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Poly(1-methyl-3,4-methylene-1-phenyl-1-sila-cis-pent-3-ene) (H_2C-I) has been prepared by cyclopropanation of the C-C double bonds of poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene) (I) by a Simmons-Smith reaction. Alternatively, H_2C-I can be prepared by a Birch reduction of the dichlorocarbene adduct of I, poly(3,4-dichloromethylene-1-methyl-1-phenyl-1-sila-cis-pent-3-ene) (Cl_2C-I). Both H_2C-I and Cl_2C-I have been characterized by 1H , ^{13}C and ^{29}Si NMR, IR and UV spectroscopy as well as by elemental analysis. Their molecular weight distributions have been determined by GPC and their thermal stabilities by TGA.

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APPENDIX I

Cyclopropanation of poly(1-Methyl-1-phenyl-1-sila-cis-pent-3-ene)
- Synthesis and Characterization of poly(1-Methyl-3,4-methylene-
1-phenyl-1-sila-cis-pent-3-ene).

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SUMMARY:

Poly(1-methyl-3,4-methylene-1-phenyl-1-sila-cis-pent-3-ene)
(H₂C-I) has been prepared by cyclopropanation of the C-C double
bonds of poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene) (I) by a
Simmons-Smith reaction. Alternatively, H₂C-I can be prepared by a
Birch reduction of the dichlorocarbene adduct of I, poly(3,4-
dichloromethylene-1-methyl-1-phenyl-1-sila-cis-pent-3-ene)
(Cl₂C-I). Both H₂C-I and Cl₂C-I have been characterized by ¹H,
¹³C and ²⁹Si NMR, IR and UV spectroscopy as well as by elemental
analysis. Their molecular weight distributions have been deter-
mined by GPC and their thermal stabilities by TGA.

Introduction

There is considerable interest in the chemical modification
of polymers ¹⁻⁴). While it has been possible to stereospecifically
quantitatively add dichlorocarbene to the C-C double bonds of
1,4-polybutadiene ⁵⁻⁸) as well as to those of poly(1,1-dimethyl-
1-sila-cis-pent-3-ene) (II) ⁹), it has not been possible to
achieve complete cyclopropanation of the C-C double bonds of
either 1,4-polybutadiene or II by use of the Simmons-Smith reac-
tion ¹⁰).

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Experimental

Analytical techniques:

^1H , ^{13}C and ^{29}Si NMR spectra were obtained either on a Bruker AM-360 or an IBM Bruker WP-270-SY spectrometer operating in the Fourier transform mode. Five to ten percent weight/volume solutions of polymers $\text{Cl}_2\text{C-I}$ and $\text{H}_2\text{C-I}$ in chloroform-*d* were used to obtain ^1H NMR spectra, whereas ten to fifteen percent solutions were utilized for ^{13}C and ^{29}Si NMR spectra. ^{13}C NMR spectra were run with broad band proton decoupling. Chloroform was used as an internal standard for ^1H and ^{13}C NMR spectra. ^{29}Si NMR spectra were externally referenced to TMS. A heteronuclear gated decoupling pulse sequence with a pulse delay of 20 sec (NONOE) was used to obtain ^{29}Si NMR spectra ¹¹). IR spectra were obtained on a Perkin-Elmer 281 spectrometer. Spectra were taken on neat films on NaCl plates. UV spectra were recorded on a Shimadzu UV-260 spectrometer.

Gel permeation chromatographic (GPC) analysis of the molecular weight distribution of the polymers was performed on a Waters system comprised of a U6K injector, 510 HPLC solvent deliver system, R401 refractive index detector, and a model 820 Maxima Control System. A Waters 7.8 mm x 30 cm, 10 μm particle size, mixed pore size, crosslinked polystyrene gel column was used for the separation. The eluting solvent was reagent THF at a flow rate of 0.6 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p 110,000; 20,400; 4,800; 1,350 whose M_w/M_n are less than 1.09.

Thermogravimetric analysis (TGA) of the polymers was carried

out on a Perkin-Elmer TGS-2 instrument at an Argon flow rate of 40 cm³/min. The temperature program for the analysis was 50°C for 10 min followed by an increase of 4°C/min to 700°C.

Elemental analysis was performed by Galbraith Laboratories Knoxville, TN.

