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Optical Properties of Poly[(disilanyl)oligophenylenes]

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ABSTRACT

Optical Properties of poly[(disilanyl)oligophenylenes] such as poly[(disilanyl) terphenylene] (PDSiTP) and poly[(disilanyl) quarterphenylene] (PDSiQP) have been studied and compared with those of poly(methylpropylsilane), p-terphenyl and p-quarterphenyl. Band-gap energies of PDSiTP and PDSiQP were 3.5 eV and 3.3 eV, respectively, which are similar to those of p-terphenyl and p-quarterphenyl. Among various poly[(disilanyl)oligophenylenes], influence of short alkyl substituents such as methyl and ethyl substituents on their properties are relatively small. However, slightly stronger photoluminescence (PL) is observed in ethyl substituted PDSiTP than in methyl substituted PDSiTP. Blue electroluminescence (EL) has been observed in diode of MgIn/PDSiTP/ITO and MgIn/PDSiQP/ITO structures. Spectral narrowing of PL of blue in color due to stimulated emission has been observed both PDSiTP and PDSiQP. Poly[(disilanyl)oligophenylenes] are much more stable than poly(methylpropylsilane) under ultraviolet light irradiation.

1. INTRODUCTION

Recently optical properties of conducting polymers with highly extended π -electron systems in their main chains have attracted much attention not only from fundamental scientific interest but also from practical view points, because electrochromic device¹⁾ and electroluminescent (EL) devices^{2,3)} utilizing conducting polymers have been proposed. In conducting polymers, even spectral narrowing due to stimulated emission and lasing have been observed under intense light excitation.⁴⁻⁶⁾

On the other hand, polysilanes, which are one-dimensional systems due to the delocalization of σ -electrons along Si backbone, have also attracted much interest, because they exhibit various interesting phenomena such as doping effects,⁷⁾ thermochromism,⁸⁾ photoconductive response with large hole mobility and large nonlinear optical effects. We have reported quenching of photoluminescence (PL) upon C_{60} doping⁹⁾ and the observation of EL in polysilanes.^{10,11)}

Recently, we have also reported novel characteristics of poly[(disilanyl)oligophenylenes] whose backbone structure consists

of silanylene and oligophenylene units.^{12,13)}

In this paper, we report the unique optical and EL characteristics of poly[(disilanylene)oligophenylenes]. Spectral narrowing in these polymers upon intense excitation and novel characteristics of C₆₀-poly[(disilanylene)oligophenylenes] systems are also discussed.

2.EXPERIMENTAL

PDSiTTP and PDSiQP, that is poly[(tetramethyldisilanylene)-*p*-terphenylene] (PMe₄DSiTTP), poly[(tetramethyldisilanylene)-*p*-quarterphenylene](PMe₄DSiQP), poly[(tetraethyldisilanylene)-*p*-terphenylene] (PEt₄DSiTTP) and poly[(tetraethyldisilanylene)-*p*-quarterphenylene] (PEt₄DSiQP) whose molecular structures are shown in Fig. 1 were synthesized through nickel-catalyzed dehalogenative coupling reaction of di-Grignard reagents prepared from the bis(4-bromophenyl)-substituted disilanes, with dibromobenzene and 4-4'-dibromobiphenyl, respectively. Procedure of synthesis and purification of these polymers have already reported in detail.¹⁴⁾

These polymers are soluble in conventional solvents such as chloroform and toluene. The films of these polymers were prepared by spin-coating onto quartz plates for optical measurements and onto In-Sn-oxide (ITO) coated quartz plates with a

