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Synthesis of silylene–phenylene and silylene–thienylene copolymers and their optical properties

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Abstract

Silylene–phenylene and silylene–thienylene copolymers were prepared by the reactions of α,ω-dichloropermethylated oligosilanes with 1,4-dilithiobenzene and 2,5-dilithiothiophene respectively. All the copolymers were soluble in a wide range of organic solvents. The influence of the chain length of the dimethylsilylene unit in the copolymer backbone on the electronic absorption spectra was investigated. The enhancement of σ–π conjugations between the dimethylsilylene units and the π-conjugated units with increasing dimethylsilylene chain length was suggested by the thermochromism.

Keywords: Silicon; Lithium; Silylene–phenylene; Silylene–thienylene; Conjugation; Thermochromism

1. Introduction

The synthesis and properties of the polymers that have a regular alternating arrangement of a silylene unit and a π-conjugated unit in the polymer backbone have been published [1]. The Si–Si σ bonds in polysilane chain have many properties which are analogous to those of C=C double bands, and the conjugation is called σ conjugation [2]. Preparation of the polymers having σ–π-conjugated systems along polymer chains has been a subject of recent interest in connection with their potential utility as polymer conductors or semiconductors [3]. In a previous paper we reported the synthesis of σ–π-conjugated alternating silylene–diacetylene copolymers by quenching of dilithiobutadiyne with α,ω-dichloropermethylated oligosilanes [4]. We showed the enhancement of the σ–π conjugation with increasing dimethylsilylene chain length. However, all copolymers were slightly soluble in common organic solvents. In this paper we report the successful synthesis of σ–π-conjugated alternating silylene–phenylene and silylene–thienylene copolymers which were soluble in a wide range of organic solvents. The synthesis of poly[*p*-(tetramethyldisilanylene)phenylene] by the sodium condensation reaction has been reported, but most of the polymers were insoluble [5]. In our study, the copolymers were synthesized by the one-pot route where dilithio compounds prepared by *n*-butyllithium-induced debromination were quenched with α,ω-dichloropermethylated oligosilanes. The chain length of α,ω-dichloropermethylated oligosilanes was varied up to six to increase the σ-conjugation of dimethylsilylene units. The thermochromism of the copolymers was investigated to discuss the effect of the dimethylsilylene chain length on σ–π conjugations between dimethylsilylene units and π units.

2. Results

The silylene–phenylene and silylene–thienylene copolymers were prepared as shown in Scheme 1. The starting compounds, 1,4-dibromobenzene and 2,5-dibromothiophene, could be directly and quantitatively converted to dilithium derivatives by reaction with two equivalents of *n*-butyllithium in diethyl ether, and quenching the solution with α,ω-dichloropermethylated oligosilanes, $Cl-(SiMe_2)_m-Cl$ ($m = 1, 3, 4$ and 6), gives the desired copolymers **1a–d** and **2a–d** respectively.

The characteristics of these copolymers are listed in Table 1. The yields are 21–49% after methanol precip-

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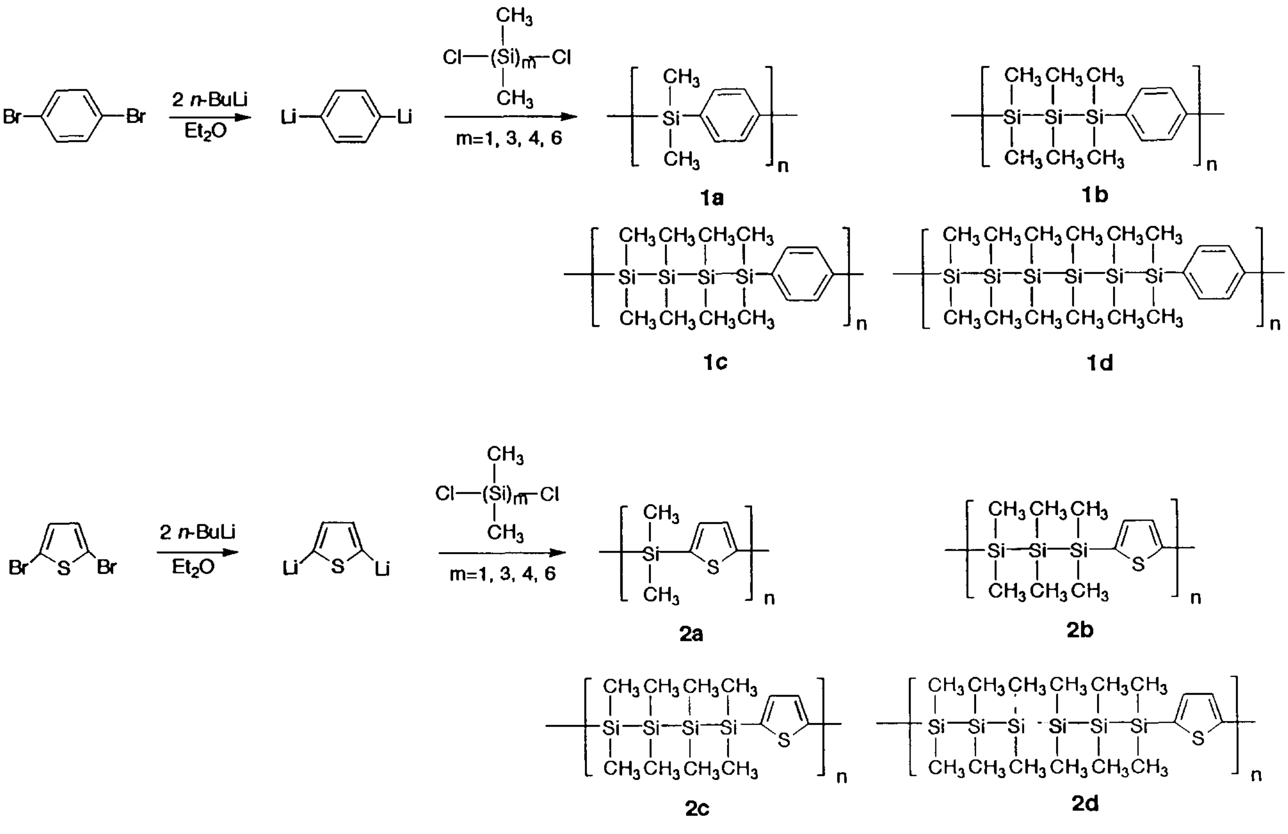
Table 1
Synthesis results of copolymers **1a–d** and **2a–d**