Syntheses:

Di-*n*-butyl ether (Aldrich) and tetrahydrofuran (THF) were distilled from deep blue solutions of sodium benzophenone ketyl immediately prior to use. All reaction were carried out under an atmosphere of purified nitrogen in flame dried glassware.

poly(1-Methyl-1-phenyl-1-sila-cis-pent-3-ene (I)

I was obtained by the anionic ring opening polymerization of 1-methyl-1-phenyl-1-silacyclopent-3-ene, $M_w/M_n = 134,000/69,000$ or $M_w/M_n = 113,000/68,000$ in successive preparations ¹²). It was stored at 0°C in the dark under Argon.

poly(1-Methyl-3,4-methylene-1-phenyl-1-sila-cis-pent-3-ene) (H₂C-I).

In a 100 mL three neck rb flask equipped with a Teflon covered magnetic stirring bar and a reflux condenser was placed 60 mL of di-*n*-butyl ether, I (0.44 g, 2.5 mmol), diiodomethane (6.7 g, 25 mmol), zinc powder (1.6 g, 25 mmol) and cuprous chloride (0.25 g, 2.5 mmol) ¹³). The mixture was heated to reflux with stirring for 5 h. The mixture was cooled to rt and the solids were removed by filtration. They were washed with ether (2 x 20 mL). The combined organic layer was washed with water (2 x 30 mL), dried over anhydrous magnesium sulfate, filtered and the solvents removed by evaporation under reduced pressure. The residue was dissolved in THF and H₂C-I was precipitated from

methanol. This process was repeated. H₂C-I was dried under vacuum for 24 h. In this way, 0.38 g, 81% yield was obtained $M_w/M_n = 4,500/3,000$. H₂C-I had the following spectral properties. ¹H NMR δ : -0.49(s,1H), 0.34(s,3H), 0.41-0.46(br.m,2H), 0.62(s,3H), 0.95(br.m, 2H), 7.32(s,3H), 7.51(s,2H). ¹³C NMR δ : -4.78, -4.62, -4.41, 11.30, 12.86, 12.91, 13.19, 14.88, 14.94, 15.00, 15.05, 127.56, 128.66, 133.96, 138.99, 139.09, 139.20. ²⁹Si NMR δ : -0.05, -0.32, -0.42. IR ν : 3080, 3060, 3000, 2960, 2910, 2880, 1430, 1360, 1250, 1190, 1115, 1030, 820, 740, 700 cm⁻¹. UV (spectra quality hexane) λ_{max} nm (ϵ) : 270(80), 266 (118), 260(92). Elemental Anal. Calc. for C₁₂H₁₆Si: C, 76.52; H, 8.56. Found: C, 75.54; H, 8.86.

This reaction was also carried out as above with I (0.44 g, 2.5 mmol), diiodomethane (3.3 g, 12.5 mmol), zinc powder (0.8 g, 12.5 mmol) and cuprous chloride (0.12 g, 1.25 mmol). The reaction was heated to reflux for 12 h. In this way, H₂C-I was obtained with $M_w/M_n = 6,500/5,000$. Finally, the reaction was repeated as above with I (0.44 g, 2.5 mmol), diiodomethane (1.3 g, 5.0 mmol), zinc powder (0.33 g, 5 mmol), and cuprous chloride (50 mg, 0.5 mmol). The reaction was heated to reflux for 12 h. In this way, a 50% cyclopropaned polymer was obtained, $M_w/M_n = 8,160/4,750$. The extent of cyclopropanation was determined by ¹H NMR integration.

Reaction of poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene) with Zinc Iodide

In a 100 mL rb flask equipped with a reflux condenser and a Teflon covered magnetic stirring bar was placed 0.43 g (2.5 mmol) of I ($M_w/M_n = 113,000/68,000$) in 60 mL of di-*n*-butyl ether. To

this mixture was added 4 g (12.5 mmol) of zinc iodide. The reaction was stirred and heated to reflux for 5 h. After cooling to rt, the mixture was filtered to remove salts and the organic layer was washed with two 30 mL aliquots of distilled water. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent was removed by evaporation under reduced pressure. The residue was taken up in a minimum volume of THF and I was precipitated from methanol. This purification procedure was repeated twice. I was dried under vacuum for 12 h. In this way, 0.42 g, a 98% yield of I ($M_w/M_n = 20,870/13,830$) was obtained. The ^1H NMR of recovered I was identical with that of starting I. *poly(3,4-Dichloromethylene-1-methyl-1-phenyl-cis-pent-3-ene)* ($\text{Cl}_2\text{C-I}$)

