Polymer Bulletin 26, 487–492 (1991)

Polymer Bulletin

Synthesis and characterization of poly(3,4-benzo-1-phenyl-1-silapentene) and poly(3,4-benzo-1-silapentene)

Young-Hoon Ko 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

Low molecular weight poly(3,4-benzo-1-phenyl-1-silapentene) (I) has been prepared by the anionic ring opening polymerization of 3,4-benzo-1-phenyl-1-silacyclopentene (II), co-catalyzed by methyllithium and HMPA in THF at low temperature. Poly(3,4-benzo-1-silapentene) (III) has been prepared similarly by polymerization of 3,4-benzo-1-silacyclopentene (IV) except that HMPA has NOT been utilized in this latter case. I and III have been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR as well as by IR and UV spectroscopy. The low molecular weight of I and III permits end group analysis by ^{29}Si NMR. The molecular weight distributions of I and III have been determined by gel permeation chromatography (GPC) and their thermal stability by thermogravimetric analysis (TGA).

INTRODUCTION

The intermediacy of poly[(methylsilylene)methylene] $[\text{-CH}_3\text{SiH-CH}_2\text{-}]_n$ in the conversion of poly(dimethylsilane) $[\text{-(CH}_3)_2\text{Si-}]_n$ fibers into silicon carbide fibers has increased interest in such carbosilane polymer systems (1,2). We have been interested in the anionic ring opening polymerization of both silacyclopent-3-enes (3-5) and 3,4-benzo-1-silacyclopentenes (6,7) since these reactions provide a convenient route to poly(1-silapent-3-enes) and poly(3,4-benzo-1-silapentenes). These unsaturated polycarbosilanes have a number of interesting properties. In particular, such polymers which possess both reactive silicon-hydrogen and carbon-carbon double bonds undergo thermal decomposition to form high ceramic char yields (4,5). Further the low molecular weight of these polymers permits end group analysis by NMR spectroscopy. This provides valuable information concerning the mechanism of this novel anionic polymerization.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC-250 MHz FT NMR spectrometer. ^{13}C NMR spectra were run with broad band proton decoupling. ^{29}Si NMR spectra were obtained on an IBM Bruker WP-270-SY spectrometer. Ten to fifteen percent (W/V) solutions in chloroform-*d* were used to obtain ^{1}H, ^{13}C and ^{29}Si NMR spectra. Chloroform was utilized as an internal standard for ^{1}H and ^{13}C NMR. All chemical shifts reported were externally referenced to TMS. A heteronuclear gated decoupling pulse sequence with a pulse delay of 20 s (NONOE) was used to obtain ^{29}Si NMR spectra (8). Infrared spectra were taken on neat films between KBr plates using an IBM FT IR/30S spectrometer. UV spectra of HPLC grade THF solutions were recorded on a Shimadzu UV-260 UV-visible spectrometer.

GPC analysis of the polymers were performed on a Waters system comprised of a U6K injector, a 510 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 gel column, packed with less than 10μm particle of mixed pore size crosslinked styrene-divinylbenzene copolymers maintained at 20°C, was used for the analysis. The eluting solvent was HPLC grade THF at a flow rate of 0.6 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p 612,000; 114,200; 47,500; 18,700 and 5,120 having M_w/M_n less than 1.09.

TGA of the polymers were carried out on a Perkin-Elmer TGS-2 instrument at a gas (nitrogen or air) flow of 40 cc/min. The temperature program for the analysis was 50°C for 10 min followed by an increase of 4°C/min to 750°C. Their glass transition temperatures (T_g) were determined using a Perkin Elmer DSC-7 differential scanning calorimeter. The melting points of indium (mp 156°C) and

---

*To whom offprint requests should be sent spectra grade hexane (mp -95^{o}C) were used to calibrate the DSC. After equilibration at -100^{o}C for 20 min, scans were conducted by increasing the temperature at a heating rate of 20^{o}C/min to 150^{o}C.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

All reactions were conducted in flame dried glassware under an atmosphere of purified Argon. THF, pentane, ether and benzene were purified by distillation from sodium benzophenone ketyl immediately prior to use. HMPA was distilled from calcium hydride and was stored over 4A^{o} molecular sieves prior to use.

