Pd-catalyzed hydrosilylation polymerization of a dihydrosilane with diyne/triyne mixed systems affording crosslinked silylene–divinylene polymers and their properties

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Abstract

Treatment of a dihydrosilane (methylphenylsilane, **1**) with mixtures of a diyne (*p*- or *m*-diethynylbenzene, **2a** or **2b**) and a triyne (1,3,5-triethynylbenzene, **3a** or *B,B′,B″*-triethynyl-*N,N′,N″*-trimethylborazine, **3b**; **1**:**2**:**3** = 100:95:5, 100:90:10, 100:80:20) in the presence of Pd–PCy$_3$ (Cy = cyclohexyl) catalyst gave new crosslinked silylenedivinylene polycarbosilanes. In TGA the resulting crosslinked polymers tended to show higher Td$_5$ values and higher char yields than the corresponding linear polymers. On the other hand, UV/vis absorption spectra of the crosslinked polymers obtained in the reactions of **2a** or **2b** with **3a** exhibited increased broad peaks around 390 nm for **2a** or 360 nm for **2b**. Coincidently, their fluorescence spectra showed significant increase of the emission peaks in 400–550 nm. The crosslinked polymer derived from **2a** and **3b**, however, showed decrease of the absorption peak around 390 nm and profound depression of fluorescence peaks in 400–550 nm.
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1. Introduction

Increasing attention has been placed on silylene-, vinylene-, and/or arylene-containing polycarbosilanes for their potential applications to optoelectric devices, heat-resistant materials, ceramic precursors, etc. [1,2]. Hydrosilylation polymerization using transition metal catalysts such as Pt [3–8] and Rh [9–20] complexes has been conveniently used to give various linear [3–6,9–16] and hyperbranched [7,17–19] polycarbosilanes with intriguing physicochemical properties. However, polycarbosilanes with partially crosslinking moieties and their properties do not seem to have been fully studied yet. Recently, we have demonstrated that Pd–PCy$_3$ catalyst is effective for hydrosilylation polymerization of tri- or dihydrosilanes with diynes affording silylene–divinylene polycarbosilanes
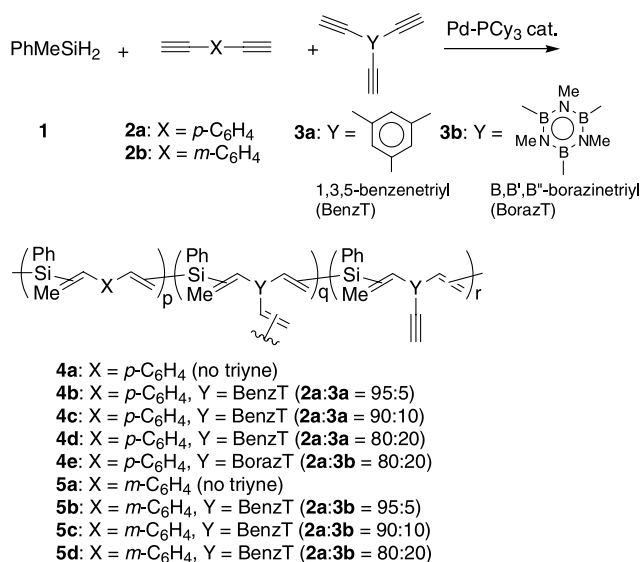
[21–23]. The catalysis is applicable to dihydrosilane/diyne/triyne three-component systems affording crosslinked silylenedivinylene polymers. Herein are reported their synthesis and thermal and photophysical properties.

