# Convenient One-pot Synthesis of Functional Alkenyl Pendant-containing Silylene-divinylene Polymers

Tumula Venkateshwar Rao,[#] Hiroshi Yamashita,* Yuko Uchimaru, Michihiko Asai, and Kazuhiko Takeuchi
*National Institute of Advanced Industrial Science and Technology (AIST),*
*Tsukuba Central 5-1, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565*

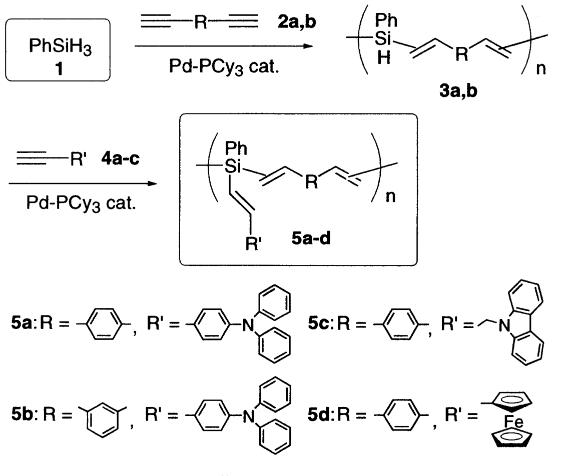
(Received April 1, 2003; CL-030280)

Successive treatment of $PhSiH_3$ with 1,4- or 1,3-diethynylbenzene (1 equiv.) and functional alkynes (1.05 equiv.) in the presence of $Pd_2(dba)_3$-$PCy_3$ (dba = dibenzylideneacetone, Cy = cyclohexyl) catalyst gave new functional alkenyl pendant-containing silylene-divinylene polymers.

---

Organosilicon polymers have attracted increasing interest for their intriguing physicochemical properties and applicability to optoelectric devices, heat-resistant materials, ceramic precursors, etc.[1] Stepwise reactions of polymerization and subsequent modification are frequently utilized to prepare functionalized organosilicon polymers. On the other hand, transition metal-catalyzed hydrosilylation is a versatile reaction affording useful organosilicon derivatives. We have recently developed an efficient Pd catalyst for hydrosilylation of alkynes with trihydrosilanes, which gives mono-, di-, and trialkenylsilanes selectively depending on the ratios of alkyne/trihydrosilane.[2] The catalysis has been found to be applicable to a very convenient polymerization-modification one-pot process, which provides new silylene-divinylene polymers with functional alkenyl pendants.[3,4]

Thus, treatment of a benzene (0.60 mL) solution of $PhSiH_3$ (**1**, 0.30 mmol) and 1,4-diethynylbenzene (**2a**, 0.30 mmol) with a $Pd_2(dba)_3$-$PCy_3$ benzene solution (0.0006 mmol Pd, P/Pd = 2, 0.03 mL) at 40 °C for 0.5 h under nitrogen cleanly gave a Si-H bond-containing silylene-divinylene polymer (**3a**) (Scheme 1, Table 1). The -C=C-Si-C=C- moieties have three possible regioisomeric structures such as -CH=CH-Si-CH=CH- (β,β), -CH=CH-Si-C(=$CH_2$)- (β,α), and -($H_2C$=)C-Si-C(=$CH_2$)- (α,α) types. $^1H$ and $^{29}Si$ NMR measurements indicated the ratio of (β,β):(β,α):(α,α) being ca. 60:35:≤5. Further treatment of the reaction mixture with a benzene (0.75 mL) solution of 4-ethynyl-*N*,*N*-diphenylaniline (**4a**, 0.315 mmol) and the Pd catalyst benzene solution (0.0036 mmol Pd, 0.18 mL) at 40 °C for 3 h transformed the Si-H bonds of **3a** in ≥95% conversion, affording a modified silylene-divinylene polymer (**5a**) with *p*-*N*,*N*-diphenylaminophenyl groups in the side chains. Purification by precipitaion from benzene/2-propanol gave **5a** as yellow powder in 80% yield. The molecular weight $M_w$ ($M_w/M_n$) was estimated by GPC (polystyrene standards) at 112000 (7.5). $^1H$ NMR and analytical data of **5a** were in good agreement with the expected structure.[5] For the regiochemistry of the modification, trans β vinylene product **6** was nearly selectively obtained in a model reaction of **4a** with a dialkenylhydrosilane (a mixture of (β,β)- and (β,α)-type isomers) which was prepared by the reaction of **1** with phenylacetylene (2 equiv.).[6] This indicates that trans β vinylene structure is preferably formed in the side chain modification process as well. On the other hand, $^{29}Si$ NMR showed the four major signals of **3a** were cleanly shifted to the three major signals of **5a** at −20.9, −20.8, and −18.6 ppm (Figure 1). By the comparison with the spectrum of **6**,[6] the signals of −20.9 and −20.8 ppm seemed to arise from the (β,β) moieties of the backbone, while the signal of −18.6 ppm would be attributed to the (β,α) moieties. The splitting of the signals observed for the (β,β) and (β,α) regions is possibly due to difference in the structure of the neighboring monomer units.

