Applied Organometallic Chemistry (1987) 1 171–176
© Longman Group UK Ltd 1987
0268-2605/87/01207171/$03.50

1,3-Adamantanyl dimethylsiloxane copolymers. Preparation and properties

Yi-Ming Pai and William P Weber*
Department of Chemistry and Loker Hydrocarbon Institute, University of Southern California, Los Angeles, California 90089-1661, USA

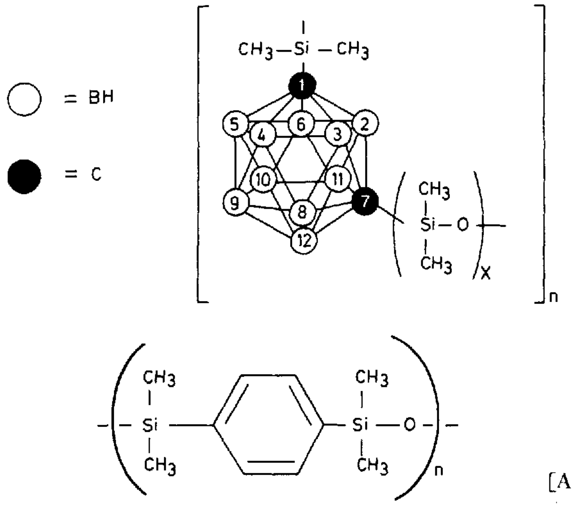
Received 27 June 1986 Accepted 6 October 1986

1,3-*bis*(Dimethylhydroxysilyl)adamantane(I) has been prepared. Thermal condensation polymerization of this monomer yields poly-1,3-adamantyl-1,1,3,3-tetramethyldisiloxane. Condensation of I with *bis*(dimethylamino)dimethylsilane or 1,3-*bis*(dimethylamino)-1,1,3,3-tetramethyldisiloxane gave the expected 1,3-adamantyl dimethylsiloxane copolymers (II and III) respectively. These polymers have been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR as well as GPC and TGA. They have unusually high thermal stability.

Keywords: Condensation, polymerization, silyladamantane, thermal stability

INTRODUCTION

Both linear *m*-carborane siloxane[1–4] and silarylene siloxane[5–8] polymers have high thermal stability [A].



[A]

Three-dimensional geometrical analysis suggested that 1,7-dicarba-*closo*-dodecacarborane ($C_2B_{10}H_{12}$) and 1,3-disubstituted adamantane polyhedra might have similar steric properties. In addition the strain free diamond like skeleton of adamantane often provides high thermal stability.[9] On the other hand, the carborane nucleus is aromatic whereas adamantane is not. For these reasons, we set out to prepare 1,3-adamantane siloxane polymers in the hope that these would possess unusual thermal stability.

It should be noted that despite considerable interest in adamantane chemistry, surprisingly few silyl adamantane derivatives have been previously prepared.[10] This probably results from the difficulty in converting adamantyl halides into the corresponding Grignard or lithium reagents.[11]

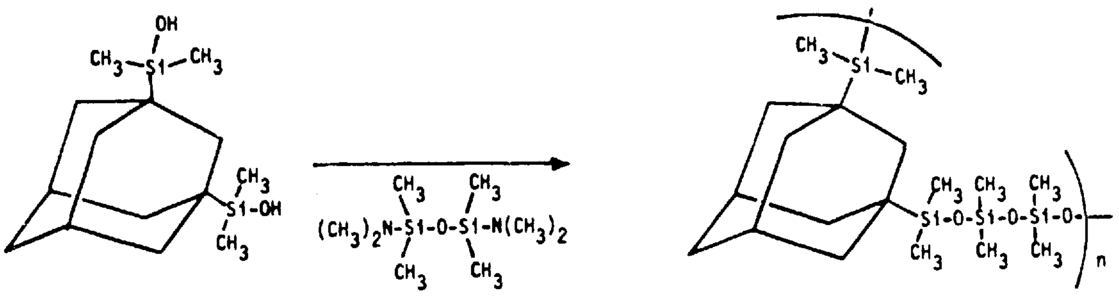
RESULTS AND DISCUSSION

The necessary monomer 1,3-*bis*(dimethylhydroxysilyl)adamantane(I) was prepared from 1,3-dibromoadamantane(IV). Phenyldimethylsilyllithium(V) reacts with IV in hydrocarbon solvent to give 1,3-*bis*-(phenyldimethylsilyl)adamantane(VI).[12] Electrophilic cleavage of aryl carbon-silicon bonds[13,14] of VI with bromine gives bromobenzene and 1,3-*bis*(dimethylbromosilyl) adamantane(VII). The silicon-bromine bonds of VII were then hydrolyzed in moist ether in the presence of sodium bicarbonate[15] to yield I.

