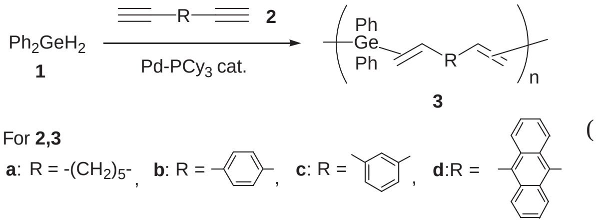
Facile Palladium-catalyzed Hydrogermylation Polymerization of a Dihydrogermane with Diynes Affording Light-emissive Germylene–Divinylene Polymers

Hiroshi Yamashita,* Somruethai Channasanon, and Yuko Uchimaru
National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba 305-8565

(Received December 21, 2005; CL-051559; E-mail: hiro-yamashita@aist.go.jp)

Hydrogermylation polymerization of diphenylgermane with aliphatic and aromatic diynes smoothly proceeded in the presence of Pd–PCy$_3$ (Cy = cyclohexyl) catalysts to give new germylene–divinylene polymers in high yields.

Increasing attention has been directed to silicon and related group 14 element polymers for their unique physicochemical properties.[1] Polyaddition of a trihydrosilane[2a,2b] or some dihydrosilanes[2c,2d,3] to diynes provides –C=C–Si–C=C– unit-containing polymers. This process is considered as a most convenient clean method for polycarbosilane synthesis. However, for germanium element, analogous polymers have not been prepared to date. We have found that a dihydrogermane can smoothly react with diynes in the presence of Pd–PCy$_3$ catalysts to give the corresponding polycarbogermanes in high yields. This is the first examples of polycarbogermane synthesis by polyaddition of dihydrogermane. In addition, an anthrylene unit-containing germanium polymer exhibits a unique light emission ranging to ≥600 nm, which is quite different from a previously reported inorganic element-containing anthrylene polymer.



(1)

Thus, when diphenylgermane (**1**) was treated with 1,8-nonadiyne (**2a**, 1 equiv.) in the presence of PdCl$_2$(PCy$_3$)$_2$ (0.9 mol % Pd) at 90 °C for 4 h, ^{1}H NMR of the reaction mixture showed complete conversion of the starting monomers along with formation of a 1:1 polyaddition product **3a** (Eq 1). In a separate reaction under similar reaction conditions, purification by precipitation from benzene/2-propanol gave **3a** as a sticky solid in 76% yield (Table 1).[4] The molecular weight M_w (M_w/M_n) was estimated by GPC at 83,000 (11) using polystyrene standards. ^{1}H NMR of **3a** showed –Ge–CH=CH– vinylene protons at 6.15 (br d, $J = 18.1$ Hz, Ge–CH=) and 6.26 (br dt, $J = 18.1$ and 5.6 Hz, Ge–C=CH) ppm, while –Ge–C(=CH$_2$)– vinylidene protons were observed at 5.50–5.93 (br m) ppm. The relatively large coupling constant (18.1 Hz) between the vinylene protons indicated trans structure of the vinylene moiety. On the basis of the proton integral ratio, the ratio of vinylene:vinylidene was estimated at 90:10. Hydrogermylation of acetylenes with a monohydrogermane (triphenylgermane) was previously reported to proceed in the presence of Pd–PPh$_3$ catalyst.[5] The use of PdCl$_2$(PPh$_3$)$_2$ in place of PdCl$_2$(PCy$_3$)$_2$ also gave **3a** (70 °C, 4 h, 61% yield, $M_w = 13{,}000$, $M_w/M_n = 3.7$) with a decreased ratio of the vinylene units (vinylene:vinylidene = 80:20). On the contrary, a platinum complex, Pt$_2$(dvs)$_3$ (dvs = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane), which is a highly efficient conventional catalyst for hydrosilylation of acetylenes, was quite ineffective in the present reaction, forming a considerable amount of a unfavorable redistribution compound (triphenylgermane, ≥15%) as a by-product.

Similarly to **2a**, *p*-diethynylbenzene (**2b**) underwent the reaction with **1** in the presence of PdCl$_2$(PCy$_3$)$_2$ at 90 °C to give the corresponding *p*-phenylene polymer **3b** ($M_w = 67{,}000$, $M_w/M_n = 12$, vinylene:vinylidene = 80:20) in 86% yield. The reactivity of **2b** was higher than that of **2a**, and the reaction was completed in 2 h. In addition to **2b**, its meta analog **2c** also reacted with **1a** to give a *m*-phenylene polymer **3c** ($M_w = 24{,}000$, $M_w/M_n = 5.8$, vinylene:vinylidene = 81:19, 92% yield). A fused-ring system, 9,10-diethynylanthracene (**2d**), could polymerize with **1** as well in the presence of Pd$_2$(dba)$_3$–PCy$_3$ (dba = dibenzylideneacetone, P/Pd = 2, 50 °C, 4 h) to form a 9,10-anthrylene unit-containing polymer **3d** ($M_w = 12{,}000$, $M_w/M_n = 3.3$, 60% yield). Interestingly, **2d** favored vinylidene units (vinylene:vinylidene = 21:79), while **2a**–**2c**