3,4-Benzo-1,1-dichloro-1-silacyclopentane (V)

V was prepared in 67% by the reaction of benzyl-chloromethyl-dichlorosilane with aluminum chloride in benzene. V was purified by fractional distillation through a 15 cm vacuum jacketed Vigreux column. A fraction bp 80-82^{o}C/4 mm (lit. bp 82-84^{o}C/4 mm) (9) was obtained. It had the following spectral properties: ^{1}H NMR δ: 2.55(s,4H), 7.14(m,2H), 7.19(m,2H); ^{13}C NMR δ: 25.14, 126.94, 129.01, 137.02; ^{29}Si NMR δ: 38.31.

3,4-Benzo-1-chloro-1-phenyl-1-silacyclopentane (VI)

In a 50 mL Schlenk flask equipped with a Teflon covered magnetic stirring bar was placed V (4.8 g, 23.6 mmol) and 5 mL of THF. The flask was sealed with a rubber septum. The mixture was cooled to -78^{o}C and a solution of phenylmagnesium chloride in THF (2M, 11.8 mL, 23.6 mmol) was slowly added via a syringe. The mixture was stirred for 2 h and then was allowed to warm to room temperature. The volatile solvents were removed by evaporation under reduced pressure. Pentane was added to residue to precipitate magnesium chloride. The pentane solution was filtered through a sintered glass funnel, and the pentane was removed by evaporation under reduced pressure. The residue was purified by fractional distillation as above. A fraction bp 117-118^{o}C/0.5 mm, 3.31 g, 57% yield was collected. ^{1}H NMR δ: 2.57(s,4H), 7.13(m, 2H), 7.27(m,2H), 7.40(m,3H), 7.67(m,2H). ^{13}C NMR δ: 22.91, 126.51, 128.24, 129.13, 130.91, 132.93, 133.65, 139.37. ^{29}Si NMR δ: 31.30. IR ν: 3139, 3071, 3016, 2938, 2883, 1591, 1571, 1477, 1454, 1429, 1336, 1305, 1284, 1266, 1209, 1190, 1168, 1157, 1130, 1114, 1067, 1030, 998, 940, 840, 789, 770, 737, 697, 679 cm^{-1}.

3,4-Benzo-1-phenyl-1-silacyclopentane (II)

Lithium aluminum hydride (0.7 g, 18.5 mmol) and 15 mL of ether were placed in a 50 mL round bottom flask equipped with a reflux condenser and a Teflon covered magnetic stirring bar. The flask and its contents were cooled to 0^{o}C and VI (3 g, 12.3 mmol) was slowly added. The mixture was stirred for 3 h at 0^{o}C and then was allowed to warm to room temperature. The ethereal solution was decanted from the excess lithium aluminum hydride and was washed with water, dried over anhydrous magnesium sulfate, filtered and the volatile solvent removed by evaporation under reduced pressure. The residue was fractionally distillation as above. A fraction, bp 153-154^{o}C/1 mm, 2.52 g, 98% yield was collected. ^{1}H NMR δ: 2.32(dd,2H, J = 17.6 and 3.3 Hz), 2.46(dd,2H, J = 17.6 and 3.3 Hz), 4.83(q,1H, J = 3.3 Hz), 7.07(m,2H), 7.26(m,5H), 7.51(m,2H). ^{13}C NMR δ: 18.34, 125.95, 127.96, 129.01, 129.83, 134.15, 134.39, 141.23. ^{29}Si NMR δ: -1.78. IR ν: 3059, 3010, 2135 (s), 1475, 1448, 1427, 1395, 1207, 1127, 1115, 937, 847, 751, 728, 695 cm^{-1}. UV λ_{max} nm (ε): 225(8317); 269(1686); 276(1285). Elemental Anal. Calcd. for $C_{14}H_{14}Si$: C, 80.00; H, 6.67. Found: C, 79.72; H, 6.73.

poly(3,4-Benzo-1-phenyl-1-silapentane) (I)