Alternate 1,3-adamantane dimethylsiloxane copolymers II and III have been prepared by condensation reactions of I with *bis*(dimethylamino)dimethylsilane or 1,3-*bis*(dimethylamino)-1,1,3,3-tetramethyldisiloxane [B]. These were characterized by gel permeation chromatography (GPC): weight average molecular weights ($\bar{M}_w$) greater than 70 000 with number average molecular

---

*Author to whom correspondence should be addressed.



[B]

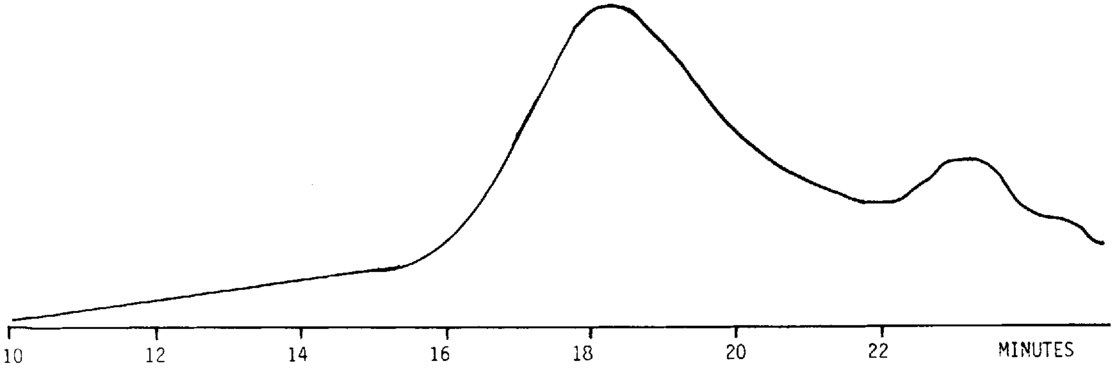


Figure 1 GPC chromatogram of 1,3-adamantanyl dimethylsiloxane copolymer III.

weights ($\bar{M}_n$) of 40000 have been found. (Figs. 1 and 2).

Homo-polymerization of I has been carried out by heating the monomer in toluene at reflux. The homo-polymer obtained has a significantly lower molecular weight, $\bar{M}_w$ equal to 7500 with a $\bar{M}_n$ equal to 2700. Despite the major difference in molecular weight between the 1,3-adamantane siloxane copolymers and the homo-polymer, both show high thermal stability by thermal gravimetric analysis (TGA). Their thermal stabilities under a nitrogen atmosphere were particularly striking. While their thermal stabilities in air were lower, they were still significantly higher than that observed for dimethylsilicone polymers of comparable molecular weight. (Figs. 3–5). These new polymers have also been characterized by ^{1}H, ^{13}C and ^{29}Si NMR, IR, and elemental analysis. They may find application as high temperature liquid phases for gas liquid phase chromatography.