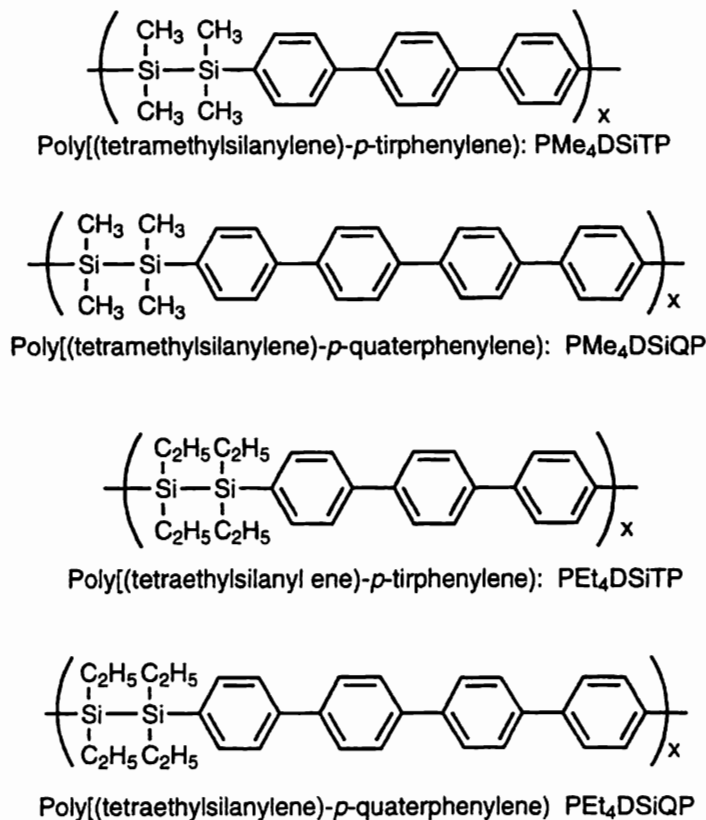


Fig. 1 Molecular structures of poly[(disilanylene)oligophenylenes] studied here.

sheet resistance of $10 \Omega/\square$ for EL measurements.

Optical absorption and PL spectra were measured using the Hitachi 330 spectrophotometer and the Hitachi F-2000 fluorescence spectrophotometer, respectively.

The EL emission spectrum was observed by a conventional method as previously reported.³⁾

Electrochemical measurements such as cyclic voltammetry were carried out with three-electrode system consisting of a

