

Platinum Complex-catalysed Polycondensation of Tetrakis(dimethylsilyl)benzene with Diynes. Synthesis of Thermally Stable and Conducting Polymers

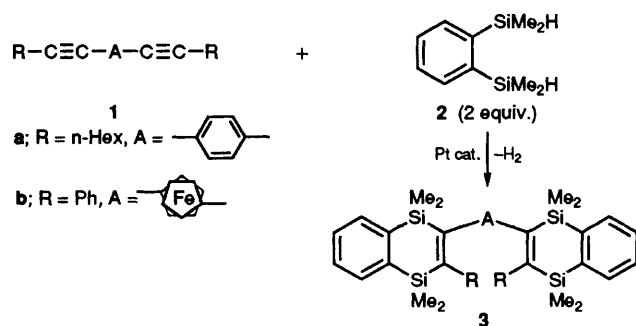
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Dehydrogenative double silylation polymerisation of diynes with 1,2,4,5-tetrakis(dimethylsilyl)benzene in the presence of a catalytic amount of (ethylene)bis(triphenylphosphine)platinum gives new silicon-based polymers, which show high thermal stability and conductivity upon doping.

Silicon-based polymers are attracting increasing attention in view of their unique chemical, physicochemical and thermal properties.¹ We now demonstrate that the dehydrogenative silylation of acetylenes² is a powerful tool for the synthesis of polymers with high thermal stability and electric conduction upon doping.

As a model experiment, *p*-di(oct-1-ynyl)benzene **1a** was treated with *o*-bis(dimethylsilyl)benzene **2** in the presence of Pt(CH₂=CH₂)(PPh₃)₂ at 30 °C for 12 h. The *p*-bis(disilacyclohexadienyl)benzene derivative **3a** was obtained in 78% yield with evolution of hydrogen, Scheme 1.†‡ 1,1'-Bis(phenylethynyl)ferrocene **1b** also reacted smoothly at 30 °C to give **3b** in 83% yield. A similar reaction between diphenylacetylene and tetrakis(dimethylsilyl)benzene **4** gave the tricyclic product **5** in excellent yield. X-Ray crystallography revealed that the tricyclic system was almost planar



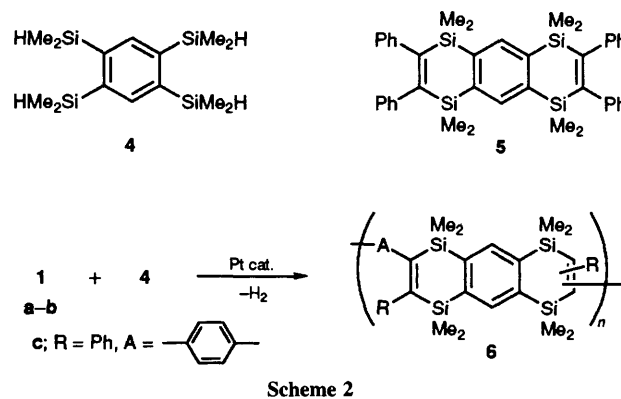
Scheme 1

† Experimental procedures are as follows, for **3a**: A mixture of **1a** (0.125 mmol), **2** (0.25 mmol), Pt(CH₂=CH₂)(PPh₃)₂ (0.005 mmol) and benzene (4 ml) was stirred at 30 °C for 12 h in a 20 ml Schlenk tube. Evaporation of the resulting solution and preparative thin layer chromatography of the residue (silica gel, hexane–benzene 3:1) afforded a white powder **3a** in 78% yield. An analytical sample was obtained by recrystallisation from ethanol. For **6b**: A mixture of **1b** (0.25 mmol), **4** (0.25 mmol), Pt(CH₂=CH₂)(PPh₃)₂ (0.01 mmol) and benzene (6 ml) was stirred at 30 °C for 15 h in a 20 ml Schlenk tube. Filtration of the deep-red mixture and addition of the filtrate to methanol (40 ml) afforded an orange powder **6b** in 94% yield.

