Synthesis of Poly[disilanyleneethynyleneoligo(thienylene)ethynylene]s and Their Photoconductivity

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ABSTRACT: Polymers having the diethynyldisilanylene and oligothienylene units were prepared by the reaction of 1,2-diethynyl-1,1,2,2-tetraethyldisilane with dibromooligothiophene in the presence of a Pd-$(PPh_3)_4$−CuI catalyst in triethylamine or a mixture of a triethylamine and toluene solution. The molecular weights of the disilanylene polymers were calculated to be 6300−19000. The polymers with more than two thienylene units in their backbone exhibit their absorption in the visible region, and their absorption maxima are red-shifted about 10−50 nm relative to poly(disilanyleneoligothienylene)s bearing the same number of a thienylene group. The present polymers showed to be photoconducting in the visible light region and showed thermal cross-linking properties.

Introduction

There has been a considerable 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.[1,2] Furthermore, polysilanes show considerably high hole-drift mobility on the order of 10^{-4} cmV^{-1} s^{-1},[3] and hence, application of these polymers to photocopiers and laser beam printers as a hole-transfer layer of organic photoreceptors has been extensively studied.[4,5]

On the other hand, the photocarrier generation efficiency of polysilanes is low, for example, it has been reported to be about 1% in ultraviolet (UV) region at high electric fields for poly(methylphenylsilane) (PMPS).[3] However, Wang et al.[6] and Kepler et al.[7] found that photocarrier generation efficiency of PMPS was significantly increased by doping with fullerene (C_{60}). We have recently reported that the photoluminescence of polysilanes bearing the aromatic side groups 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.[8] Unfortunately, high photocarrier generation efficiency in this system is limited in the UV region, and therefore, it is impractical to apply this system to the photocarrier generation layer with the use of visible light.

Recently, Malliaras et al.[9] and Kunai et al.[10] reported the synthesis of polymers that have a regular alternating arrangement of a silylene or disilanylene unit and oligothienylene system in the polymer backbone, whose absorption and luminescence can be observed in the visible region. More recently, we have reported that poly[(disilanylene)oligo(2,5-thienylene)]s [PDS(Th)$_m$; $m = 2-4$] showed the photoconductivity in the visible light region, and these photoconductivities are greatly enhanced by C_{60} doping.[11] The electronic structures of simplified PDS(Th)$_m$, $m = 1-5$, have also been reported by Tanaka et al.[12]

On the other hand, Corriu et al. have reported the preparation of poly(diethynylenearylenesilylenes) by the coupling reaction of diethynylsilanes and dihaloarylene using a palladium complex and copper(I) iodide in triethylamine,[13−16] using the method developed by Sonogashira et al.[17] Kunai et al. also reported the synthesis of poly(diethynylenepyridylene)disilanylenes with the use of this method.[18]

In this paper, we report the preparation of the novel polymers having a diethynyldisilanylene and an oligothienylene unit in the polymer backbone, poly[disilanyleneethynyleneoligo(thienylene)ethynylene]s [PDSE(Th)$_m$E; $m = 1-4$]. We also report photoconductivities of these polymers in visible light region and their thermal properties.

Experimental Section

Method of Calculations. All calculations for the electronic structure of the polymers were performed on the basis of the one-dimensional tight-binding self-consistent field-crystal orbital (SCF−CO) method at the level of the MNDO−AM1 (modified neglect of diatomic overlap, Austin model 1) approximation, using the geometries obtained from the MNDO−AM1 solid-state calculations considering all the valence electrons.[19] The resonance integrals and the electron repulsion integrals were considered as far as the second nearest neighboring cell at a maximum (ca. 30−50 Å from the central cell on average). The polymers for all the geometry optimizations were presumed to possess two energetically stable *trans*-conformations on the neighboring disilanylene unit[12] as illustrated in Tables 1 and 2, respectively.

General Procedures for Synthesis. All reactions were carried out under an atmosphere of dry nitrogen. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a JEOL model JNM-A400 spectrometer using deuteriochloroform as a solvent. Mass spectra were measured with a Hewlett-Packard model HP5972A spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. UV−Vis spectra were recorded on a Hitachi U-3210 spectrophotometer. Molecular weights of polymers were determined by gel permeation chromatography using Shodex System 11 and using THF as the eluent, relative to polystyrene standards.