In a 50 mL round bottom flask equipped with a Teflon covered magnetic stirring bar was placed II (3.6 g, 17.3 mmol), THF (20 mL) and HMPA (0.1 mL). The flask was sealed with a rubber septum and was cooled to -78^{o}C. Methyllithium(0.6 mL, 0.85 mmol) was slowly added via a syringe. The mixture was stirred at -78^{o}C for 4 h. It was quenched at -78^{o}C by addition of 10 mL of saturated aqueous NH_4Cl. Ten mL of ether was added and the organic layer was separated, washed with water, dried over anhydrous magnesium sulfate, filtered and the volatile solvent removed by evaporation under reduced pressure. The residue was taken up in ether and I was precipitated by addition of 15 mL of methanol. In this way, 1.4 g, 40% yield of a sticky material was obtained. M_w/M_n = 2130/1900. T_g = 13.87 ^{o}C. ^{1}H NMR : 2.20(m,4H), 4.27(m,0.9H), 7.13(m,9H). ^{13}C NMR δ: 18.48, 19.13, 19.21, 19.41, 20.25, 20.45, 124.90, 125.84, 127.75, 127.87, 127.92, 127.95, 129.03, 129.51, 129.53, 129.55, 134.02, 134.78, 134.80, 135.27, 136.00, 136.06, 141.32. ^{29}Si NMR δ: 13.54, -11.08, -11.30, -31.15. IR ν: 3067, 3012, 2898, 2134 (s), 1598, 1483, 1449, 1429, 1396, 1212, 1189, 1153, 1115, 1053, 939, 864, 807, 759, 737, 699 cm^{-1}. UV λ_{max} nm (ε): 238(10,225), 272(3,360). Elemental Anal. Calcd. for $C_{14}H_{14}Si$: C, 80.00; H, 6.67. Found: C, 79.32; H, 6.71.

3,4-Benzo-1,1-diphenyl-1-silacyclopentene (VII)

In a 50 mL round bottom flask equipped with a Teflon-covered magnetic stirring bar was placed V (2.35 g, 11.6 mmol) and 5 mL of THF. The flask was sealed with a rubber septum. The flask and its contents were cooled to 0°C in an ice-water bath. Phenylmagnesium chloride in THF (22.6 mL, 46.6 mmol) was added via a syringe to the well stirred reaction mixture. The reaction was allowed to stir for 3 h. The reaction was quenched by addition of water. Ether (10 mL) was added. The solution was extracted twice with water, dried over anhydrous magnesium sulfate, filtered, and the volatile solvents were removed by evaporation under reduced pressure. The residue was distilled under reduced pressure. A fraction bp 200-201°C/3.2 mm, 2.23 g, 67% yield was obtained. ^{1}H NMR δ: 2.58(s,4H), 7.07(m,2H), 7.30(m,8H), 7.55(m, 4H). ^{13}C NMR δ: 19.90, 125.97, 127.96, 128.69, 129.15, 129.69, 134.74, 134.81, 141.38. ^{29}Si NMR δ: 7.97. Elemental Anal. Calcd. for $C_{20}H_{18}Si$: C, 83.86; H, 6.33. Found: C, 84.03; H, 5.93.

3,4-Benzo-1-silacyclopentene (IV)

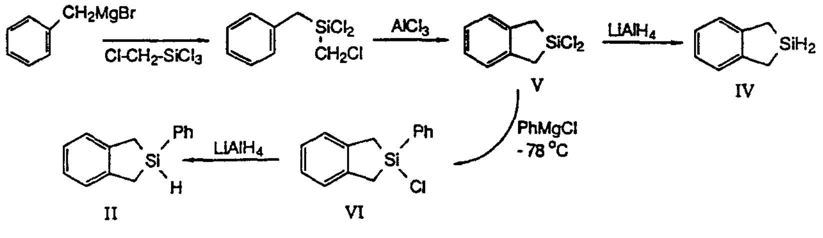
In a 100 mL round bottom flask equipped with reflux condenser and a Teflon covered magnetic stirring bar was placed lithium aluminum hydride (2.4 g, 64 mmol) and ether 50 mL. The flask and its contents were immersed in an ice-water bath. To the well stirred solution was added V (8.5 g, 42 mmol) via a syringe. The ice-water bath was removed and the reaction was allowed to warm to room temperature over 3 h. The reaction was quenched by addition of water. The ether layer was separated, dried over anhydrous magnesium sulfate, filtered and the ether solvent removed by evaporation under reduced pressure. The residue was purified by fractional distillation as above. A central fraction, bp 55°C/4 mm (lit. bp 190.5-192.5 °C) [9] 4.0 g, 71% yield was obtained. ^{1}H NMR δ: 2.25(t,4H, J = 3.8 Hz), 4.08(q,2H, J = 3.8 Hz), 7.05(m,2H), 7.23(m,2H). ^{13}C NMR δ: 14.74, 125.82, 128.89, 141.17. ^{29}Si NMR δ: -24.88.

