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Articles

Synthesis of Silicon-Containing Unsaturated Polymers by Hydrosilylation Reactions. Photophysical Studies

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ABSTRACT: Silicon-containing unsaturated polymers have been synthesized using the Pt(acac)$_2$-catalyzed photoactivated hydrosilylation of alkynes. These polymers fluoresce at 360 nm when excited at 270 nm due to the π-conjugated vinylphenyl segment in the polymer chain. The polymers have excellent solubility in several organic solvents.

Introduction

Conjugated polymers are of interest as emissive layers in organic light-emitting devices.[1,2] The emission can be controlled by use of a spacer between chromophores in the polymer chain; the extent of control depends on the choice of chromophore. It is also possible to tune the luminescence properties of such polymers at the molecular level. Electroluminescence from a polymer containing well-defined fluorophores linked by flexible spacers has been studied.[3] Polymers utilizing silicon-based spacers have several advantages, and a wide variety of such silicon-containing polymers have been designed and synthesized.[4] The solubility and processability of the polymer can be improved due to the chain flexibility arising from the silicon atom. Absorption and emission data suggest only weak $\sigma-\pi$ conjugation coupling between chromophores by way of the silicon linker.[5,6]

Kim[7] studied the synthesis and optical properties of poly(*p*-phenylenevinylene)-like polymers containing silicon atoms in the main chain. The photoluminescence of these polymers between 440 and 480 nm indicates that the regular π-conjugated system is effectively interrupted by the organosilicon units, thus resulting in a blue emission. These units improve processing and limit the π-conjugation length.[7]

Hydrosilylation is an effective method for preparing silicon-containing polymers.[8−13] Platinum and rhodium complexes such as Karstedt's catalyst,[8] chloroplatinic acid,[9,10] and RhI(PPh$_3$)$_3$[11−13] are the common catalysts for such reactions. Hyperbranched polycarbosilanes were also synthesized by hydrosilylation addition reactions.[14−16]

Kepler[8] reported the synthesis of light-emitting oligocarbosilanes with Karstedt's catalyst. The model compound that is the repeat unit in the oligocarbosilane was also synthesized. Kepler observed a red shift of the fluorescence of the polymer over the model compound. This red shift was proposed to be due to the weak $\sigma-\pi$ conjugation through the silicon atoms in the polymer chain or due to interchain aggregation of oligomer chains.

In this paper, conjugated polymers with organosilicons as the spacer were synthesized using platinum(II) bis(acetylacetonato) [Pt(acac)$_2$]-catalyzed photohydrosilylation of alkynes. These polymers photoluminesce when excited at 270 nm.

Experimental Section

Materials and Instruments. THF was purchased from Aldrich Chemical Co. and refluxed with sodium and benzophenone until the color turned blue to remove moisture. Triethylamine was freshly distilled. All other reagents were purchased from Acros Chemical Co. and used as received unless otherwise noted. Irradiations were carried out in a Rayonet photochemical reactor (350 nm lamps) equipped with a jacketed beaker (Pyrex). NMR spectra were obtained using a Varian Gemini 200 NMR spectrometer, and chemical shifts are in parts per million with the corresponding deuterated solvents as the internal standard. GC/MS spectra were obtained on a Shimadzu GC/MS-QP5050 mass spectrometer coupled to a GC-17A (Restek ST1-5 column, 30 m × 0.25 mm × 0.25 μm).

((*p*-Bromophenyl)ethynyl)trimethylsilane (2) was synthesized via the Sonogashira coupling reaction.[17] To a solution of 5.1 g (18 mmol) of 1-bromo-4-iodobenzene and 2.1 g (21 mmol) of ethynyltrimethylsilane in 80 mL of anhydrous triethylamine were added 0.23 g (0.33 mmol) of bis(triphenylphosphine)palladium(II) chloride and 19 mg (0.10 mmol) of cuprous iodide. The reaction mixture was stirred at room temperature under argon overnight, then diluted with benzene, washed twice with 200 mL of water, and dried over MgSO$_4$. Solvent was evaporated under vacuum and the residue purified by chromatography on silica gel with hexanes as the eluent. A colorless liquid was obtained (90% yield) and characterized by ^{1}H NMR and GC/MS. ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.25 (s, 9H), 7.34 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H). MS (m/z): 252.