Table 1. Pd-catalyzed hydrogermylation polymerization of diphenylgermane **1** with diynes **2**[a]

2	Catalyst (0.9 mol %/1)	Temp. /°C	Time /h	3 [Yield[b] /%]	M_w (M_w/M_n)[c]	VL:VD[d]	Absorption[e] λ_{max}/nm [$\varepsilon_{monomer\ unit}$]	Emission[e] λ_{max}/nm [excitation/nm]	TGA[f] Td$_5$ /°C	Char[g] /%
2a	PdCl$_2$(PCy$_3$)$_2$	90	4	**3a** [76]	83,000 (11)	90:10	—	—	343	9
2b	PdCl$_2$(PCy$_3$)$_2$	90	2	**3b** [86]	67,000 (12)	80:20	301 [2.6×10^4]	353, 373, 392, 419 [331]	363	33
2c	PdCl$_2$(PCy$_3$)$_2$	90	4	**3c** [92]	24,000 (5.8)	81:19	260 [3.0×10^4]	336, 353 [287]	392	40
2d	1/2Pd$_2$(dba)$_3$–2PCy$_3$	50	4	**3d** [60]	12,000 (3.3)	21:79	258 [4.8×10^4], 375 [7.0×10^3], 396 [1.2×10^4], 421 [1.2×10^4]	440, 464, 534 [417]	407	43

[a]Reaction conditions: **1** (0.30 mmol), **2** (0.30 mmol), Pd catalyst (0.0027 mmol), benzene-d_6 or benzene (0.30 mL). [b]Yield after precipitation from benzene/2-propanol. [c]Estimated by GPC using polystyrene standards. [d]VL = vinylene, VD = vinylidene. The ratios were estimated by ^{1}H NMR. [e]In chloroform, $c = 6.67 \times 10^{-5}$ M (mol monomer unit/L). [f]Under N$_2$. [g]Char yield at 980 °C.

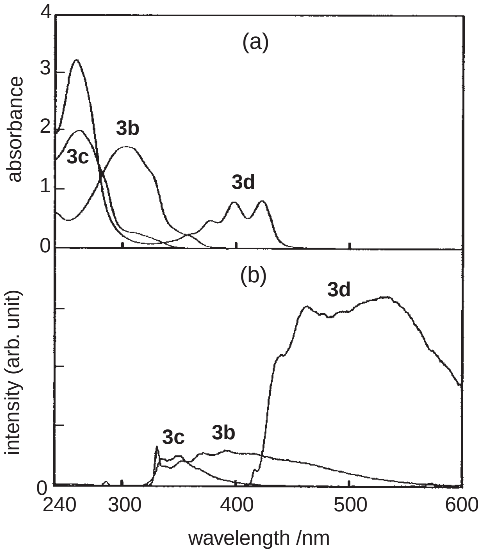


Figure 1. UV–vis absorption (a) and emission (b) spectra of **3b**–**3d** (in chloroform, $c = 6.67 \times 10^{-5}$ M (mol monomer unit/L), excitation at 331 (**3b**), 287 (**3c**), and 417 (**3d**) nm).

formed vinylene units preferentially. In **2a**–**2d**, crosslinked structures resulting from the reactions of the main chain C=C moieties with Ge–H bonds were not found by NMR. All new polymers **3a**–**3d** showed satisfactory spectral and analytical data.[4]

Polymer **3b** with *p*-phenylene linkage showed UV–vis absorption peak at 301 nm (Table 1, Figure 1). On the other hand, **3c** with *m*-phenylene linkage exhibited the $\lambda_{\max}$ peak at shorter wavelength of 260 nm, presumably because of shorter conjugation length of the phenylene–divinylene linkage. Anthrylene unit-containing **3d** displayed several peaks in the region of 340–440 nm due to the anthrylene ring incorporated in the backbone. In fluorescence emission spectra, **3b** and **3c** showed several peaks in the region of 330–600 and 330–430 nm, respectively. In remarkable contrast with **3b** and **3c**, anthrylene polymer **3d** gave very intense and broad spectra ranging from 420 to ≥600 nm with $\lambda_{\max}$ peaks at 440, 464, and 534 nm. The emergence of the intense peak around 530 nm is quite different from a previously reported boron-containing anthrylene-divinylene polymer $[B(R)–CH=CH–X–CH=CH]_n$ (R = mesityl, X = 9,10-anthrylene);[6] the boron polymer shows most intense peaks in 400–450 nm and only tailing profile in ≥500 nm. The emission in the long wavelength region for **3d** might originate from possile interaction between the adjacent anthracene rings in the main chain, which causes excimer-type light emission (Figure 2).[7] The photoluminescence quantum yield was estimated at ca. 0.74. In thermogravimetric analysis (TGA), the 5% weight loss temperature (Td_5) and char yield at 980 °C under nitrogen increased in the order of **3a** (343 °C and 9%, respectively) < **3b** (363 and 33) < **3c** (392 and 40) < **3d** (407 and 43), revealing anthrylene-containing **3d** being thermally most stable.