Materials. Triethylamine was dried over NaOH and distilled before use. Toluene was dried over sodium benzophenone and distilled before use. A Pd catalyst, tetrakis(triphenylphos-

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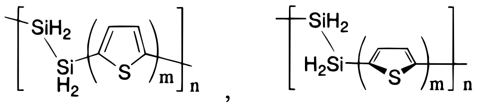
Table 1. Electronic Properties of Simplified PDS(Th)$_m$, m = 1, 2, and 4[a]

	$m = 1$		$m = 2$		$m = 4$		
	PF[b]	NPF[b]	PF[b]	NPF[b]	PF[b]	NPF[b]	PTh[c]
ionization potential	9.26	8.54	8.70	8.27	8.15	8.03	7.80
electron affinity	0.34	1.31	0.86	1.37	1.24	1.42	1.51
band gap	8.92	7.21	7.84	6.90	6.91	6.61	6.29
HOCO(π) bandwidth	<0.01	0.40	<0.01	0.55	<0.01	0.16	1.57
LUCO(π*) bandwidth	0.01	0.20	0.01	0.36	0.01	0.21	1.25
total energy[d]	4.2	0.0	2.3	0.0	2.5	0.0	

[a] MNDO−AM1 results. All values are in eV except total energy. [b] PF and NPF represent the planar form and the nonplanar form, respectively. The unit cells of PF and NPF are shown, respectively as follows:

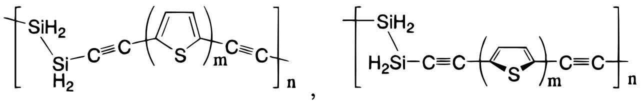


[c] Polythiophene. [d] kcal/(mol·unit cell). The NPF energies have been taken as a standard. The positive value stands for instability.

Table 2. Electronic Properties of Simplified PDS(Th)$_m$E, m = 1, 2, and 4[a]

	$m = 1$		$m = 2$		$m = 4$		
	PF[b]	NPF[b]	PF[b]	NPF[b]	PF[b]	NPF[b]	PTh[c]
ionization potential	9.10	8.64	8.58	8.37	8.19	8.13	7.80
electron affinity	1.02	1.53	1.25	1.51	1.42	1.53	1.51
band gap	8.08	7.11	7.33	6.86	6.77	6.60	6.29
HOCO(π) bandwidth	<0.01	0.20	<0.01	0.28	<0.01	0.09	1.57
LUCO(π*) bandwidth	0.02	0.14	<0.01	0.31	<0.01	0.13	1.25
total energy[d]	0.45	0.0	0.21	0.0	0.19	0.0	

[a] MNDO−AM1 results. All values are in eV except total energy. [b] PF and NPF represent the planar form and the nonplanar form, respectively. The unit cells of PF and NPF are shown, respectively, as follows:



[c] Polythiophene. [d] kcal/(mol·unit cell). The NPF energies have been taken as a standard. The positive value stands for instability.

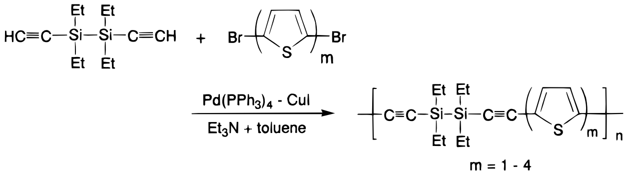
phine)palladium(0), Pd(PPh$_3$)$_4$ obtained from Tokyo Chemical Industry Co., Ltd. was used as received. 2,5-Dibromothiophene was purchased from Tokyo Chemical Industry Co., Ltd. and distilled before use.