2. Results and discussion

Treatment of a toluene solution of methylphenylsilane (**1**) with *p*-diethynylbenzene (**2a**, 1 equiv) in the presence of Pd$_2$(dba)$_3$–PCy$_3$ (dba = dibenzylideneacetone) catalyst at 60 °C for 4 h gave a linear 1:1 addition polymer (**4a**) (Scheme 1, Table 1, Run 1). Polymer **4a** was obtained in 75% yield after purification by precipitation from toluene/2-propanol. When a crosslinking agent, 1,3,5-triethynylbenzene (**3a**, **1**:**2a**:**3a** = 100:95:5, 100:90:10, and 100:80:20) was added to the reaction system, crosslinked polymers **4b**–**d** were formed, respectively (Runs 2–4). The reaction times were usually within 4.5 h. Prolonging the reaction time sometimes caused gelation. The reaction was terminated by pouring the reaction mixture into 2-propanol to precipitate the produced polymer before gelation took place.

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Scheme 1.

In ^{29}Si NMR of crosslinked polymer **4d**, two major signals were observed at −15.6 and −13.4 ppm, which would be assigned as –CH=CH–SiMePh–CH=CH– (β,β) and –CH=CH–SiMePh–C(=CH₂)– (β,α) regioisomeric structures, respectively (Fig. 2(a)) [23]. *m*-Phenylene analog **5d** also gave a similar spectral pattern, showing two major signals at −15.6 and −13.6 ppm (Fig. 2(b)). Meanwhile, borazine-containing polymer **4e** exhibited three major signals at −17.7, −15.6, and −13.4 ppm (Fig. 2(c)). The signal at −17.7 ppm seemed to arise from boron-containing B–CH=CH–SiPhMe– moieties. On the other hand, ^{1}H NMR of crosslinked polymers **4b–e** and **5b–d** showed the vinylene proton signals of Si–C=CH moieties at 6.4–6.9 ppm, while the vinylidene proton signals of Si–C=CH₂ moieties emerged at 5.5–5.9 and 5.9–6.2 ppm. The ^{1}H NMR spectra of **4d**, **5d**, and **4e** are shown in Fig. 2(d)–(f). On the basis of their ^{1}H NMR integral curves the ratios of the (β,β):(β,α) structures were estimated at about 7:3. As for the ratios of *p:q:r* of the crosslinked polymers, elemental analyses indicated almost all of the crosslinking agent was incorporated into the polymers. Thus, in the polymers of **4d**, **5d**, and **4e**, the ratios of *p:q + r* were estimated at ca. 8:2. In ^{1}H NMR of **4b–d** and **5b–d**, small signals for acetylenic protons were observed at 2.6–2.8 ppm, although such acetylenic signals were not clearly recognized in **4e** because of the signal overlapping between acetylenic and *N*-methyl protons. From the ^{1}H NMR integral values the ratios of *q:r* in **4b–d** and **5b–d** were estimated at about 8:2–9:1, indicating the approximate degree of branching being in the range of 0.04–0.045 for **4b** and **5b** to 0.16–0.18 for **4d** and **5d**.

Similarly, *m*-diethynylbenzene (**2b**) reacted with **1** in the absence or presence of **3a** to afford the corresponding linear and crosslinked polymers, **5a** or **5b–d**, respectively (Runs 6–9). In addition, a boron-containing six-membered triyne, triethynylborazine (**3b**), also gave a borazine-containing crosslinked polymer **4e** in the reaction with **1** and **2a** (Run 5), although the reactivity of **3b** was considerably lower than that of **3a** presumably because of steric hindrance of **3b**.

When the ratio of **1:2:3** was in the range of 100:95:5–100:80:20 and the reaction time was appropriately controlled, soluble crosslinked polymers were obtained. The polymers were soluble in common organic solvents such as toluene, tetrahydrofuran, chloroform, etc. GPC analysis showed use of more amount of the crosslinking agent **3** tended to give larger molecular weight M_w and larger polydispersity M_w/M_n. In GPC profiles of **4a** and **5a**, the peaks were broadened and shifted to high molecular weight region by addition of **3a** as shown in Fig. 1 for **4a,c,d** and **5a,c,d**.