Copolymer	yield (%)	M_w	M_w/M_n	λ_{max} [a] (nm)	ϵ [a]	Melting point (°C)
1a	49	2460	1.2	234.5	9700	181–184
1b	35	2520	1.2	253.0	13200	107–109
1c	26	2710	1.2	263.5	18200	123–125
1d	21	3080	1.3	269.0	22000	150–152
2a	33	3360	1.7	249.5	10200	127–129
2b	28	5470	1.8	268.0	17850	84–86
2c	26	6120	2.1	271.0	20200	92–95
2d	21	7440	2.1	241.0, 273.5	19450, 24850	121–124

[a] In THF solution at room temperature.

itation. These copolymers are light-yellow powders and soluble in common organic solvents such as tetrahydrofuran (THF), chloroform and aromatic solvents, but slightly soluble in saturated hydrocarbons and insoluble in alcohols. The molecular weights were determined to be $M_w = 2460–3080$ and 3360–7440 for **1a–d** and **2a–d** respectively. The copolymers **1a** ($M_w = 2460$; $M_w/M_n = 1.2$) and **2a** ($M_w = 3360$; $M_w/M_n = 1.7$) which have the alternating sequence of a dimethylsilylene unit and a π-electron system in the main chain, produced from rigid chains show a higher melting temperature T_m than do all other copolymers. On the other hand, T_m increased with increasing number of dimethylsilylene unit in the copolymers **1b–d** and **2b–d**.

The structures of **1a–d** and **2a–d** were verified by spectroscopic analysis. The FT IR spectra of **1a–d** and **2a–d** are shown in Figs. 1 and 2 respectively. In Fig. 1, the absorption bands in the region 1124–1132 cm^{-1} are assigned to the stretching vibration of the Si-phenyl in silylene–phenylene copolymers **1a–d**, while the bonds in the region 728–831 cm^{-1} can be ascribed to the C–H out-of-plane vibrations [6]. In Fig. 2, the bands due to the vibrational modes of the Si-thienyl in silylene–thienylene copolymers **2a–d** appear in the region 1481–1490 cm^{-1} and those due to the C–H out-of-plane modes in the region 732–833 cm^{-1} [7]. Further, the deformation vibration of the Si-methyl at around 1250 cm^{-1} appears in all spectra. The symmetric and asymmetric vibration of the C–H band of the methyl group are also observed for all copolymers at around 2860 cm^{-1} and 2895 cm^{-1} respectively. In Fig. 3, the IR absorbance ratio for the Si-methyl at around 1250 cm^{-1} and the Si-phenyl in the region 1124–1132 cm^{-1} or the Si-thienyl in the region 1481–1490 cm^{-1} is plotted against the number of dimethylsilylene units. A



Scheme 1.

linear relationship which is consistent with the expected structures is observed.

Characteristic of these copolymers is the strong absorption in the UV region. The absorption spectra of copolymers **1a–d** and **2a–d** are shown in Figs. 4 and 5 respectively. The absorption maxima of the copolymers shift to longer wavelengths with increasing dimethylsilylene chain length. The thermochromism of the copolymers **1a–d** and **2a–d** was investigated. With decreasing temperature, the absorption spectra of the silylene–phenylene copolymer **1a** (dimethylsilylene chain length $m = 1$) and silylene–thienylene copolymer **2a** ($m = 1$) do not show the red shift of the absorption peak in Figs. 6 and 7 respectively. In Fig. 8, **1d** ($m = 6$; $M_w = 3080$; $M_w/M_n = 1.3$) shows two absorption peaks at low temperatures, and the ratio changes with tem-