α,ω-Dibromo-2,5-oligothiophenes were prepared as reported in the literature procedure.[20] 5,5′-Dibromo-2,2′-bithiophene, 5,5″-dibromo-2,2′:5′,2″-terthiophene, and 5,5‴-dibromo-2,2′:5′,2″:5″,2‴-quaterthiophene were prepared by bromination of 2,2′-bithiophene (Tokyo Chemical Industry Co., Ltd.), 2,2′:5′,2″-terthiophene, and 2,2′:5′,2″:5″,2‴-quaterthiophene, respectively with 2 equiv of *N*-bromosuccinimide (NBS). 2,2′:5′,2″-Terthiophene and 2,2′:5′,2″:5″,2‴-quaterthiophene were prepared by the Ni-catalyzed Grignard coupling reaction[21] of 2-thienylmagnesium bromide with 2,5-dibromothiophene and 5,5′-dibromo-2,2′-bithiophene, respectively, and purified by silica gel column chromatography, followed by recrystallization from ethanol.

1,2-Diethynyl-1,1,2,2-tetraethyldisilane[22] and diethynylmethylphenylsilane[23] were prepared as reported previously.

Preparation of Diethynyldi(*n*-hexyl)silane. To a solution of 0.5 M ethynylmagnesium bromide (400 mL, 0.20 mol, Aldrich Chemical Co. Inc.) in a 1 L three-naked flask was added 26.9 g (0.10 mol) of dichlorodi(*n*-hexyl)silane (LS-4460, Shin-Etsu Chemical) through a dropping funnel over a period of 30 min. The resulting solution was allowed to stand overnight at room temperature and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and dried over magnesium bromide. After the solvent was evaporated, the residue was distilled under reduced pressure to give 15.7 g (63% yield) of diethynyldi(*n*-hexyl)silane: bp 90−92 °C (0.5 mmHg); MS *m/z* 223 ((M − CCH)$^+$), 222 ((M − CCH,H)$^+$), 194, 163 ((M − Hex)$^+$), 135, 121, 109, 107, 95, 79 (M$^+$ was not found); IR ν(≡CH) 3293, ν(C≡C) 2039 cm^{-1}; ^{1}H NMR (in CDCl$_3$) δ 0.75 (t, 4H, Si−C*H*$_2$−), 0.89 (t, 6H, −C*H*$_3$), 1.26−1.52 (m, 16H, Si−CH$_2$(C*H*$_2$)$_4$CH$_3$), 2.47 (s, 2H, acetylenic protons); ^{13}C NMR (in CDCl$_3$) δ 14.12, 14.15, 22.58, 23.40, 31.48, 32.68 (hexyl carbons), 84.92, 95.06 (acetylenic carbons); ^{29}Si NMR (in CDCl$_3$) δ −28.54. Anal. Calcd for $C_{16}H_{28}Si$: C, 77.34; H, 11.36. Found: C, 77.22; H, 11.44.

Scheme 1



Preparation of PDSE(Th)$_3$E. The following is a typical procedure used for cross-coupling polymerization (see Scheme 1).

A mixture consisting of 1.2-diethynyl-1,1,2,2-tetraethyldisilane (0.222 g; 1.00 mmol), 5,5″-dibromo-2,2′:5′,2″-terthiophene (0.406 g; 1.00 mmol), Pd(PPh$_3$)$_4$ (0,023 g; 0,02 mmol), copper(I) iodide (0.004 g; 0.02 mmol), 5 mL of triethylamine, and 5 mL of toluene was stirred at 89 °C under a nitrogen atmosphere for 16 h. The resulting solution was filtered, and the solution was evaporated off. The residue was reprecipitated twice from benzene−methanol and dried under reduced pressure to give 0.283 g (61% yield) of PDSE(Th)$_3$E as a brown powder; M_w = 12 000, M_w/M_n = 2.3; IR ν(C≡C) 2141 cm^{-1}; UV (λ_{max} 395 nm), ^{1}H NMR (in CDCl$_3$) δ 0.90 (q, 8H, Si−CH$_2$), 1.15 (t, 12H, −CH$_3$), 6.98−7.10 (m, 6H, thienylene protons) ppm (TMS); ^{13}C NMR (in CDCl$_3$) δ 4.87 (Si−CH$_2$), 8.39 (−CH$_3$), 97.49 (Si−C≡), 101.10 (−C≡); 122.48, 123.37, 124.86, 133.33, 136.03, 138.15 (thienylene C) ppm (CHCl$_3$), ^{29}Si NMR (in CDCl$_3$) δ −28.54 ppm (TMS). Anal. Calcd for $(C_{24}H_{26}S_3Si_2)_n$: C, 61.75; H, 5.61. Found: C, 59.66; H, 5.69%.[24]

