Synthesis and reactions of poly[(ethoxysilylene)phenylenevinylene]s and chain-to-pendant energy transfer in the resulting polymer

Joji Ohshita,* Ryosuke Taketsugu, Koichi Hino, and Atsutaka Kunai*

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

Abstract

Reactions of (bromophenylethenyl)diethoxysilanes with magnesium in THF gave poly[(ethoxysilylene)phenylenevinylene]s. The ethoxy group of the polymers could be readily replaced with other substituents by treating them with nucleophiles. Optical properties of the resulting poly(silylenephenylenevinylene)s were examined with respect to their UV absorption and emission spectra. Of those, pyrenyl-ethynyl-substituted one exhibited energy transfer from the backbone to the substituent in the photo-excited state.

Key words: Polycarbosilane; Hydrosilation; Polymer reaction; Energy transfer

1. Introduction

There has been an interest in polymers having an alternate arrangement of an organosilanylene unit and a π-electron system [1, 2]. In these polymers, the interaction between the silicon σ-orbital and the π-orbital (σ-π conjugation) in the polymer backbone [1] and/or electron-donating properties of the silicon unit, which would elevate the HOMO energy level of the π-electron system, allow to use the polymers as p-type organic semi conductors for electroluminescent devices [3] and thin film transistors [4]. It may be also noted that this type of the polymers are usable as heat-resistant materials and preceramics with high ceramic yield [5].

Recently, we have demonstrated that synthesis of poly[(ethoxysilylene)-phenylene]s, followed by transformation of the Si-OEt bond by nucleophilic substitution, can be a convenient method to prepare variously substituted poly(silylenephenylene)s [6]. Indeed, utilizing this method, we recently prepared poly(silylenephenylene)s bearing a pendant fluorophor as highly photoluminescent materials [7]. In this paper, we report the synthesis of poly[(ethoxysilylene)-phenylenevinylene]s and their substitution reactions with organic nucleophiles. Organosilylene-divinylarene alternate polymers have been well studied very recently as materials with unique optical properties [8, 9]. However, no papers concerning silylene-phenylenevinylene alternate polymers have been published to date, in spite of the fact that phenylenevinylene skeleton is often employed as a core fragment of π-conjugated functionality materials. Optical properties of the resulting silylene-phenylenevinylene polymers also are described.

2. Results and discussion

2.1. Monomer synthesis

We recently reported that palladium-catalyzed selective dehydrogenation of trihydrosilanes with 2 quiv of ethanol produced diethoxyhydrosilanes in good yield [10]. With diethoxyhydrosilanes thus prepared, we examined model reactions for the preparation of monomers (Table 1). As presented in Table 1, hydrosilation using the Wilkinson's catalyst proceeded most selectively to give the highest *trans*/*gem* ratios among those examined. In most of the reactions, triethoxysilanes were formed as the by-products. Since the sterically less hindered *trans*-isomers seemed to be more preferable as the monomers rather than the *gem*-isomers, we carried out the following monomer synthesis by using the Wilkinson's catalyst in toluene at room temperature.

[Table 1]

Table 2 summarizes the results of the monomer synthesis by hydrosilation of (bromophenyl)acetylene with diethoxysilanes under the conditions as mentioned above. In these reactions, triethoxysilanes were again found to be formed, but they were readily removed by fractional distillation. Carrying out the reaction at higher temperature led to less selective formation of the *trans*-isomer. The monomers were used for the following polymerization as the *trans*/*gem* mixtures, since they could not be isolated.

[Table 2]

2.2. Synthesis and reactions of polymers

When monomers **1a**-**1c** were treated with an excess of magnesium in refluxing THF and the resulting products were reprecipitated from chloroform/ethanol, polymers **2a**-**2c** were obtained, respectively, as shown in Table 3. Polymers **2a**-**2c** are soluble in common organic solvents, such as ethers, chlorocarbons, and aromatic hydrocarbons. Polymers **2a** and **2c** are soluble also in saturated hydrocarbons. However, for **2b**, the high molecular weight fraction is not soluble in pentane, and thus could be separated by reprecipitation from chloroform/pentane (Table 3).

The polymer structures were verified mainly by the NMR spectra. The *trans*/*gem* ratios (x/y) determined by integration in the ^{1}H NMR spectra are similar to those of the monomers, indicating that non-chemoselective polymerization had occurred. The ^{1}H and ^{13}C NMR spectra reveal only two sets of the ethoxy signals, due to the *trans* and *gem* segments. Furthermore, the integration ratios are almost consistent with the ideal structures. These results clearly indicate that only one ethoxy group of the monomers reacted during the polymerization to produce monoethoxysilylene units, selectively, in the resulting polymer backbone.