EXPERIMENTAL

^{1}H, ^{13}C and ^{29}Si NMR spectra were obtained on an IBM–Bruker WP-270-SY spectrometer operating in the Fourier Transform mode using 5%, 15% and 20% solutions respectively in deuteriochloroform. Chloroform was utilized as an internal stadard for both ^{1}H and ^{13}C NMR spectra. Tetramethylsilane was used as an external standard for ^{29}Si NMR spectra. ^{13}C NMR spectra were run with broad band proton decoupling. ^{29}Si NMR spectra were run with DEPT (Distortionless Enhancement by Polarization Transfer) pulse sequences.[16] IR spectra were obtained of chloroform solutions on a Perkin–Elmer 281 spectrometer. Low resolution mass spectra were obtained on a Hewlett–Packard 5985A mass spectrometer at an ionizing voltage of 70 eV. High resolution mass spectra were obtained on an A.E.I. MS-902 mass spectrometer at an ionizing voltage of 70 eV. Exact masses were determined by peak matching against peaks of known mass of perfluoro kerosene. GPC analysis of molecular weight distribution of polymers was performed on a Perkin–Elmer series 10 liquid chromatograph equipped with a 30 cm × 7.7 mm Perkin–Elmer PL Gel mixed bead 10 μm column, LC-25 refractive index detector (maintained at 25°C), a 3600 data station and a 660 printer. Chloroform was used as the carrier solvent at a

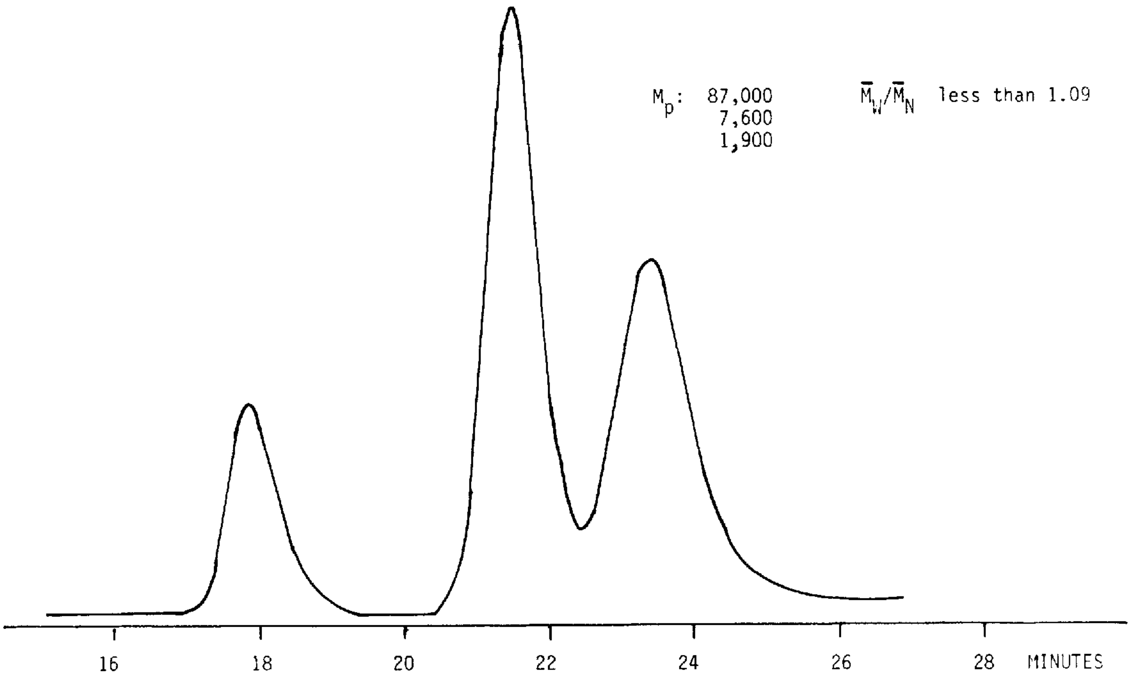


Figure 2 GPC chromatogram of polystyrene standards.

