Polymer Bulletin 28, 17–21 (1992)

Polymer Bulletin

Stereoselective anionic ring opening polymerization of 1,1-dimethyl-1-silacyclobutene

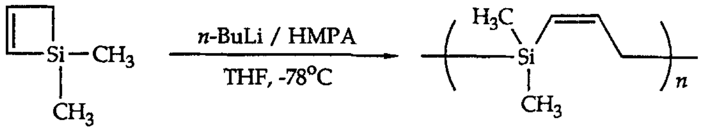
Characterization of poly(1,1-dimethyl-1-sila-*cis*-but-2-ene)

Marcus Theurig and William P. Weber*

D. P. and K. B. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, USA

SUMMARY

Stereoselective anionic ring opening polymerization of 1,1-dimethyl-1-silacyclobutene co-catalyzed by *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at -78^{o}C yields predominantly poly(1,1-dimethyl- 1-sila-*cis*-but-2-ene). The polymer has been characterized by ^{1}H, ^{13}C, ^{29}Si NMR spectroscopy, gel permeation chromatography (GPC), thermogravimetric analysis (TGA) and elemental analysis.



EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-360 spectrometer operating in the Fourier Transform mode (FT). ^{29}Si NMR spectra were recorded on an IBM-Bruker WP-270-SY spectrometer. Five to ten percent weight/volume solutions of polymer in chloroform-*d* were used for ^{1}H NMR spectra, whereas fifteen percent solutions were utilized for ^{13}C and ^{29}Si NMR spectra. ^{13}C NMR spectra were run with broad band proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 20 sec delay was used to acquire ^{29}Si NMR spectra (1). These were externally referenced to TMS. Chloroform was used as an internal reference for ^{1}H and ^{13} NMR spectra. IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer.

Gel permeation chromatographic analysis of the molecular weight distribution of the polymer was performed on a Waters system comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 refractive index detector and a Model 820 Maxima control system. A Waters 7.8 mm x 30 cm Ultrastyragel linear column packed with less than 10 m particles of mixed pore size crosslinked styrene divinylbenzene copolymer maintained at 20^{o}C was used for the analysis. The eluting solvent was HPLC grade THF at a flow rate of 0.8 mL/min. The retention times were calibrated against those of known monodisperse polystyrene standards: M_p 612,000; 114,000; 47,500; 18,700 and 5,120 whose M_w/M_n are less than 1.09.

Thermogravimetric analysis of the polymer was carried out on a Perkin-Elmer TGS-2 instrument with a nitrogen flow rate of 40 cm^{3}/min. The temperature program for the analysis was 50^{o}C for 10 min followed by an increase of 4^{o}C/min to 750^{o}C.

Elemental analysis was performed by Galbraith Laboratories, Knoxville TN.

All reactions were carried out under an atmosphere of argon in flame dried glassware. THF was dried by distillation from a deep blue solution of sodium/benzophenone ketyl immediately prior to use. HMPA was distilled from calcium hydride and stored over activated 4 A^{o} molecular sieves.

1,1-Dimethyl-1-silacyclobutene (I)

I was prepared by flash vacuum pyrolysis of diallyldimethylsilane (Aldrich) at 750^{o}C. The ^{1}H and

---

*To whom offprint requests should be sent

^{13}C NMR spectra were in agreement with those previously reported (2). ^{29}Si NMRδ : 14.85.

Poly(1,1-dimethyl-1-sila-*cis*-but-2-ene)

In a 100 mL round bottom flask equipped with a Teflon covered magnetic stirring bar was placed 1,1-dimethyl-1-silacyclobutene (0.35 g, 3.6 mmol), THF (20 mL), HMPA (200µL). The flask was sealed with a rubber septum and was cooled to -78^{o}C. The contents of the flask were stirred and a hexane solution of *n*-butyllithium (100µ L, 2.5 M, 0.25 mmol) was added via a syringe. The reaction was continued for 2 h at -78^{o}C. The reaction was quenched at -78^{o}C by addition of 10 mL of saturated aqueous ammonium chloride. The reaction was allowed to warm to room temperature and the organic layer was separated. It was washed with water (20 mL), dried over anhydrous magnesium sulfate, filtered and the volatile solvents removed by evaporation under reduced pressure. The residue was dissolved in the minimum amount of THF and the polymer was precipitated from methanol. In this way, 0.3 g, 86% yield, M_w/M_n = 7020/4770 was obtained. ^{1}H NMRδ : 0.12(s,6H), 1.68(d,2H, J = 8.5 Hz), 5.28(d,1H, J = 14.0 Hz), 6.37(dt,1H, J = 14.0 and 8.6 Hz). ^{13}C NMR δ : -1.24, 25.65, 124.12, 146.39. ^{29}Si NMR δ : -11.07. Anal. Calcd for $C_5H_{10}Si$: C, 61.14; H, 10.26. Found: C, 59.97; H, 10.29.