[Table 3]

The ethoxy group on the silicon atom of the polymers thus obtained was readily replaced with other groups. As summarized in Table 4, the reactions of polymer **2b** with organic nucleophiles proceeded in THF at room temperature. The reactions with 1 equiv of butyllithum and vinylmagnesium chloride afforded the respective substituted polymers **3b** and **4b**, although complete substitution could not be performed and partially substituted products were always obtained. The reaction of pyrenylethnynyllithium gave polymer **5b** with only 23% of the silylene units replaced by the pyrenylethynyl units.

[Table 4]

*2.3. Optical properties of polymers **2b** and **5b***

Figure 1 shows the UV absorption spectra of polymers **2b** and **5b** in THF. As can be seen in Figure 1, the spectrum of polymer **5b** shows a broad absorption band due to the pyrenylethynyl unit at 347 nm. In addition to this, an absorption due to the phenylenevinylene unit appears at 278 nm in this spectrum, which is almost at the same wavelength as that of polymer **2b** (λ_{max} = 274 nm), indicating that no significant interaction takes place between these chromophors with respect to the absorption spectra. In contrast, as shown in Figure 2, the emission spectra of polymer **5b** show a broad band, which would arise mainly from the emission form the pyrenylethynyl unit. Although a broad shoulder around at 360 nm in these spectra seems to be ascribed to the phenylenevinylene emission, no evident peaks from the phenylenevinylene unit are observed, even when the phenylenevinylene unit is excited at 278 nm. Figure 3 shows an emission spectrum of (trimethylsilylethynyl)pyrene [7]. The spectrum involves two maxima at 386 and 407 nm, corresponding to two broad peaks around 400 nm of polymer **5b**. Broadening of the spectra of polymer **5b** is probably due to its polymeric structure. These are indicative of that energy transfer from the phenylenevinylene unit in the backbone to the pendant pyrenylethynyl unit occurs in the excited state. Intrachain energy transfer has been reported for alternate polymers composed of a silylene-π-electron system [9, 11]. However, little is known for chain-to-pendant energy transfer in this type of the polymers. The emission quantum efficiencies were determined to be $\Phi = 0.31$ and 0.15 for THF solutions of polymers **2b** and **5b**, respectively.

[Figures 1 and 2]

3. Conclusion

In conclusion, on the basis of the results described above, we demonstrated that the formation of ethoxy-substituted poly(silylenephenylenevinylene)s, followed by nucleophilic substitution, is a convenient method leading to a variety of poly(silylenephenylenevinylene)s.

4. Experimental Section

4.1. General

(Bromophenyl)(trimethylsily)acetylene [6], diethoxysilanes [10], pyrenylethynyllithium [7] were prepared as reported in the literature. All reactions were carried out in an atmosphere of dry nitrogen. Toluene and THF were dried over sodium and distilled just before use. Emission quantum efficiencies (Φ) were determined relative to a THF solution of 9,10-diphenylanthracene as a standard. Some NMR signals for the minor *gem*-isomer and fragment could not be observed, probably due to their low intensities and/or overlapping with those of the major *trans*-isomer and fragment. The ratios of subunits in the present polymers (x/y and a/b in Tables 3 and 4, respectively) were determined on the basis of integration ratios in the ^1H NMR spectra. Molecular weights of the polymers were determined by GPC eluting with THF, relative to polystyrene standards. By using seven polystyrene standards with different molecular weights, we obtained a second order calibration curve with a correlation coefficient of 0.99932.

4.2. Preparation of monomers

A mixture of (bromophenyl)(trimethylsily)acetylene (14.2 g, 56.1 mmol), potassium carbonate (30.2 g, 219 mmol), and methanol (500 mL) was stirred at room temperature for 4h. The mixture was hydrolyzed and extracted three times with ether. The extracts were combined and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave (bromophenyl)acetylene as yellow solids (8.55 g, 47.2 mmol, 84% yield): ^1H NMR (δ in $CDCl_3$) 7.44 (d, J = 8.4 Hz, 2H, Ph), 7.32 (d, J = 8.4 Hz, 2H, Ph), 3.10 (s, 1H, $-C\equiv\underline{CH}$); ^{13}C NMR (δ in $CDCl_3$) 133.51 (Ph CH), 131.57 (ipso Ph), 123.11, 120.99 (Ph CH), 82.55 ($-\underline{C}\equiv CH$), 78.25 ($-C\equiv\underline{CH}$); GC/MS m/z 180 (M^+).