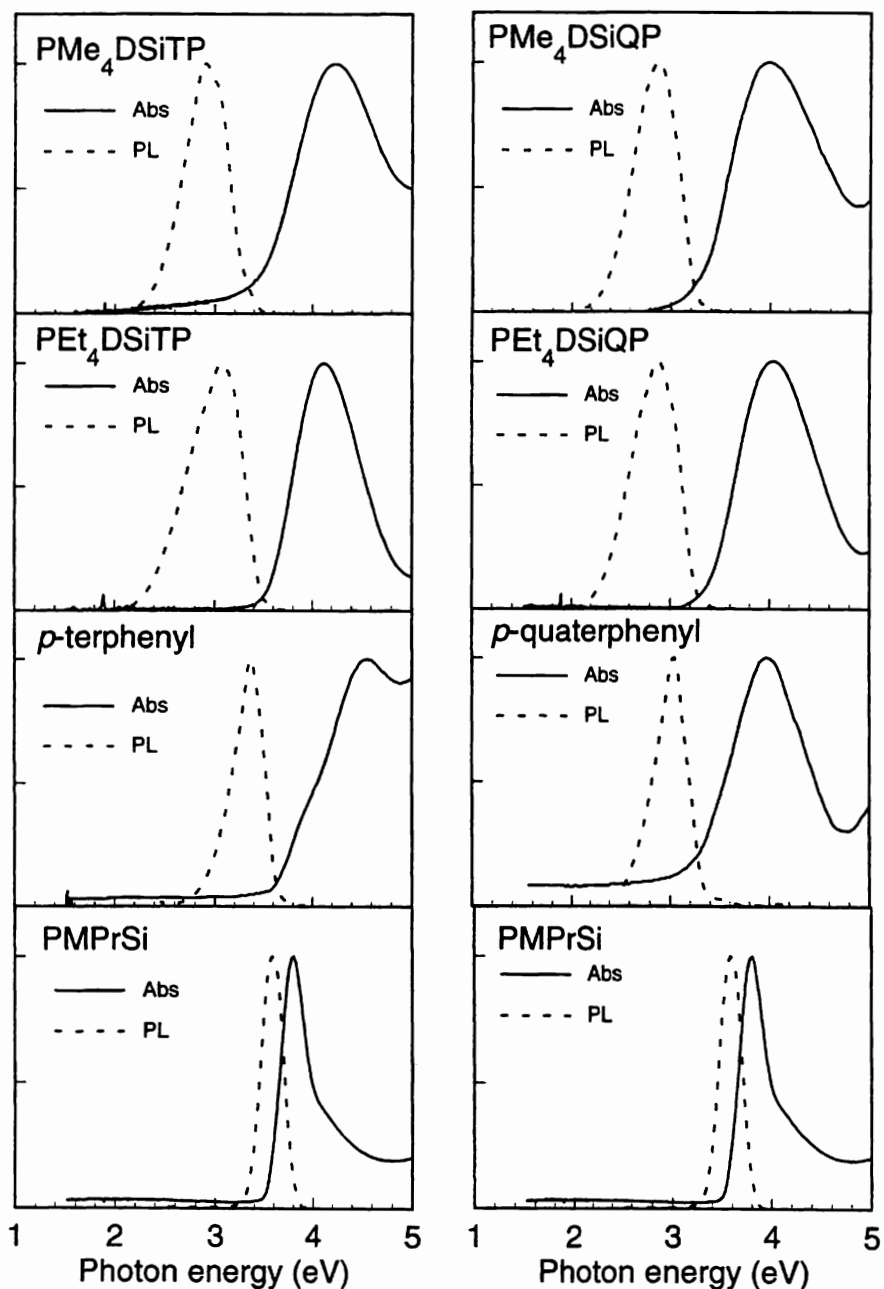


Fig. 2. Optical Absorption spectra and PL spectra of various poly[(disilanyl)oligophenylenes], corresponding phenylene oligomers and PMPrSi.

working electrode with the sample, a platinum counter electrode and a silver reference electrode utilizing the Hokuto-Denko HB-105 function generator and the HA-501 potentiostat. Tetrabutylammonium tetrafluoroborate (TBABF₄)/benzonitrile was used as the electrolyte solution.

For the study of C₆₀-poly[(disilanylene)oligophenylenes] system, C₆₀ prepared by means of arc-discharge from graphite and washing with toluene, and provided by Science Laboratories Co. Ltd. was used.

C₆₀ doped poly[(disilanylene)oligophenylenes] films were prepared by spin coating of the toluene solution containing appropriate concentrations of both components onto appropriate substrate.

C₆₀/poly[(disilanylene)oligophenylene] junction devices were prepared by deposition of C₆₀ by vacuum evaporation on poly[(disilanylene)oligophenylenes] film prepared by spin-coating on appropriate substrates.

Photoconductivity and photovoltaic effect were studied utilizing conventional method already reported by us.¹³⁾

For the measurement of spectral narrowing, the Third Harmonics Generation (THG) light (355 nm) of Nd:YAG laser (1064 nm) of 10 ns in pulse width was used as excitation light source and Hamamatsu Photonics PMA-11 spectrophotometer as the detection system, respectively.

3. RESULTS AND DISCUSSION

As shown in Fig. 2, the absorption spectra of poly[(disilanylene)oligophenylenes] were dependent on the oligophenylene such as p-terphenyl and p-quarterphenyl but not dependent on alkyl substituents of silanylene such as methyl and ethyl substituents. From the analysis of the absorption spectral edge of PDSiTP and PDSiQP using the relationship of $(h\nu\alpha)^2$ vs. $h\nu$ (α : absorption coefficient at frequency ν , h : Planck constant) under the assumption of direct transition, the band gap energies were evaluated to be 3.5 eV and 3.3 eV, respectively. Though these band gap are comparable to that of PMPrSi (3.5 eV), the spectral shapes of PDSiTP and PDSiQP are much different from that of PMPrSi but resemble to those of p-terphenyl and p-quarterphenyl,