In a 300 mL three neck rb flask equipped with a pressure equalizing addition funnel and a Teflon covered magnetic stirring bar was placed I (11.5 mmol, 2.0 g) ($M_w/M_n = 113,000/68,000$) methylene chloride 120 mL, chloroform 60 mL and tetra-*n*-butylammonium bromide 0.2 g. The mixture was vigorously stirred and was cooled to -10°C . To this mixture was slowly added a solution comprised of 25.5 g of potassium hydroxide dissolved in 24 mL of water. The addition rate was controlled so that temperature of the reaction mixture was maintained at -10°C . The reaction was stirred at -10°C for 4 h. The organic layer was separated and was washed several times with an equal volume of ice-water until the aqueous layer was neutral. The organic layer was separated, dried over anhydrous magnesium sulfate, filtered and the volatile organic solvents removed by evaporation under reduced pressure. $\text{Cl}_2\text{C-I}$ was dissolved in THF and purified by precipitation from

methanol. This process was repeated. In this way, 1.95 g, a 66% yield of $\text{Cl}_2\text{C-I}$ was obtained. It had the following properties. $M_w/M_n = 62,600/35,300$. $^1\text{H NMR } \delta$: 7.48(br.s,2H), 7.38(br.s,3h), 1.52(br.s,2H), 0.85(br.s,2H), 0.77(br.s,2H), 0.47(br.s,3H). $^{13}\text{C NMR } \delta$: -5.54, -5.11, -4.55, 9.08, 9.40, 9.72, 29.51, 67.92, 67.96, 127.98, 129.51, 133.89, 136.17, 136.22. $^{29}\text{Si NMR } \delta$: -1.38 and -1.65. IR ν : 3070, 3049, 3000, 2957, 2887, 1428, 1409, 1256, 1184, 1114, 972, 839 and 700 cm^{-1} . UV (THF) λ_{max} nm (ϵ): 271.4 (260), 265.8(390), 259.6(435), 253.6(425). Elemental Anal. Calc. for $\text{C}_{11}\text{H}_{14}\text{SiCl}_2$: C, 56.03; H, 5.49; Cl, 27.56. Found: C, 55.81; H, 5.65; Cl, 27.52.

Synthesis of $\text{H}_2\text{C-I}$ by Birch Reduction of $\text{Cl}_2\text{C-I}$.

In a 500 mL three neck rb flask equipped with a cold finger reflux condenser and pressure equalizing addition funnel was placed 1.6 g (70 mmol) of freshly prepared sodium dispersion and 150 mL of THF and a glass covered magnetic stirring bar. Dry ice and acetone were added to the cold finger condenser. The flask was partially immersed in a Dewar flask containing dry ice and acetone. Ammonia gas was condensed into the flask until a deep blue color appeared. The reaction mixture was stirred and the temperature was maintained at -78°C while a solution of 1.8 g (7 mmol) of $\text{Cl}_2\text{C-I}$ in 120 mL of THF was slowly added. The reaction was stirred while the temperature was maintained at -78°C for 3.5 h. It was then allowed to slowly warm to rt. The THF solution was decanted from the unreacted lumps of sodium. These were washed with ether. The combined organic layer was washed several times with saturated ammonium chloride. It was separated, dried over

anhydrous magnesium sulfate, filtered and the solvents removed by evaporation under reduced pressure. $\text{H}_2\text{C-I}$ was dissolved in THF and was purified by precipitation from methanol. $\text{H}_2\text{C-I}$ was dried under vacuum overnight. In this way, 1.13 g, 86% yield of $\text{H}_2\text{C-I}$ ($M_w/M_n = 60,900/21,300$) was obtained. Its spectral properties were in complete agreement with those of $\text{H}_2\text{C-I}$ prepared by the Simmons-Smith reaction above.