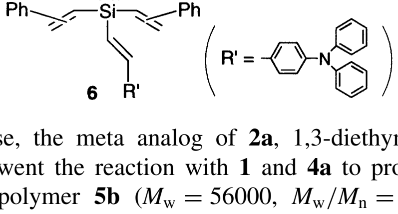


**Scheme 1.**

**Table 1.** Reactions of phenylsilane (**1**) with diynes (**2**) and functional acetylenes (**4**)[a]

| 2 | 4 | 5 | Yield/%[b] | $M_w$ ($M_w/M_n$)[c] |
|---|---|---|---|---|
| **2a** | **4a** | **5a** | 80 | 112000 (7.5) |
| **2b** | **4a** | **5b** | 79 | 56000 (9.4) |
| **2a** | **4b** | **5c** | 85 | 61000 (5.7) |
| **2a** | **4c** | **5d** | 85 | 42000 (4.1) |

[a] **1** (0.30 mmol), **2** (0.30 mmol), **4** (0.315 mmol), $Pd_2(dba)_3$-$PCy_3$ (totally 0.0042 mmol Pd, P/Pd = 2), benzene (1.56 mL). [b] Yield after purification by precipitation from benzene/2-propanol. [c] Estimated by GPC using polystyrene standards.



6

Likewise, the meta analog of **2a**, 1,3-diethynylbenezene (**2b**), underwent the reaction with **1** and **4a** to provide a 1,3-phenylene polymer **5b** ($M_w$ = 56000, $M_w/M_n$ = 9.4), via a Si-H bond-containing polymer **3b** whose (β,β):(β,α):(α,α) ratio estimated by NMR was similar to that of **3a**. In addition, modification of **3a** with *N*-(2-propargyl)carbazole (**4b**) and ethynyl-

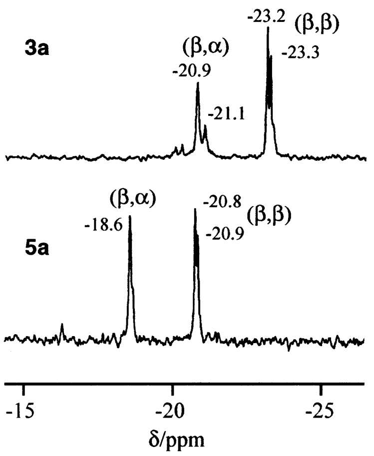


**Figure 1.** $^{29}$Si NMR spectra of **3a** and **5a** (in benzene-$d_6$).

ferrocene (**4c**) also smoothly proceeded to give modified polymers **5c** ($M_w = 61000$, $M_w/M_n = 5.7$) and **5d** ($M_w = 42000$, $M_w/M_n = 4.1$), respectively. Polymers **5b–d** showed satisfactory spectral and analytical data as **5a**.[5] Partial modification was also possible by controlling the reaction conditions; for instance, in the reaction with **4b** reducing the catalyst to one-third of the standard amount gave a partially (63%) modified polymer with remaining Si-H bonds.

In the UV–vis absorption spectra, 1,4-phenylene polymer **5a** showed a large peak at a longer wavelength (306 nm) than the corresponding 1,3-phenylene polymer **5b** (262 nm) with shorter π-electron conjugated system (Figure 2). Similarly to **5a**, other 1,4-phenylene polymers **5c**,**d** also displayed largest peaks at around 300 nm. On the other hand, these polymers exhibited unique fluorescence emission spectra in 300–600 nm. The position of the $\lambda_{max}$ peak was tunable by the linkage type of the phenylene ring; 1,4-phenylene polymer **5a** showed an emission peak (477 nm) in significantly longer wavelength region than the 1,3-phenylene polymer **5b** (430 nm), as observed in their absorption spectra. The alkenyl side chain also strongly affected the position of the $\lambda_{max}$ peak and the spectral pattern; the wavelength of the largest peak is in the order of **5a** (477 nm) > **5c** (426) > **5d** (357).

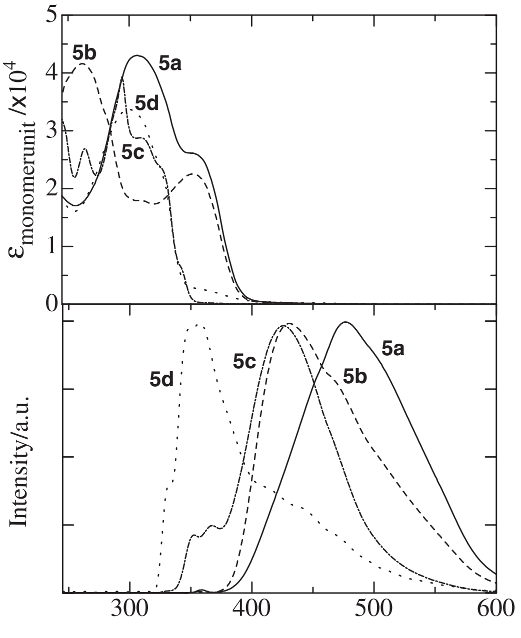


**Figure 2.** UV–vis absorption (top) and fluorescence emission (bottom) spectra of **5a–d**. $c = 6.67 \times 10^{-5}$ M (mol monomer unit/L, in chloroform); emission spectra were normalized in the intensity scale.