In thermogravimetric analysis (TGA) the 5% weight loss temperature (Td_5) of linear polymer **4a** under nitrogen was 437 °C (Table 2). When crosslinking agent **3a** was added, the Td_5 value increased up to 460 °C (**2a**:**3a** = 80:20). Similarly, thermal stability of the meta analog **5a** was improved by addition of **3a** to give the Td_5 value of 449 °C (**2b**:**3a** = 80:20). The char yield at 980 °C under nitrogen also tended to rise as **3a** was added; the char yield increased from 57% (**4a**) to 68% (**4d**) and from 61% (**5a**) to 66% (**5d**).
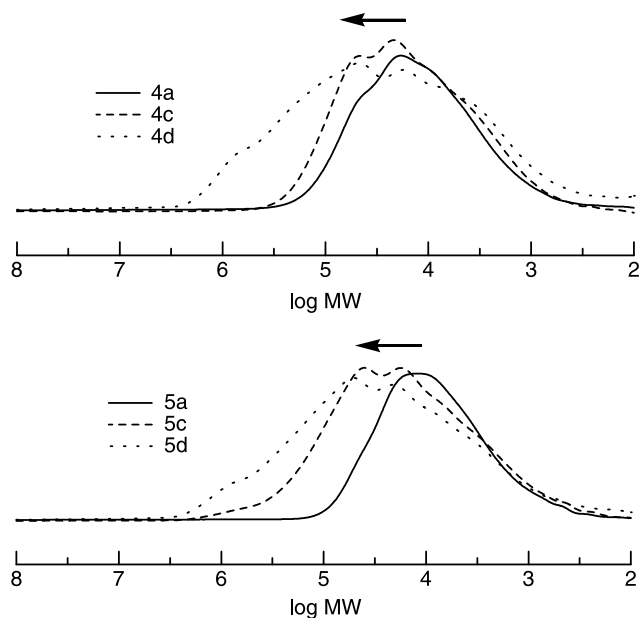
Table 1
Pd-catalyzed reactions of a dihydrosilane **1** with diyne/triyne (**2/3**) mixed systems

Run	2	3	2:3	Temp. (°C)	Time (h)	Polymer (Yield[a], %)	M_w (M_w/M_n)[b]
1	**2a**	–	100:0	60	4	**4a** (75)	24,000 (3.8)
2	**2a**	**3a**	95:5	60	4	**4b** (70)	26,000 (4.1)
3	**2a**	**3a**	90:10	60	4.5	**4c** (68)	30,000 (5.0)
4	**2a**	**3a**	80:20	60	3.5	**4d** (80)	130,000 (16)
5	**2a**	**3b**	80:20	80	4.5	**4e** (70)	59,000 (7.2)
6	**2b**	–	100:0	70	5	**5a** (65)	15,000 (3.1)
7	**2b**	**3a**	95:5	70	4	**5b** (70)	21,000 (4.0)
8	**2b**	**3a**	90:10	70	5	**5c** (64)	59,000 (9.7)
9	**2b**	**3a**	80:20	70	3	**5d** (75)	110,000 (14)

Reaction conditions: **1** 0.50 mmol, **2** + **3** 0.50 mmol, Pd₂(dba)₃–PCy₃ (0.005–0.01 mmol Pd, P/Pd = 2), toluene 1.2 ml.
[a] Yield after purification by precipitation from toluene/2-propanol.
[b] Estimated by GPC using polystyrene standards.

Fig. 1. GPC profiles of **4a,c,d** (top) and **5a,c,d** (bottom); MW=molecular weight with reference to polystyrene standards.