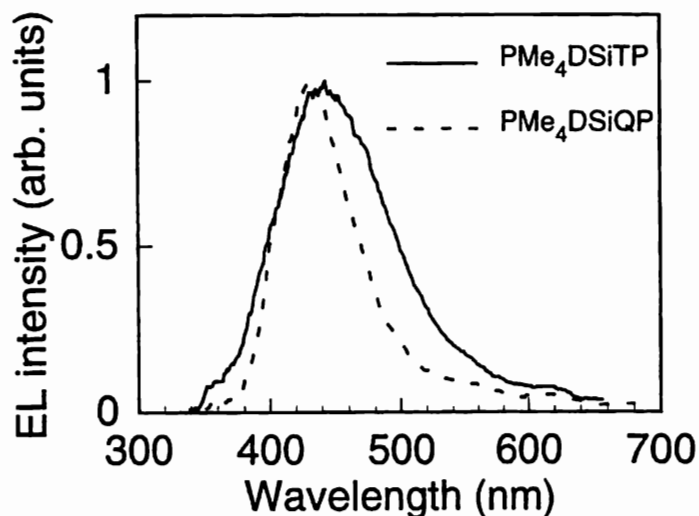


Fig. 3. EL spectra of poly[(disilanylene)oligophenylenes].

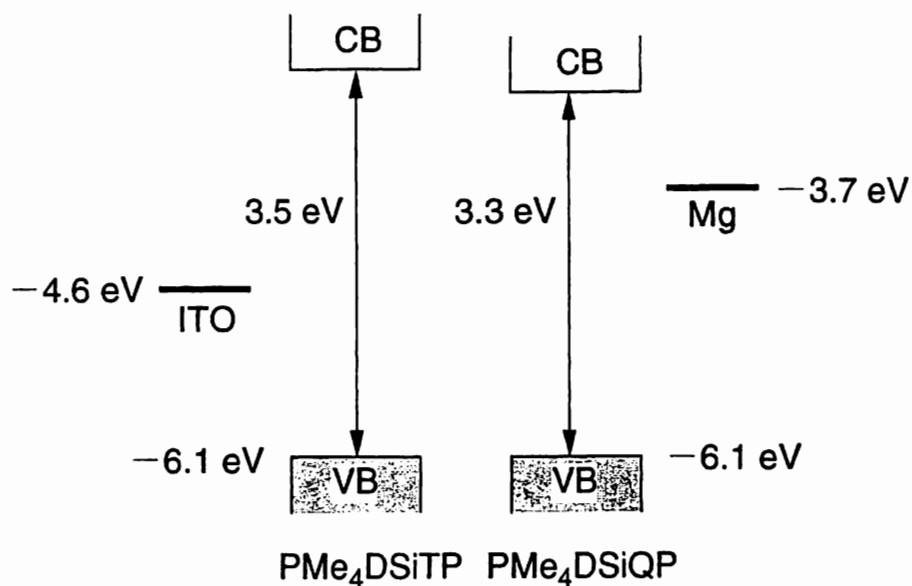


Fig. 4 Electronic energy structures of PMe₄DSiTP and PMe₄DSiQP. Fermi levels of ITO and Mg are also shown.

respectively.

PL spectral shape of PDSiTP and PDSiQP were also similar to those of p-terphenyl and p-quarterphenyl, though the PL peaks were slightly red-shifted compared with those of corresponding phenylene oligomers. It should be noted in Fig. 3, that the Stokes shift of PL in poly[(disilanylene)oligophenylene]s are larger than those of phenylene oligomers, which may be related to the increase of one-dimensionality of π -electron systems in polymers compared with oligomers.

The influence of length of alkyl substituents of silanylene on absorption and PL was relatively small. However, the PL intensity of PDSiTP with ethyl substituents (PEt₄DSiTP) in solution was stronger than that of methyl substituents (PMe₄DSiTP). On the other hand, the effect of alkyl substituent effect on PL was much less in PDSiQP. The origin of this small effect is not clear at this stage but interchain interaction may be influenced by the alkyl substituent in poly[(disilanylene)oligophenylene]s with short phenylene oligomers, that is, in PDSiTP. We are now studying effect of longer alkyl substituents now.

In the diode with MgAg/PDSiTP/ITO and MgAg/PDSiQP/ITO structures, blue EL peaked at 440 nm and 443 nm was observed, respectively, under the forward biased condition, in which MgAg electrode is negatively biased against the ITO electrode as shown in Fig. 3. The spectral width of EL in both PDSiTP and PDSiQP diodes was about 0.3 eV and much wider than that (0.17 eV) in the diode with PMPPrSi.