A mixture of bromophenylacetylene (2.40 g, 13.3 mmol), diethoxyhexylsilane (2.63 g, 12.9 mmol), $RhCl(PPh_3)_3$ (0.015 g, 0.016 mmol), and toluene (10 mL) was stirred at room temperature for 48 h. To this was added ca. 10 mg of a triazine-based complexing agent (Sankyo Kasei Co. Ltd.) to remove the catalyst. After filtration, the solvent was removed and the residue was distilled under reduced pressure to give monomer **1a** (2.53 g, 6.56 mmol, 51% yield): bp 155 °C (4×10^{-6} mmHg); ^1H NMR (δ in $CDCl_3$) 7.45-7.39 (m, phenylene), 7.34-7.29 (m, phenylene), 7.02 (d, J = 19.1 Hz, CH=CH), 6.23 (d, J = 19.1 Hz, CH=CH), 6.04 (d, J = 1.9 Hz, $C=CH_2$), 5.84 (d, J = 1.9 Hz, $C=CH_2$), 3.80 (q, J = 6.8 Hz, *trans* OCH_2), 3.71 (q, J = 6.8 Hz, *gem* OCH_2), 1.40-1.15 (m, $SiCH_2\underline{(CH_2)_4}$ and $OCH_2\underline{CH_3}$), 0.83 (t, J = 6.8 Hz, CH_3 of Hex), 0.72 (br t, J = 6.7 Hz, $SiCH_2$); ^{13}C NMR (δ in $CDCl_3$) 140.07 (CH=CH), 138.87 ($\underline{C}=CH_2$), 133.43, 131.62, 130.12, 128.15, 122.66, 119.26 (phenylene, CH=CH, and $C=\underline{CH_2}$), 58.42 (*trans* OCH_2), 58.40 (*gem* OCH_2), 32.94, 31.47, 22.64, 22.54 (Hex), 19.39 (*trans* $OCH_2\underline{CH_3}$), 19.21 (*gem* $OCH_2\underline{CH_3}$), 14.07, 12.94 (Hex); GC/MS m/z 384 (M^+), 339 (M^+-OEt), 307 (M^+-Br). Anal. Calcd for $C_{18}H_{29}BrO_2Si$: C, 56.09; H, 7.58. Found: C, 56.47; H, 7.44. Adding the complexing agent and filtration of the precipitates before distillation must not be skipped. The products, otherwise, underwent thermal decomposition during distillation.

Other monomers were prepared in a similar fashion to above. Data for **1b**: bp 175 °C (6×10^{-6} mmHg); ^1H NMR (δ in $CDCl_3$) 7.70-7.61 (m, phenylene), 7.44-7.26 (m, Ph and phenylene), 7.04 (d, J = 19.2 Hz, CH=CH), 6.39 (d, J = 19.2 Hz, CH=CH), 6.16 (d, J = 2.6 Hz, $C=CH_2$), 5.94 (d, J = 2.6 Hz, $C=CH_2$), 3.86 (q, J = 7.0 Hz, *trans* OCH_2), 3.71 (q, J = 7.0 Hz, *gem* OCH_2), 1.26 (t, J = 7.0 Hz, *trans* $OCH_2\underline{CH_3}$), 1.13 (t, J = 7.0 Hz, *gem* $OCH_2\underline{CH_3}$); ^{13}C NMR (δ in $CDCl_3$) 147.40 (CH=CH), 136.61 ($\underline{C}=CH_2$), 134.63, 134.30, 131.64, 130.24, 130.07, 128.27, 127.86, 127.75, 122.59, 121.96 (ring carbons, CH=CH, and $C=\underline{CH_2}$), 58.86 (*trans* OCH_2), 58.64 (*gem* OCH_2), 18.35 (*trans* $OCH_2\underline{CH_3}$), 18.11 (*gem* $OCH_2\underline{CH_3}$); GC/MS m/z 376 (M^+), 331 (M^+-OEt), 299 (M^+-Br). Anal. Calcd for $C_{18}H_{21}BrO_2Si$: C, 57.29; H, 5.61. Found: C, 57.27; H, 5.53. Data for **1c**: bp 150 °C (4×10^{-6} mmHg); ^1H NMR (δ in $CDCl_3$) 7.45-7.42 (m, phenylene), 7.32-7.29 (m, phenylene), 7.02 (d, J = 19.0 Hz, CH=CH), 6.24 (d, J = 19.0 Hz, CH=CH), 6.04 (d, J = 2.9 Hz, $C=CH_2$), 5.85 (d, J = 2.9 Hz, $C=CH_2$), 3.81 (q, J = 7.0 Hz, *trans* OCH_2), 3.70 (t, J = 7.0 Hz, *gem* OCH_2), 1.37-1.19 (m, $SiCH_2\underline{(CH_2)_2}CH_3$ and $OCH_2\underline{CH_3}$), 0.87 (t, J = 7.0 Hz, CH_3 of Bu), 0.73 (br t, J = 7.0 Hz, $SiCH_2$); ^{13}C NMR (δ in $CDCl_3$) 145.44 (CH=CH), 139.84 ($\underline{C}=CH_2$), 133.26, 131.09, 128.89, 126.32, 122.98, 120.31 (ring carbons, CH=CH, and $C=\underline{CH_2}$), 58.74 (*trans* OCH_2), 58.55 (*gem* OCH_2), 26.75, 26.13 (Bu), 19.79 (*trans* $OCH_2\underline{CH_3}$), 19.58 (*gem* $OCH_2\underline{CH_3}$), 13.81, 13.75 (Bu); GC/MS m/z 356 (M^+), 331 (M^+-OEt), 299 (M^+-Bu). Anal. Calcd for $C_{16}H_{25}BrO_2Si$: C, 53.78; H, 7.05. Found: C, 53.72; H, 7.05.