Preparation of PDSE(Th)E. PDSE(Th)E was prepared by the reaction of 1,2-diethynyl-1,1,2,2-tetraethyldisilane and 2,5-dibromothiophene as above: this yields a brown viscous liquid (0.140 g 46% yield); M_w = 6900, M_w/M_n = 2.9; IR ν(C≡C) 2143 cm^{-1}; UV (λ_{max} 340 nm), ^{1}H NMR (in CDCl$_3$) δ 0.87−1.16 (m, 20H, Si−CH$_2$CH$_3$), 6.90−7.20 (m, 2H, thienylene protons) ppm (TMS); ^{13}C NMR (in CDCl$_3$) δ 4.81 (Si−CH$_2$), 8.38 (−CH$_3$), 97.03 (Si−C≡), 100.52 (−C≡); 124.69, 127.93, 132.06, 134.37 (thienylene C) ppm (CHCl$_3$), ^{29}Si NMR (in CDCl$_3$) δ −28.81 ppm (TMS). Anal. Calcd for $(C_{12}H_{12}SSi_2)_n$: C, 63.51; H, 7.33. Found: C, 60.16; H, 6.57.[24]

Preparation of PDSE(Th)$_2$E. PDSE(Th)$_2$E was prepared as above from 1,2-diethynyl-1,1,2,2-tetraethyldisilane and 5,5′-dibromo-2,2′-bithiophene: this yields a brown powder (0.125 g, 33% yield), M_w = 6300, M_w/M_n = 2.9, IR ν(C≡C) 2141 cm^{-1}; UV (λ_{max} 363, 375 nm), ^{1}H NMR (in CDCl$_3$) δ 0.87−1.16 (m, 20H, Si−CH$_2$CH$_3$), 6.90−7.20 (m, 4H, thienylene protons) ppm (TMS); ^{13}C NMR (in CDCl$_3$) δ 4.89 (Si−CH$_2$), 8.46 (−CH$_3$), 97.56 (Si−C≡), 100.80 (−C≡); 123.75, 127.92, 133.31, 137.97 (thienylene C) ppm (CHCl$_3$), ^{29}Si NMR (in CDCl$_3$) δ −19.49 ppm (TMS). Anal. Calcd for $(C_{20}H_{24}S_2Si_2)_n$: C, 62.44; H, 6.29. Found: C, 51.59; H, 6.18.[24]

Preparation of PDSE(Th)$_4$E. PDSE(Th)$_4$E was prepared as above from 1,2-diethynyl-1,1,2,2-tetraethyldisilane and 5,5‴-dibromo-2,2′:5′,2″:5″,2‴-quaterthiophene: this yields an orange brown powder (0.312 g, 57% yield), M_w = 18 700, M_w/M_n = 3.2, IR ν(C≡C) 2141 cm^{-1}; UV (λ_{max} 425 nm); ^{1}H NMR (in CDCl$_3$) δ 0.92 (q, 8H, Si−CH$_2$), 1.17(t, 12H, −CH$_3$), 7.10−7.26 (m, 8H, thienylene protons) ppm (TMS); ^{13}C NMR (in CDCl$_3$) δ 4.89 (Si−CH$_2$), 8.47 (−CH$_3$), 97.49 (Si−C≡), 101.10-(−C≡); 122.42, 123.26, 124.49, 127.92, 133.30, 135.68, 136.23, 138.35 (thienylene C) ppm (CHCl$_3$), ^{29}Si NMR (in CDCl$_3$) δ −28.25 ppm (TMS). Anal. Calcd for $(C_{28}H_{28}S_4Si_2)_n$: C, 61.26; H, 5.14. Found: C, 55.14; H, 6.02%.[24]

Photoconductivity Measurements. The samples used for the photoconductivity measurements are composed of an indium tin oxide (ITO)/PDSE(Th)$_3$E/Au sandwich-type cell. Polymer films (2−4 μm) were prepared by spin coating of a toluene solution of PDSE(Th)$_3$E 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. 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. Monochromic 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).