***p*-Bromophenylacetylene (3)** was synthesized in 91% yield following a literature procedure.[18] The light yellow compound was characterized by ^{1}H NMR and GC/MS. ^{1}H NMR (200 MHz, CDCl$_3$): δ 3.13 (s, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H). MS (m/z): 180.

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(*p*-(Dimethylsilyl)phenyl)acetylene (4) was synthesized following a literature procedure (63% yield) as a colorless liquid that turned yellow on standing.[5] The compound was characterized by ^{1}H NMR and GC/MS. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.33 (d, $J = 4.0$ Hz, 6H), 3.10 (s, 1H), 4.42 (m, 1H), 7.49 (s, 4H). MS (*m*/*z*): 160.

1,4-Diethynylbenzene (6) was obtained as the side product of the synthesis of **4**. It is a white solid with a melting point of 91−93 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.18 (s, 2H), 7.45 (s, 4H). MS (*m*/*z*): 126.

2-((Trimethylsilyl)ethynyl)thiophene (8) was synthesized as **2**, with 2-bromothiophene as the starting material. The residue was purified by chromatography on silica gel using hexanes as the eluent. A yellow liquid was obtained (50%). The compound was characterized by ^{1}H NMR and GC/MS. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.26 (s, 9H), 6.96 (t, 1H), 7.25 (d, 2H). MS (*m*/*z*): 180.

2-Iodo-5-ethynylthiophene (10) was synthesized in 84% yield following a literature procedure.[16] ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.39 (s, 1H), 6.90 (d, $J = 3.6$ Hz, 1H), 7.09 (d, $J = 4$ Hz, 1H). MS (*m*/*z*): 234.

2-((Dimethylsilyl)ethynyl)thiophene (11) was synthesized as **4**, with **10** as the starting material. A yellow liquid was obtained in a yield of 91%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.31 (d, 6H), 4.27 (m, 1H), 6.93 (t, 1H), 7.26 (d, 2H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 132.88 (CH), 127.57 (CH), 126.86 (CH), 122.80 (CH), 98.84 (C), 95.69 (C), −3.0 (CH_3), −3.10(CH_3). HRMS (*m*/*z*): calcd for $C_8H_{10}SiS$ 166.3189, found 166.0279.

1,3,5-((Trimethylsilyl)ethynyl)benzene (14) was synthesized as **2**, with 1,3,5-tribromobenzene as the starting material. The residue was purified by chromatography on silica gel with hexanes as the eluent. A colorless liquid was obtained (70% yield). The compound was characterized by ^{1}H NMR and GC/MS. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.23 (s, 27 H), 7.49 (s, 3H). MS (*m*/*z*): 262.

1,3,5-Triethynylbenzene (15)[19] was synthesized via a procedure similar to that of **3**, with **14** as the starting material. A light yellow solid was obtained in a yield of 91%. The melting point is 100−101 °C. The compound was characterized by ^{1}H NMR and GC/MS. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.11 (s, 3H), 7.57 (s, 3H). MS (*m*/*z*): 150.

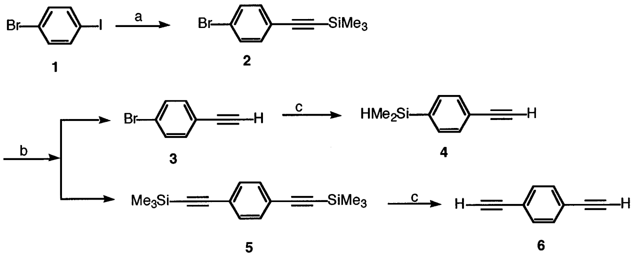
((*p*-(Dimethylsilyl)phenyl)ethynyl)trimethysilane (16) was synthesized as **2**, with **2** as the starting material. After hydrolytic workup and rotary evaporation of the solvent, the residue was purified by flash chromatography (silica gel, hexanes) to provide a colorless liquid (3.2 g, 86%). The compound was characterized by ^{1}H NMR and GC/MS. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.26 (s, 9H), 0.34 (d, 6H), 7.58 (d, 2H), 7.60 (d, 2H). Anal. Calcd: C, 67.17; H, 8.67. Found: C, 67.20; H, 8.46.