4.3. Synthesis of ethoxy-substituted polymers

A mixture of **1a** (1.10 g, 2.85 mmol), magnesium powder (0.11 g, 4.60 mmol), and

THF (15 mL) was heated to reflux for 120 h. The resulting magnesium salts and excess magnesium were removed by filtration. After the solvent was evaporated, the residue was reprecipitated from chloroform/ethanol to give polymer **2a** (0.28 g, 38% yield) as colorless solids: IR 2972, 2873 (C-H), 1069, 912 (Si-O) cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 7.59-7.40 (m, phenylene), 7.01 (d, *J* = 19.0 Hz, CH=CH), 6.24 (d, *J* = 19.0 Hz, CH=CH), 6.03 (d, *J* = 2.7 Hz, $C=CH_2$), 5.85 (d, *J* = 2.7 Hz, $C=CH_2$), 3.70 (q, *J* = 6.9 Hz, *trans* OCH_2), 3.47 (q, *J* = 6.9 Hz, *gem* OCH_2), 1.29-1.14 (m, $SiCH_2\underline{(CH_2)_4}CH_3$ and $OCH_2\underline{CH_3}$), 0.85-0.71 (m, $Si\underline{CH_2}(CH_2)_4\underline{CH_3}$); ^{13}C NMR (δ in $CDCl_3$) 148.47 (CH=CH), 137.04 ($\underline{C}=CH_2$), 133.48, 131.60, 128.02, 126.14, 122.06, 119.42 (ring carbons, CH=CH, and $C=\underline{CH_2}$), 58.68 (*trans* OCH_2), 58.46 (*gem* OCH_2), 33.21, 31.51, 23.01, 22.59 (Hex), 18.57 (*trans* $OCH_2\underline{CH_3}$), 18.31 (*gem* $OCH_2\underline{CH_3}$), 14.11, 13.80 (Hex).

Polymers **2b** and **2c** were prepared in a similar fashion to above. Data for **2b**: yellow solids; IR 2978, 2867 (C-H), 1070, 911 (Si-O) cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 7.78-7.28 (m, ring protons), 7.08 (d, *J* = 19.0 Hz, CH=CH), 6.74 (d, *J* = 19.0 Hz, CH=CH), 6.01 (d, *J* = 2.8 Hz, $C=CH_2$), 5.80 (d, *J* = 2.8 Hz, $C=CH_2$), 3.93 (q, *J* = 6.9 Hz, *trans* OCH_2), 3.80 (q, *J* = 6.9 Hz, *gem* OCH_2), 1.33 (t, *J* = 7.0 Hz, *trans* $OCH_2\underline{CH_3}$), 1.20 (t, *J* = 7.0 Hz, *gem* $OCH_2\underline{CH_3}$); ^{13}C NMR (δ in $CDCl_3$) 148.70 (CH=CH), 139.04 ($\underline{C}=CH_2$), 134.98, 134.38, 131.63, 130.18, 128.26, 127.89, 127.81, 126.19, 122.60, 122.06 (ring carbons, CH=CH, and $C=\underline{CH_2}$), 58.81 (*trans* OCH_2), 58.57 (*gem* OCH_2), 18.43 (*trans* $OCH_2\underline{CH_3}$), 18.08 (*gem* $OCH_2\underline{CH_3}$); ^{29}Si NMR (δ in $CDCl_3$) -12.01, -13.98. Data for **2c**: colorless oil; ^{1}H NMR (δ in $CDCl_3$) 7.60-7.45 (m, phenylene), 7.05 (d, *J* = 19.0 Hz, CH=CH), 6.60 (d, *J* = 19.0 Hz, CH=CH), 6.09 (d, *J* = 2.9 Hz, $C=CH_2$), 5.87 (d, *J* = 2.9 Hz, $C=CH_2$), 3.76 (q, *J* = 6.9 Hz, *trans* OCH_2), 3.58 (q, *J* = 6.9 Hz, *gem* OCH_2), 1.37-1.14 (m, $SiCH_2\underline{(CH_2)_2}CH_3$ and $OCH_2\underline{CH_3}$), 1.01-0.76 (m, $Si\underline{CH_2}(CH_2)_2\underline{CH_3}$); ^{13}C NMR (δ in $CDCl_3$) 145.71 (CH=CH), 139.69 ($\underline{C}=CH_2$), 134.16, 131.36, 128.41, 126.19, 122.89, 119.78 (ring carbons, CH=CH, and $C=\underline{CH_2}$), 58.65 (*trans* OCH_2), 58.42 (*gem* OCH_2), 27.41, 26.04 (Bu), 19.43 (*trans* $OCH_2\underline{CH_3}$), 19.21 (*gem* $OCH_2\underline{CH_3}$), 13.78, 13.69 (Bu).