The quantum efficiency is defined as the ratio of the number of photogenerated carriers collected to the number of photons absorbed by the polymer film (amps/photons). The photogenerated carriers collected were calculated as measured photocurrent minus measured darkcurrent. The number of photons was calculated based on a standard photodiode photocurrent, which was placed at the same position.

Thermogravimetric Analysis for Polymers. Thermal behavior of the polymers was examined by thermogravimetry under nitrogen. A sample (5−10 mg) of PDSE(Th)$_3$E in sealed aluminum pans was heated from 20 to 800 °C at a heating rate of 20 min^{-1}.

Results and Discussion

Calculation of the Band Gap of PDSE(Th)$_m$E Compared with PDS(Th)$_m$ and PTh. First, we studied the electronic properties of the polymers, PDSE(Th)$_m$E by the use of the SCF−CO method, to estimate their properties. We also carried out the calculation for PDS(Th)$_m$ and polythiophene (PTh) for comparison. The ionization potential (IP), electron affinity (EA), band gap (=IP − EA) and the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO) bandwidths of the polymers are given in Tables 1 and 2. All the values with one exception of the relative total energy are mainly concerned to the π-type bands formed by the thienylene unit. The contribution of the σ-type bands formed by the disilanylene unit to the electronic structures is very small, as reported previously for the similar calculations of PDS(Th)$_m$.[12]

Though the difference of the electronic structures between PDSE(Th)$_m$E and PDS(Th)$_m$ is small, the π−π* band gap is somewhat smaller in the former than in the latter, due to the long effective π-conjugation between the thienylene and ethynylene units in the former. It can be seen in Tables 1 and 2 that in both PDSE(Th)$_m$E and PDS(Th)$_m$, the π−π* band gaps in $m = 4$ are smaller than those in $m = 1$ and 2 indicating the extension of the π-conjugation through the thiophene rings in $m = 4$. In the polymers with $m = 4$, whose conformation is nonplanar, the π−π* band gaps are also smaller than in the planar conformation, because the nonplanar structures must have the σ−π conjugation due to the disilanylene−thienylene bond. The HOCO and LUCO bandwidths in both PDSE(Th)$_m$E and PDS(Th)$_m$ are calculated to be narrow compared with those in PTh, implying that the disilanylene group cuts off the long π-conjugation in the thiophene rings. The bandwidths in the nonplanar conformation are somewhat wider than those in the planar conformation, and this indicates the contribution of the σ−π conjugation to the delocalization of the electrons in the former. As can be seen in Tables 1 and 2, the relative total energy difference between the planar and nonplanar conformations is very small. Therefore, it can be expected that the real conformation of the PDSE(Th)$_m$E or PDS(Th)$_m$ would be the mixed form of the planar and nonplanar in room temperature.

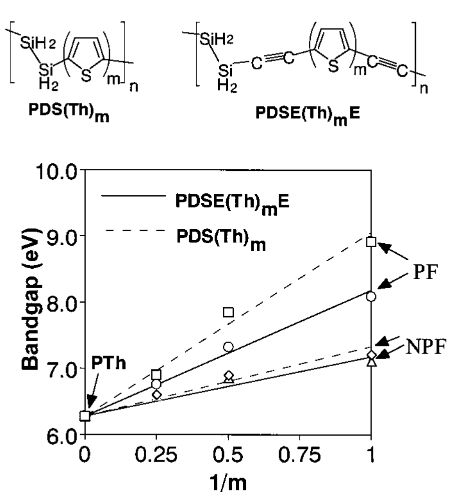


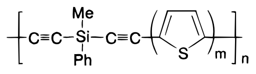
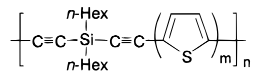
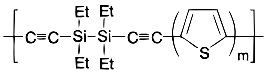
Figure 1. π−π* band gaps as a function of the inverse number of thiophene rings (m) for PDSE(Th)$_m$E and PDS(Th)$_m$ ($m = 1, 2, 4$). The squares, open circles, and triangle represent the planar forms (PF), nonplanar forms (NPF), and PTh, respectively. The solid and dashed lines are guides to eye.