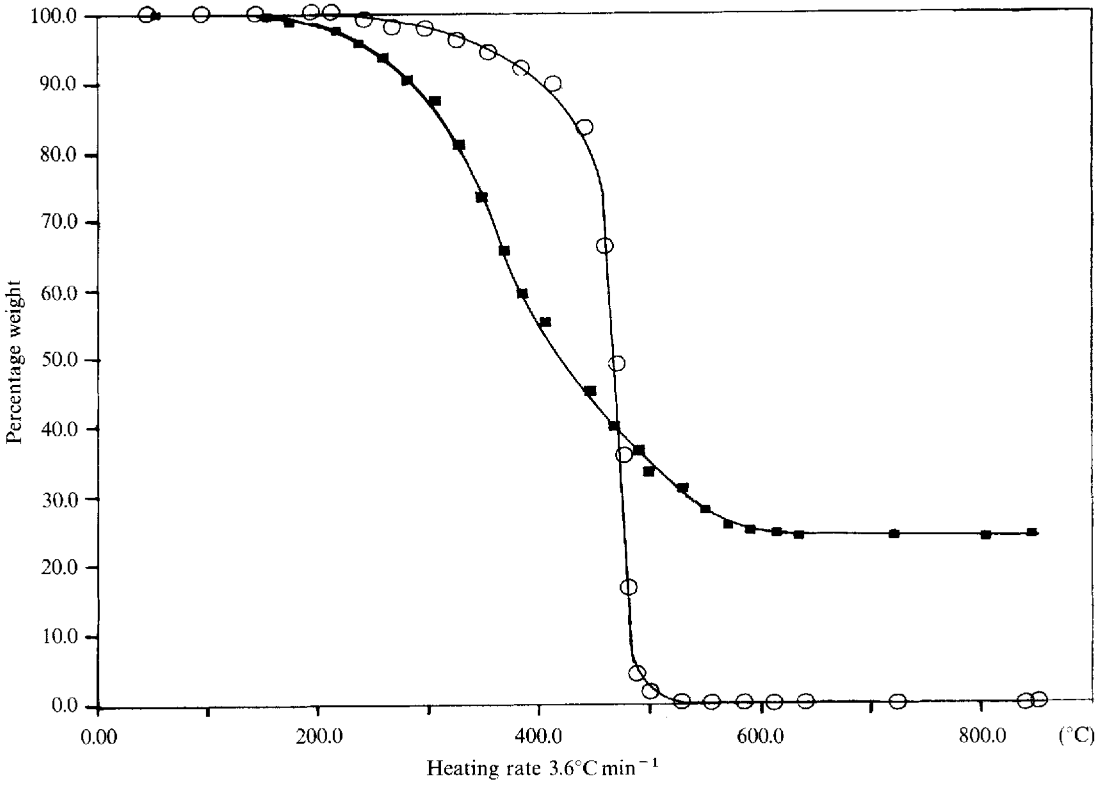


Figure 3 Thermal stability of poly-1,3-adamantyl-1,1,3,3-tetramethyldisiloxane.