4.4. Reactions of polymer ***2b***

To a solution of polymer **2b** (5.6 mg, 0.22 unit mol) in THF (5 mL) was added a 1.60 M of butyllithium in hexane (0.14 mL, 0.22 mmol) at –40˚C. The mixture was stirred for 16 h at room temperature. After hydrolysis, the organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was reprecipitated from chloroform/ethanol to give polymer **3b** (0.018 g, 31% yield) as colorless solids: IR 2963, 2855 (C-H), 1067, 914 (Si-O) cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 7.53-7.34 (m, phenylene), 6.95 (d, J = 19.2 Hz, CH=CH), 6.76 (d, J = 19.1 Hz, CH=CH), 6.22 (d, J = 2.8 Hz, $C=CH_2$), 5.92 (d, J = 2.8 Hz, $C=CH_2$), 3.70 (q, J = 6.9 Hz, *trans* OCH_2), 3.54-3.48 (m, *gem* OCH_2), 1.39-1.18 (m, $SiCH_2\underline{CH_2CH_2}CH_3$ and $OCH_2\underline{CH_3}$), 0.94-0.84 (m, $Si\underline{CH_2}CH_2CH_2\underline{CH_3}$); ^{13}C NMR ($\delta$ in $CDCl_3$) 148.37 (CH=CH), 138.24 ($\underline{C}=CH_2$), 135.57, 135.24, 134.55, 134.26, 129.33, 127.85, 127.71, 127.78, 126.00, 121.79 (ring carbons, CH=CH, and $C=\underline{CH_2}$), 58.84 (*trans* OCH_2), 58.56 (*gem* OCH_2), 26.66, 26.06 (Bu), 18.61 (*trans* $OCH_2\underline{CH_3}$), 18.45 (*gem* $OCH_2\underline{CH_3}$), 13.74, 13.70 (Bu).