1,3,5-Trivinylbenzene (17) was synthesized in 60% yield following a literature procedure.[20] It was characterized by ^{1}H NMR and GC/MS. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.23 (d, $J = 10.6$ Hz, 3H), 5.72 (d, $J = 17.6$ Hz, 3H), 6.72 (dd, $J = 11.0$ Hz, $J = 17.6$ Hz, 3H), 7.33 (s, 1H). MS (*m*/*z*): 156.

The First Generation of a Star Polymer (16a) was synthesized by Pt(acac)$_2$-catalyzed hydrosilylation of **15** and **16** with a molar ratio of 1:3. It was characterized by GC/MS and elementary analysis. Anal. Calcd for $C_{51}H_{66}Si_6\cdot{}^1/_2H_2O$: C, 71.51; H, 7.88. Found: C, 71.17; H, 7.91.

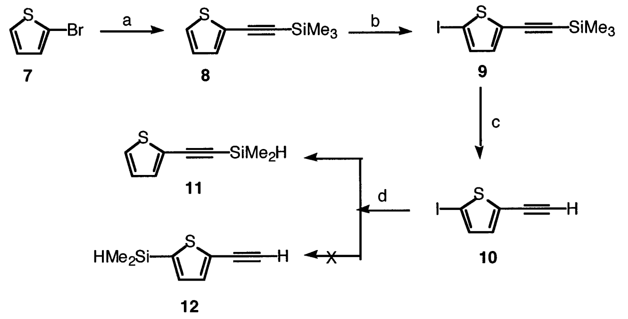
General Procedure for Photopolymerization of Carbosilane Monomers. All the polymerizations were conducted in bulk at a molar ratio of Pt(acac)$_2$ to the monomer of 10^{-3}:1. The reaction mixture was stirred well before irradiation at 350 nm in the Rayonet reactor. In most of the cases, after a short period of irradiation the reaction mixtures were kept in the dark overnight at room temperature before workup and analysis. Control experiments were conducted for the same reaction mixtures under the same conditions without irradiation. The polymers were isolated by dissolution in CH_2Cl_2 and precipitated three times with MeOH. Polymers were characterized by GPC, ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, and FT-IR. Cross-linked polymers were extracted in a Soxhlet extractor with CH_2Cl_2 for 2 days and dried in an oven.

Scheme 1. Synthesis of 4[a]



[a] Reagents and conditions: (a) Pd(PPh$_3$)$_2$Cl$_2$, CuI, NEt$_3$, HCCSiMe$_3$, argon, 15 h; (b) MeOH, K_2CO_3, 5 h; (c) (1) *n*-BuLi, THF, −78 °C, argon; (2) ClSiMe$_2$H.

Scheme 2. Synthesis of 11[a]



[a] Reagents and conditions: (a) Pd(PPh$_3$)$_2$Cl$_2$, CuI, NEt$_3$, HCCSiMe$_3$, argon, 15 h; (b) LDA, I$_2$, −78 °C; (c) MeOH, K_2CO_3, 5 h; (d) (1) *n*-BuLi, THF, −78 °C, argon; (2) ClSiMe$_2$H.

General Procedure for Fluorescence Quantum Yield Measurement.[21] Fluorescence quantum yields were measured in cyclohexane using naphthalene as the standard. Using the same apparatus, the quantum yield of an unknown is related to that of a standard by eq 1. The subscript u refers to the

$$\phi_u = \frac{A_sF_u}{A_uF_s}\left(\frac{\eta}{\eta_0}\right)^2\phi_s \qquad (1)$$

unknown and s to the standard, and the other symbols have the following meanings: ϕ is the quantum yield, A is the UV−vis absorption at the excitation wavelength, F is the integrated emission area across the band, and η is the index of refraction of the solvent containing the unknown (η) and the standard (η_0) at the sodium D line and the temperature of the emission measurement. In this case, naphthalene in cyclohexane was used as the standard so $\phi_s = 0.19$, $\eta_0 = 1.363$ (cyclohexane), and $\eta = 1.424$ (dichloromethane).