Further investigations on extension of the catalysis and application of the resulting polymers are under way.

## References and Notes

\# Present address: Indian Institute of Petroleum, Dehradun-248005, India.

1 For recent progress: “Silicon-Containing Polymers,” ed. by R. G. Jones, W. Ando, and J. Chojnowski, Kluwer, Dordrecht (2000).

2 H. Yamashita and Y. Uchimaru, *Chem. Commun.*, **1999**, 1763.

3 For some examples of polycarbosilanes and their applications: J. Ohshita, *Yuki Gosei Kagaku Kyokaishi*, **59**, 11 (2001), see also: Ref. 4.

4 For recent studies on hydrosilylation polymerization: G. Kwak and T. Masuda, *Kobunshi Ronbunshu*, **59**, 332 (2002), and references cited therein; A. Mori, E. Takahisa, H. Kajiro, Y. Nishihara, and T. Hiyama, *Macromolecules*, **33**, 1115 (2000); D. S. Kim and S. C. Shim, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 2933 (1999).

5 Selected spectral and analytical data for **5a–d**. **5a**: $^1$H NMR ($C_6D_6$) δ 5.60–5.98 and 6.03–6.35 (each br m, $=CH_2$), 6.50–7.90 (br m, CH=CH and ring H); $^{29}$Si NMR ($C_6D_6$) δ −20.9, −20.8, −18.6; UV–vis absorption ($CHCl_3$) 306, 353 sh nm; emission ($CHCl_3$) 477 nm. Anal. Calcd for $(C_{36}H_{29}NSi)_n$: C, 85.84; H, 5.80; N, 2.78. Found: C, 85.82; H, 5.81; N, 2.65; **5b**: $^1$H NMR $C_6D_6$) δ 5.57–5.95 and 6.00–6.30 (each br m, $=CH_2$), 6.55–7.91 (br m, CH=CH and ring H); $^{29}$Si NMR ($C_6D_6$) δ −20.9, −20.8, −18.9; UV–vis absorption ($CHCl_3$) 262, 352 sh nm; emission ($CHCl_3$) 430, 467 sh nm. Anal. Calcd for $(C_{36}H_{29}NSi)_n$: C, 85.84; H, 5.80; N, 2.78. Found: C, 85.33; H, 5.84; N, 2.53; **5c**: $^1$H NMR ($C_6D_6$) δ 4.20–4.87 (br m, N-$CH_2$), 5.40–6.40 (br m, pendant CH=CH and $=CH_2$), 6.40–8.10 (br m, backbone CH=CH and ring H); $^{29}$Si NMR ($C_6D_6$) δ −21.7, −21.6, −19.8; UV–vis absorption ($CHCl_3$) 264, 294, 309 nm; emission ($CHCl_3$) 353, 367, 426 nm. Anal. Calcd for $(C_{31}H_{25}NSi)_n$: C, 84.69; H, 5.73; N, 3.19. Found: C, 84.22; H, 5.81; N, 3.18; **5d**: $^1$H NMR ($C_6D_6$) δ 3.83–4.12 and 4.17–4.40 (each br m, ferrocene ring H), 5.80–6.00 and 6.10–6.33 (each br m, $=CH_2$), 6.37–6.57 (pendant CH=CH), 6.74–7.64 and 7.73–7.97 (each br m, backbone CH=CH and benzene ring H); $^{29}$Si NMR ($C_6D_6$) δ −21.3, −21.2, −19.2; UV–vis absorption ($CHCl_3$) 299, 358 sh nm; emission ($CHCl_3$) 332 sh, 349, 357, 410 sh, 438 sh, 466 sh nm. Anal. Calcd for $(C_{28}H_{24}FeSi)_n$: C, 75.67; H, 5.44. Found: C, 75.38; H, 5.45.

6 $^1$H and $^{29}$Si NMR monitoring of the reaction showed nearly selective formation of trans β vinylene structure; the proton signal for the formed Si-CH=C moiety was observed at 6.75 ppm with a relatively large coupling constant between the vinylene protons ($J = 19.2$ Hz), while two $^{29}$Si NMR signals emerged at −20.9 and −18.8 ppm which corresponded to the (β,β)- and (β,α)-type isomers of **6**, respectively.

Published on the web (Advance View) June 10, 2003; DOI 10.1246/cl.2003.580