Poly(3,4-benzo-1-silapentene) (III)

In a 50 mL Schlenk flask equipped with a Teflon covered magnetic stirring bar was placed IV (1.0 g, 7.5 mmol) and THF (5 mL). The flask was sealed with a rubber septum and was cooled to -78°C. *n*-Butyllithium (0.1 mL, 0.25 mmol) was slowly added via a syringe to the well stirred reaction mixture. The solution became pale yellow. The mixture was stirred at -78°C for 3 h. The reaction was then quenched by the dropwise addition of 10 mL of a saturated solution of aqueous NH_4Cl at -78°C. Ether (15 mL) was added and the organic layer was extracted with water, dried over anhydrous magnesium sulfate, filtered and the volatile solvents removed by evaporation under reduced pressure. The residue (0.72 g) was dissolved in a minimum amount of THF and was precipitated by addition of 6 mL of methanol. In this way 0.5 g, 50% yield of a white fluffy polymer was obtained. It had the following properties: M_w/M_n = 23,900/8050, T_g 37 °C, T_m 59-61 °C. ^{1}H NMR δ: 0.85(m, 0.08H), 1.26(m, 0.06H), 1.7-2.1(br.m,4H), 3.4-3.8(br.m, 1.25H), 6.8-7.1(br.m,4H). ^{13}C NMR δ: 8.79, 13.11, 13.71, 16.41, 17.26, 17.30, 18.42, 19.66, 21.04, 25.75, 27.36, 124.70, 125.22, 125.72, 125.85, 128.18, 128.34, 128.50, 128.83, 129.07, 129.29, 136.05, 136.68, 138.96, 141.09, 141.26. ^{29}Si NMR δ: 21.40, 1.01, -3.08, -6.44, -28.85, -29.20, -57.55, -57.84. IR : 3040, 3000, 2900, 2132 (s), 1600, 1560, 1480, 1450, 1400, 1300, 1260, 1210, 1190, 1150 (br.s), 1050 (br.s), 940, 920, 850 (s) cm^{-1}. Elemental Anal. Calcd. for $C_8H_{10}Si$: C, 71.66; H, 7.46. Found: C, 71.32; H, 7.29.

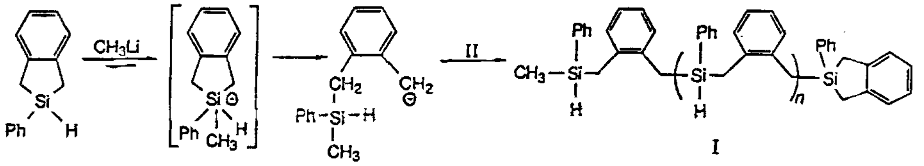
RESULTS AND DISCUSSION

3,4-Benzo-1,1-dichloro-1-silacyclopentene is a key intermediate in the preparation of II and IV.



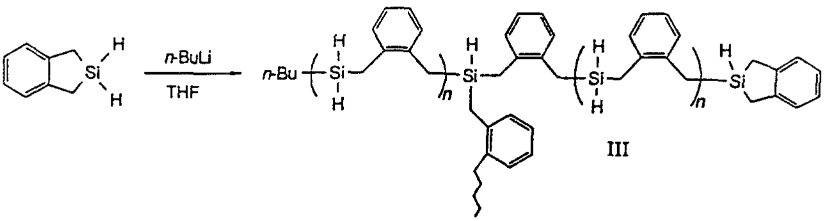
3,4-Benzo-1-phenyl-1-silacyclopentene (II) undergoes anionic ring opening oligomerization on treatment with a catalytic amount of methyllithium and hexamethylphosphoramide (HMPA) in THF at -78°C to yield low molecular weight poly(3,4-benzo-1-phenyl-1-silapentene) (I). Similar anionic ring opening polymerizations of 3,4-benzo-1,1-dimethyl-1-silacyclopentene (VIII)(6), 3,4-benzo-1-methyl-1-silacyclopentene (IX) (7) 1,1-dimethyl-1-silacyclopent-3-ene (X)(3), 1-methyl-1-silacyclopent-3-ene (XI) (4) and 1-phenyl-1-silacyclopent-3-ene (XII)(5) have been reported. These polymerizations have been proposed to proceed by nucleophilic addition of an alkyllithium reagent to the silyl center of the monomer to yield an anionic pentacoordinate siliconate intermediate which undergoes ring opening to yield an allyl or benzyl anion. This may involve relief of ring strain. Attack of the allyl or benzyl anion on the silyl center of another molecule of monomer results in chain growth and formation of another negatively charged pentacoordinate silicon intermediate. The anionic polymerization of II to yield I probably follows a similar mechanistic pathway. The ^{29}Si NMR resonances at -11.08 and -11.30 ppm in the spectrum of I may be assigned to the 3,4-benzo-1-phenyl-1-silapentene units of the polymer. For comparison, the ^{29}Si NMR resonances for 1-phenyl-1-silapentene units of poly(1-phenyl-1-silapentene) are found at -15.74 ppm.