Z- and E-1,3-*bis*(Trimethylsilyl)propene

In a 250 mL three neck round bottom flask equipped with a Teflon covered magnetic stirring bar, a pressure equalizing addition funnel and a reflux condenser was placed 1.39 g (57 mmol) of magnesium powder and THF (60 mL)). A crystal of iodine was added to activate the magnesium. After the brown color of the iodine had faded, chlorotrimethylsilane (5.8 g, 53 mmol) in THF (30 mL) was added and the reaction mixture was allowed to stir for one h. A 1:1 mixture of Z- and E-1,3-dibromopropene (Aldrich) (5.0 g, 25 mmol) in THF (30 mL) was added dropwise over 1 h. The reaction was stirred at rt for 24 h and was then quenched by addition of 50 mL of saturated aqueous ammonium chloride. The organic layer was separated, dried over anhydrous magnesium sulfate, filtered and the organic solvents removed by evaporation under reduced pressure. The residue was transferred to a 25 mL round bottom flask. The product was purified by fractional distillation through a 15 cm vacuum jacketed Vigreux column. A fraction bp 85^{o}C/45 mm, 3.35 g, 72% yield was isolated. Z and E isomers 1:5 can be separated by GLPC. IR ν :2965, 2898, 1606, 1401, 1250, 1143, 1050, 1014, 987, 841, 757, 721, 690, 669 cm^{-1}.

E-1,3-*bis*(trimethylsilyl)propene (3)

^{1}H NMR δ : -0.02(s,9H), 0.017(s,9H), 1.61(dd,2H, J = 7.7 and 1.0 Hz), 5.41(dt, 1H, J = 18.0 and 1.0 Hz), 6.00(dt, 1H, J = 18.4 and 7.8 Hz). ^{13}C NMR δ: -2.0, -1.0, 28.4, 128.0, 143.7. ^{29}Si NMR δ : 0.135, -8.66. MS m/e (rel. intensity): 188(0.1), 187(0.4), 186(1.8) $M^{+\cdot}$, 173(0.5), 172(1.1), 171(5.9) M-15^{+}, 100(2.0), 99(6.0), 98(49.9), 97(5.1), 85(1.7), 84(1.5), 83(14.9), 75(4.52), 74(10.7), 73(100.0).

Z-1,3-*bis*(trimethylsilyl)propene

^{1}H NMR δ: 0.05(s,9H), 0.03(s,9H), 1.65(d,2H, J = 8.4 Hz), 5.30(dt,1H, J = 14.1 and 1.2 Hz), 6.31(dt,1H, J = 13.9 and 8.5 Hz). ^{13}C NMR δ : -0.5, 0.5, 25.3, 125.9, 144.3. ^{29}Si NMR δ: 0.26, -11.0. MS m/e (rel. intensity): 188(0.1), 187(0.5), 186(2.6) $M^{+\cdot}$, 173(0.7), 172(1.5), 171(7.8) M-15^{+}, 100(1.7), 99(5.3), 98(44.0), 97(3.4), 85(1.6), 84(1.2), 83(13.6), 75(3.5), 74(8.5), 73(100.0).

RESULTS and DISCUSSION

While considerable work has been done on the anionic (4), thermal (5) and platinum (6) catalyzed ring opening polymerization of silacyclobutanes and on the anionic (7,8) and metathesis (9) ring opening polymerization silacyclopent-3-enes, **no previous work has been reported on the polymerization of silacyclobutenes.** This situation may reflect the difficult in the preparation of silacyclobutenes (2,10-13).