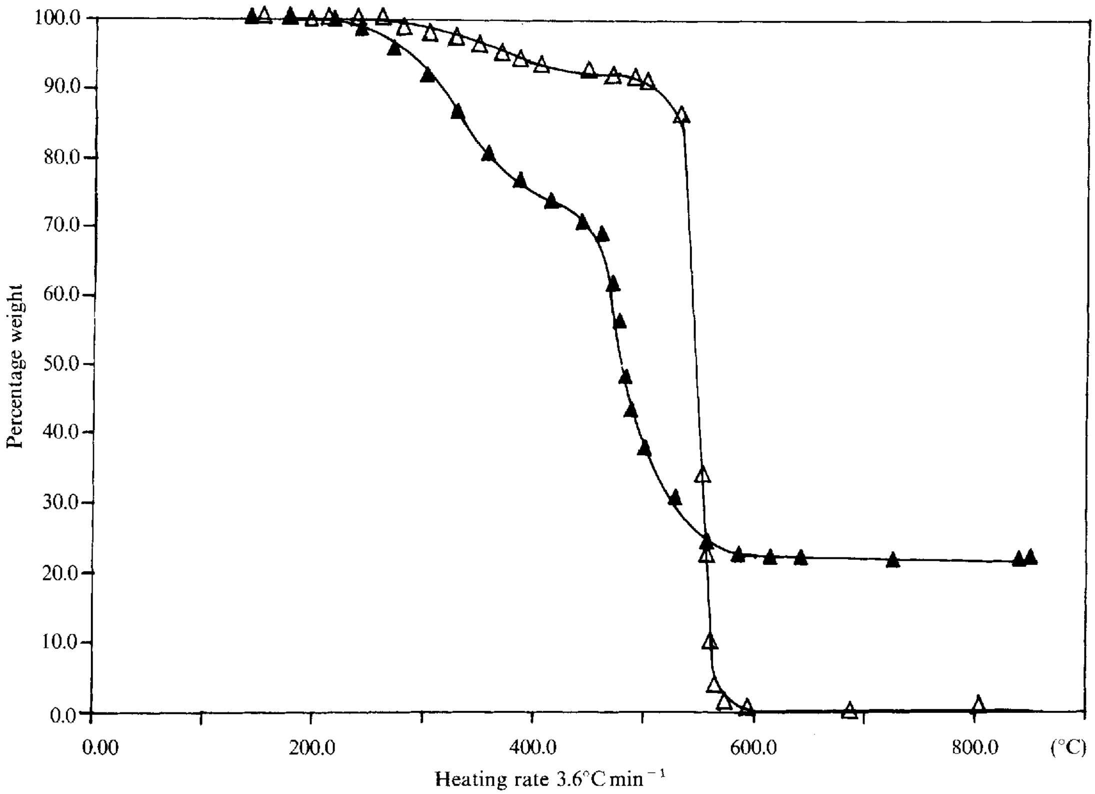


Figure 4 Thermal stability of 1,3-adamantyl dimethylsiloxane copolymer III.

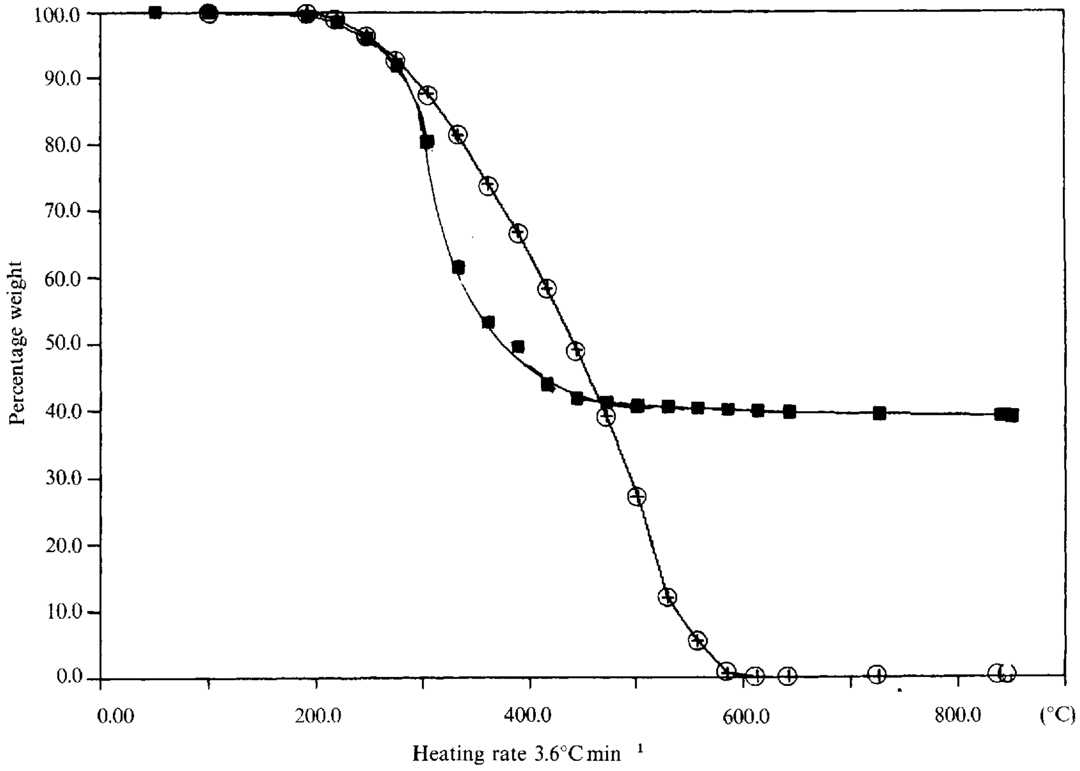


Figure 5 Thermal stability of polydimethylsiloxane ($\bar{M}_w \sim 100\,000$).