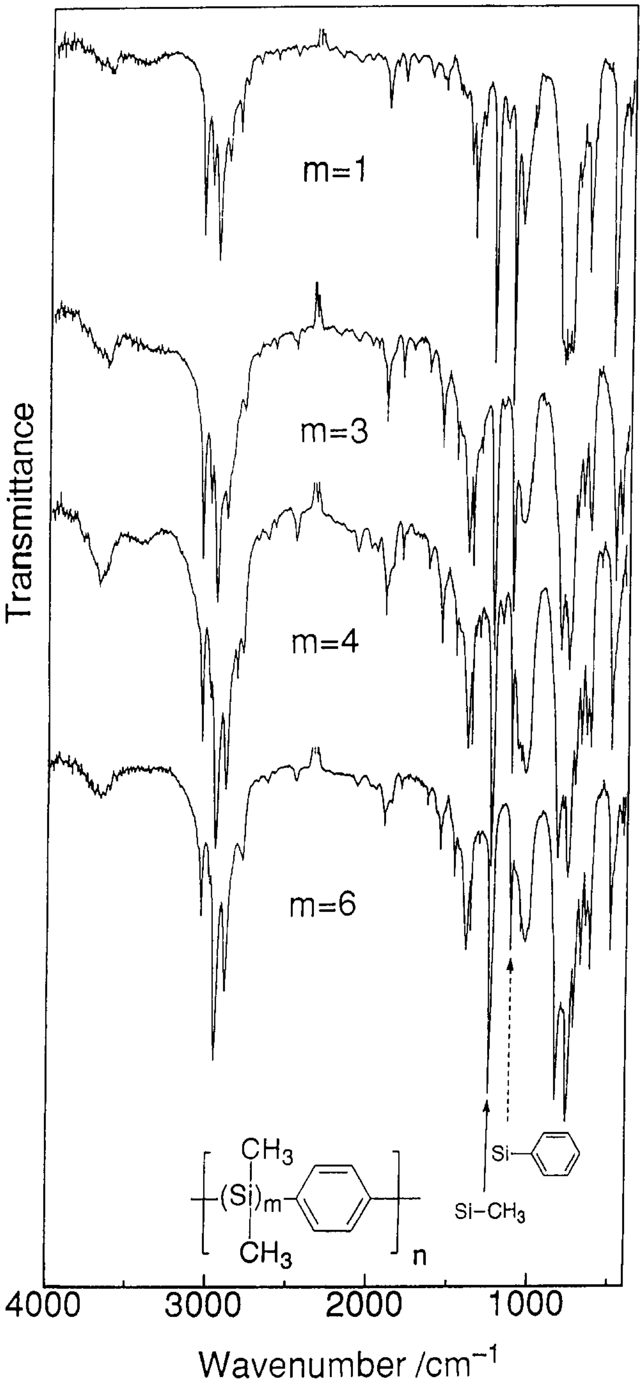


Fig. 1. The IR spectra of silylene–phenylene copolymers **1a–d**.

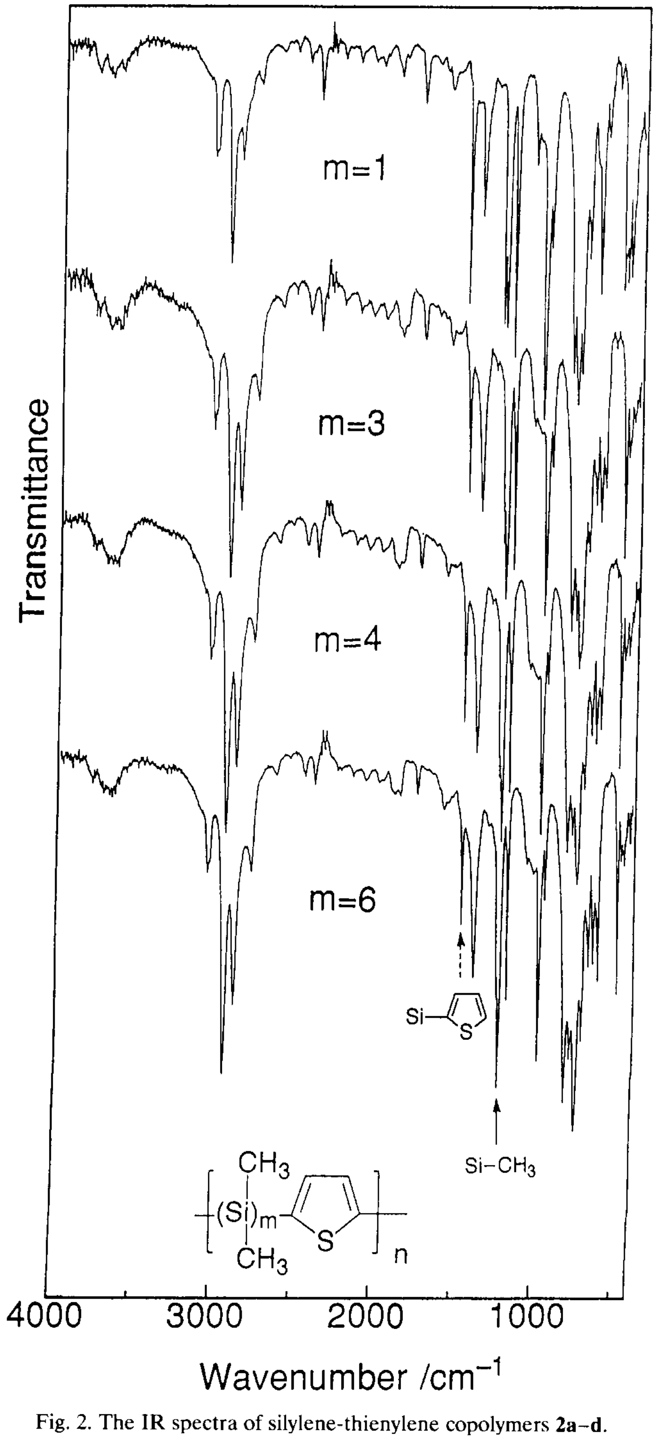


Fig. 2. The IR spectra of silylene-thienylene copolymers **2a–d**.