Results and discussion

We have been able to achieve quantitative stereospecific *cis*-cyclopropanation of the C-C double bonds of I to yield $\text{H}_2\text{C-I}$ by utilization of the Simmons-Smith reaction ^{13,14}). Unfortunately, the molecular weight of $\text{H}_2\text{C-I}$ ($M_w/M_n = 4,500/3,000$) is considerably decreased compared to the starting polymer I ($M_w/M_n = 134,000/69,000$). It is well known that allylic silanes undergo electrophilic cleavage ¹⁵). In a control experiment I ($M_w/M_n = 113,000/68,000$) was treated with zinc iodide as above. The molecular weight of recovered I was significantly decreased ($M_w/M_n = 20,870/13,830$). This demonstrates that the Lewis acid, zinc iodide, generated in the Simmons-Smith reaction is able to cleave the allylic Si-C sigma bonds of the backbone of I.

Alternatively, we have prepared $\text{H}_2\text{C-I}$ by a two step process. Addition of dichlorocarbene, generated under phase transfer catalysis (PTC), to I yields $\text{Cl}_2\text{C-I}$. We have found that polymer scission is minimized by maintaining low temperature (-10°C) during both the reaction and workup. Even with this precaution the molecular weight of $\text{Cl}_2\text{C-I}$ ($M_w/M_n = 62,600/35,300$) is approximately half that of the precursor polymer I ($M_w/M_n = 113,000/68,000$). A dramatic effect of reaction temperature on the

molecular weight of $\text{Cl}_2\text{C-I}$ is observed. Thus when this reaction is conducted at 0°C the molecular weight of $\text{Cl}_2\text{C-I}$ is $M_w/M_n = 24,000/7,400$. Scission of I may partially result from nucleophilic attack by hydroxide ion on a silyl center with loss of an allylic anion. Transfer of hydroxide anion into organic solvents has been suggested to occur under PTC conditions (16,17).

$\text{Cl}_2\text{C-I}$ ($M_w/M_n = 62,600/35,300$) has been converted to $\text{H}_2\text{C-I}$ by a Birch reduction with sodium in liquid ammonia. Little or no degradation of polymer occurs in this process ($\text{H}_2\text{C-I}$, $M_w/M_n = 60,900/21,000$) (Fig. 1).

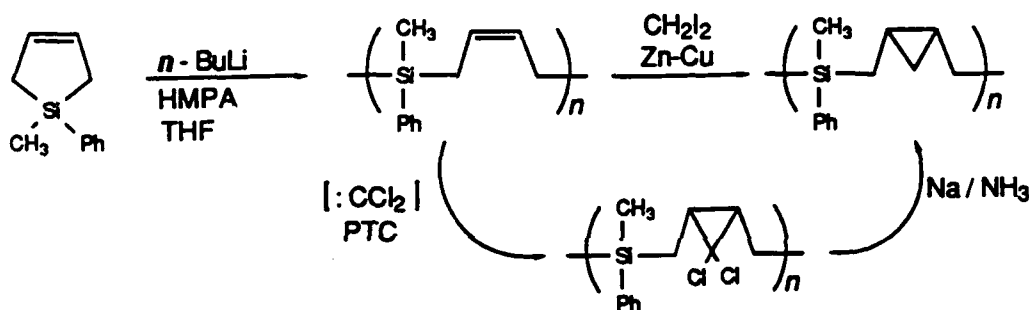


Fig. 1. Synthesis of $\text{H}_2\text{C-I}$

^{13}C and ^{29}Si NMR spectroscopy is informative concerning the microstructure of $\text{H}_2\text{C-I}$. A dyad analysis predicts three distinct environments for the methylphenylsilylene units. These are determined by the stereochemical arrangements of the neighboring cyclopropane rings (Fig. 2). In fact, three ^{29}Si NMR signals in approximately a 1:2:1 intensity ratio are observed at -0.05 , -0.32 and -0.42 ppm. Similarly three ^{13}C resonances in a 1:2:1 intensity ratio are observed for the methyl group bonded to silicon at -4.78 , -4.62 and -4.41 ppm. The first and third result

from methyl groups bonded to silicon in which adjacent cyclopropane rings are on the same side of the polymer chain. On the other hand, the resonance at -4.62 ppm arises from the methyl groups bonded to silicon in which neighboring cyclopropane rings are on opposite sides of the polymer chain. Likewise, three distinct resonances are observed for the *ipso* carbon of the phenyl group bonded to silicon at 138.99, 139.09 and 139.20. On the other hand, the *ortho*, *meta* and *para* carbons each give rise to only one ^{13}C signal. This probably results from their more remote location from the center of assymmetry.