flow rate of 0.5 cm^3 min^{-1}. The retention times were calibrated against known polystyrene standards: M_p 194 000, 87 000, 19 000, 10 200, 7600 and 1900 whose $\bar{M}_w/\bar{M}_n$ were less than 1.09. A Perkin–Elmer TGS-2 instrument equipped with a system 7/4 Thermal Analysis Controller was used to perform the TGA measurements. These were carried out in both nitrogen and air at a gas flow rate of 40 cm^3 min^{-1} between 50°C and 850°C at a heating rate of 3.6°C min^{-1}. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

All reactions were run under an atmosphere of purified nitrogen and all solvents were rigorously anhydrous unless otherwise noted. 1,3-Dichloro-1,1,3,3-tetramethylisiloxane(VIII) and *bis*(dimethylaminodimethylsilane were obtained from Petrarch Systems Inc., and were distilled immediately before use. 1,3-*bis*(Phenyldimethylsilyl) adamantane(VI) was prepared by the reaction of V with IV.[12]

Preparation of 1,3-*bis*(dimethylamino)-1,1,3,3-tetramethyldisiloxane(IX)[17]

Freshly distilled VIII (10.5 g, 50 mmol) in 30 cm^3 of ether was added to 15 cm^3 of dimethylamine in 30 cm^3 of ether at -5°C. After the addition was complete, the reaction mixture was allowed to warm slowly to room temperature. It was then refluxed for 1 h. The dimethylammonium hydrochloride salts were removed by filtration. They were washed twice with 30 cm^3 portions of ether. The ether was removed from the combined organic solutions by distillation. The residue was fractionally distilled through a 15 cm vacuum jacketed Vigreux column. IX (8.0 g, bp 55–57°C/5 mm) was collected, 70% yield. It had the following spectral properties: ^{1}H NMR δ: 0.0259 (s, 12H), 2.4361 (s, 12H); ^{13}C NMR δ: -1.404 (4C), 37.259 (4C); ^{29}Si NMR δ: -10.412.

Preparation of 1,3-*bis*-(Dimethylbromosilyl)adamantane(VII)

1,3-*bis*(Phenyldimethylsilyl)adamantane(VI) (5.3 g, 13 mmol) dissolved in 20 cm^3 of dichloromethane was cooled to 0°C and was added to a solution of bromine (2 cm^3, 20 mmol) in 5 cm^3 dichloromethane. The reaction mixture was warmed to room temperature and was stirred for 2 h. Excess bromine and dichloromethane were removed by distillation. The residue was bulb-to-bulb distilled at 120°C/10^{-3} mm. VII was obtained in 92% yield. It has the following spectral properties: ^{1}H NMR δ: 0.458 (s, 12H), 1.738–1.708 (m, 14H). ^{13}C NMR δ: -1.672 (4C), 22.221 (2C), 26.285 (2C), 34.575 (1C), 35.631 (4C), 36.688 (1C). ^{29}Si NMR δ: 32.40. IR ν: 2900, 1430, 1250 cm^{-1}. Mass spectrum (rel. intensities) m/e 412 (56%), 410 (100%), 408 (49%) M$^{+\bullet}$, 273 (100%), 271 (97%) M-Si(CH$_3$)$_2$Br$^+$, 231 (12%), 229 (12%), 139 (48%), 137 (47%) Si(CH$_3$)$_2$Br$^+$. High resolution mass spectrum m/e calcd. for $Si_2C_{14}H_{26}{}^{79}Br_2$ 407.99391; found 407.99390. Elemental analysis calcd. for $Si_2C_{14}H_{26}Br_2$: C, 40.98%; H, 5.46%, Br, 38.94%. Found: C, 40.32%; H, 6.39%; Br, 36.05%.

Preparation of 1,3-*bis*-(Dimethylhydroxysilyl)adamantane(I)