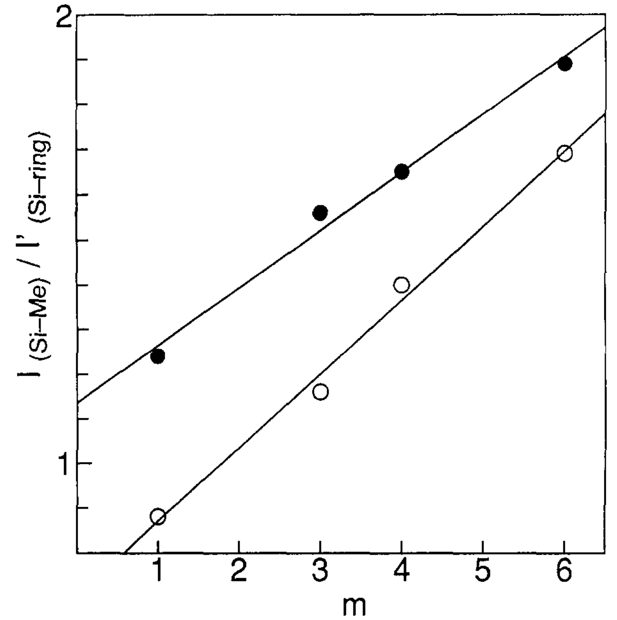


Fig. 3. The IR absorbance ratio ($I_{(\text{Si-Me})}/I'_{(\text{Si-ring})}$) of the Si-methyl band to the Si-ring band vs. the chain length m of dimethylsilylene unit for the copolymers **1a–d** (○) and **2a–d** (●).

perature change. The red shifts with decreasing temperature are also shown in Fig. 9 for **2d** ($m = 6$; $M_w = 7440$; $M_w/M_n = 2.1$).

3. Discussion

The absorption maxima and the extinction coefficient ε per repeating unit in the solution state increase

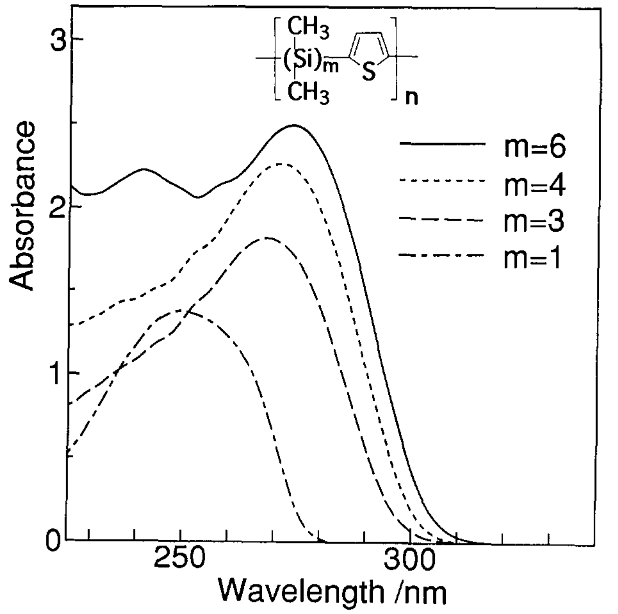


Fig. 5. Absorption spectra of silylene–thienylene copolymers **2a–d** in THF at room temperature.

with increasing number of silylene units. This means that conjugation along the backbone is enhanced by increasing the number of silylene units. Moreover, these show the red shift of UV absorption by introducing a π-electron-conjugating system in the main chain in comparison with those of the corresponding α,ω-dichloropermethylated oligosilanes. The absorption maxima and the molar absorptivities of α,ω-dichloropermethylated oligosilanes are $\lambda_{\text{max}} = 219$ nm ($\epsilon = 9200$)

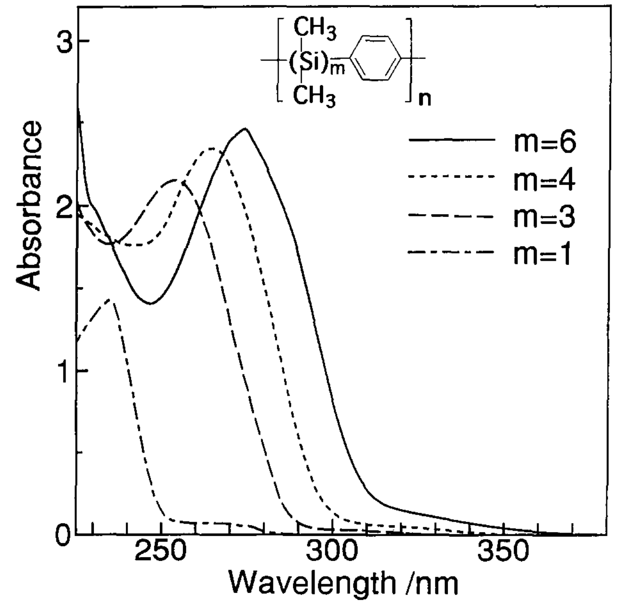


Fig. 4. Absorption spectra of silylene–phenylene copolymers **1a–d** in THF at room temperature.