The dependence of the π−π* band gap on the inverse number of thienylene rings is illustrated in Figure 1. The π−π* band gap in PDSE(Th)$_m$E approaches to that of PTh as $1/m$ decreases analogous to that of PDS(Th)$_m$. It is assumed that these two polymers with a large number of thiophene rings have similar electronic properties to those of PTh. As shown in Figure 1, the difference of the π−π* band gaps between the planar and nonplanar conformation is large in PDSE(Th)E and PDS(Th), implying that the contribution of the σ−π conjugation between the disilanylene and thienylene units to their band gaps is large in these polymers with a small number of thiophene rings. Since the Hartree−Fock-type SCF−CO method used in the present calculations always leads to the overestimation of the value for the band gap by a factor of 3−4,[25] the actual band gaps of the present polymers are expected to be 2−3 eV.

Synthesis of PDSE(Th)$_m$E and Their Absorption Spectra. The polymers PDSE(Th)$_m$E were synthesized by the Pd(PPh$_3$)$_4$−CuI catalyzed cross-coupling reaction of 1,2-diethynyl-1,1,2,2-tetraethydisilane with the respective dibromooligothiophenes (Scheme 1). Methylphenylsilylene and di(n-hexyl)silylene polymers were also prepared by the similar cross coupling reaction of the respective diethynylsilanes with dibromooligothiophenes. All the polymerization reactions were almost completed for 16 h, and the results are shown in Table 3. For the synthesis of the silylene polymers, a large amount of insoluble materials was always produced. Moreover, the molecular weights of the resulting polymers were rather low ($M_w = 1200−5600$). On the other hand, in the case of the disilanylene polymers, no insoluble substances were formed, and the polymers whose molecular weights were calculated to be 6300−19 000 were obtained in high yields. Presumably, the presence of the tetraethyldisilanylene unit in the polymer chain greatly enhances solubility of the polymers in organic solvents.

Absorption spectra of dihexyl-substituted poly[silyleneethynyleneoligo(thienylene)ethynylene]s, PSE(Th)$_m$E ($m = 1, 2, 3$) are shown in Figure 2. The absorption maxima of PSE(Th)$_m$E, which correspond to the α,ω-

Table 3. Molecular Weight and Absorption λ_{max} of Poly[(di)silanyleneethynyleneoligo(thienylene)-ethynylene]s

Polymer	m	Mw^a	Mw/Mn^a	Absorption λmax (nm)
	1	3,600	1.8	340^b
	2	2,800	1.6	400
	3	1,200	1.2	422
	1	5,600	1.7	315, 334
	2	4,800	1.6	378, 400
	3	2,000	1.8	411, 424^b
	1	6,900	2.9	340
	2	6,300	2.9	363, 375, 404^b
	3	12,000	2.3	395, 425^b
	4	18,700	3.2	425

^{a} Determined by GPC, relative to polystyrene standards. ^{b} Shoulder.

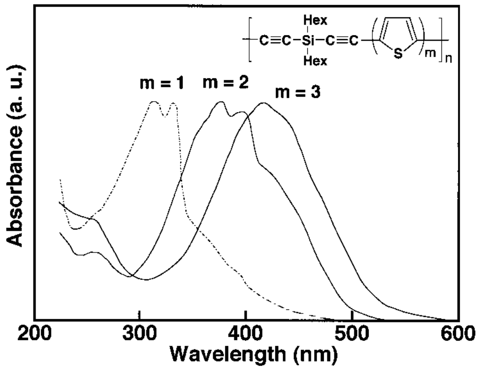


Figure 2. Absorption spectra of poly[di-*n*-hexylsilanylene-ethenyleneoligo(thienylene)ethenylene]s [PSE(Th)$_m$E, $m = 1$, 2, 3].

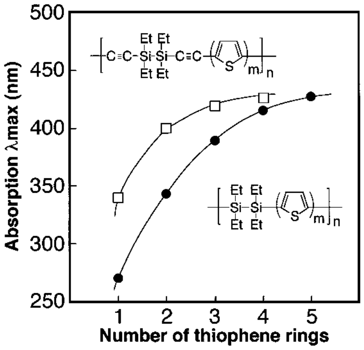


Figure 3. Relationship between the number of thiophene and absorption λ_{max} of PDSE(Th)$_m$E in THF solution compared with that of PDS(Th)$_m$ (λ_{max} data from ref 10).