The fact that monomers substituted with Si-H bonds give low molecular weight polymers has been interpreted as resulting from the ease of loss of lithium hydride from such pentacoordinate siliconate intermediates. Silacyclopentene rings observed in the ^{29}Si NMR of these low molecular weight polymers have been interpreted as end groups formed by this process. The observation of a signal at 13.54 ppm in the ^{29}Si NMR of I is consistent with the presence of a 3,4-benzo-1-silacyclopentene ring in which the silyl center is substituted with a phenyl group as well as an allyl group from the polymer chain. This value is intermediate between that of the ^{29}Si NMR chemical shift of VII which is found at 7.97 ppm and that for 3,4-benzo-1,1-dimethyl-1-silacyclopentene which is observed at 18.3 ppm.



On the other hand, it was essential to eliminate HMPA to achieve successful anionic ring opening polymerization of IV to yield III. In the presence of HMPA, polymerization of IV gave a polymer which contained little or no Si-H bonds. The fact that silanes are known to reduce P=O bonds of phosphine oxides may provide an explanation for this observation (12). On the other hand, problems with HMPA have not been observed in the polymerization of II, XI or XII. At this time, IV is the only 3,4-benzo-1-silacyclopentene or for that matter 1-silacyclopent-3-ene system we have been able to anionically polymerize without co-catalysis by HMPA, TMEDA or N,N'dimethylpropyleneurea (DMPU). In addition, we have been unable to polymerize VII. The reasons for this is not understood at present.

^{29}Si NMR spectra of III indicates a more complex microstructure for this polymer than has been proposed for I. Four sets of resonances are observed in the ^{29}Si NMR of III. The resonances between -28.4 and -29.7 can be assigned to 3,4-benzo-1-silapentene units. A number of ^{29}Si signals can be assigned to branch points. These can be formed by nucleophilic attack of a propagating benzyl anion on one of the silyl centers in the polymer chain with loss of hydride. Hydride is well known to function as a leaving group in nucleophilic substitution reactions at silyl centers (10,11). Specifically, the ^{29}Si signal at 21.4 ppm is assign to a 3,4-benzo-1-silacyclopentene ring in which both of the hydrogens bonded to silicon have been displaced by benzyl anions. For comparison, the ^{29}Si resonance of 3,4-benzo-1,1-dimethyl-1-silacyclopentene is found at 18.31 ppm. The signals at 1.1 and 1.0 probably arise from end groups formed by loss of hydride from the pentacoordinate siliconate intermediate rather than ring opening to a benzyl anion. Consistent with this interpretation, the integration of the ^{1}H NMR signal for the Si-H bonds is only 1.25H instead of the predicted value of 2H. Branch points may permit the union of several polymer chains. This may account for the high molecular weight observed for III compared to I.



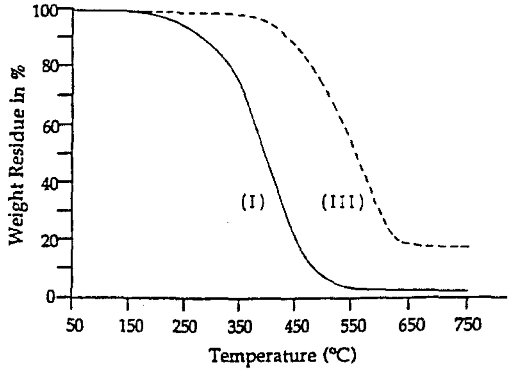
III

While the elemental analysis of both I and III are acceptable both of these polymers contain a small number of siloxane bonds. This is evident from the IR spectra which show siloxane bands between 1150 and 1050 cm^{-1} as well as from the ^{29}Si NMR spectra. In the case of I, ^{29}Si resonances are observed at -31 ppm while for III resonances at -57.6 and -57.8 ppm are observed. These may be assigned to the siloxane microstructures below.