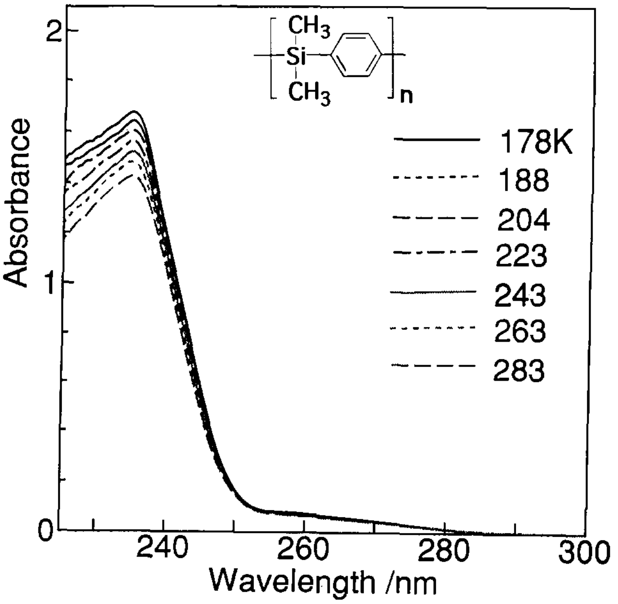


Fig. 6. The temperature dependence of the absorption spectra of silylene–phenylene copolymer **1a** (8.5×10^{-4} M, per repeating unit) in THF.

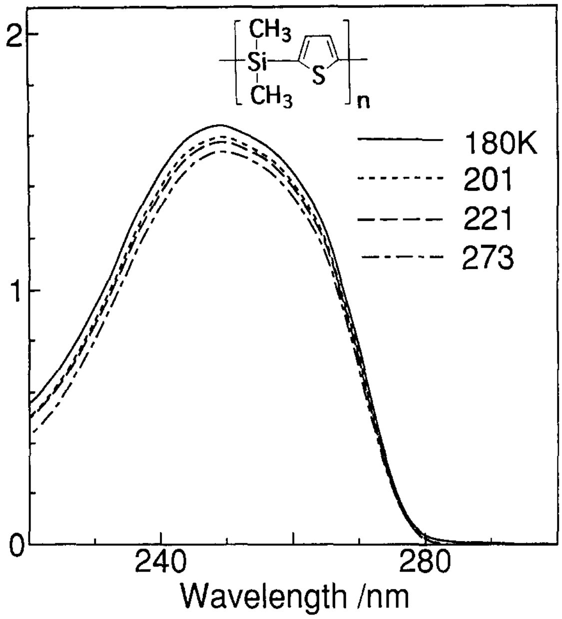


Fig. 7. The temperature dependence of the absorption spectra of silylene–phenylene copolymer **2a** (8.5×10^{-4} M, per repeating unit) in THF.

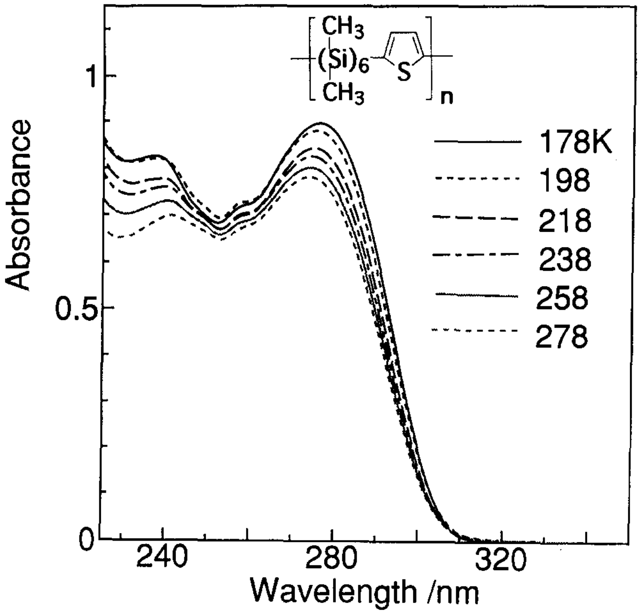


Fig. 9. The temperature dependence of the absorption spectra of silylene–phenylene copolymer **2d** (1.8×10^{-4} M, per repeating unit) in THF.