The EL peaks in PDSiTP and PDSiQP coincide almost with their PL spectral peaks as evident in Fig. 2 and Fig. 3. Therefore, the Stokes shift of EL in these polymers are also large. This suggests that EL in these new polymers originates from exciton or exciton polaron formation in phenylene oligomer units of the main chain formed by the recombination of electrons and holes injected from the cathode and the anode, respectively.

Figure 4 shows electronic energy structures of PDSiTP and PDSiQP evaluated from cyclic voltammogram and absorption

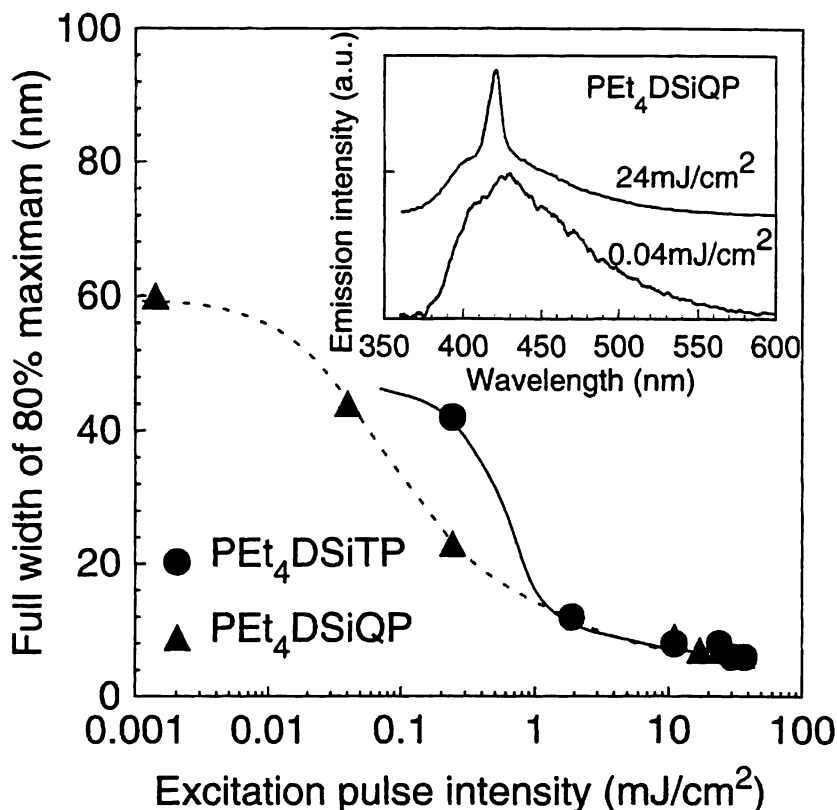


Fig. 5. Dependence of line width of photoluminescence of poly[(disilanyl)oligophenylenes] on excitation pulse intensity. Inset: emission spectra of PEt₄DSiQP at weak(0.04 mJ/cm²) and strong (24 mJ/cm²)

spectra measurements together with Fermi level of MgAg and ITO electrodes. These electronic energy schemes are consisted with above interpretation.

The diode made by incorporating an electron transporting layer of PBD between MgAg and poly[(disilanyl)oligophenylenes] film also exhibited strong blue EL at the same wavelength.

Highly efficient PL and the large stokes shift of PL suggests that poly[(disilanyl)oligophenylenes] are good candidates for lasing devise. Therefore, we have also studied PL under intense excitation.

As shown in the inset of Fig. 5 the remarkable spectral narrowing was observed with increasing exciting intensity of THG light (355nm), which was interpreted by the stimulated emission and lasing. The dependence of spectral width on excitation intensity is shown in Fig.5. These spectra narrowing was observed in all the poly[(disilanyl)oligophenylenes] so far studied. Detailed characteristics of lasing in these polymers are now under study.

It should also be mentioned that poly[(disilanyl)oligophenylenes] were much more stable under ultraviolet irradiation than PMPrSi.