Anionic ring opening polymerization of 1,1-dimethyl-1-silacyclobutene co-catalyzed by *n*-butyllithium and HMPA at -78^{o}C proceeds in a stereoselective manner. Only four major resonances are observed in the ^{13}C NMR spectrum of poly(1,1-dimethyl-1-silabut-2-ene) and only a major single ^{29}Si NMR signal is detected. The predominant *cis* stereochemistry of the polymer has been assigned on the basis of comparison with model compounds: E- and Z-1,3-*bis*(trimethylsilyl)propene. In particular, the ^{13}C NMR resonances for the allylic carbons are characteristic (See Figure 1). The observation of a small peak in the ^{13}C NMR at 28.6 ppm in addition to the large peak at 25.65 ppm and a small ^{29}Si NMR peak at -8.79 ppm in addition to the major peak at -11.07 ppm is consistent with the presence of a small number of *trans* units in the polymer. The intensity ratios of these peaks is consistent with the presence of less than six percent *trans* units.

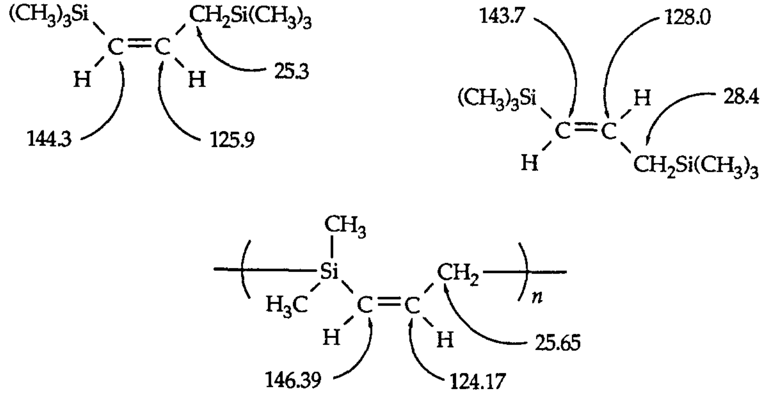


Figure 1. ^{13}C NMR Chemical Shifts (δ) of Z- and E-1,3-*bis*(trimethylsilyl)propene and poly(1,1-dimethyl-1-sila-*cis*-but-2-ene)

The vicinal H-H coupling constants for the vinyl hydrogens observed in the ^{1}H NMR confirm this assignment. Thus the H-H coupling constant between the vinyl hydrogens of poly(1,1-dimethyl-1-sila-*cis*-but-2-ene) is found to be 14.0 Hz. This is identical with the H-H coupling constant between the vinyl hydrogens of Z-1,3-*bis*(trimethylsilyl)propene [14.0 Hz] and significantly smaller than the vicinal H-H coupling constant observed for vinyl hydrogens of E-1,3-*bis*(trimethylsilyl)propene [18.0 Hz] (See Figure 2).

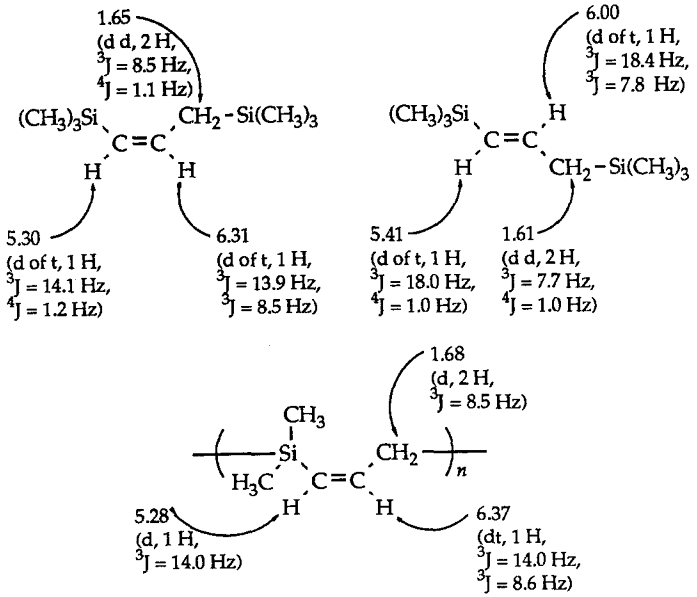


Figure 2. ^{1}H NMR Chemical Shifts (δ) of Z- and E-1,3-*bis*(trimethylsilyl)propene and poly(1,1-dimethyl-1-sila-*cis*-but-2-ene)

Finally, the predominant ^{29}Si NMR resonance is consistent with the *cis* stereoselectivity (See Figure 3).