for $m = 3$, $\lambda_{max} = 235$ nm ($\epsilon = 17100$) for $m = 4$, and $\lambda_{max} = 259$ nm ($\epsilon = 23\,000$) for $m = 6$ [8]. The wavenumbers of absorption maxima of the silylene–phenylene copolymers **1a–d**, silylene–thienylene copolymers **2a–d** and α,ω-dichloropermethylated oligosilanes are compared in Fig. 10. The α,ω-dichloropermethylated oligosilanes show the dependence of the absorption peak on the dimethylsilylene chain length m, which is due to the enhancement of the σ conjugation with increase in m. The red shift of the silylene–phenylene and silylene–thienylene copolymers compared with α,ω-dichloropermethylated oligosilanes may

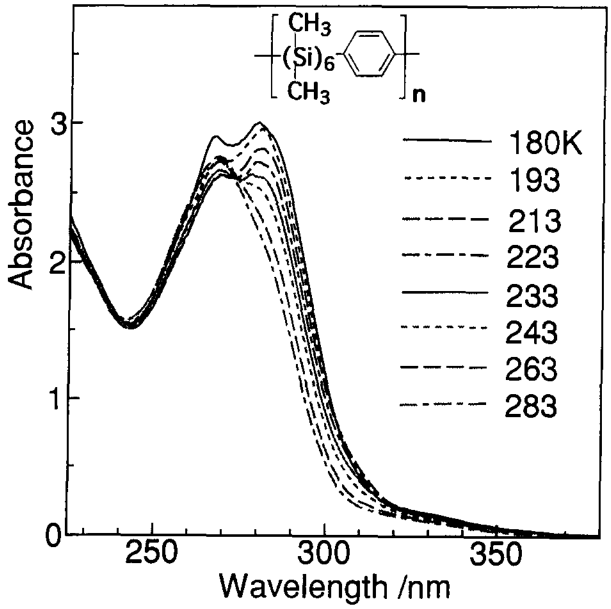


Fig. 8. The temperature dependence of the absorption spectra of silylene–phenylene copolymer **1d** (7.2×10^{-4} M, per repeating unit) in THF.

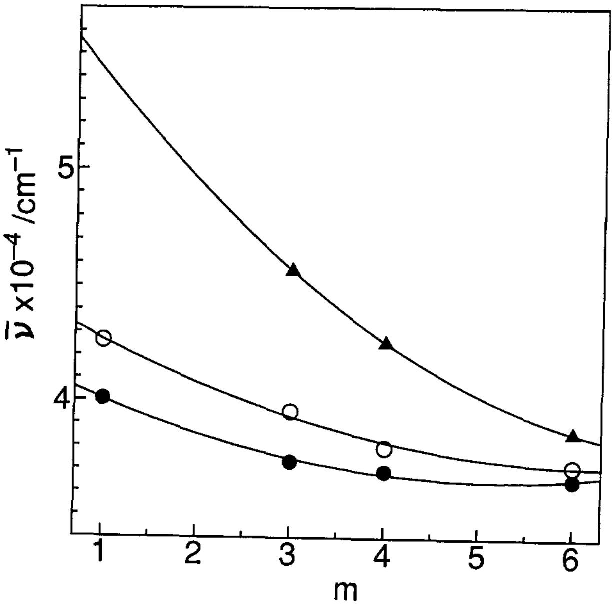


Fig. 10. The plot of the wavenumber $\tilde{\nu}$ of the absorption maximum vs. chain length m for silylene–phenylene copolymers **1a–d** (○), silylene–thienylene copolymers **2a–d** (●) and α,ω-dichloromethylated oligosilanes (▲) in THF at room temperature.

be caused by electron delocalization through the σ–π conjugation.

The thermochromism of the polysilanes is caused by the conformational change of the Si–Si chain [9]. With decreasing temperature, the absorption peak of polysilane shows a red shift with increasing ratio of *trans* conformation to *gauche* conformation. The red shift is caused by the increase in the overlapping of σ electrons in the *trans* conformation. The thermochromism is one piece of evidence for the σ conjugation of polysilanes. If there is a σ–π conjugation effect between the dimethylsilylene units and π units along the polymer chain, the conjugation must be enhanced by the increase in the σ conjugation with decreasing temperature. The linear dependence of wavenumber of absorption maxima upon reciprocal temperature is shown in Figs. 11 and 12 for **1a–d** and **2a–d** respectively. In Fig. 11, the broken line represents the fact that the longer-wavelength absorption band became a shoulder in the range 243–263 K and disappeared above approximately 263 K for **2d**. The red shift was scarcely observed for **1a** and **2a**. This result suggests that the chain length of the dimethylsilylene unit (m = 1) is not effective in inducing σ–π conjugation. The red shift was observed for **1b–d** and **2b–d** which have dimethylsilylene chain lengths greater than three. In particular, **1d** (m = 6) shows a new UV band near 280 nm with decrease temperature, as shown in Fig. 8. These results suggest the existence of σ–π conjugation between dimethylsilylene units and π units and that the conjugation is enhanced by an increase in the dimethylsilylene chain length.