Result and Discussion

Photopolymerization of Monomers 4, 11, and 18. Polymers **4a**, **11a**, and **18a** were synthesized by Pt(acac)$_2$-catalyzed photoactivated hydrosilylation reactions of the appropriate silanes. The latter contained both a Si−H bond and a carbon−carbon triple bond. Monomers **4** and **11** were synthesized as shown in Schemes 1 and 2. Oligomers **11a** and **18a** were obtained after 30 min of irradiation from photopolymerization of monomers **11** and **18** through Pt(acac)$_2$-catalyzed photoactivated hydrosilylation (Scheme 3). Efforts to precipitate oligomers with methanol were not successful. Both oligomers are brown glassy solids. The polymerization result is shown in Table 1.

In the photopolymerization of monomer **4** via the Pt(acac)$_2$-catalyzed photoactivated hydrosilylation, vigorous and exothermic polymerization was observed after less than 3 min of irradiation. The products are mostly cross-linked polymers that cannot be dissolved in or-

Scheme 3. Synthesis of Silicon-Containing Polymers from Monomers 11 and 18

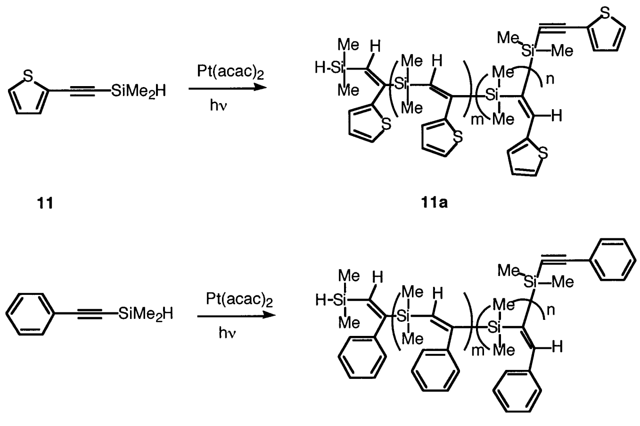
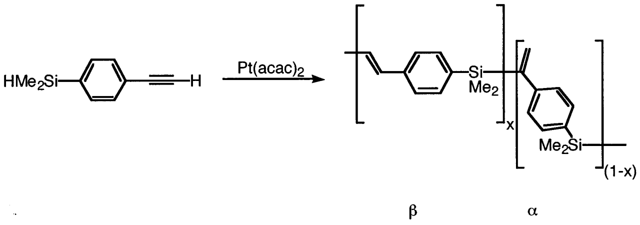


Table 1. Polymerization Results of Monomers 4, 11, and 18

polymer	M_w (g/mol)	PD	yield (%)
18a	735	1.2	
11a	811	1.3	
4a[a]			66
4a[b]	16890	2.5	
4a[c]	8899	3.0	55

[a] Cross-linked polymer from photopolymerization of **4** after extraction in CH_2Cl_2 for 48 h. [b] Soluble polymer from photopolymerization of **4**. [c] Control polymerization of **4** in the dark for 2 days.

Scheme 4. Polymerization of (*p*-(Dimethylsilyl)phenyl)acetylene



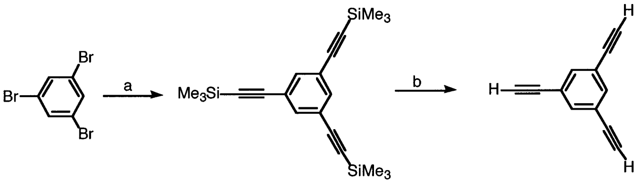
ganic solvents such as CH_2Cl_2, $CHCl_3$, benzene, and hexanes. The cross-linked polymers obtained have a large swelling ratio (5.1 in CH_2Cl_2); therefore, the degree of cross-linking cannot be high. A small amount of soluble polymer was obtained following precipitation by a large amount of methanol (Scheme 4). In the control reaction, soluble polymer was obtained after 2 days of dark reaction. The polymerization was smooth and slow. The molecular weights of the polymers are listed in Table 1.

The Pt(acac)$_2$-catalyzed hydrosilylation reaction of alkyne occurs via *cis* addition and forms three kinds of products, with the β-*trans* isomer predominating over the α isomer.[22] The oligomers **11a** and **18a** as well as polymer **4a** contain both conjugated and cross-conjugated segments as a consequence of the formation of both β-*trans* and α isomers. These polymers have good solubility in common organic solvents.

