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Synthesis of polycarbosilanes with pendant functional groups via simultaneous platinum-catalyzed hydrosilation/ ring-opening polymerization of 1-phenyl-1-silacyclobutane[†]

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Summary – Six polycarbosilanes with pendant functional groups (poly[1-(3′-phenoxypropyl)-1-phenyl-1-silabutane]; poly[1-(3′-(biphenyl-4-yloxy)propyl)-1-phenyl-1-silabutane]; poly[1-(3′-(4-nitrophenoxy)propyl)-1-phenyl-1-silabutane]; poly [1-(3′-(4-cyanophenoxy)propyl)-1-phenyl-1-silabutane]; poly[1-(3′-(4-cyanobiphenyl-4-yloxy)propyl)-1-phenyl-1-silabutane]; and poly[1-(5′-(4-cyanobiphenyl-4-yloxy)pentyl)-1-phenyl-1-silabutane]) have been prepared by platinum-catalyzed reaction of 1-phenyl-1-silacyclobutane with allyl phenyl ether, allyl biphenyl-4-yl ether, allyl 4-nitrophenyl ether, allyl 4-cyanophenyl ether, allyl 4-cyanobiphenyl-4-yl ether, and 4-pentenyl 4-cyanobiphenyl-4-yl ether, respectively. In these reactions, platinum simultaneously catalyzes the hydrosilation and ring-opening polymerization of 1-phenyl-1-silacyclobutane. The polymers have been characterized by ^{1}H, ^{13}C, ^{29}Si NMR, FTIR and UV spectroscopy. The molecular weight distributions of these polymers have been determined by gel permeation chromatography (GPC), and their glass transition temperatures (T_g) by differential scanning calorimetry (DSC).

platinum catalysis / hydrosilation / ring opening / 1-phenyl-1-silacyclobutane / polycarbosilane

Introduction and background

Polycarbosilanes are a broad class of polymers in which the polymer backbone contains silicon-carbon bonds [1]. The backbone of these polymers can be made up of diverse types of organic groups which alternate with silylene or disilylene units. Variation is possible not only in the organic units but also in the substituents bonded to silicon. The combination of possibilities makes tremendous structural variation possible. While polycarbosilanes have received less attention than either polysilanes [2, 3] or commercially significant silicone polymers [4, 5], there has been growing interest in these polymers over the last 15 years.

Anionic [6], platinum-catalyzed [7-9] and thermal polymerization [10, 11] of 1,1-dimethyl-1-silacyclobutane and related systems are well known. Ring-opening polymerization of functionally substituted silacyclobutanes is not suitable for the preparation of functionally substituted poly(1-silabutanes) due to the incompatibility of many functional groups with the synthetic methodology (Grignard cyclization) necessary to prepare silacyclobutanes [12].

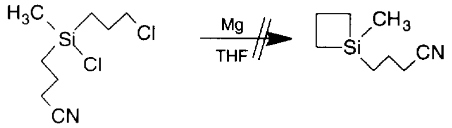

Fig 1

Previously, we have used a two-step approach to solve this problem. The first involves the anionic ring-opening polymerization of Si-H silacyclobutanes such as 1-methyl-1-silacyclobutane, 1-phenyl-1-silacyclobutane and 1-silacyclobutane to yield poly(1-methyl-1-silabutane), poly(1-phenyl-1-silabutane), and poly(1-silabutane) respectively [13]. In the second step, Si-functionally substituted polycarbosilanes have been prepared by platinum-catalyzed graft hydrosilation reactions between the Si-H polycarbosilane poly(1-methyl-1-silabutane) and functionally substituted alkenes [14]. This method is based on the chemical modification of an intact Si-H polycarbosilane. There is considerable interest in such methods since they often permit the synthesis of polymers which cannot be prepared directly [15-18].