Other substitution reactions were carried out as above. Data for **4b**: colorless solids; IR 2979, 2864 (C-H), 1106, 960 (Si-O) cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 7.65-7.31 (m, phenylene), 7.11 (d, J = 18.8 Hz, CH=CH), 6.82 (d, J = 18.8 Hz, CH=CH), 6.28-6.22 (m, vinyl), 6.05-6.02 (m, $C=CH_2$), 5.94-5.87 (m, vinyl), 5.83-5.80 (m, $C=CH_2$), 3.87 (q, J = 6.9 Hz, *trans* OCH_2), 3.71-3.67 (m, *gem* OCH_2), 1.25 (t, J = 6.9 Hz, *trans* $OCH_2\underline{CH_3}$), 1.17-1.12 (m, *gem* $OCH_2\underline{CH_3}$); ^{13}C NMR (δ in $CDCl_3$) 148.81 (CH=CH), 139.12 ($\underline{C}=CH_2$), 135.35, 135.00, 134.67, 134.43, 131.68, 130.05, 128.55, 128.30, 127.92, 126.81, 126.24, 123.49 (ring carbons, CH=CH, $C=\underline{CH_2}$, and $SiCH=CH_2$), 59.65 (*trans* OCH_2), 59.45 (*gem* OCH_2), 18.45 (*trans* $OCH_2\underline{CH_3}$), 18.21 (*gem* $OCH_2\underline{CH_3}$). Data for **5b**: blue purple solids; IR 2972, 2871 (C-H), 1067 (Si-O) cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 8.25-7.27 (m, ring protons), 7.08 (d, J = 19.0 Hz, CH=CH), 6.80 (d, J = 19.0 Hz, CH=CH), 6.18 (d, J = 2.9 Hz, $\mathrm{C{=}CH_2}$), 5.84 (d, J = 2.9 Hz, $\mathrm{C{=}CH_2}$), 3.86 (q, J = 6.8 Hz, *trans* $\mathrm{OCH_2}$), 3.71-3.62 (m, *gem* $\mathrm{OCH_2}$), 1.24 (t, J = 6.8 Hz, *trans* $\mathrm{OCH_2\underline{CH_3}}$), 1.11 (t, J = 6.8 Hz, *gem* $\mathrm{OCH_2\underline{CH_3}}$); ^{13}C NMR ($\delta$ in $\mathrm{CDCl_3}$) 147.82 (CH=CH), 139.44 ($\mathrm{\underline{C}{=}CH_2}$), 135.35, 135.34, 135.00, 132.68, 131.87, 130.75, 130.18, 130.05, 129.84, 128.19, 128.02, 127.91, 127.84, 126.74, 126.26, 126.23, 126.20, 125.89, 125.28, 125.29, 124.86, 124.73, 124.09, 123.68, 122.57, 116.19 (ring carbons, CH=CH, and $\mathrm{C{=}\underline{CH_2}}$), 86.03 ($\mathrm{Py\text{-}\underline{C}{\equiv}C}$), 80.14 ($\mathrm{Si\text{-}\underline{C}{\equiv}C}$), 59.64 (*trans* $\mathrm{OCH_2}$), 59.47 (*gem* $\mathrm{OCH_2}$), 18.46 (*trans* $\mathrm{OCH_2\underline{CH_3}}$), 18.23 (*gem* $\mathrm{OCH_2\underline{CH_3}}$). For this polymer, ^{1}H NMR signals of the pyrene units were observed as overlapped with those of the phenylene units in its backbone. Therefore, we estimated the integration value for the pyrene protons by subtracting the calculated value for the phenylene protons based on the integration of the methyl-Si protons, from that for the whole sp^2 protons. The integration value of the pyrene protons, thus obtained, was compared with that of the ethoxy protons to give the a/b ratio of 7.7/2.3 as shown in Table 4.

Acknowledgement

This work was supported by a Grant-in Aid for Scientific Research (No. 17550105) from the Ministry of Education, Science, Sports, and Culture of Japan and NEDO (project No. 04A25015). We thank Sankyo Kasei Co. Ltd., Tokuyama Co. Ltd., and Tokuyama Science Foundation for financial support. We thank Sankyo Kasei Co. Ltd. also for the gift of the complexing agent that was used to remove the Rh-catalyst from the reaction mixtures of hydrosilation.

References and notes

[1] For reviews, see: (a) J. Ohshita, A. Kunai, Acta Polymerica, 49 (1998) 379;

(b) W. Uhlig, Prog. Polym. Sci., 27 (2002) 255.

[2] For recent works, see: (a) Mori, E. Takahisa, Y. Yamamura, T. Kato, A. P. Mudalige,

H. Kajiro, K. Hirabayashi, Y. Nishihara, T. Hiyama, Organometallics, 23 (2004) 1755 ;

(b) F. Wang, B. R. Kaafarani, D. C. Neckers, Macromolecules, 36 (2003) 8225;

(c) Y. Morisaki, F. Fujimura, Y. Chujo, Organometallics, 17 (2003) 3553;

(d) Y.-J. Cheng, T.-Y. Liu, Chemistry A, Europ. J., 10 (2004) 5361.

[3] (a) J. Ohshita, T. Sumida, A. Kunai, A. Adachi, K. Sakamaki, K. Okita, Macromolecules, 33 (2000) 8890;

(b) J. Ohshita, A. Takata, H. Kai, A. Kunai, K. Komaguchi, M. Shiotani, A. Adachi, K. Okita, Y. Harima, Y. Kunugi, K. Yamashita, M. Ishikawa, Organometallics, 19 (2000) 4492;

(c) J. Ohshita, D. Nada, Y. Tada, Y. Kimura, H. Yoshida, A. Kunai, Y. Kunugi, J. Organomet. Chem., 690 (2005) 3591.

[4] J. Ohshita, D.-H. Kim, Y. Kunugi, A. Kunai, Organometallics, 24 (2005) 4494.

[5] (a) J. Ohshita, T. Iida, M. Ikeda, T. Uemura, N. Ohta, A. Kunai, J. Organomet. Chem., 689 (2004) 1540;

(b) H. Yamashita, M. S. Leon, S. Channasannon, Y. Suzuki, Y. Uchimaru, K. Takeuchi, Polymer, 44 (2003) 7089.

[6] J. Ohshita, A. Yamashita, T. Hiraoka, A. Shinpo, A. Kunai, M. Ishikawa, Macromolecules, 30 (1997) 1540.