Photopolymerization of Monomers 4 and 15 and 4 and 6. To synthesize longer conjugated polymers containing both π conjugation and $\sigma-\sigma$ conjugation, compounds **6** and **15** were prepared (Schemes 5 and 1). Photopolymerization of **15** and **4** at molar ratios of 1:10 and 1:20 gave soluble star polymer **15a** (Scheme 6). After 30 min of irradiation, the polymers were glassy solids though they were of low molecular weight. After postpolymerization in the dark at room temperature for three weeks, hard solid polymers formed with much higher molecular weights. Photopolymerization of **6** and **4** at a molar ratio of 1:10 also gave soluble polymer **6a** (Scheme 7). All these polymers were yellow powders after purification and are soluble in common organic solvents. See Table 2 for the results.

Photopolymerization of **15** and **4** at a molar ratio of 1:50 gave partially cross-linked polymer. The high concentration of **4** is responsible for the formation of cross-linked polymer. This is probably due to the hy-

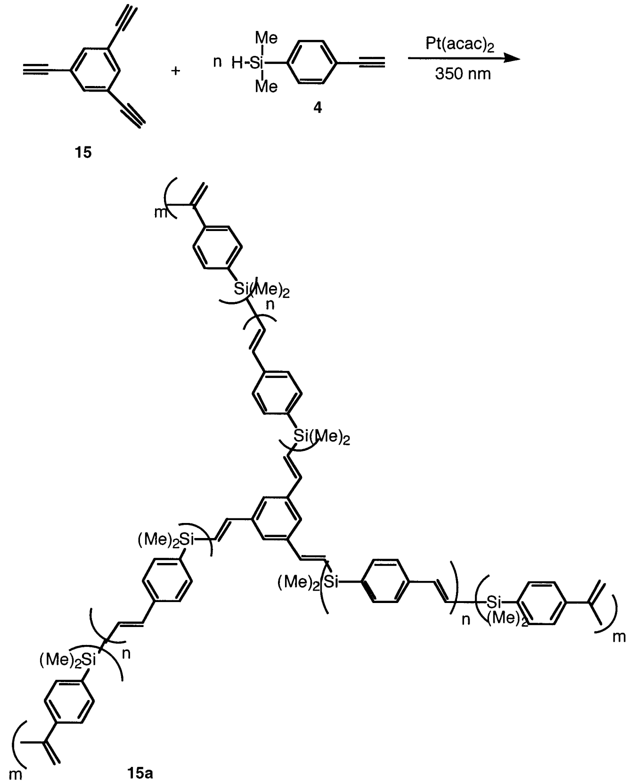
Scheme 5. Synthesis of 15[a]



13 14 15

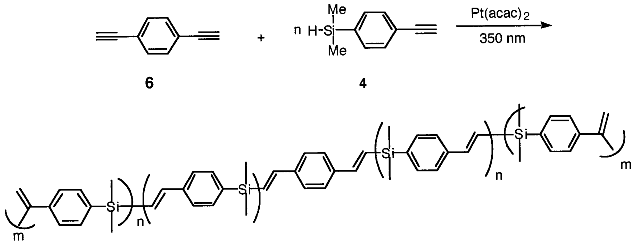
[a] Reagents and conditions: (a) $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, $HCCSiMe_3$, argon, 15 h; (b) MeOH, K_2CO_3, 5 h.

Scheme 6. Synthesis of a Silicon-Containing Star Polymer with Pt(acac)$_2$-Catalyzed Photoactivated Hydrosilylation of 1,3,5-Triethynylbenzene



15 4 15a

Scheme 7. Synthesis of a Linear Silicon-Containing Polymer with Pt(acac)$_2$-Catalyzed Photoactivated Hydrosilylation of Alkyne