In this paper, we report the successful synthesis of Si-functionally substituted poly(1-phenyl-1-silabutanes) in a single step process by simultaneous platinum cat-

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[†] This manuscript is dedicated to Professor Raymond Calas. Professor Calas work on the formation of carbon silicon bonds by treatment of unsaturated organic compounds with magnesium and trimethylchlorosilane in HMPT or lithium and trimethylchlorosilane in THF has made possible the preparation of numerous interesting and useful organosilicon compounds. Professor Calas' work has been a major contribution to the development of Organosilicon Chemistry.

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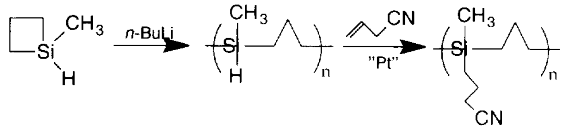


Fig 2

alyzed ring opening polymerization and hydrosilation of 1-phenyl-1-silacyclobutanes with functionally substituted alkenes. While we do not know which step proceeds first or if they occur competitively, the method described herein constitutes an efficient method to prepare functionally substituted poly(1-phenyl-1-silabutanes).

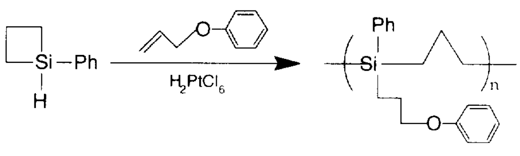


Fig 3

Experimental section

^{1}H and ^{13}C NMR spectra were run on a Bruker AM-250 spectrometer operating in the Fourier transform (FT) mode. ^{13}C NMR spectra were run with broad-band proton decoupling. ^{29}Si NMR spectra were recorded on an IBM-Bruker 270-SY spectrometer. ^{29}Si NMR spectra were obtained by use of a heteronuclear gated decoupling pulse sequence (INVGATE) with a relaxation delay of 15-30 s [19]. All spectra were run using 10% chloroform-*d* solution. Chloroform was used as an internal standard for ^{1}H and ^{13}C NMR spectra. ^{29}Si NMR spectra were externally referenced to TMS.

IR spectra of neat films on NaCl plates were recorded on an IBM FTIR/30s, DTGS/CSI spectrometer. UV spectra of THF solutions were recorded on a Milton Roy-3000/Spectronic Array.

Gel permeation chromatographic analysis (GPC) of the molecular weight distribution of the polymers was performed on a Waters system, comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 differential refractive index detector and a Maxima 820 control system. A series of three 7.8 mm × 30 cm columns packed with < 10 μm particles of monodisperse crosslinked styrene/divinyl benzene copolymer. These contain pore sizes of 1×10^4 Å (Waters Ultrastyragel), 1×10^3 Å (Waters Ultrastyragel) and finally 500 Å (Polymer Laboratories PLgel). The elution solvent was HPLC grade THF at a flow rate of 0.7 mL/min. The retention times were calibrated against known monodisperse polystyrene standards : M_w = 612,000; 114,200; 53,100; 18,700; 5,120; and 2,200 whose M_w/M_n are less than 1.09.

The glass transition temperatures (T_gs) of the polymers were determined on a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC). The melting points of indium (mp 156°C) and spectral grade *n*-hexane (mp −95°C) were used to calibrate the DSC. Temperature scans were begun at −100°C. The temperature was increased at a heating rate of 10°C/min to 150°C.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGS-2 instrument. The temperature program for the analysis was at 50°C for 10 min followed by an increase of 4°C/min to 800°C with a nitrogen flow rate of 40 cc/min.

GC/MS analysis was performed on a Hewlett-Packard 5871A instrument which was equipped with a MSD. The gas chromatograph inlet was furnished with a 30 m × 25 μ film thickness DB-5 column. Helium at a linear velocity of 20 m/min was used as the carrier gas. The temperature program was 60°C for 3 min, followed by an increase of 15°C/min to 240°C. High resolution mass spectra were run at the University of California Riverside Mass Spectrometry Facility on a VG-7070 EHF mass spectrometer at an ionizing voltage of 70 eV. Exact masses were determined by peak matching against known masses of perfluorokerocene.