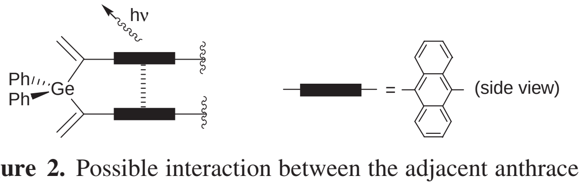


Figure 2. Possible interaction between the adjacent anthracene rings.

In summary, Pd–PCy_3 catalyst system effectively promotes hydrogermylation polymerization of a dihydrogermane with diynes to give new germylene–divinylene polymers. An anthrylene-containing polymer shows intense light emission with $\lambda_{\max}$ peaks in 440–540 nm. Further investigations on extension of monomers and detailed properties and applications of the germanium and related polymers are in progress.

References and Notes

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4 Typically, a mixture of **1** (0.30 mmol), **2a** (0.30 mmol), $PdCl_2(PCy_3)_2$ (0.0027 mmol), and benzene-d_6 (0.30 mL) was heated at 90 °C under nitrogen in a NMR tube. The progress of the reaction was monitored by ^{1}H NMR. When remaining acetylenic protons became negligible (≤5%), heating was discontinued. Separate reaction using benzene in place of benzene-d_6 gave essentially the same result. Precipitation from benzene/2-propanol gave **3a** as a colorless sticky solid (0.23 mmol, 76% yield). Similarly, **3b**–**3d** were obtained as pale yellow powder solids. Spectral and analytical data for **3a**–**3d** are as follows. **3a**: ^{1}H NMR (C_6D_6): δ 0.97–2.52 (br m, $(CH_2)_5$), 5.50–5.93 (br m, Ge–C=CH_2), 6.15 (br d, $J = 18.1$ Hz, Ge–CH=), 6.26 (br dt, $J = 18.1$ and 5.6 Hz, Ge–C=CH), 6.95–7.88 (br m, aromatic H); ^{13}C NMR (C_6D_6): δ 28.8, 29.2, 37.0, 124.7, 128.5, 129.1, 135.2, 138.2, 139.1, 149.6, 150.3; IR (KBr): 1612, 1483, 1431, 1306, 1186, 1092, 1026, 987, 849, 735, 696, 465 cm^{-1}. Anal. Calcd for $(C_{21}H_{24}Ge)_n$: C, 72.27; H, 6.93%. Found: C, 71.71; H, 6.92%. **3b**: ^{1}H NMR (C_6D_6): δ 5.50–6.30 (br m, Ge–C=CH_2), 6.78–7.88 (br m, Ge–CH=CH and aromatic H); ^{13}C NMR (C_6D_6): δ 125.2, 127.4, 128.8, 129.5, 132.7, 135.4, 137.0, 138.2, 143.3, 146.8; IR (KBr): 1595, 1504, 1483, 1429, 1184, 1090, 984, 768, 735, 696, 463 cm^{-1}. Anal. Calcd for $(C_{22}H_{18}Ge)_n$: C, 74.44; H, 5.11%. Found: C, 74.15; H, 5.13%. **3c**: ^{1}H NMR (C_6D_6): δ 5.55–6.27 (br m, Ge–C=CH_2), 6.72–7.88 (br m, Ge–CH=CH and aromatic H); ^{13}C NMR (C_6D_6): δ 125.2, 126.8, 128.8, 129.0, 129.5, 135.4, 135.9, 137.1, 138.5, 144.0, 147.0; IR (KBr): 1570, 1483, 1429, 1186, 1090, 987, 760, 735, 698, 465 cm^{-1}. Anal. Calcd for $(C_{22}H_{18}Ge)_n$: C, 74.44; H, 5.11%. Found: C, 74.46; H, 5.14%. **3d**: ^{1}H NMR (C_6D_6): δ 5.50–6.35 (br m, Ge–C=CH_2), 6.55–8.75 (br m, Ge–CH=CH and aromatic H); ^{13}C NMR (C_6D_6): δ 124.8, 127.2, 127.9, 128.9, 129.3, 135.0, 137.2, 137.6, 138.4, 149.2; IR (KBr): 1431, 1348, 1088, 1028, 999, 939, 766, 733, 698, 679, 607, 521, 467 cm^{-1}. Anal. Calcd for $(C_{30}H_{22}Ge)_n$: C, 79.17; H, 4.87%. Found: C, 80.07; H, 4.78%.

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7 Dilution of the solution (10–100 times) did not affect the spectral shape, indicating intramolecular excimer formation.

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