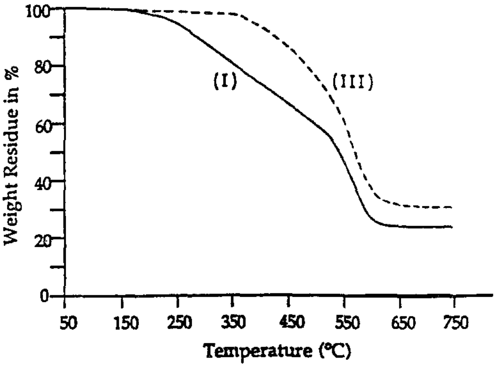
The thermal stability of I and III in the presence of both nitrogen and air was determined by TGA. In an atmosphere of nitrogen, I is stable to 150^{o}C. Between 150 and 250^{o}C I loses four percent of its initial weight. Between 250 and 350^{o}C an additional fifteen percent weight loss is observed. Above 350^{o}C rapid **catastrophic weight loss** occurs. By 500^{o}C less than ten percent of the initial sample weight remains. Above 550^{o}C less than one percent residue remains (Figure 1). III is also stable to 150^{o}C. Between 150 and 400^{o}C three percent of the initial sample weight is lost. Rapid weight loss occurs between 400 and 600^{o}C. A black residue amounting to sixteen percent of the sample weight is found.

In the presence of air, I is likewise stable to 150^{o}C. Between 150 and 225^{o}C three percent weight loss occurs. Between 225 and 550^{o}C, forty-three percent weight loss occurs at a steady rate. Between 550 and 600^{o}C an additional thirty percent weight loss rapidly occurs. Above 625^{o}C no further weight loss is observed. A white colored residue amounting to twenty-five percent of the initial sample weight is found. This is most probably silicon dioxide. The theoretical yield of silicon dioxide would be twenty-eight and a half percent.

On the other hand, III does not lose weight in air until 350^{o}C. Rapid weight loss occurs between 375 and 600^{o}C occurs. A white residue amounting to thirty-one percent of the initial sample weight is found. The theoretical yield of silicon dioxide would be almost forty-five percent.



THERMOGRAVIMETRIC ANALYSIS OF I AND III IN NITROGEN



THERMOGRAVIMETRIC ANALYSIS OF I AND III IN AIR

The thermal decomposition in an inert atmosphere of these poly(silapent-3-enes) [X, XI and XII] and poly(3,4-benzo-1-silapentenes) [I, VIII, IX] demonstrates two types of behavior. Those which have both reactive Si-H and C-C double bonds, such as XI and XII, undergo decomposition to yield a ceramic (SiC) char. On the other hand, those which do not possess **both** of these reactive units, such as I, VIII, and X, undergo catastrophic decomposition. These observations are consistent with the hypothesis that crosslinking via thermal intra-chain hydrosilation reactions are critical for the formation of high char yields from such unsaturated carbosilane polymers (13-15). The observation of a significant char yield in the thermal decomposition of III is exceptional. This may result from the branched nature of III as it is formed under the anionic polymerization conditions.

Acknowledgements: This work was supported in part by the Office of Naval Research and the Air Force Office of Scientific Research.

REFERENCES

1. Yajima S, Hasegawa Y, Hayashi J, Iimura M (1978) J Mater Sci **13**: 2569
2. Bacque E, Pillot J-P, Birot M, Dunogues J (1988) Macromolecules **21**: 30
3. Zhang X, Zhou Q, Weber W-P, Horvath R-F, Chan T-H, Manuel G (1988) Macromolecules **22**: 1563
4. Zhou S-Q, Weber W-P (1990) Macromolecules **23**: 1915
5. Liao X, Ko Y-H, Manuel G, Weber W-P (1990) Polym Bull **25**: 63
6. Park Y-T, Zhou Q, Weber W-P (1989) Polym Bull **22**: 349
7. Zhou S-Q, Weber W-P (1990) Makromol Chem Rapid Commun **11**: 19
8. Freeman R, Hill H-D-W, Kaptein R (1972) J Magn Reson **7**: 327
9. Nametkin N-S, Vdovin V-M, Finkel'shtein E-Sh, Arkhipove T-N, Oppengeim V-D (1964) Dokl Akad Nauk SSSR **154**: 383
10. Peake J-S, Nebergall W-H, Chen Y-T (1952) J Am Chem Soc **74**: 1526
11. Gilman H, Zeuch E-A (1957) J Am Chem Soc **79**: 4560
12. Weber W-P (1983) Silicon Reagents for Organic Synthesis, Springer-Verlag, Berlin, pp 328-332
13. Baney R-H, Gaul J-H Jr., Hilty T-K (1983) Organometallics **2**: 859
14. Schilling C-L Jr, Wesson J-P, Williams T-C (1983) Ceramic Bull **62**: 859
15. Boury B, Carpenter L, Corriu R-J-P (1990) Angew Chem Int Ed **29**: 785

Accepted April 29, 1991 K