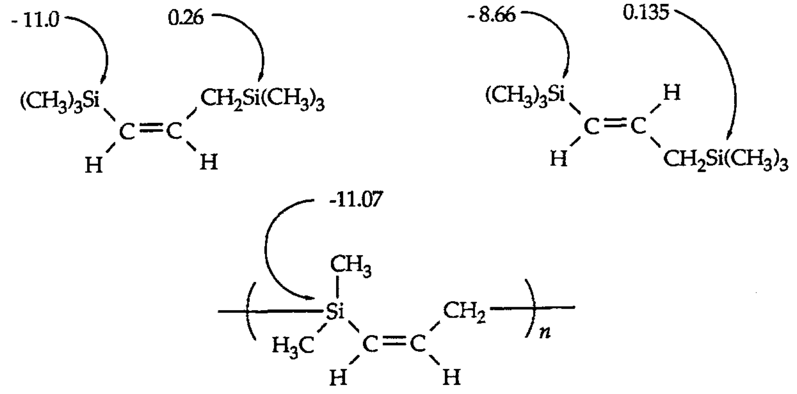


Figure 3. ^{29}Si NMR Chemical Shifts (δ) of Z- and E-1,3-*bis*(trimethylsilyl)propene and poly(1,1-dimethyl-1-sila-*cis*-but-2-ene)

We believe that the mechanism of this stereoselective anionic ring opening polymerization of 1,1-dimethyl-1-silacyclobutene proceeds by nucleophilic attack at the silyl center to form a pentacoordinate anionic silicon intermediate. Ring opening of this intermediate leads to a *cis*-allyl anion which reacts rapidly with another molecule of 1,1-dimethyl-1-silacyclobutene. This process leads to a new pentacoordinate siliconate species. This reaction must occur faster than the isomerization of the *cis*-allyl anion into a *trans*-allyl anion by rotation about the partial carbon-carbon double bond to account for the predominant *cis* stereospecificity observed. This is not unreasonable at the low temperature utilized for the polymerization (-78^{o}C), since the energy of activation for such isomerization process has been determined to be between 10 and 17 kcal/mol (14,15). This mechanism is similar to that previously proposed for the anionic ring opening polymerization of 1,1-dimethyl-1-silacyclobutane (16,17) and 1-silacyclopent-3-enes (7,8,18).

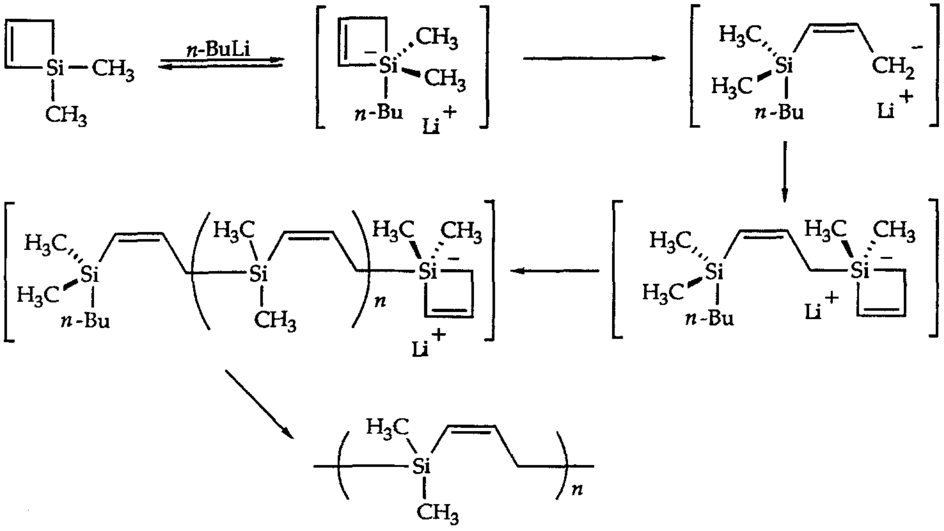


Figure 4. Mechanism of Anionic Ring Opening Polymerization of 1,1-Dimethyl-1-silacyclobutene

The thermal stability of poly(1,1-dimethyl-1-sila-*cis*-but-2-ene) has determined by TGA. The polymer is thermally stable to 225°C. Between 225 and 300°C the polymer loses five percent of its initial weight. Above 300°C rapid catastrophic decomposition occurs. By 430°C complete weight loss has occurred.