The photoconductivity of poly[(disilanyl)oligophenylenes] was remarkably enhanced and PL was notably quenched upon doping of C₆₀ as shown in Fig. 6. These characteristics are similar to those in conducting polymers and can be interpreted in

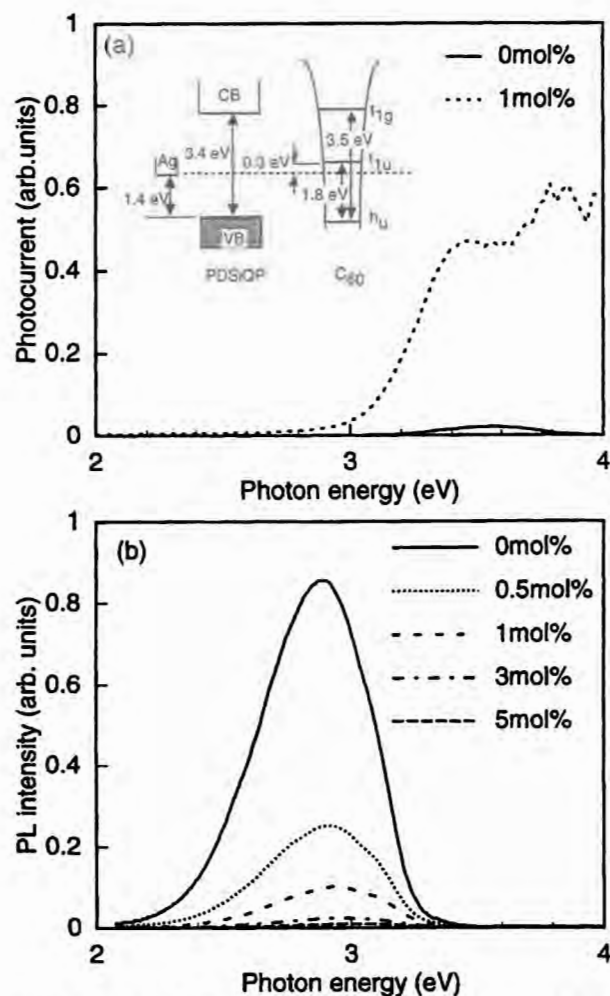


Fig. 6. Enhancement of photoconductivity (a) and quenching of photoluminescence in PDSiQP upon C_{60} doping.

terms of highly efficient photoinduced charge transfer between oligophenylenes in the main chain and C_{60} . This also suggests the important role of oligophenylenes in these polymers. The spectral response of photoconductivity also supported this interpretation.

In the C_{60} /poly[(disilanyl)oligophenylenes] junction device, notable photovoltaic effect was also confirmed.

4. SUMMARY

Present experimental results are summarized as follows.

- (1) Band gap energies of poly[(disilanyl)oligophenylenes], PDSiQP and PDSiTP were evaluated to be 3.3 eV and 3.5 eV, respectively.
- (2) The effect of length of alkyl substituents of silanyl units on the band gap was small.
- (3) From the spectral shape of absorption and PL, the optical properties of poly[(disilanyl)oligophenylenes] are interpreted

to be determined by those of oligophenylene units in the main chain.

- (4) Blue EL was realized with diodes of MgAg/PDSiTP/ITO and MgIn/PDSiQP/ITO structures.
- (5) These optical properties and EL characteristics were consistent with electronic energy schemes determined on the basis of absorption spectra and cyclic voltammogram measurements.
- (6) Spectral narrowing in blue range was observed in poly[(disilanylene)oligophenylenes] under intense optical excitation.
- (7) Poly[(disilanylene)oligophenylenes] were confirmed to be much more stable than polysilanes under ultraviolet irradiation.
- (8) Remarkable photoconductivity enhancement and notable PL quenching was observed in poly[(disilanylene)oligophenylenes] upon C₆₀ doping, which is interpreted in terms of highly efficient photoinduced charge transfer between oligophenylene units in the backbone structure and C₆₀.
- (9) Notable photovoltaic effect was confirmed in C₆₀/poly[(disilanylene)oligophenylenes] junction device.

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