Elemental analysis was performed by Oneida Research Services, Inc, Whitesboro, NY.

All reactions were conducted under an atmosphere of purified nitrogen. All glassware was flamed out under dry nitrogen before use. THF was distilled immediately before use from a deep blue solution of sodium benzophenone ketyl. Allyl chloride, allyl phenyl ether, chlorotrimethylsilane, 4-nitrophenol, 4-cyanophenol, 4-phenylphenol, 4′-hydroxy-4-biphenylcarbonitrile, 5-bromo-1-pentene, and chloroplatinic acid were purchased from Aldrich.

1-Phenyl-1-silacyclobutane [13], allyl *p*-nitrophenyl ether [20], allyl *p*-cyanophenyl ether [20], allyl *p*-biphenylyl ether [21], and allyl 4-cyanobiphenyl-4-yl ether [21], were prepared following literature methods.

4-Pentenyl p-*cyanobiphenylyl ether*

In a 50 mL round-bottomed flask equipped with a Teflon covered magnetic stirring bar was placed potassium hydroxide (0.6 g, 10.7 mmol), water (15 mL), 5-bromo-1-pentene (1.5 g, 10 mmol), 4′-hydroxybiphenyl-4-carbonitrile (1.9 g, 9.7 mmol), THF (15 mL) and tetra-*n*-butylammonium bromide (0.3 g, 2 mmol) as a phase-transfer catalyst. The reaction was stirred at room temperature for 48 h. The reaction mixture was extracted with three 40 mL aliquots of ethyl ether. The combined organic extracts were dried over anhydrous magnesium sulfate, filtered and the volatile solvents removed by evaporation under reduced pressure. In this way, 1.8 g of crude product was obtained. The material was purified by chromatography on a silica gel column using pentane/ether (4:1) as eluent. In this way, 1.5 g, 58% of product was obtained. It had the following properties.

IR ν : 3 074, 2 928, 2 222, 1 698, 1 640, 1 604, 1 579, 1 553, 1 519, 1 495, 1 469, 1 440, 1 394, 1 314, 1 291, 1 245, 1 181, 1 115, 1 055, 1 001, 954, 924, 913, 856, 850, 832, 821, 814, 701 cm^{-1}.

UV λ_{max} nm (ε) : 228 (6 580), 285 (7 980).

High resolution MS ($M^{+\cdot}$) Calc for $C_{18}H_{17}NO$: 263.131. Found : 263.132.

^{1}H NMR δ : 1.90 (dt, 2H, J = 13 and 7 Hz), 2.24 (q, 2H, J = 7 Hz), 4.00 (t, 2H, J = 6.4 Hz), 4.99 (d, 1H, J = 10 Hz), 5.05 (d, 1H, J = 17 Hz), 5.84 (ddt, 1H, J = 17, 10, and 7 Hz), 6.97 (d, 2H, J = 9 Hz), 7.50 (d, 2H, J = 9 Hz), 7.64 (dd, 4H, J = 15 and 8.5 Hz).

^{13}C NMR δ : 28.32, 30.06, 67.28, 110.01, 115.06, 115.32, 119.12, 127.06, 128.31, 131.33, 132.56, 137.66, 145.24, 159.68.