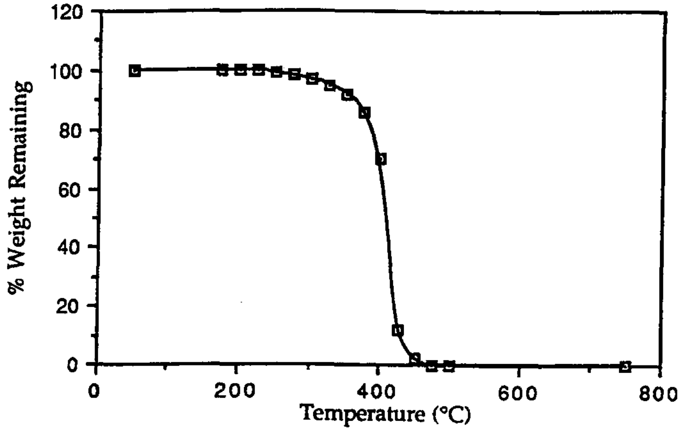


Figure 5. TGA of Poly(1,1-dimethyl-1-sila-*cis*-but-2-ene)

Acknowledgements

This work was supported by the Office of Naval Research and the Air Force Office of Scientific Research. M. Theurig thanks Professor H. Hopf of the Technical University of Braunschweig, Germany.

REFERENCES

1. Freeman, R.; Hill, H. D. W.; Kaptein, R. *J. Magn. Reson.*, **1972**, *7*, 327.
2. Block, E.; Revelle, L. K. *J. Am. Chem. Soc.*, **1978**, *100*, 1630.
3. House, H. O.; Goa, P. D.; Lee, J. H. C.; Van Derveer, D. *J. Org. Chem.*, **1983**, *48*, 1670.
4. Nametkin. N. S.; Vdovin, V. M.; Poletaev, V. A.; Zav'yalov, V. I. *Dokl. Akad. Nauk SSSR* **1967**, *175*, 1068.
5. Vdovin, V. M.; Pushchevaya, K. S.; Belikova, N. A.; Sultanov, R.; Plate, A. F.; Petrov, A. D. *Dokl. Akad. Nauk SSSR* **1961**, *136*, 96.
6. Weyenberg, D. R.; Nelson, L. E. *J. Org. Chem.* **1965**, *30*, 2618.
7. Zhang, X.; Zhou, Q.; Weber, W. P.; Horvath, R. F.; Chan, T. H.; Manuel, G. *Macromolecules*, **1988**, *21*, 1563.
8. Weber, W. P., Park, Y. T.; Zhou, S. Q. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43* 259.
9. Stonich, D. A.; Weber, W. P. *Polymer Bull*, **1991**, *25*, 629.
10. Gilman, H.; Atwell, W. H. *J. Am. Chem. Soc.*, **1965**, *87*, 2678.
11. Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.*, **1983**, *105*, 2006.
12. Conlin, R. T.; Kwak, Y.-W.; Huffacker, H. B. *Organometallics* **1983**, *2*, 343.
13. Auner, N.; Seidenschwarz, C.; Herdtweck, E. *Angew. Chem.*, **1991**, *103*, 1172.
14. Fraenkel, G.; Winchester, W. R.; *Organometallics* **1990**, *9*, 1314.
15. West, P.; Purmort, J. I.; McKinley, S. V.; Freedman, H. H. *J. Am. Chem. Soc.*, **1968**, *90*, 495.
16. Gilman, H.; Atwell, W. H. *J. Am. Chem. Soc.*, **1964**, *86*, 2687.
17. Vdovin, V. M.; Grinberg, P. L.; Babich, E. D. *Dokl. Akad. Nauk SSSR*, **1965**, *161*, 268.
18. Park, Y. T.; Manuel, G.; Weber, W. P. *Macromolecules*, **1990**, *23*, 1911.

Accepted January 8, 1992 K