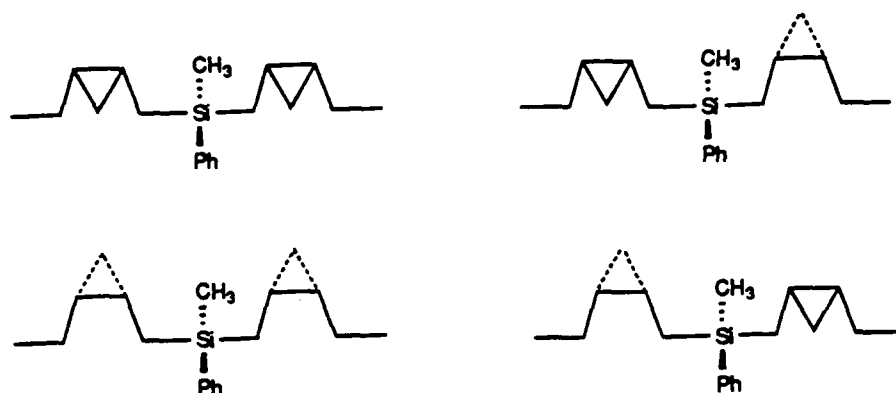


Fig. 2. Dyad microstructures of $\text{H}_2\text{C}-1$

A triad analysis of the microenvironments of the *cis*-2,3-methylene-1,4-butane units predicts that there will be three distinct cyclopropane methylene carbons, four unique methylene carbons bonded to silicon and four different cyclopropane methine carbons (Fig. 3). In fact, three distinct cyclopropane methylene carbons are observed at 12.86, 12.91 and 13.19 ppm as well as four signals which can be assigned to methylene carbons bonded to silicon at 14.88, 14.94, 15.00 and 15.05 ppm. However, only one

signal is observed for the cyclopropane methine carbons at 11.30 ppm ⁹). The ¹H NMR spectrum of H₂C-I can be assigned by comparison with that reported for *cis*-1,2-dimethylcyclopropane ¹⁴) as well as that observed for poly(1,1-dimethyl-3,4-methylene-1-sila-*cis*-pent-3-ene) ⁹).

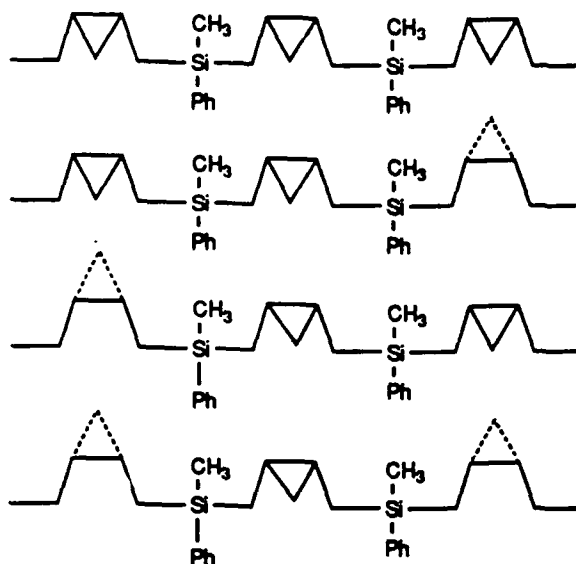


Fig. 3. Triad microstructures of H₂C-I

¹³C and ²⁹Si NMR spectroscopy are informative concerning the microstructure of Cl₂C-I. A dyad analysis predicts three distinct microenvironments for the methylphenylsilylene units (Fig. 4). In fact, three resonances are observed for the methyl carbon bonded to silicon at -4.56, -5.10 and -5.45 in a 1:2:1 intensity ratio. Of the phenyl carbons only the *ipso* carbon is sensitive to microstructure. While three distinct signals are predicted, only two are observed at 136.17 and 136.22 ppm. Similarly, three distinct resonances are expected in the ²⁹Si NMR. In fact, only two are observed at -1.39 and -1.65 ppm in a 1:3 ratio. Apparently, there is fortuitous overlap of two of the silicon signals at -1.65 ppm.

A triad analysis of the microenvironments of the *cis*-2,3-

dichloromethylene-1,4-butane units predicts that there will be three distinct cyclopropane methylene carbons, four unique methylene carbons bonded to silicon and four different cyclopropane methine carbons as above. In fact, only one cyclopropane methine carbon is observed at 29.51 ppm. Three methylene carbons bonded to silicon are seen at 9.08, 9.40 and 9.72 ppm in a 2:1:1 ratio. Apparently two of these resonances fortuitously have the same chemical shift at 9.08 ppm. Finally two cyclopropane methylenes are observed at 67.92 and 67.96 ppm.