[7] J. Ohshita, T. Uemura, D.-H. Kim, A. Kunai, Y. Kunugi, M. Kakimoto, Macromolecules, 38 (2005) 730.

[8] (a) G. Kwak, K. Sumiya, F. Sanda, Y. Masuda, J. Polym. Sci., A, Polym. Chem., 41 (2003) 3615;

(b) T. V. Rao, H. Yamashita, Y. Uchimaru, J. Sugiyama, K. Takeuchi, Polymer, 46 (2005) 9736.

[9] (a) Y.-J. Cheng, T.-Y. Liu, Macromolecules, 38 (2005) 4563;

(b) Y.-J. Cheng, S. Basu, S.-J. Luo, T.-Y. Liu, Macromolecules, 38 (2005) 1442.

[10] J. Ohshita, R. Taketsugu, Y. Nakahara, A. Kunai, J. Organomet. Chem., 689 (2004)

3258.

[11] J. Ohshita, K. Kawashima, A. Iwata, H. Tang, M. Higashi, A. Kunai, Z. Naturforshung B, 59 (2004) 1332.

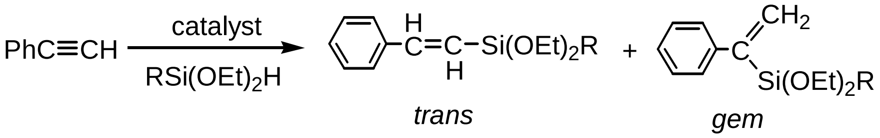
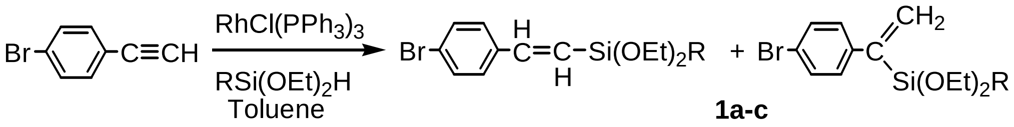


Table 1. Optimization of hydrosilation.

catalyst	R	solvent	temp	GC yield (%)		
				trans	*gem*	$RSi(OEt)_3$
$RhCl(PPh_3)_3$	Hex	toluene	rt	83	2	7
	Ph	toluene	rt	76	1	6
	Ph	THF	rt	49	48	0
	Ph	ether	rt	67	29	2
H_2PtCl_6 $6H_2O$/ 2-PrOH	Hex	toluene	rt	15	34	33
	Ph	ether	rt	71	19	9
	Hex	none	rt	60	32	4
$IrCl(CO)(PPh_3)_2$	Hex	THF	reflux	41	21	10



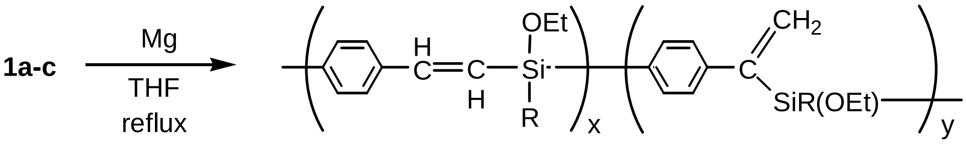
1a-c

Table 2. Monomer synthesis

R	temp	product (*trans* / *gem*)^a	isolated yield (%)^b	GC yield (%) *trans*	 *gem*	 RSi(OEt)$_3$
Hex	rt	**1a** (88/12)	51	85	4	6
Ph	rt	**1b** (91/9)	67	89	6	3
	50°C	**1b** (68/32)	71	54	32	3
Bu	rt	**1c** (94/6)	41	77	6	5

[a] Determined by ^{1}H NMR;

[b] Isolated by distillation.



2a-c

Table 3. Polymer synthesis

monomer (*trans*/*gem*)	time (h)	polymer	yield[a] (%)	x/y[b]	Mw (Mw/Mn)[c]	m.p (°C)
1a (88/12)	120	**2a**	38	92 / 8	2230 (1.06)	52-56
1b (91/9)	17	**2b**	66	87 / 13	3170 (1.13)	57-64
	24	**2b**	56	88 / 12	3730 (1.19)	63-71
	24	**2b**	16[d]	82 / 18	5470 (1.35)	93-105
1c (94/6)	40	**2c**	21	89 / 11	5580 (1.16)	oil

[a] After reprecipitation from chloroform/EtOH;

[b] Determined by ^{1}H NMR;

[c] Determined by GPC, relative to polystyrene standards;

[d] Purified by reprecipitation from chloroform/pentane.