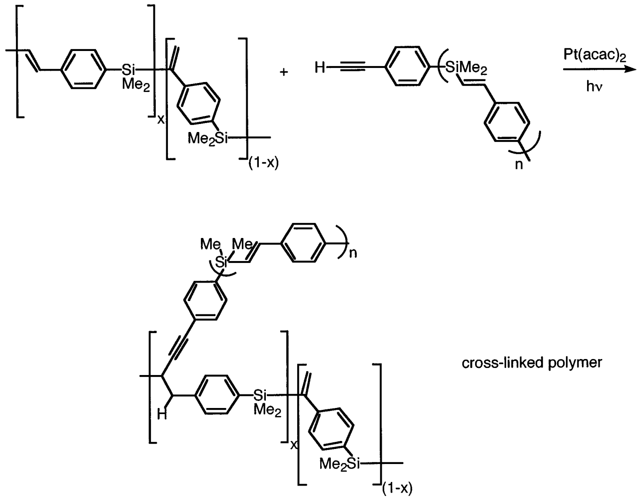
6 4 6a

Table 2. Photopolymerization Results of 15 and 4 and 6 and 4

monomers	molar ratio	M_n (g/mol)	M_w (g/mol)	PD
6 and **4**	1:10	3788	6421	1.69
	1:20^a	1555	3121	1.71
15 and **4**	1:10	1080	1738	1.61
	1:10^b	2616	4652	1.78
	1:20	2003	3703	1.85
	1:20^b	4660	8790	1.89
	1:50	5941	14480	2.4

[a] Thermal polymerization (room temperature, dark). [b] After postpolymerization for 3 weeks (room temperature, dark).

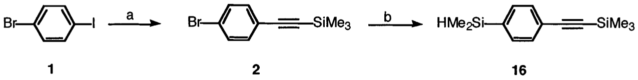
Scheme 8. Mechanism of the Formation of a Cross-Linked Polymer



drosilylation of the terminal Si−H bond of H across the C−C double bond in the polymer chain (Scheme 8). In the photoreaction of **15** with **4** at a lower molar ratio the terminal Si−H bond reacts first with the C−C triple bond of compound **15**. There is no terminal Si−H bond remaining as the polymerization becomes complete. No cross-linked polymer was formed. On the other hand, hydrosilylation of the internal C−C double bond is difficult due to steric considerations. In the photopolymerization of monomer **4**, the exothermic hydrosilylation of the terminal alkynes along the polymer chain is very rapid. A large amount of heat is released following a short induction period, promoting the hydrosilylation reaction of some of the internal C−C double bonds and resulting in cross-linked polymers.

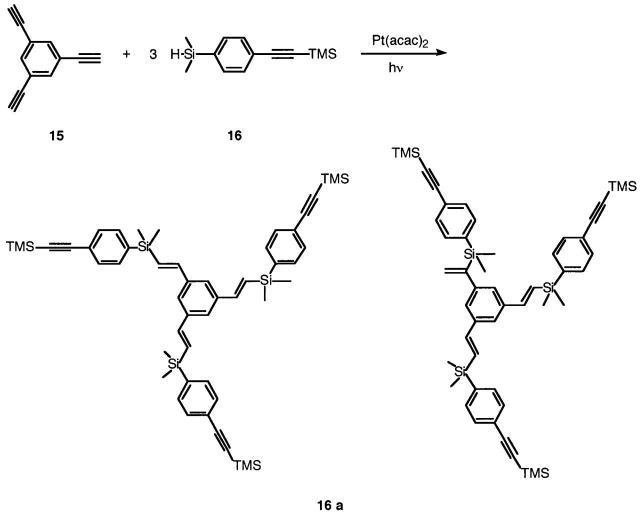
All the polymers were characterized by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, and FT-IR. For the linear polymer formed from monomer **4**, a doublet of doublets at chemical shifts of 6.65 and 6.88 ppm with a large coupling constant (J = 19 Hz) is characteristic of the β-*trans* isomer. The two broad singlet peaks belonging to the α isomer at chemical shifts of 5.67 and 6.01 ppm were also observed in the ^{1}H NMR spectrum. The two vinyl carbons of the β-*trans* isomer are clearly shown at 146.5 and 125.1 ppm in the ^{13}C NMR. In the ^{29}Si NMR, two signals from the β-*trans* and α isomers in the polymer chain are at chemical shifts of −8.417 and −10.579 ppm, respectively.

Scheme 9. Synthesis of 16[a]



[a] Reagents and conditions: (a) Pd(PPh$_3$)$_2$Cl$_2$, CuI, NEt$_3$, HCCSiMe$_3$, argon, 15 h; (b) (1) n-BuLi, THF, −78 °C, argon, 2. ClSiMe$_2$H.