Poly[1-(3′-phenoxypropyl)-1-phenyl-1-silabutane]

In a 25 mL round-bottomed flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar was placed 1-phenyl-1-silacyclobutane (0.84 g, 5.67 mmol) and allyl phenyl ether (0.76 g, 5.67 mmol). A THF solution (10 mL) of chloroplatinic acid (5 mg, 10^{-2} mmol) and chlorotrimethylsilane (1 g, 9 mmol) was then added to the flask. After 0.5 h of reflux, THF and excess chlorotrimethylsilane were distilled out at 90°C. During this distillation the color of the reaction mixture became darker. The mixture was stirred at 90°C for 24 h. During this time it became very viscous. The crude polymer, 1.66 g, 100% yield, was dissolved in THF and was chromatographed through a short column of silica gel to remove the platinum catalyst. The polymer was purified by precipitation three times from chloroform solution by addition of pentane. The polymer was then triturated three times with ethyl ether to remove oligomers. In this way, 1.21 g, 73% yield of light yellow polymer, $M_w/M_n = 13{,}000/6{,}900$; $T_g = -7°C$ was obtained.

IR ν : 3 068, 3 042, 2 917, 2 875, 1 601, 1 586, 1 498, 1 471, 1 456, 1 428, 1 413, 1 387, 1 337, 1 302, 1 290, 1 245, 1 272, 1 141, 1 110, 1 079, 1 034, 941, 904, 797, 754, 737, 701, 692 cm^{-1}.

UV λ_{max} nm (ε) : 239 (3 300), 265 (10 100), 280 (3 700).

^{1}H NMR δ : 0.80 (s, 6H), 1.33 (s, 2H), 1.71 (s, 2H), 3.79 (s, 2H), 6.85 (s, 2H), 6.93 (s, 1H), 7.27 (s, 7H).

^{13}C NMR δ : 8.30, 17.08, 18.21, 23.69, 70.19, 114.34, 120.36, 127.68, 127.79, 128.77, 128.90, 133.94, 158.93.

^{29}Si NMR δ : −3.92, −2.89, −1.82.

Elemental Anal calc for $C_{18}H_{22}OSi$: C, 76.53; H, 7.87. Found : C, 74.29; H, 7.85.

Poly[1-(3′-(biphenyl-4-yloxy)propyl)-1-phenyl-1-silabutane]

In a 25 mL round-bottomed flask fitted with a reflux condenser and a Teflon-covered stirring bar was placed 1-phenyl-1-silacyclobutane (1.04 g, 7.03 mmol) and allyl biphenyl ether (1.52 g, 7.23 mmol). A THF (10 mL) solution of chloroplatinic acid (5 mg, 10^{-2} mmol) and chlorotrimethylsilane (2 g, 18 mmol) was added to the flask. After 0.5 h at reflux, THF and excess chlorotrimethylsilane were distilled off at 90°C. During the distillation, the color of the reaction mixture turned from light yellow to orange red. The mixture was stirred at 80°C for 24 h while the temperature was allowed to rise to 100°C. After another 24 h of stirring at 100°C, the contents of the flask had become very viscous. A THF solution of the crude polymer was passed through a short column of a silica gel to remove platinum catalyst. The crude polymer, 2.3 g, 90% yield, was purified by precipitation three times from chloroform solution by addition of pentane. After that the polymer was triturated three times with ethyl ether to remove oligomers. In this way, a light yellow polymer, 1.70 g, 65% yield, $M_w/M_n = 24{,}400/15{,}300$; $T_g = 32°C$ was obtained.

IR ν : 3 068, 3 032, 2 920, 2 875, 1 610, 1 584, 1 569, 1 519, 1 487, 1 471, 1 451, 1 428, 1 412, 1 387, 1 291, 1 270, 1 246, 1 185, 1 176, 1 141, 1 110, 1 046, 1 028, 1 013, 1 004, 994, 941, 907, 833, 763, 698, 668, 640 cm^{-1}.

UV λ_{max} nm (ε) : 214 (14 100), 263 (16 800).

^{1}H NMR δ : 0.97 (s, 6H), 1.50 (s, 2H), 1.87 (s, 2H), 3.95 (s, 2H), 7.01 (s, 2H), 7.40-7.62 (m, 12H).