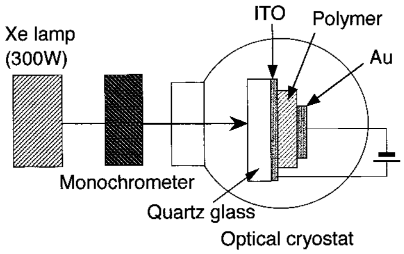


Figure 4. Steady-state photocurrent measurement.

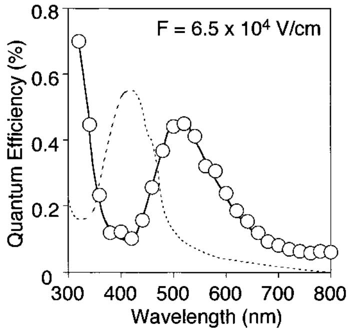


Figure 5. Wavelength dependence of photocurrent quantum efficiency of PDSE(Th)$_3$E with its absorption spectrum of thin film (dashed line, arbitrary unit).

diethynyl-substituted oligothiophenes, shift to a longer wavelength as the number of the thienylene rings increases. The relationship between the number of thiophenes in the polymer unit (m) and the absorption maxima of PDSE(Th)$_m$E is shown in Figure 3, compared with those of poly(disilanyleneoligothienylene)s, PDS-(Th)$_m$. The polymers with more than two thienylene units in their backbone show their absorbance in the visible region. The absorption maxima of PDSE(Th)$_m$E are red-shifted about 10–50 nm, compared with those of the corresponding PDS(Th)$_m$ with the same number of thiophenes in polymer unit. These results clearly show that π-conjugation of PDSE(Th)$_m$E, which is divided by disilanylene units, can be extended by the addition of two ethynylene groups to oligothienylene. However, the absorption maxima in both polymers seem to be saturated in the region around 450 nm. These results are wholly consistent with those of the calculations described above.

Photoconductivity Measurements of PDSE(Th)$_3$-E. The cell structure and the steady-state photocurrent measurement equipment used in this study are shown in Figure 4. The wavelength dependence of the photocurrent quantum efficiency of the PDSE(Th)$_3$E is shown in Figure 5, together with the absorption spectrum of the thin film. The maximum of the photocurrent quantum efficiency appears at 500–520 nm, close to the absorption edge of the polymers and about 100 nm longer wavelength than that of the respective absorption maximum. This type of phenomena has also been observed in the case of poly(disilanyleneoligothienylene)s, PDS(Th)$_m$.[11] 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 strong absorption bands of the polymers. The difference of the wavelength of PDSE(Th)$_m$E is larger than that of PDS(Th)$_m$, because the absorption band of PDSE(Th)$_m$E is broader than that of PDS(Th)$_m$ and its absorption edge appears at longer wavelength. Therefore, the maximum of photocarrier generation quantum efficiency is also red-shifted.

The electric field dependence of the photocurrent quantum efficiency of PDSE(Th)$_3$E at 520 nm is shown in Figure 6. The quantum efficiency showed the logarithmic dependence on the electric field strength. The maximum quantum efficiency was determined to be 4.7% at $F = 1.6 \times 10^5$ V/cm. This efficiency is almost the same level as those of PDS(Th)$_3$ and PDS(Th)$_4$ reported previously.

Thermal Cross-Linking of the Polymers. Recently, it has been reported that some poly(silylene-ethynylenearyleneethynylene)s showed high thermal stability because of the cross-linking reaction of a C≡C bond in the polymer backbone.[26] Therefore, the present polymers, PDSE(Th)$_m$E, can also be expected to have high thermal stability.