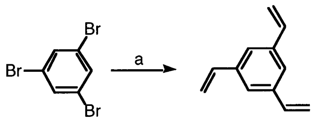
Scheme 10. Synthesis of the First Generation of a Star Polymer (Two Possible Isomers)



Few differences in ^{1}H NMR, ^{13}C NMR, and FT-IR are observed when one compares the structure of the star polymer with that of the linear polymer formed from **4**. The ^{1}H NMR clearly shows the star polymer has a terminal acetylenic proton at 3.1 ppm while the linear polymer of monomer **4** has no signals around 3.1 ppm because of its high molecular weight. In the ^{13}C NMR spectrum, the star polymers have a new signal at 131.25 ppm belonging to the carbon of the −CH group on the core benzene ring. Other peaks have the same chemical shifts as those found in the spectrum of the linear polymer from **4**. In the FT-IR spectrum, the star polymer has a much stronger absorption of the terminal alkyne group at 3316 and 2108 (weak) cm^{-1} than does the linear polymer formed from monomer **4**. Furthermore, there is almost no absorption of the Si−H bond at 2116 cm^{-1} in the star polymer, while there is an absorption at 2116 cm^{-1} in the thermal polymer formed from monomer **4**. This clearly shows that there is no terminal Si−H bond in the star polymer while there is a terminal Si−H bond in the linear polymer formed from monomer **4**. No difference is observed in the ^{29}Si NMR spectra of the star polymers and the linear polymer formed from monomer **4**.

All these polymers and oligomers fluoresce when excited at wavelengths from 250 to 300 nm. The fluorescence of the oligomers and linear polymers is weak compared with that of the star polymer ($\Phi_{\mathrm{fl}} \approx 10^{-3}$). The fluorescence maxima of the star polymers are observed at ~360 nm. The fluorescence quantum yield decreases as the length of the star polymer increases. To clarify the fluorescence chromophore, the first generation of a star polymer (**16a**) was synthesized by hydrosilylation of **15** and **16** (Schemes 9 and 10). The core molecule 1,3,5-trivinylbenzene (**17**) was also synthesized (Scheme 11). The UV−vis absorption spectrum of **17** has an absorption maximum at 248 nm. The maxima of the fluorescence are at 346 and 362 nm. The normalized fluorescence spectra ($\lambda_{\max}$ = 346 and 362 nm) of compound **17** and the star polymers are shown in Figure 1. A red shift of 10 nm was observed between **17** and **16a**, spectrum a. There is no red shift in the fluorescence spectra of **16a** or the star polymers formed from 1:10 and 1:20 molar ratios of **15** and **4,** spectrum b. However, the fluorescence spectrum of the star

Scheme 11. Synthesis of 17[a]



13 **17**

[a] Reagents and conditions: (a) LiCl, Pd(PPh$_3$)$_4$, vinyltributylstannane, anhydrous dioxane, argon, 100 °C, 15 h.

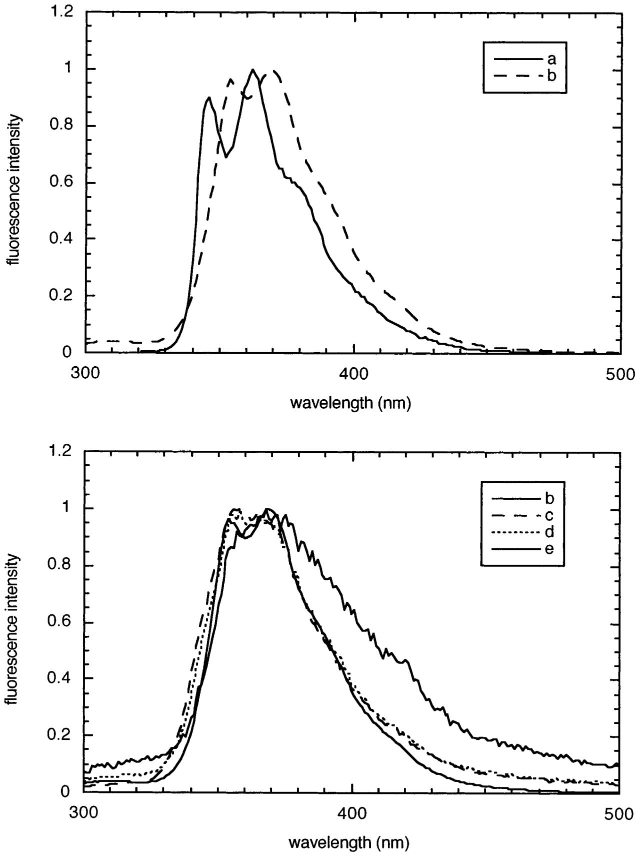


Figure 1. Fluorescence spectra of 1,3,5-trivinylbenzene and star polymers: (a) 1,3,5-trivinylbenzene; (b) first generation of a star polymer; (c–e) star polymers from a molar ratio of **6.15** and **6.4** of 1:10, 1:20, and 1:50, respectively.