^{13}C NMR δ : 8.27, 17.09, 18.25, 23.63, 70.36, 114.62, 126.54, 127.69, 127.80, 127.95, 128.62, 128.80, 133.27, 133.93, 137.00, 140.66, 158.58.

^{29}Si NMR δ : −3.07, −2.85, −1.84.

Elemental anal calc for $C_{24}H_{26}OSi$: C, 80.39; H, 7.32. Found : C, 78.53; H, 7.62.

Poly[1-(3′-(4-nitrophenoxy)propyl)-1-phenyl-1-silabutane]

In a 25 mL round-bottomed flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar was placed 1-phenyl-1-silacyclobutane (1.01 g, 6.82 mmol) and allyl *p*-nitrophenyl ether (1.23 g, 6.87 mmol). A THF solution (10 mL) of chloroplatinic acid (5 mg, 10^{-2} mmol) and chlorotrimethylsilane (2 g, 18 mmol) was then added to the flask. After an hour of reflux, THF and excess chlorotrimethylsilane were removed by distillation at 85°C. During the distillation, the color of the reaction mixture became darker. The mixture was stirred at 85°C for 12 h. During this time, the reaction mixture became quite viscous. The reaction temperature was then raised to 100°C for another 36 h. A THF solution of the crude polymer was passed through a short column of a silica gel to remove the platinum catalyst. The resulted crude polymer, 2.0 g, 85% yield, was purified by precipitation three times from chloroform solution by addition of pentane. The polymer was then triturated three times with ethyl ether to remove oligomers. In this way, light yellow polymer, 1.59 g, 68% yield, $M_w/M_n = 13{,}800/7{,}200$; $T_g = 23°C$ was obtained.

IR ν : 3 070, 3 050, 3 018, 2 922, 2 876, 1 607, 1 592, 1 511, 1 498, 1 468, 1 428, 1 342, 1 297, 1 264, 1 174, 1 142, 1 111, 1 046, 998, 909, 845, 796, 753, 735, 701, 653 cm^{-1}.

UV λ_{max} nm (ε) : 220 (8 300), 308 (8 600).

^{1}H NMR δ : 0.79 (s, 6H), 1.33 (s, 2H), 1.67 (s, 2H), 3.83 (m, 2H), 6.81 (s, 2H), 7.28 (s, 5H), 8.11 (s, 2H).

^{13}C NMR δ : 8.15, 16.74, 18.11, 23.31, 70.86, 114.17, 125.72, 127.69, 128.86, 133.20, 133.80, 141.07, 163.84.

^{29}Si δ : −3.95, −2.99, −1.84.

Elemental anal calc for $C_{18}H_{21}NO_3Si$: C, 66.01; H, 6.47; N, 4.28. Found : C, 64.34; H, 6.31; N, 3.56.

Poly[1-(3′-(4-cyanophenoxy)propyl)-1-phenyl-1-silabutane]

In a 10 mL round-bottomed flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar was placed 1-phenyl-1-silacyclobutane (1.02 g, 6.89 mmol) and allyl *p*-cyanophenyl ether (1.16 g, 7.29 mmol). A THF (10 mL) solution of chloroplatinic acid (5 mg, 10^{-2} mmol) and chlorotrimethylsilane (2 g, 18 mmol) was then added to the flask. After 2 h of reflux, most of the THF and excess chlorotrimethylsilane were removed by distillation at 90°C. During the distillation, the color of the reaction mixture became darker. The reaction mixture was stirred at 90-100°C for 72 h. A THF solution of the crude product, 2.0 g, 91% yield, was passed though a short column of silica gel to remove the platinum catalyst. The polymer was purified by precipitation three times from chloroform solution by addition of pentane. The polymer was then triturated three times with ethyl ether to remove oligomers. The very sticky purified polymer, 1.37 g, 63% yield, $M_w/M_n = 6{,}600/5{,}500$; $T_g = 5°C$ was obtained.