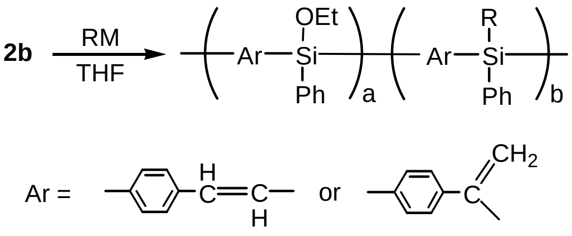
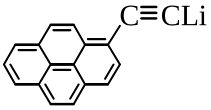


Table 4. Reactions of **2b**

RM	**2b** Mw (Mw/Mn)[c]	time (h)	product	yield (%)[a]	a / b[b]	Mw (Mw/Mn)[c]	m.p (°C)
n-BuLi	5467 (1.35)	16	**3b**	31	2.4 / 7.6	5730 (1.33)	92-102
CH_2=CHMgCl	3697 (1.18)	16	**4b**	23	7.6 / 2.4	3070 (1.04)	61-65
		40	**4b**	61	0.5 / 9.5	3540 (1.16)	54-60
	3729 (1.19)	24	**5b**	39	7.7 / 2.3	4400 (1.26)	141-147

[a] After reprecipitation from chloroform/EtOH;
[b] Determined by ^{1}H NMR;
[c] Determined by GPC, relative to polystyrene standards.

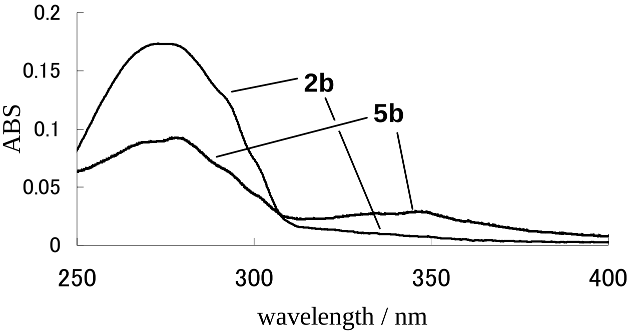


Figure 1. UV absorption spectra of polymers **2b** and **5b** in THF.

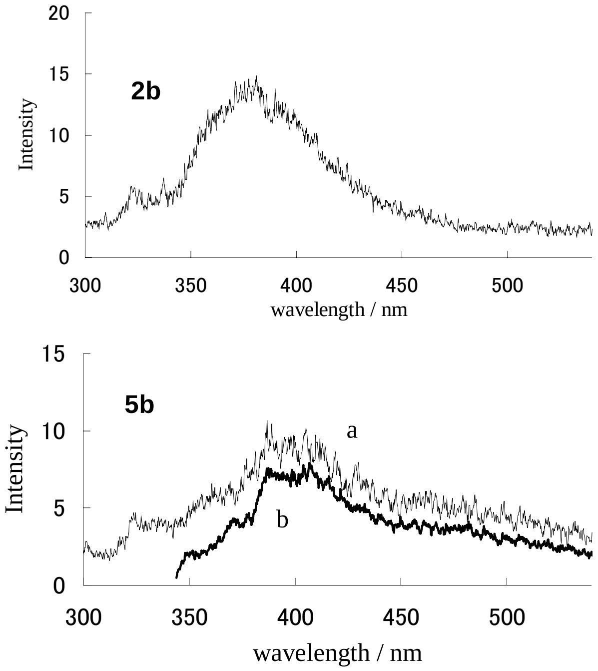


Figure 2. Emission spectra of polymers **2b** (top) and **5b** (bottom) excited at 278 nm (a) and 334 nm (b) in THF.

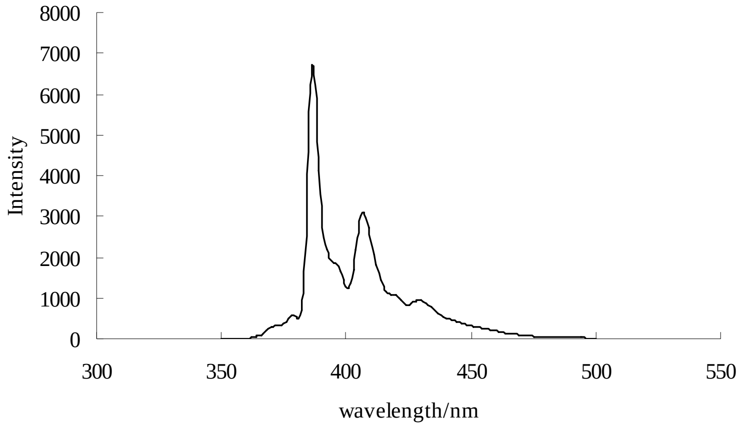


Figure 3. Emission spectrum of (trimethylsilylethynyl)pyrene excited at 350 nm in THF.