On the other hand, six-membered borazine-containing polymers with hydrogen substituents at boron and/or nitrogen atoms have been used to prepare boron nitride ceramics. We have previously synthesized a new borazine polymer with organic groups at boron and nitrogen atoms by the reaction of B,B',B''-trietynyl-N,N',N''-trimethylborazine

Table 2
Photophysical and thermal properties of **4** and **5**

Polymer	TGA[a]		UV/vis absorption[b]	Fluorescence emission[b]
	Td_5 (°C)	Char yield[c] (%)	λ_{max} (nm) (absorbance)	λ_{max} (nm) (excitation)
4a	437 [298]	57 [18]	305 (1.64), 393 (0.12)	346, 358, 399, 461, 484 (330)
4b	444	62	300 (1.53), 393 (0.18)	358, 398, 461, 482 (329)
4c	457	67	296 (1.53), 391 (0.21)	358, 398, 461, 482 (325)
4d	460 [330]	68 [20]	292 (1.43), 388 (0.20)	358, 377, 398, 462, 482 (325)
4e	431 [304]	65 [39]	304 (1.54)	347, 358, 458 (329)
5a	438	61	260 (2.01)	341, 353, 419, 442 (279)
5b	435	60	260 (1.98), 351 (0.10)	356, 369, 420, 441 (278)
5c	440	63	260 (1.88), 354 (0.13)	357, 370, 424, 445 (283)
5d	449	66	260 (1.87), 363 (0.13)	358, 371, 425, 446 (284)

[a] Under nitrogen, 10 °C/min heating rate. Figures in brackets are the values under air.
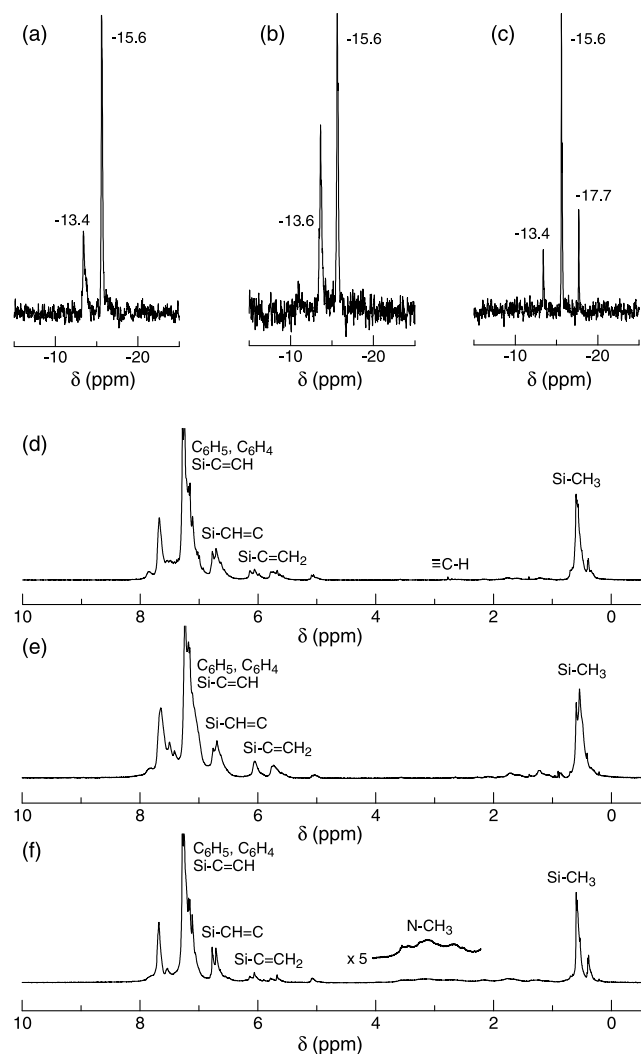[b] In chloroform.
[c] At 980 °C.

Fig. 2. ^{29}Si NMR of (a) **4d**, (b) **5d**, and (c) **4e** in benzene-d_6.