IR ν : 3 069, 3 048, 3 017, 2 920, 2 875, 2 797, 2 224, 1 607, 1 574, 1 510, 1 469, 1 428, 1 419, 1 303, 1 259, 1 172, 1 142, 1 112, 1 047, 998, 942, 909, 835, 790, 702 cm^{-1}.

UV λ_{max} nm (ε) : 212 (9 000), 248 (16 700).

^{1}H NMR δ : 0.79 (br s, 4H), 1.11 (br s, 2H), 1.32 (br s, 2H), 1.73 (br s, 2H), 3.86 (br s, 2H), 6.82 (br s, 2H), 7.24-7.33 (br s, 5H), 7.50 (br s, 2H).

^{13}C NMR δ : 8.13, 16.88, 18.09, 23.27, 70.48, 103.36, 114.93, 119.00, 127.59, 128.75, 133.17, 133.70, 136.80, 162.02.

^{29}Si NMR δ : −3.90, −2.89, −1.74.

Elemental anal calc for $C_{19}H_{21}NOSi$: C, 74.21; H, 6.90; N, 4.56. Found : C, 71.76; H, 6.62; N, 4.02.

Poly[1-(3′-(4-cyanobiphenyl-4-yloxy)propyl)-1-phenyl-1-silabutane]

In a 10 mL round-bottomed flask fitted with a reflux condenser and a Teflon-covered magnetic stirring bar was placed

1-phenyl-1-silacyclobutane (0.17 g, 1.15 mmol) and allyl cyanobiphenylyl ether (0.28 g, 1.21 mmol). A THF solution (5 mL) of chloroplatinic acid (1 mg, 2×10^{-3} mmol) and chlorotrimethylsilane (0.5 g, 4.5 mmol) was then added to the flask. After 0.5 h of reflux, most of the THF and chlorotrimethylsilane were removed by distillation at 95°C. During the distillation, the color of the reaction mixture turned from colorless to yellow. The reaction mixture was stirred at 110°C for 48 h. During this time the reaction mixture became very viscous. A THF solution of the crude polymer was passed through a short column of silica gel to remove the platinum catalyst. The polymer, 0.35 g, 78% yield, was purified by precipitation three times from chloroform solution by addition of pentane. The polymer was then triturated three times with ethyl ether to remove oligomers. In this way, light yellow polymer, 0.28 g, 63% yield, $M_w/M_n = 5{,}400/4{,}700$; $T_g = -9.9°C$ was obtained.

IR ν : 3 070, 3 045, 2 924, 2 872, 2 226, 1 890, 1 725, 1 657, 1 604, 1 581, 1 520, 1 495, 1 469, 1 428, 1 405, 1 315, 1 290, 1 250, 1 180, 1 114, 1 064, 999, 910, 823, 737, 702 cm^{-1}.

UV λ_{max} nm (ε) : 235 (3 200), 297 (17 000).

^1H NMR δ : 0.83 (s, 4H), 1.28 (s, 2H), 1.35 (s, 2H), 1.71 (s, 2H), 3.85 (s, 2H), 6.90 (s, 2H), 7.31-7.60 (m, 11H).

^{13}C NMR δ : 8.37, 16.88, 18.27, 23.65, 70.27, 110.03, 114.99, 118.96, 126.93, 127.80, 128.22, 131.17, 128.22, 131.17, 132.48, 133.33, 133.94, 134.75, 145.01, 159.58.

^{29}Si NMR δ : −2.89.

Elemental anal calc for $C_{25}H_{25}NOSi$: C, 78.28; H, 6.57; N, 3.65. Found : C, 76.21; H, 6.70; N, 3.44.