‡ Satisfactory analytical data were obtained for all synthesised compounds. **3a**: white powder; m.p. 130–132 °C; ¹H NMR (200 MHz, CDCl₃): δ 0.18 (s, 12H), 0.41 (s, 12H), 0.83 (t, 7 Hz, 6H), 1.1–1.4 (br s, 16H), 2.18 (t, 7 Hz, 4H), 6.90 (s, 4H), 7.35–7.4 (m, 4H), 7.55–7.65 (m, 4H); ¹³C NMR (50.3 MHz, CDCl₃): δ –1.0 (4C), –0.3 (4C), 14.0 (2C), 22.6 (2C), 29.7 (2C), 30.2 (2C), 31.4 (2C), 33.6 (2C), 127.1 (4C), 128.06 (2C), 128.14 (2C), 132.9 (2C), 133.2 (2C), 140.4 (2C), 144.9 (2C), 145.2 (2C), 155.0 (2C), 156.2 (2C). **3b**: orange powder; m.p. 229–230.5 °C; ¹H NMR (CDCl₃): δ 0.12 (s, 12H), 0.57 (s, 12H), 3.70 (m, 4H), 3.89 (m, 4H), 6.8–7.0 (m, 4H), 7.15–7.7 (m, 14H); ¹³C NMR (CDCl₃): δ –0.6 (4C), 2.4 (4C), 71.2 (4C), 71.8 (4C), 85.5 (2C), 125.7 (2C), 127.6 (4C), 128.0 (2C), 128.4 (6C), 132.7 (2C), 133.2 (2C), 143.5 (2C), 145.8 (2C), 145.9 (2C), 148.2 (2C), 155.5 (2C). **5**: m.p. >300 °C; ¹H NMR (C₆D₆): δ 0.4 (s, 12H), 0.5 (s, 12H), 6.8–7.1 (m, 20H), 8.1 (s, 2H).

and that the four phenyl groups were nearly perpendicular to this plane (Fig. 1).§

Based on the results of the model systems, we could develop a dehydrogenative double silylation polymerisation reaction as follows.¶ The polymerisation between **1b** and **4** proceeded at 30 °C over 15 h in the presence of the same platinum catalyst, and **6b** which contains the ferrocene structure in the backbone was obtained in 94% yield, Scheme 2, Table 1. The molecular mass [*M*_w, gel-permeation chromatography (GPC), polystyrene standards] was 2.3 × 10⁴ and the polydispersity (*M*_w/*M*_n) was estimated at 2.9.∥ Analytical and spectral data were all in agreement with the proposed structure. Other diacetylenes also underwent the polycondensation with **4**



Scheme 2

§ Crystal data for **5**: Crystal size 0.2 × 0.14 × 0.5 mm, triclinic, *a* = 8.5468(6), *b* = 9.1680(6), *c* = 20.689(5) Å, α = 79.502(5), β = 72.387(6), γ = 88.061(5)°, *V* = 977.8(1) Å³, *P*1̄, *Z* = 1, *D*_c = 1.003 g cm⁻³, μ = 14.93 cm⁻¹. Data collection on an Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Cu-Kα radiation (λ = 1.5418 Å). An empirical absorption correction using Ψ scans (transmission factors 0.9689/1.0000). The 2929 observed reflections (2θ ≤ 120°; |*F*_o| > 3σ|*F*_o|). The structure was solved by MULTAN78. Final *R* = 0.051 (*R*_w = 0.079). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ Satisfactory analytical data were obtained for all synthesised polymers. **6a**: pale-yellow powder; ¹H NMR (CDCl₃): δ 0.19 (s, 6H), 0.21 (s, 6H), 0.42 (s, 6H), 0.44 (s, 6H), 0.82 (t, 7.5 Hz, 6H), 1.05–1.4 (br s, 16H), 2.15–2.25 (br s, 4H), 6.8–6.95 (br s, 4H), 7.75, 7.80 and 7.85 [three singlets, total 2H (1:2:1)]; ¹³C NMR (CDCl₃): δ –1.1 (4C), –0.3 (4C), 14.0 (2C), 22.6 (2C), 29.7 (2C), 30.2 (2C), 31.4 (2C), 33.7 (2C), 127.1 (4C), 137.0, 137.2 and 137.4 [total 2C (1:2:1)], 140.4 (2C), 144.1, 144.2, 144.4, 144.5, 155.1 (2C), 156.2 (2C). **6b**: orange powder; ¹H NMR (CDCl₃): δ 0.07 (s, 6H), 0.12 (s, 6H), 0.52 (s, 6H), 0.57 (s, 6H), 3.7 (s, 4H), 3.8 (s, 4H), 6.9 (br s, 4H), 7.25 (br s, 6H), 7.6, 7.7 and 7.8 [three singlets, total 2H (1:2:1)]; ¹³C NMR (CDCl₃): δ –0.58 (2C), –0.52 (2C), 2.45 (2C), 2.51 (2C), 71.1 (4C), 71.8 (4C), 85.2 (2C), 125.8 (2C), 127.6 (4C), 128.5 (4C), 136.4, 137.1 and 137.7 [total 2C (1:2:1)], 142.7, 143.1, 145.1, 145.5, 145.8 (2C), 148.3, 148.4, 155.6, 155.7.

∥ The molecular mass (*M*_n) of the polymer **6b** obtained by vapour-pressure osmometry (benzene, 40 °C) was 6.5 × 10³.

