a function of oligothiophene length.

strongly by C_{60} doping. For example, the PL intensity of PDSiOT ($m=5$) excited by violet light at 450 nm changed markedly upon C_{60} doping as shown in Fig. 11. Though the wavelength of the emission peak did not change markedly, its intensity decreased drastically with increasing C_{60} concentration.

As shown in Fig. 12, PC of PDSiOT ($m=5$) was enhanced significantly upon C_{60} doping. The photoconduction response at the photon energy corresponding to the band-gap energy of PDSiOT was notably enhanced by the introduction of a small amount of C_{60} . This observation of enhancement of PC in PDSiOT upon C_{60} doping can also be explained by photoinduced charge transfer from the excitons in PDSiOT to C_{60} by formation of stable C_{60}^{-1} . The remaining positive carriers on the main chain of PDSiOT contribute to enhanced photoconduction.¹⁴

The HOMO of PDSiOT is lower than the LUMO of C_{60} , as shown in Fig. 13. Therefore, electron transfer from PDSiOT to C_{60} is difficult in the ground state which is consistent with the small changes in the absorption spectrum in PDSiOT by C_{60} doping under dark conditions.

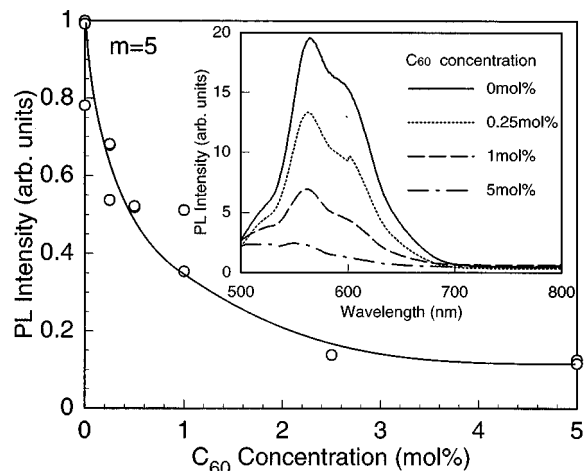


FIG. 11. Dependence of photoluminescence intensity of PDSiOT ($m=5$) on the concentration of C_{60} . Inset shows photoluminescence spectra of PDSiOT ($m=5$) with C_{60} doping.

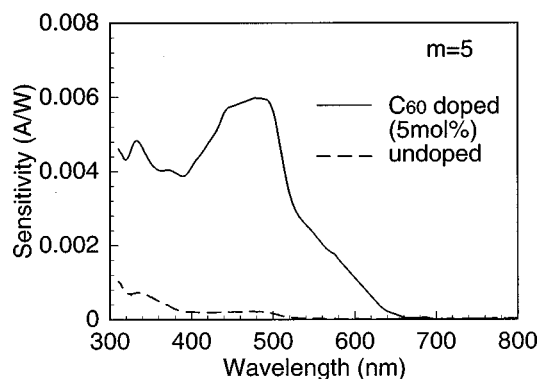


FIG. 12. Photoconduction spectra of PDSiOT ($m=5$) as a function of C_{60} concentration.

Upon irradiation of light with a photon energy exceeding the band-gap energy of PDSiOT ($m=5$), 2.5 eV, the inter-band optical transition will create excitons in PDSiOT. When excitons migrating along the main chain of PDSiOT encounter with C_{60} , electrons are transferred to C_{60} , resulting in dissociation of excitons and hence quenching of PL and also enhancement of PC due to migration of remaining positive carriers on the polymer chain as schematically shown in Fig. 13.

We have already reported that in polysilanes with saturated hydrocarbon side chains, PL quenching was not clearly

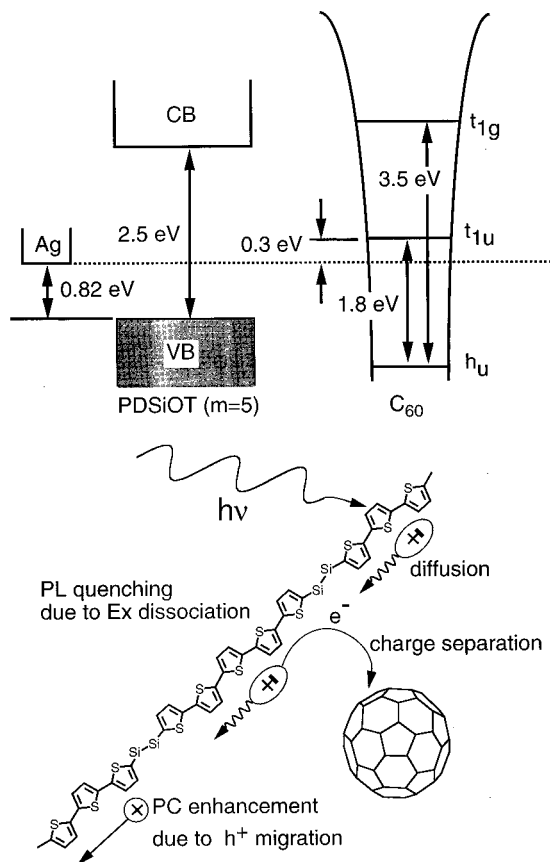


FIG. 13. Schematic explanation of photoinduced charge transfer between PDSiOT and C_{60} .

observed but clear PL quenching was confirmed to occur in polysilanes with aromatic units in the side chain.⁹ In that case, aromatic units are interpreted to play a role as mediators of charge transfer, which is consistent with the present observation of the important role of thienylene units in PDSiOT for C_{60} doping.

IV. SUMMARY

Absorption and PL spectra in PDSiOT exhibit remarkable redshift with increasing the number of thienylene rings. The Stokes shift also depends on the number of thienylene rings. The color of EL changes from green to red with increasing number of thienylene rings from three to seven. The stability was still enhanced upon C_{60} doping. PL was remarkably quenched and photoconductivity was strongly enhanced upon C_{60} doping, which were explained by the photoinduced electron transfer between aromatic units in these polymers and C_{60} . These facts also indicate that the properties of these polymers are mainly determined by the aromatic units such as oligothiophene in the main chain.

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