Poly[1-(5'-(4-cyanobiphenyl-4-yloxy)pentyl)-1-phenyl-1-silabutane]

In a 10 mL round-bottomed flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar was placed 1-phenyl-1-silacyclobutane (0.17 g, 1.14 mmol) and 4-pentenyl *p*-biphenyl-4-yl ether (0.30 g, 1.14 mmol). A THF (10 mL) solution of chloroplatinic acid (1 mg, 2×10^{-3} mmol) and chlorotrimethylsilane (0.5 g, 4.5 mmol) was then added to the flask. After 0.5 h of reflux, most of the THF and excess chlorotrimethylsilane were removed by distillation at 100°C. During the distillation, the color of the reaction mixture became darker. The mixture was stirred at 110°C for 72 h. During this time, the reaction mixture became very viscous. A THF solution of the crude polymer was passed through a short column of silica gel to remove the platinum catalyst. The polymer, 0.36 g, 75% yield, was purified by precipitation three times from chloroform solution by addition of pentane. The polymer was then triturated three times with ethyl ether to remove oligomers. A light yellow polymer, 0.29 g, 61% yield, $M_w/M_n = 5{,}000/4{,}300$; $T_g = 11.5°C$ was obtained.

IR ν : 3 068, 3 045, 2 921, 2 872, 2 226, 1 888, 1 604, 1 581, 1 524, 1 495, 1 473, 1 428, 1 404, 1 314, 1 292, 1 251, 1 181, 1 112, 1 067, 1 033, 1 000, 985, 905, 852, 823, 737, 701 cm^{-1}.

UV λ_{max} nm (ε) : 209 (6 000), 223 (4 900), 297 (12 600).

^1H NMR δ : 0.82 (s, 6H), 1.37 (s, 2H), 1.46 (s, 4H), 1.76 (s, 2H), 3.94 (s, 2H), 6.96 (s, 2H), 7.33 (s, 5H), 7.50 (s, 2H), 7.62 (s, 2H), 7.66 (s, 2H).

^{13}C NMR δ : 12.32, 17.21, 18.26, 23.56, 28.74, 29.94, 68.01, 109.92, 114.98, 118.95, 126.90, 127.59, 128.18, 128.62, 131.10, 132.43, 133.30, 133.92, 145.07, 159.66.

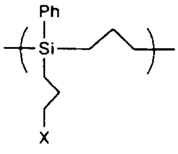
^{29}Si NMR δ : −4.03, −3.42, −2.85.

Elemental anal calc for $C_{27}H_{29}NOSi$: C, 78.78; H, 7.10; N, 3.40. Found : C, 77.11; H, 7.05; N, 3.11.

Results and discussion

In this paper, we report the novel preparation and properties of six saturated polycarbosilanes which have pendant functional groups. These Si-functionally substituted poly(1-phenyl-1-silabutanes) have been prepared by platinum catalyzed simultaneous hydrosilation and ring-opening polymerization reactions of 1-phenyl-1-silacyclobutane with either ω-functionally substituted 1-alkenes. In this way, good yields of polycarbosilanes with reasonable molecular weights were obtained (see table I). From an architectural point of view, these are comb polymers.

Table I. Molecular weights and glass transition temperatures of the polycarbosilanes obtained.

	M_w/M_n	T_g°C
Ph–O–	13.000/6.900	−7
p-Ph–Ph–O–	24.400/15.300	32
p-O_2N–Ph–O–	13.800/7.200	23
p-NC–Ph–O–	6.600/5.500	5
p-NC–Ph–Ph–O–	5.400/4.700	−9.9
p-NC–Ph–Ph–O–$(CH_2)_2$–	5.000/4.300	11.5

Trimethylchlorosilane was added to remove water by formation of hexamethyldisiloxane and HCl. Excess trimethylchlorosilane, hydrochloric acid, and THF were removed by distillation. In every case the elemental analysis results for carbon are low. Similar low carbon analysis have been previously observed in graft hydrosilation of Si-H polycarbosilanes with functional alkenes [22]. This may result from a platinum-catalyzed side reaction between adventitious water and Si-H bonds of poly(1-phenyl-1-silabutane). This results in formation of silanol (Si-OH) bonds which would undergo dehydration to form siloxane bonds [23].