3b with p-bis(dimethylsilyl)benzene [8]. Since the polymer has exhibited high thermal stability under air, incorporation of borazine ring into other polymers is also expected to improve thermal stability under air. Indeed, when the borazine agent **3b** was used in place of **3a**, the resulting crosslinked polymer **4e** showed higher thermal stability under air; the char yields at 980 °C under air were 18% for linear polymer **4a**, 20% for crosslinked polymer **4d**, and 39% for borazine-containing crosslinked polymer **4e**. Although the reason for the improvement of thermal stability by incorporation of borazine has not been elucidated, oxidation-stable boron and silicon oxides might be formed on the surface of borazine-containing polymers during heating under air, which prevent further oxidative degradation of the polymers. Formation of boron and silicon oxides in heating process under air was suggested in some silicon and boron-containing polymers [24,25].

In UV/vis absorption spectra of p-phenylene polymers **4a–d**, the peaks around 390 nm increased as the ratio of

crosslinking agent **3a** to **2a** became large. Meanwhile, the λ_{max} peak at 305 nm (**2a**:**3a**=100:0) was shifted to a low wavelength of 292 nm (**2a**:**3a**=80:20) with decrease of the intensity (Table 2, Fig. 3). Fluororescence emission spectra showed increase of the peaks in the region of 420–550 nm. From these absorption and emission spectra, the emission at 420–550 nm appeared to be connected with the absorption around 390 nm. In *m*-phenylene polymers **5a**–**d** also, the shoulder peaks around 360 nm increased by raising the amount of **3a**, while the intensity of the λ_{max} peak at 260 nm slightly decreased (Fig. 4). In addition, *m*-phenylene polymers **5a**–**d** displayed significant increase of the fluorescence emission in 400–550 nm with decrease of the emission in 320–400 nm as **3a** was increased. This indicates the absorption peaks around 360 nm and 260 nm are correlated with the emission peaks in 400–550 and 320–400 nm, respectively. In these spectra, the wavelength values corresponding to isosbestic points were estimated at about 340 nm (absorption for **4a**–**d**), 425 nm (emission for **4a**–**d**), 285 nm (absorption for **5a**–**d**), and 380 nm (emission for **5a**–**d**). The λ_{max} peaks around 300 nm for **4a**–**d** and 260 nm for **5a**–**d** would originate from π–π* transition of the phenylenedivinylene moieties, while the weak absorption around 390 nm for **4a**–**d** and 360 nm for **5a**–**d** may arise from phenylenedivinylene π to silylene σ charge transfer as suggested for a hyperbranched phenylenevinylene–silylene polymer [17,18]. If this is the case, addition of crosslinking agent **3a** would promote the π to σ charge transfer by facilitating through-space interaction, resulting in the increase of the absorption around 390 nm for **4a**–**d** and

Fig. 4. UV/vis absorption (top) and fluorescence emission (bottom) spectra of **5a**–**d** in chloroform (c=6.67×10^{-5} mol Si/l).