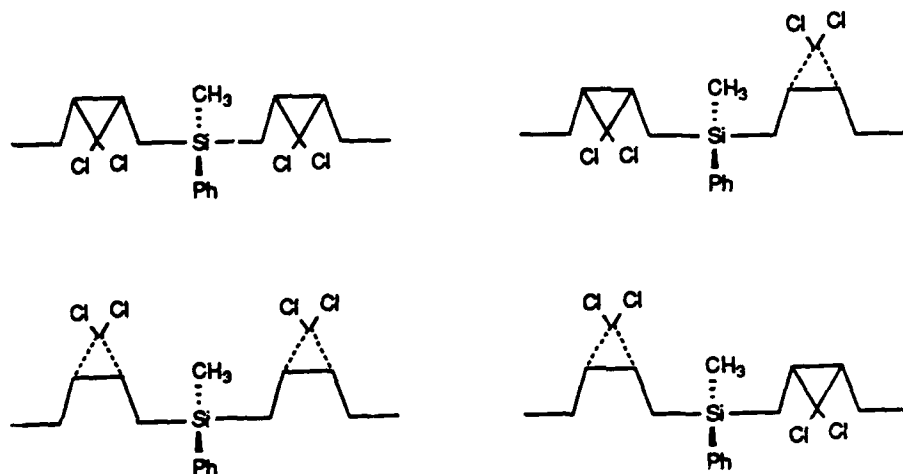


Fig. 4. Dyad microstructures of $\text{Cl}_2\text{C-I}$

$\text{H}_2\text{C-I}$ is stable to 220°C as determined by TGA. Between 220 and 350°C $\text{H}_2\text{C-I}$ loses five percent of its initial weight. Above 350°C rapid weight loss occurs. By 450°C complete weight loss is observed (Fig. 5). The thermal stability of $\text{H}_2\text{C-I}$ and I are comparable ¹²). On the other hand, $\text{Cl}_2\text{C-I}$ is only thermally stable to 98°C . Between 98 and 210°C it loses 22% of its initial weight. Rapid weight loss occurs between 270 and 470°C . A black residue equal to 9% of the initial sample weight is stable to at least 650°C (Fig. 6).