First, we examined the TG–DTA analysis for the polymers under a nitrogen atmosphere, and the result

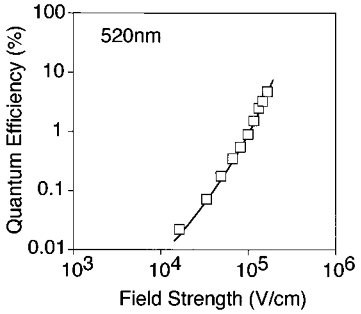


Figure 6. Field dependence of the photocurrent quantum efficiency of PDSE(Th)$_3$E under irradiation of 520 nm monochromatic light.

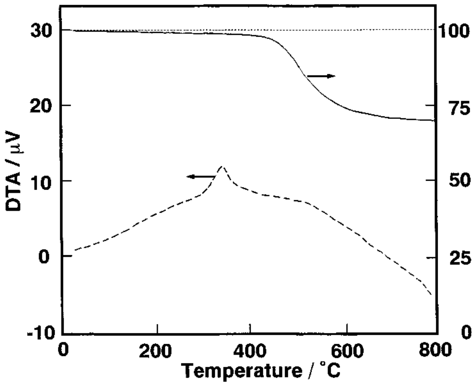


Figure 7. TG−DTA curves of PDSE(Th)$_3$E in N_2.

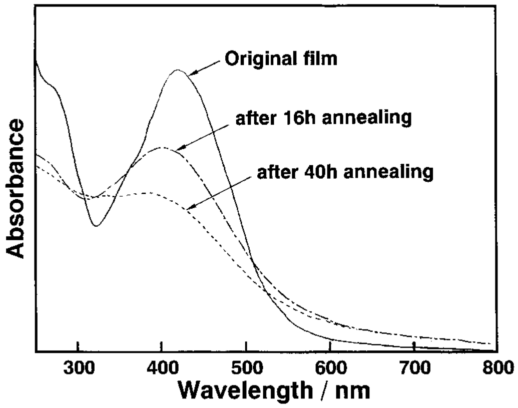


Figure 8. UV−Vis absorptional changes of PDSE(Th)$_4$E film annealed at 200 °C.

obtained from PDSE(Th)$_3$E is shown in Figure 7. Weight loss commenced at ca. 450 °C and attained about 30% at 800 °C. This type of weight loss is almost the same as that of other poly(silyleneethnyleneaRyleneethynylene)s. DTA showed an exothermic peak at 340 °C. This seems to be due to the cross-linking reaction originating from ethynylene units.

Next, we followed the changes of absorption spectra of a PDSE(Th)$_4$E film during annealing at 200 °C in the air (see Figure 8). Comparing the original film, the absorption peak at around 425 nm gradually decreased by annealing, and the tail of the absorption at around 600−700 nm increased slightly. At this time, the color of the film changed from orange to dark brown. After annealing, the film became insoluble in organic solvents such as THF, benzene, etc. Absorptional change means some extensions of π-conjugation, which are probably established by cross-linking of ethynylene units. This cross-linking reactions concerning the ethynylene units took place was confirmed by IR spectrum observation, the absorption at 2141 cm^{-1} that is due to the C≡C units was almost disappeared after annealing. This cross-linking of the polymer might afford the possibility to increase the mechanical strength of the film.

Conclusion

Polymers having the diethynylsilylene or diethynyldisilanylene and oligothienylene units were prepared by the reaction of diethynyldihexylsilane, diethynylmethylphenylsilane, 1,2-diethynyl-1,1,2,2-tetraethyldisilane with dibromooligothiophene in the presence of a Pd(PPh$_3$)$_4$−CuI catalyst in triethylamine or a mixture of triethylamine and toluene. Their molecular weights were determined to be 1200−5600 for monosilylene polymers and 6300−19 000 for disilanylene polymers. The polymers with more than two thienylene units in their backbone showed the absorption in the visible region and their absorption maxima were red-shifted about 10−50 nm, compared with those of poly(disilanyleneoligothienylene)s with the same number of thiophenes in the polymer backbone. This result was wholly consistent with those of our calculations. Poly[disilanyleneethynyleneoligo(thienylene)ethynylene]s, PDSE(Th)$_m$E also showed high photoconductivity in visible light region as did PDS(Th)$_m$. It has been also shown that thermal cross-linking originated from the carbon−carbon triple bonds occurred for the present polymers.

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