Table 1 Polymers **6** from 1,2,4,5-tetrakis(dimethylsilyl)benzene **4** and diynes **1**^a

Polymer	Time/h	Yield (%)	$M_w/(M_w/M_n)$	M.p./°C	$T_5^b/°C$	Char ^c (Wt%)	Conductivity ^d S cm ⁻¹
6a	18	72 ^e	1.2×10^4 (2.1) ^f	—	—	—	—
		25 ^g	2.1×10^4 (2.8) ^f	>300	424	24	1×10^{-4}
6b	15	94	2.3×10^4 (2.9) ^h	>300	454	49	7×10^{-3}
6c	18	91	Insoluble	>300	496	62	6×10^{-4}

^a Reaction conditions: **1** 0.25 mmol, **4** 0.25 mmol, Pt(CH₂=CH₂)(PPh₃)₂ 0.01 mmol, benzene 6 ml, 30 °C. ^b Temperature of 5% weight loss in TGA. ^c Wt% of the char formed in TGA up to 900 °C. ^d Conductivity of the FeCl₃-doped polymer. ^e Benzene-soluble fraction. ^f GPC, 1,2-dichlorobenzene, 135 °C, polystyrene standards. ^g Benzene insoluble fraction. ^h GPC, tetrahydrofuran, 40 °C, polystyrene standards.

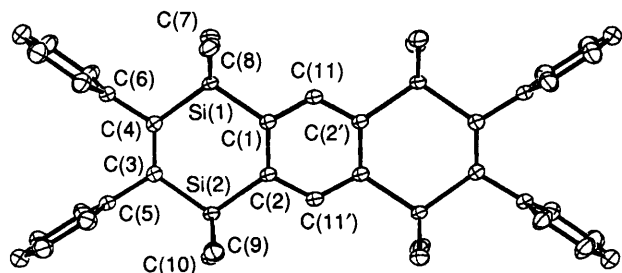


Fig. 1 Perspective view of **5**. The molecule itself has a centre of symmetry. Selected bond lengths (Å) and angles (°): Si(1)–C(1) 1.871(2), Si(1)–C(4) 1.882(2), Si(1)–C(7) 1.868(4), Si(1)–C(8) 1.862(4), Si(2)–C(2) 1.872(2), Si(2)–C(3) 1.881(2), Si(2)–C(9) 1.864(5), Si(2)–C(10) 1.873(3), C(1)–C(2) 1.412(3), C(1)–C(11) 1.401(3), C(2)–C(11') 1.402(3), C(3)–C(4) 1.346(3); C(1)–Si(1)–C(4) 110.8(1), C(2)–Si(2)–C(3) 111.1(1), Si(1)–C(1)–C(2) 123.9, Si(1)–C(4)–C(3) 125.3(2), Si(1)–C(4)–C(6) 112.7(2), Si(2)–C(2)–C(1) 124.1(2), Si(2)–C(3)–C(4) 124.6(2), Si(2)–C(3)–C(5) 114.3(2), C(7)–Si(1)–C(8) 108.3(2), C(9)–Si(2)–C(10) 108.0(2), C(2)–C(1)–C(11) 118.2(2), C(1)–C(2)–C(11) 118.2(2), C(1)–C(11)–C(2') 123.7(2).

under mild conditions to give the polymers in good to excellent yields. The polymer **6b** was soluble in benzene, chloroform and tetrahydrofuran. The solubility of **6a** in these solvents was dependent on the molecular mass, and was generally lower. However, **6c** was not soluble at all, and hence its structure determination is only based on elemental analysis and the comparison with **5** in the IR spectrum.

Thermogravimetric analysis (TGA, 10 °C min⁻¹ raising rate, under He stream) of the polymers revealed that T_5 's (temperature of 5% weight loss) were all higher than 420 °C.

The weights of the black residues obtained after pyrolysis up to 900 °C ranged from 24 to 62% of the originals. In addition, their differential scanning calorimetry did not indicate distinct melting points nor glass transition temperatures between 50 and 450 °C. Although mechanical properties of these polymers have not yet been evaluated, the thermal behaviour suggests that these polymers are promising as structural materials and as precursors for SiC/C composite materials.

The polymers proved to be insulators (conductivity < 10⁻¹⁰ S cm⁻¹). However, when doped with FeCl₃, the polymers exhibited electrical conductivity. Thus, the polymers suspended in nitromethane were treated with a nitromethane solution of FeCl₃. The resulting homogeneous mixture was evaporated and the residue was processed into a pellet.³ Measurement by the two-probe method showed conductivities ranging from 10⁻⁴ to 10⁻³ S cm⁻¹ at 25 °C.

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