VII (5.0 g, 12 mmol) in 20 cm^3 of ether was cooled to 0°C. To this solution was added dropwise 60 cm^3 of ether which had been previously saturated with water. The reaction mixture was stirred for 1 h at 0°C and then warmed to room temperature. Sodium bicarbonate was added to neutralize the HBr generated. The solution was dried over anhydrous magnesium sulfate, filtered and the ether solvent removed by evaporation under reduced pressure. The white solid was recrystallized from pentane mp 145–147°C. In this manner, 2.87 g of I was obtained, 84.2% yield. I has the following spectral properties: ^{1}H NMR δ: 0.0234 (s, 12H), 1.2287 (br. s, 2H) Si-OH, 1.6250–1.8199 (m, 14H); ^{13}C NMR δ: -4.419 (4C), 21.655 (2C), 26.635 (2C), 35.393 (1C), 36.557 (4C), 37.592 (1C); ^{29}Si NMR δ: 7.55 (2Si). IR ν: 3660 Si-OH)[18], 2900, 1250, 1060 cm^{-1}. Mass spectrum (rel. intensities) m/e 284 (91%) M$^{+\bullet}$, 269 (5%) M-15$^+$, 209 (12%), 149 (71%), 75 (100%). High resolution mass spectrum m/e: calcd. for $Si_2C_{14}H_{28}O_2$ 284.16278. Found 284.16260. Elemental analysis calcd. for $Si_2C_{14}H_{28}O_2$: C, 58.90%; H, 9.86%. Found: C, 59.15%; H, 9.52%.

Homo-polymerization of 1,3-*bis*-(Dimethylhydroxysilyl)adamantane(I)

I, (2.84 g, 10 mmol) was dissolved in 20 cm^3 of dry toluene. The solution was placed in a 50 cm^3 round bottom flask equipped with a magnetic stirring bar and a reflux condenser. The solution was heated to reflux for 1 h and was then allowed to slowly cool to room temperature. The solvent was removed by evaporation under reduced pressure. The crude polymer, a white powder, was recrystallized from methanol, 70% yield. After drying for 48 h at high vacuum the polymer had a mp 125–127°C. It has the following properties: $M_w = 7480$, $M_n = 2716$ (GPC). TGA see Fig. 3. ^{1}H NMR δ: -0.0614 (s, 12H), 1.865–1.545 (m, 14H). ^{13}C NMR δ: -3.7314 (4C), 21.6973 (2C), 26.7748 (2C), 35.2995 (1C), 36.6116 (4C), 37.7877 (1C). ^{29}Si NMR δ: 6.50. IR ν: 2900, 1400, 1250, 1050, 800 cm^{-1}. Elemental analysis calcd. for $Si_2C_{14}H_{26}O$: C, 63.31%; H, 9.83%. Found: C, 60.82%; H, 9.46%.

Copolymerization of *bis*(dimethylamino)dimethylsilane with 1,3-*bis*-(dimethylhydroxysilyl)adamantane(I)

I, (1.42 g, 5 mmol) was placed in a 25 cm^3 round bottom flask with 10 cm^3 of dry toluene and *bis*(dimethylamino)dimethylsilane, (0.73 g, 5 mmol) was added. The mixture was heated to reflux for 1 h. 10 mg of *bis*-(dimethylamino)dimethylsilane was added and the mixture was heated for 1 h. The reaction was cooled and the solvent removed by evaporation under reduced pressure. The slightly yellow clear viscous oil was washed with 5 cm^3 of methanol and dried under high vacuum. A 70% yield of polymer II was obtained. It had the following properties: $\bar{M}_w = 70\,000$, $\bar{M}_n = 40\,000$ (GPC). TGA was similar to that of polymer III (see Fig. 4). ^{1}H NMR δ: -0.0399 (s, 12H), 0.0134 (s, 6H), 1.534–1.7865 (m, 14H). ^{13}C NMR δ: -3.838 (4C), 1.425 (2C), 21.741 (2C), 26.893 (2C), 35.357 (1C), 36.645 (4C), 37.820 (1C). ^{29}Si NMR δ: -22.243 (2Si), 6.350 (1Si). IR ν: 1250 and 1100–1030 cm^{-1}.