360 nm for **5a**–**d** as well as the emission in 400–550 nm. On the other hand, addition of borazine crosslinking agent **3b** in the reaction of **1** with **2a** caused significant decrease of the absorption peak around 390 nm (Fig. 5). Coincidently, the emission peaks in 400–550 nm showed profound decrease.
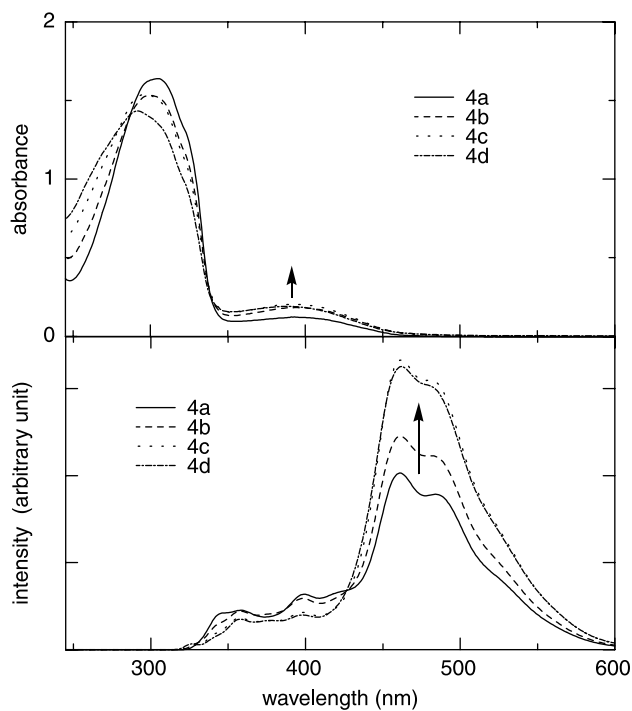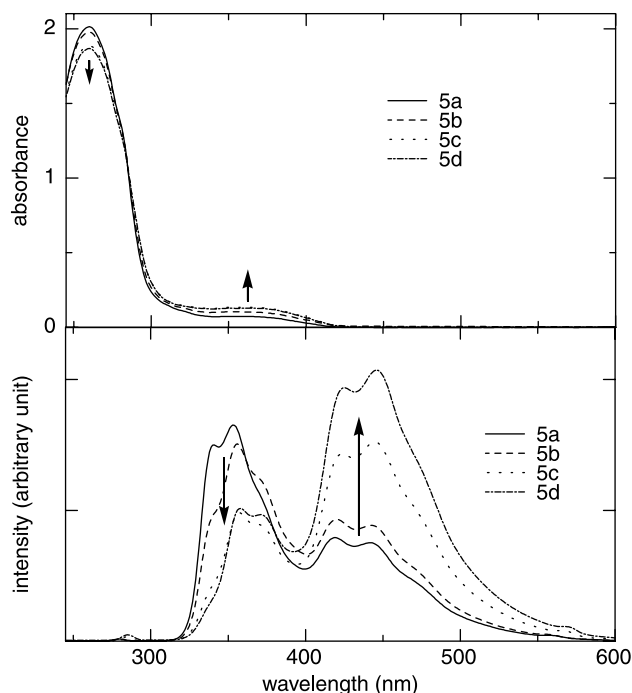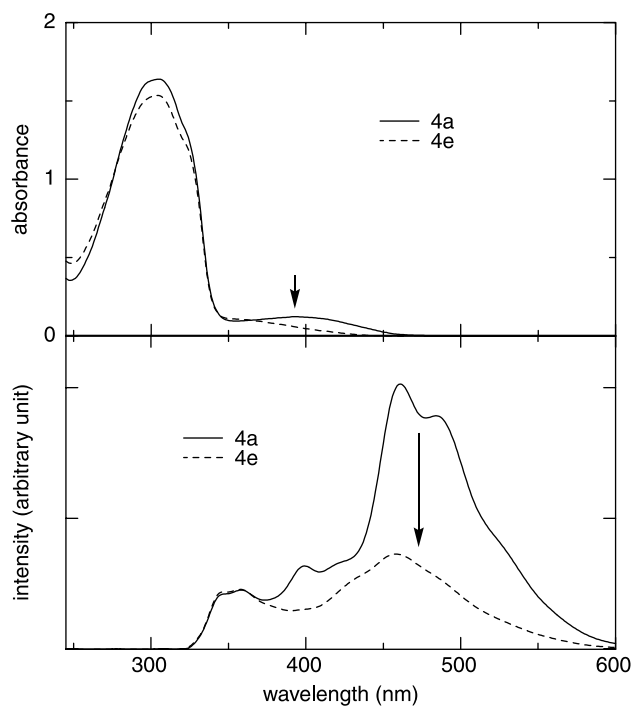

Fig. 3. UV/vis absorption (top) and fluorescence emission (bottom) spectra of **4a**–**d** in chloroform (c=6.67×10^{-5} mol Si/l).

Fig. 5. UV/vis absorption (top) and fluorescence emission (bottom) spectra of **4a**,**e** in chloroform (c=6.67×10^{-5} mol Si/l).