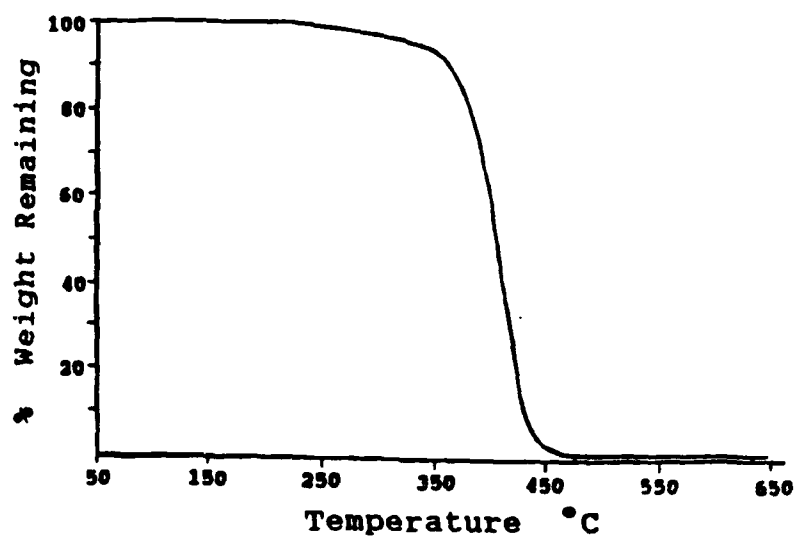


Fig. 5. TGA of H₂C-I

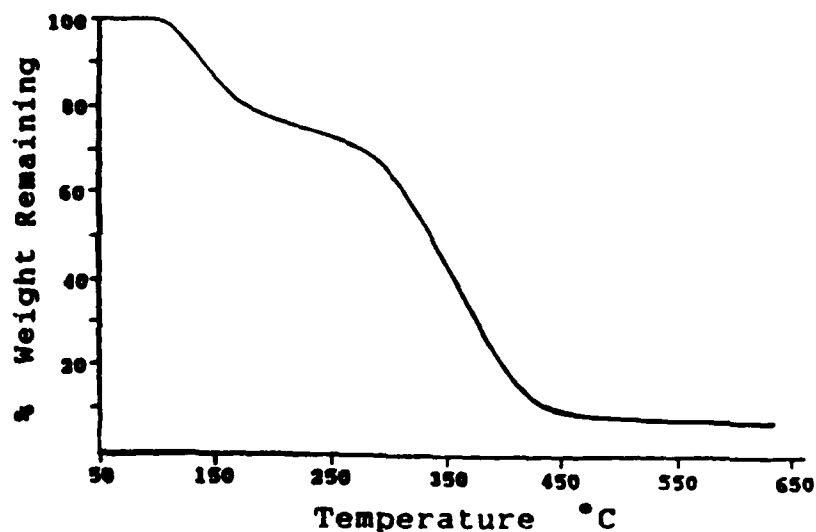


Fig. 6. TGA of Cl₂C-I

The stability of Cl₂C-I is also low in ionizing solvents. Thus heating a chloroform solution of Cl₂C-I ($M_w/M_n = 62,000/35,000$) at reflux overnight yields material of significantly lower molecular weight ($M_w/M_n = 2,600/1,900$). We believe this degradation process occurs by ionization of one of the carbon-chlorine bonds with concerted disrotatory opening of the

cyclopropane ring to yield an allylic cation ¹⁸). This symmetry allowed process is accelerated due to stabilization of the allylic cation by two *beta*-methylphenylsilyl groups. It is well-known that silicon has a significant stabilizing effect on *beta*-carbocation centers ¹⁹). Nucleophilic attack by the chloride anion on the methylphenylsilyl center results in scission of the polymer chain. One end of which is terminated by a methylphenylchlorosilyl group while the other has a 2-chloro-1,3-butadiene end group (Fig. 7). Reaction with adventitious water converts the methylphenylchlorosilyl group to a disiloxane units. Absorption bands consistent with Si-O-Si units are observed in the IR at 1050 cm⁻¹. Evidence for 2-chloro-1,3-butadiene end groups is found in the ¹H NMR. In the ¹H NMR four vinyl-CH resonances of equal intensity are observed at 5.04(d, J = 10.4 Hz), 5.44(d, J = 16.6 Hz), 5.78(t, J = 7.8 Hz), 6.31(d of d, J = 16.6 and 10.4 Hz). For comparison, the dichlorocarbene adduct of allyltrimethylsilane is stable to distillation at 185°C. However, on treatment with zinc chloride at 110°C for 4 h, it decomposes to 2-chloro-1,3-butadiene and trimethylchlorosilane ²⁰).