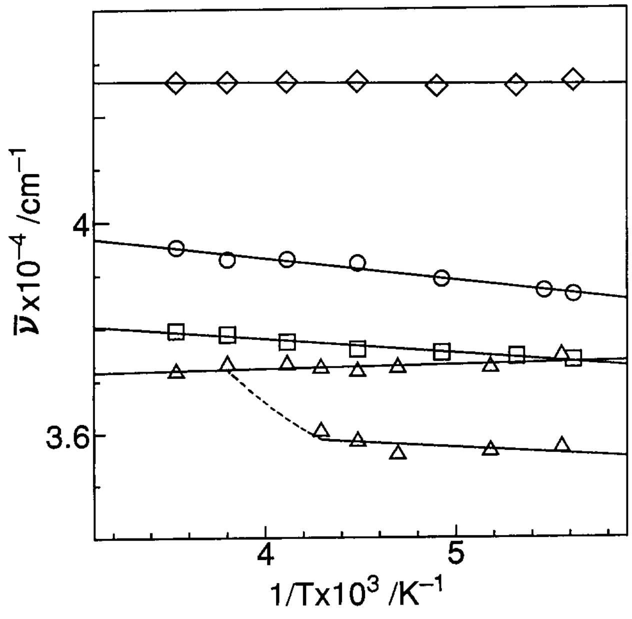


Fig. 11. The wavenumber ($\tilde{\nu}$) of the absorption maximum as a function of the reciprocal temperature for silylene–phenylene copolymers **1a–d** in THF: ◇, m = 1; ○, m = 3; □, m = 4; △, m = 6.

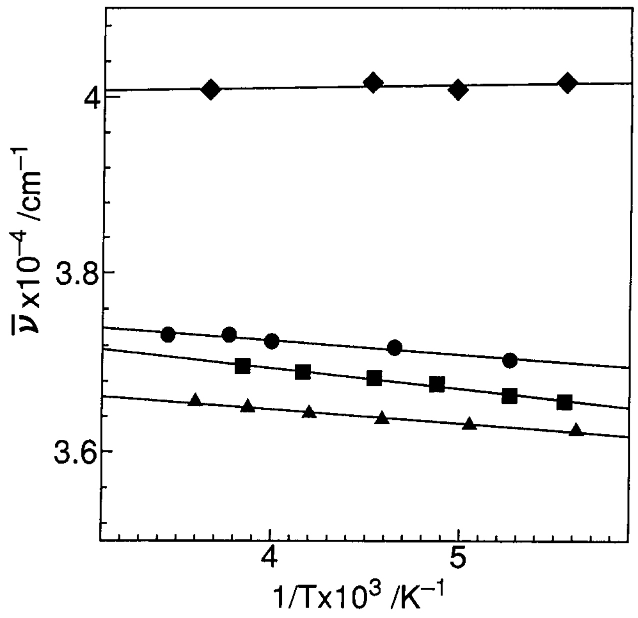


Fig. 12. The wavenumber $\tilde{\nu}$ of the absorption maximum as a function of the reciprocal temperature for silylene–phenylene copolymers **2a–d** in THF: ◆, m = 1; ●, m = 3; ■, m = 4; ▲, m = 6.

In conclusion, we have been able to achieve a successful synthesis of the alternating silylene–phenylene and silylene–thienylene copolymers which have various silylene chains. This is an efficient and convenient one-pot synthesis. The σ–π conjugation of the silylene–phenylene and silylene–thienylene copolymers was suggested by measurements of the thermochromism.

4. Experimental details

4.1. General procedures

All reactions were carried out under an atmosphere of dry argon. The FT IR spectra were recorded on a Japan Electric Co. Ltd. JIR-100 FT IR spectrophotometer using copolymer samples mixed with KBr powder (0.2 wt.%). Electronic absorption spectra were measured on a Hitachi U-3400 spectrophotometer. Spectra-quality THF was used as the solvent to prepare solutions for UV analysis. ^{1}H and ^{13}C NMR spectra were determined with a Bruker AC 250 NMR spectrometer using deuteriochloroform as a solvent. The molecular weight was determined by a Toyo Soda HLC-802VR gel permeation chromatography. The eluting solvent was reagent THF at a flow rate of 1 ml min^{-1}. The column was calibrated using a series of polystyrene standards of a narrow molecular weight distribution. The melting points of copolymers were determined using a prismscope melting-point determinator. Diethyl ether (Et$_2$O) was distilled after refluxing with sodium-benzophenone ketyl. All other solvents were nitrogen saturated and dried according to standard procedures. Commercially available 1,4-dibromobenzene and 2,5-dibromothiophene were recrystallized from hexane. The α,ω-dichloropermethylated oligosilanes Cl–(SiMe$_2$)$_m$–Cl ($m = 3$, 4 and 6) were prepared by the reaction of dodecamethylcyclohexasilane with phosphorous pentachloride in *sym*-tetrachloroethane according to literature preparations [10]. Dimethyldichlorosilane was obtained from a commercial source and distilled just before use.