This seems to indicate incorporation of the borazine unit retards the π to σ charge transfer, possibly because of much less π-electron conjugated and/or more sterically hindered properties in comparison with the benzene unit.

In summary, new crosslinked silylene–divinylene polymers were prepared by Pd-catalyzed hydrosilylation polymerization using triethynyl compounds as crosslinking agents. Thermal and photophysical properties of the resulting polymers could be effectively controlled by the kind and the amount of the crosslinking agent. Application of the crosslinked polymers and extension of monomers will be the coming subjects.

3. Experimental

3.1. Materials

Dihydrosilane **1** and diynes **2a,b** were commercially available, and used after purification by distillation in the presence of CaH_2 under nitrogen or by sublimation. Triethynyl compounds **3a** [26] and **3b** [8] were synthesized by literature methods. Toluene, chloroform, and benzene-d_6 were dried with CaH_2 and distilled under nitrogen. $Pd_2(dba)_3$ and PCy_3 were purchased and used as they were.

3.2. Instruments

^1H and ^{29}Si NMR spectra were measured by a Bruker ARX-300 instrument using benzene-d_6 solvent. IR spectra were recorded on a Perkin Elmer Spectrum One spectrometer. TGA measurements were carried out using a Seiko TG/DTA 6200 instrument. UV/vis absorption and fluorescence emission spectra were collected with Hitachi U-3010 and Jasco FP-6500 spectrometers, respectively, using chloroform solvent ($c = 6.67 \times 10^{-5}$ mol Si/l). Molecular weights of polymers were estimated by a GPC system equipped with a high pressure Shimadzu 10ADp pump, Polymer Laboratories PLgel MIXED-B columns, and a Shimadzu RID-10A detector using polystyrene standards and toluene eluent. Softening points of polymers were measured by Stuart Scientific Melting Point Apparatus SMP3.

3.3. Polymerization reactions of *1* with *2* and *3*

Typically, to a mixture of **1** (0.50 mmol), **2a** (0.40 mmol), **3a** (0.10 mmol) and toluene (1 ml) in a glass tube with a Young cock was added a $Pd_2(dba)_3$–PCy_3 toluene solution (0.005 mmol Pd, P/Pd = 2, 0.2 ml) under nitrogen. The mixture was stirred at 60 °C for 3.5 h. The reaction mixture was poured into 2-propanol under stirring to give analytically pure **4d** as a pale yellow powder solid (80% yield). Similarly, other crosslinked polymers were obtained as pale yellow powder solids.

Physical, spectral, and/or analytical data for crosslinked polymers **4b–e** and **5b–d** are as follows.

4b: Softening point 145–150 °C; ^1H NMR (C_6D_6, nm) δ 0.30–0.75 (br m, Si–CH_3), 2.68–2.81 (m, ≡CH), 4.98–5.13 (br m, terminal Si–H), 5.56–5.83 and 5.93–6.22 (each br m, Si–C=CH_2), 6.48–6.83 (br m, Si–CH=C), 6.90–7.97 (br m, aromatic H and Si–C=CH).

4c: Softening point 145–150 °C; ^1H NMR (C_6D_6) δ 0.30–0.74 (br m, Si–CH_3), 2.70–2.81 (m, ≡CH), 5.01–5.11 (br m, terminal Si–H), 5.65–5.85 and 6.00–6.20 (each br m, Si–C=CH_2), 6.50–6.80 (br m, Si–CH=C), 6.80–7.90 (br m, aromatic H and Si–C=CH); ^{29}Si NMR (C_6D_6) δ −15.7, −15.6, −13.6; IR (KBr) 2120 (ν_{Si-H}), 1605, 1570, 1429, 1251, 1191, 1110, 988, 828, 789, 735, 696 cm^{-1}. Anal. Calcd for $(C_{172}H_{160}Si_{10})_n$: C, 82.37; H, 6.43. Found: C, 82.96; H, 6.57.