Table 3. Absorption Maxima of the UV–Vis Spectra of the Core Molecule and Star Polymers

compound	$\lambda_{\max}$ (nm)
1,3,5-triethynylbenzene	235, 253
1,3,5-trivinylbenzene	248
first generation of a star polymer	258, 270
star polymers	270 (br)

polymer obtained from a 1:50 molar ratio of **15** and **4** has a red shift compared with those of other star polymers prepared using lower ratios of starting materials (1:10, 1:20). Furthermore, the red shift of 10 nm was also observed in the UV–vis spectrum of **17** when compared with spectra from the star polymers (Table 3). These results suggest a very weak $\sigma-\pi$ conjugation in the polymer chain. The silicon atom actually inhibits π conjugation, and the conjugation is restricted to a single repeating unit.

Table 4. Fluorescence Quantum Yields of Polymers[a]

compound[b]	a	b	c	d	e	f
ϕ	0.90	0.68	0.18	0.12	0.06	0.0090

[a] The excitation wavelength is 270 nm, and naphthalene was used as the standard (ϕ = 0.19 in cyclohexane). [b] Compounds: a = 1,3,5-trivinylbenzene; b = first generation of a star polymer; c = star polymer from a molar ratio of **15** and **4** of 1:10; d = star polymer from a molar ratio of **15** and **4** of 1:20; e = star polymer from a molar ratio of **15** and **4** of 1:50; f = 1,3,5-triethynylbenzene.

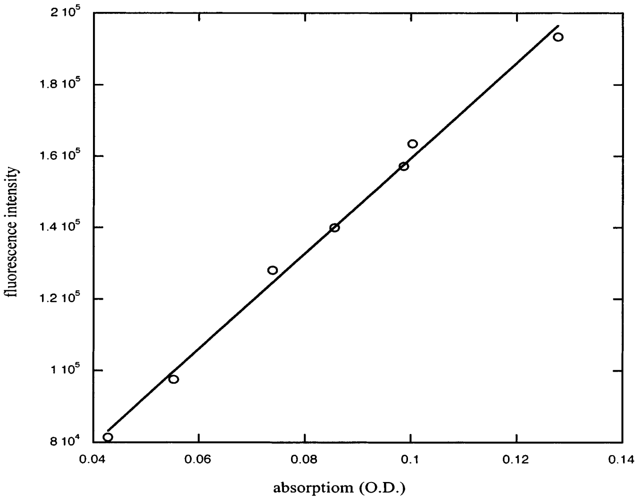


Figure 2. Relationship of the UV absorption and intensity of the fluorescence of the star polymer (1:10 molar ratio).

1,3,5-Triethynylbenzene has a very small fluorescence quantum yield, whereas the fluorescence quantum yield of **17** is 0.90 when it is excited at 270 nm. This fluorescence quantum yield is larger than those of all the star polymers, Table 4, and suggests that the fluorescing chromophore is the core molecule **17**. There is no intermolecular self-quenching in that there is a linear relationship between the fluorescence intensity and concentration of the star polymer (Figure 2).

The longer the arm of the star polymer, the lower the fluorescence quantum yield. This might be associated with an intramolecular self-quenching of the star polymer. Because of the flexibility of the polymer chain containing a silicon atom, the arms of the star polymer can be highly folded and, thus, interact with other arms in the polymer. Intrachain chromophore interaction due to folding of the polymer has been reported for silylene–divinylbenzene copolymers.[23,24] This idea, however, must be tested with further experiments.

Conclusion

Photoluminescent silicon-containing polymers have been efficiently synthesized using the Pt(acac)$_2$-catalyzed photoactivated hydrosilylation of alkynes. The fluorescent chromophore derived is mainly due to the π-conjugated vinylphenyl segment. The polymers have excellent solubility in organic solvents.

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References and Notes

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