*4.2. Synthesis of polymer **1a** as a general example of silylene–phenylene and silylene–thienylene copolymers **1a–d** and **2a–d***

In a 200 ml three-necked flask fitted with a condenser, stirrer and dropping funnel was placed 4.72 g (0.02 mol) of 1,4-dibromobenzene dissolved in 60 ml of Et$_2$O. The flask was flushed with argon and 25 ml of 1.6 N solution of *n*-butyllithium in *n*-hexane was added with stirring. The mixture warmed slightly and a heavy white precipitate formed. The mixture was then stirred and refluxed for 3 h until color test A [11] was negative. The reaction mixture was cooled to 0°C, a solution of 2.58 g (0.02 mol) of dichlorodimethylsilane in 20 ml of Et$_2$O was added over a 10 min period, and the solution was warmed to room temperature. The mixture was stirred for 1 h and refluxed for 5 h. The mixture was hydrolyzed with 50 ml of 2 N hydrochloric acid. The organic layer was separated off, washed with water and evaporated to dryness. The residue was redissolved in 5 ml of THF and added to 200 ml of methanol to precipitate copolymer **1a**, which was filtered and dried in vacuo (yield, 49%). The silylene–phenylene copolymers **1b–d** and silylene–thienylene copolymers **2a–d** were prepared by similar procedures.

1a: ^{1}H NMR (CDCl$_3$): δ 0.53 (6H, Si–Me), 7.49 (4H, phenylene ring). ^{13}C NMR (CDCl$_3$): δ −2.6 (Si–Me), 129.8, 133.5 (phenylene ring). IR: 3049, 2997, 2956, 2897, 2831, 1919, 1381, 1252, 1132, 1088, 771, 820, 673, 517 cm^{-1}. Anal. Found: C, 69.25; H, 7.47. Calc.: C, 70.24; H, 7.32%.

1b: ^{1}H NMR (CDCl$_3$): δ 0.08, 0.31 (18H, Si–Me), 7.37 (4H, phenylene ring). ^{13}C NMR (CDCl$_3$): δ −3.3, −6.5 (Si–Me), 129.6, 133.0 (phenylene ring). IR: 3045, 2995, 2955, 2895, 2810, 1917, 1378, 1248, 1132, 1068, 770, 831, 661, 511 cm^{-1}. Anal. Found: C, 45.78; H, 6.34. Calc.: C, 46.87; H, 6.25%.

1c: ^{1}H NMR (CDCl$_3$): δ 0.07, 0.30 (24H, Si–Me), 7.34 (4H, phenylene ring). ^{13}C NMR (CDCl$_3$): δ −3.2, −5.6 (Si–Me), 129.6, 133.0 (phenylene ring). IR: 3041, 2991, 2951, 2893, 2791, 1913, 1377, 1248, 1126, 1066, 767, 831, 659, 509 cm^{-1}. Anal. Found: C, 41.17; H, 6.19, Calc.: C, 41.78; H, 6.04%.

1d: ^{1}H NMR (CDCl$_3$): δ 0.06, 0.10, 0.29 (36H, Si–Me), 7.31 (4H, phenylene ring). ^{13}C NMR (CDCl$_3$); δ −3.2, −4.6, −5.5 (Si–Me), 129.5, 133.0 (phenylene ring). IR: 3040, 2991, 2951, 2892, 2791, 1913, 1377, 1247, 1125, 1037, 761, 831, 657 cm^{-1}. Anal. Found: C, 35.39; H, 5.74. Calc.: C, 35.45; H, 5.68%.

2a: ^{1}H NMR (CDCl$_3$): δ 0.63 (6H, Si–Me), 7.37 (2H, thienylene ring). ^{13}C NMR (CDCl$_3$): δ 0.2 (Si–Me), 136.6, 144.1 (thienylene ring). IR: 3056, 2962, 2897, 1490, 1267, 1252, 1205, 1011, 833, 807, 783, 744, 675 cm^{-1}. Anal. Found: C, 48.97; H, 5.73. Calc.: C, 50.36; H, 5.60%.

2b: ^{1}H NMR (CDCl$_3$): δ 0.09, 0.37 (18H, Si–Me), 7.22 (2H, thienylene ring). ^{13}C NMR (CDCl$_3$): δ −1.6, −6.4 (Si–Me), 135.1, 143.8 (thienylene ring). IR: 3054, 2956, 2896, 1486, 1265, 1249, 1203, 1005, 833, 806, 775, 741, 666 cm^{-1}. Anal. Found: C, 45.88; H, 7.84. Calc.: C, 46.07; H, 7.68%.

2c: ^{1}H NMR (CDCl$_3$): δ 0.08, 0.37 (24H, Si–Me), 7.20 (2H, thienylene ring). ^{13}C NMR (CDCl$_3$): δ −1.5, −5.6 (Si–Me), 135.1, 143.8 (thienylene ring). IR: 3052, 2950, 2895, 1485, 1263, 1248, 1202, 1001, 832, 805, 771, 732, 663 cm^{-1}. Anal. Found: C, 43.45; H, 8.17. Calc.: C, 44.71; H, 8.07%.

2d: ^{1}H NMR (CDCl$_3$): δ 0.08, 0.12, 0.36 (36H, Si–Me), 7.18 (2H, thienylene ring). ^{13}C NMR (CDCl$_3$): δ −1.4, −4.5, −5.4 (Si–Me), 135.0, 143.7 (thienylene ring). IR: 3051, 2950, 2893, 1485, 1262, 1248, 1200, 1001, 831, 801, 763, 731, 661 cm^{-1}. Anal. Found: C, 42.93; H, 8.75. Calc.: C, 43.87; H, 8.68%.

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