The ^{29}Si NMR spectra of these polymers can be understood on the basis of triad analysis. Three resonances are observed in every case except poly[1-(3'-(4-cyanobiphenyl-4-yloxy)propyl)-1-phenyl-1-silabutane]. The intensity ratio of these peaks is close to the predicted 1:2:1 (fig 4). Evidently silicon is sensitive to the chirality of the adjacent silyl centers.

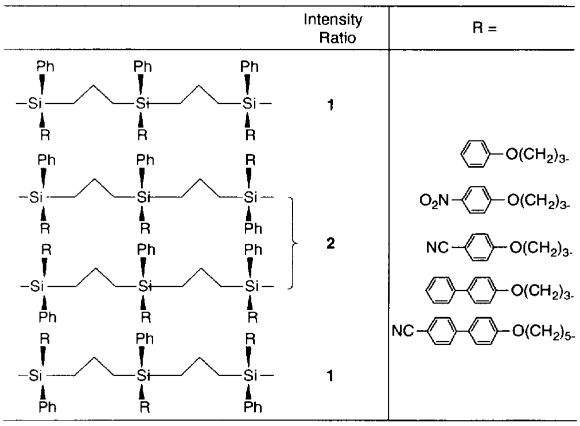


Fig 4

Liquid crystalline behavior is observed in the DSC of poly[1-(3′-phenoxypropyl)-1-phenyl-1-silabutane], poly [1-(3′-(4-cyanophenoxy)propyl)-1-silabutane], and poly[1-(3′-biphenoxypropyl)-1-silabutane]. On initial heating, in addition to T_g at −7°C, poly[1-(3′-(biphenyl-4-yloxy)propyl)-1-phenyl-1-silabutane] shows a T_{m1} at 17°C and a T_{m2} at 25°C (see figures). On cooling, a single broad exothermic transition at −7°C is detected. On the other hand, on initial heating of poly[1-(3′-(4-cyanophenoxy)propyl)-1-phenyl-1-silabutane] in addition to T_g at 5°C, three endothermic transitions are observed at 14, 21, and 85°C. On heating poly[1-(3′-(biphenyl-4-yloxy)propyl)-1-phenyl-1-silabutane] in addition to T_g at 32°C, a second endothermic transition at 96°C is detected. Liquid crystalline materials demonstrate unusual phase behavior which combines properties of the homogeneous liquid and the ordered crystalline states [24, 25]. Polymeric side chain [26-28] liquid crystalline materials comprised of a highly flexible, low T_g, siloxane backbone in which the silyl centers are substituted with pendant aryl or aryloxy mesogenic groups have been prepared [26, 29]. These materials represent an important class of side chain liquid crystalline polymers because of their many desirable properties.

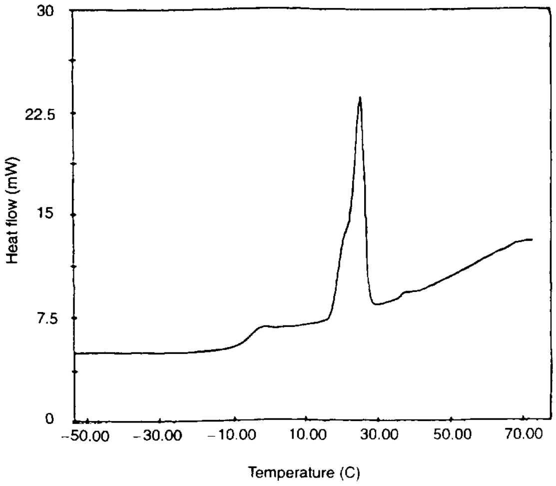


Fig 5. DSC of poly[1-(3′-phenoxypropyl)-1-phenyl-1-silabutane].

Acknowledgments

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