4d: Softening point 145–155 °C; ^1H NMR (C_6D_6) δ 0.30–0.80 (br m, Si–CH_3), 2.68–2.81 (m, ≡CH), 4.98–5.12 (br m, terminal Si–H), 5.55–5.83 and 5.91–6.20 (each br m, Si–C=CH_2), 6.45–6.87 (br m, Si–CH=C), 6.80–7.97 (br m, aromatic H and Si–C=CH); ^{29}Si NMR (C_6D_6) δ −15.6, −13.4; IR (KBr) 2153 (ν_{Si-H}), 1599, 1506, 1428, 1250, 1110, 987, 801, 736, 698 cm^{-1}. Anal. Calcd for $(C_{87}H_{80}Si_5)_n$: C, 82.54; H, 6.37. Found: C, 83.05; H, 6.42.

4e: Softening point 150–160 °C; ^1H NMR (C_6D_6) δ 0.30–0.82 (br m, Si–CH_3), 2.50–3.70 (br m, ≡CH, N–CH_3), 4.94–5.13 (br m, terminal Si–H), 5.56–6.21 (br m, Si–C=CH_2), 6.46–6.83 (br m, Si–CH=C), 6.90–7.95 (br m, aromatic H and Si–C=CH); ^{29}Si NMR (C_6D_6) δ −17.7, −15.6, −13.4; IR (KBr) 2152 (ν_{Si-H}), 1599, 1506, 1444, 1428, 1397, 1251, 1110, 987, 799, 736, 699 cm^{-1}. Anal. Calcd for $(C_{84}H_{86}B_3N_3Si_5)_n$: C, 76.99; H, 6.61; N, 3.21. Found: C, 76.08; H, 6.56; N, 2.76.

5b: Softening point 135–140 °C; ^1H NMR (C_6D_6, nm) δ 0.27–0.74 (br m, Si–CH_3), 2.61–2.73 (m, ≡CH), 4.97–5.11 (br m, terminal Si–H), 5.53–5.83 and 5.90–6.16 (each br m, Si–C=CH_2), 6.47–6.85 (br m, Si–CH=C), 6.85–7.95 (br m, aromatic H and Si–C=CH).

5c: Softening point 135–140 °C; ^1H NMR (C_6D_6) δ 0.27–0.77 (br m, Si–CH_3), 2.62–2.73 (m, ≡CH), 4.96–5.11 (br m, terminal Si–H), 5.55–5.83 and 5.90–6.17 (each br m, Si–C=CH_2), 6.48–6.85 (br m, Si–CH=C), 6.85–7.95 (br m, aromatic H and Si–C=CH); IR (KBr) 2152 (ν_{Si-H}), 1605, 1571, 1428, 1250, 1193, 1110, 988, 829, 791, 735, 698, 475 cm^{-1}. Anal. Calcd for $(C_{172}H_{160}Si_{10})_n$: C, 82.37; H, 6.43. Found: C, 82.71; H, 6.60.

5d: Softening point 140–145 °C; ^1H NMR (C_6D_6) δ 0.24–0.76 (br m, Si–CH_3), 2.63–2.73 (m, ≡CH), 4.95–5.12 (br m, terminal Si–H), 5.50–5.83 and 5.86–6.18 (each br m, Si–C=CH_2), 6.43–6.87 (br m, Si–CH=C), 6.87–8.02 (br m, aromatic H and Si–C=CH); ^{29}Si NMR (C_6D_6) δ −15.6, −13.6; IR (KBr) 2152 (ν_{Si-H}), 1606, 1572, 1428, 1250, 1194, 1110, 988, 826, 795, 735, 698, 475 cm^{-1}. Anal. Calcd for $(C_{87}H_{80}Si_5)_n$: C, 82.54; H, 6.37. Found: C, 82.63; H, 6.38.

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