Copolymerization of 1,3-*bis*(dimethylamino)-1,1,3,3-tetramethyldisiloxane(IX) with 1,3-*bis*(dimethylhydroxysilyl)adamantane(I)

I, (1.42 g, 5 mmol) was placed in a 50 cm^3 round bottom flask with 10 cm^3 of dry toluene and IX, (1.09 g, 4.95 mmol) was added. The mixture was warmed to reflux over a period of 2 h. During this time dimethylamine was evolved. IX, (10 mg) was added from a syringe to the reaction mixture.[19] Heating was continued for 1 h. The solution was allowed to cool to room temperature and the solvent was removed by evaporation under reduced pressure. The colorless viscous oil was washed twice with 5 cm^3 portions of methanol and then was dried under a high vacuum for 48 h. A 63% yield of polymer III was obtained. It had the following properties: $\bar{M}_w = 74\,000$, $\bar{M}_n = 43\,000$ (GPC). TGA see Fig. 4. A small amount of a lower molecular weight component ($\bar{M}_w \cong 2000$) can be seen in the GPC (Fig. 1). This may be cyclic oligomer. This may account for the initial 5% weight loss in the TGA which begins at 300°C. ^{1}H NMR δ: -0.0469 (s, 12H), 0.0257 (s, 12H), 1.7279–1.5279 (m, 14H). ^{13}C NMR δ: -3.959 (4C), 1.2821 (4C), 21.5260 (2C), 26.6948 (2C), 35.1224 (1C), 36.4357 (4C), 37.6869 (1C). ^{29}Si NMR δ: -22.442 (2Si), 6.696 (2Si). IR ν: 2900, 1250, 1050, 800 cm^{-1}. Elemental analysis calcd. for $Si_4C_{18}H_{38}O_3$: C, 52.12%; H, 9.23%. Found: C, 52.12%; H, 8.47%.

Acknowledgements This work was supported by the Air Force Office of Scientific Research 86-0042.

REFERENCES

1. Peters, EN *Ind. Eng. Chem., Prod. Res. Dev.*, 1984, 23: 28; and references cited therein
2. Peters, EN *J. Macromol. Sci. Rev. Macromol. Chem.*, 1979, C17: 173; and references cited therein
3. Roller, MB and Gillham, JK *Polymer Eng. Sci.*, 1974, 14: 567
4. Stewart, DD, Peters, EN, Beard, CD, Dunks, GB, Hedaya, E, Kwiatkowski, GT, Moffitt, RB and Bohan, JJ *Macromolecules*, 1979, 12: 373
5. Dvornic, PR and Lenz, RW *Polymer*, 1983, 24: 763
6. Koide, N and Lenz, RW, *J. Polym. Sci., Polym. Symp.*, 1983, 70: 91
7. Dvornic, PR and Lenz, RW *J. Polym. Sci., Polym. Chem. Ed.*, 1982, 20: 593
8. Lai, YC, Dvornic PR and Lenz, RW *J. Polym. Sci., Polym. Chem. Ed.*, 1982, 20: 2277; and references cited therein
9. Fort, RC, Jr, *Adamantane. The Chemistry of Diamond Molecules*, Marcel Dekker, Inc., New York, 1976
10. Mironov, VF, Gar, TK, Fedotov, NS and Evert, GE *Russ. Chem. Rev.*, 1981, 50: 262
11. Molle, G, Bauer, P and Dubois, JE *J. Org. Chem.*, 1983, 48: 2975; and references cited therein
12. Pai, YM, Wanek, E and Weber, WP *J. Organomet. Chem.*, 1984, 279: 271
13. Eaborn, C and Bott, RW Synthesis and Reactions of the Silicon-Carbon Bond. In: *Organometallic Compounds of the Group IV Elements*, Vol. 1, MacDiarmid, AG (ed), Marcel Dekker, New York, 1968, pp 407–437
14. Guindon, Y, Fortin, R, Yoakim, C and Gillard, JW *Tetrahedron Lett.*, 1984, 4717
15. Novikov, SS, No, BI and Ushchenko, VP *Zh. Obshc. Khim.*, 1975, 45: 2029
16. Blinka, TA, Helmer, BJ and West, R *Adv. Organomet. Chem.*, 1984, 23: 193
17. Pittman, CU, Jr, Patterson, WJ and McManus, SP *J. Polym. Sci., Polym. Chem. Ed.*, 1976, 14: 1715
18. Firgo, HA and Weber, WP *Organometallics*, 1982, 1: 649
19. Burks, RE, Jr, Covington, ER, Jackson, MV and Curry, JE *J. Polym. Sci., Polym. Chem. Ed.*, 1973, 11: 319