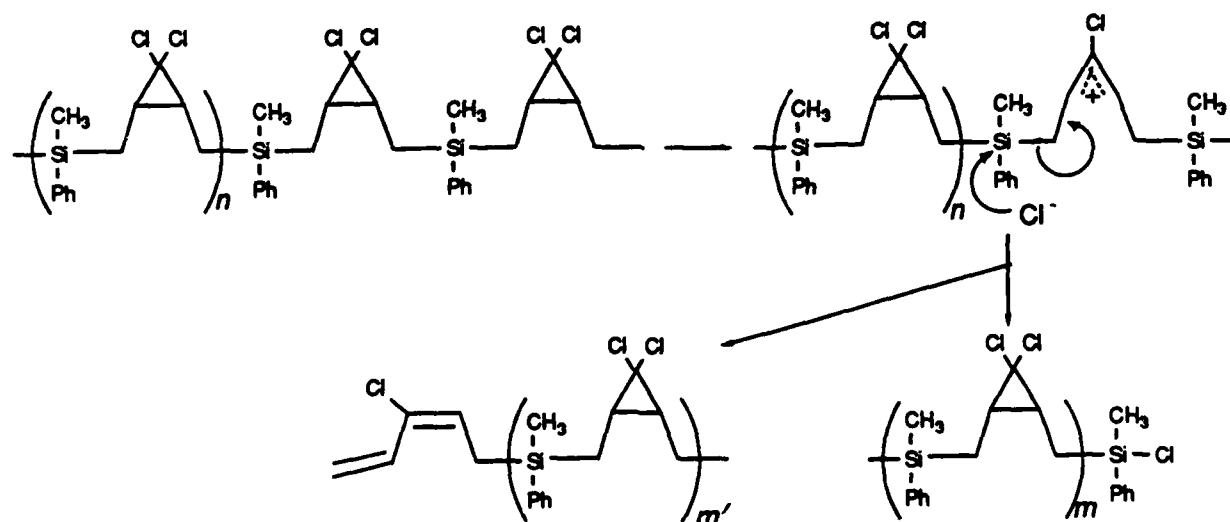


Fig. 7. Heterolytic decomposition of $\text{Cl}_2\text{C}-\text{I}$

Conclusion

Low molecular weight poly(1-methyl-3,4-methylene-1-phenyl-1-sila-cis-pent-3-ene) ($\text{H}_2\text{C-I}$) has been prepared directly by Simmons Smith reaction of poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene) (I). Higher molecular weight $\text{CH}_2\text{-I}$ can be prepared by dichlorocyclopropanation of I under PTC conditions, followed by Birch reduction of poly(3,4-dichloromethylene-1-methyl-1-phenyl-1-sila-cis-pent-3-ene) $\text{Cl}_2\text{C-I}$.

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References

1. Fettes, E. M., ed. *Chemical Reactions of Polymers* Interscience Publishers: New York, 1964.
2. Benhman, J. L. Kinstle, J. F., eds. *Chemical Reactions on Polymers* ACS Symposium Series 364, American Chemical Society: Washington, DC, 1988.
3. Carraher, C. E., Jr. Moore, J. A., eds. *Modification of Polymers* Plenum: New York, 1983.
4. Mathias, L. J. Carraher, C. E., Jr., eds. *Crown Ethers and Phase Transfer Catalysis in Polymer Science* Plenum: New York, 1984.
5. Huvard, G. S. Nicholas, P. P. Horne, S. E., Jr. *J. Polym. Sci., Polym. Chem. Ed.*, 23, 2005 (1985)
6. Komoroski, R. A. Horne, S. E., Jr. Carman, C. J. *J. Polym. Sci., Polym. Chem. Ed.*, 21, 89 (1983)
7. Carman, C. J. Komorski, R. A. Horne, S. E., Jr. *NMR and Macro-*

molecules; Randall, J. C., Ed.; ACS Symposium Series 247; American Chemical Society: Washington, DC, 1984, p 167.

8. Hummel, K. Martl, M. G. Chemelli, R. Greiser, H. Wakovnig, S. Zekoll, H. *Macromol. Chem.*, **185**, 2489 (1984)

9. Zhou, Q. Weber, W. P. *Macromolecules*, **22**, 1300 (1989)

10. Zhou, Q. Weber, W. P. *Polymer Bull.*, **21**, 173 (1989)

11. Freeman, R. Hill, H. D. W. Kaptein, R. J. *Magn. Reson.*, **7**, 327 (1972)

12. Zhang, X. Zhou, Q. Weber, W. P. Horvath, R. F. Chan, T. H. Manuel, G. *Macromolecules*, **21**, 1563 (1988)

13. Rawson, R. J. Harrison, I. T. *J. Org. Chem.*, **35**, 2057 (1970)

14. For a review on the Simmons-Smith Reactions see: Simmons, H. E. Cairns, T. L. Vladuchick, S. A. Hoiness, C. M. *Organic Reactions Vol. 20*, J. Wiley & Sons: 1973, p 1-131.

15. For a review on Electrophilic Cleavage of Allylic Silanes see: Weber, W. P. *Silicon Reagents for Organic Synthesis*, Springer-Verlag: Berlin, 1983, p 173-191.

16. Dehmlow, E. V. Thieser, R. Sasson, Y. Pross, E. *Tetrahedron*, **41**, 2972 (1985)

17. Dehmlow, E. V. Lissel, M. *Tetrahedron* **37**, 1653 (1981)

18. Woodward, R. B. Hoffmann, R. J. *Am. Chem. Soc.* **87**, 395 (1965)

19. Lambert, J. B. Wang, G. T. Finzel, R. B. Teramura, D. H. J. *Am. Chem. Soc.* **109**, 7838 (1987) and references cited therein.

20. Seyferth, D. Julia, F. T. J. *Am. Chem. Soc.*, **90**, 2938 (1968)