Linear Hybrid Polymer Building Blocks: Methacrylate-Functionalized Polyhedral Oligomeric Silsesquioxane Monomers and Polymers

Joseph D. Lichtenhan,* Yoshiko A. Otonari, and Michael J. Carr

Propulsion Directorate, Phillips Laboratory, Edwards Air Force Base, California 93524

Received June 26, 1995
Revised Manuscript Received September 19, 1995

Introduction. The development of materials with enhanced properties that can be understood and tailored at the molecular level is the premier challenge for materials chemists. In an effort to meet this challenge, new classes of monomers capable of imparting novel properties to common classes of polymeric materials have been prepared. Polyhedral oligomeric silsesquioxanes (POSS) are a class of compounds which have recently received a considerable amount of interest for application in catalysis,[1] modeling of silica surfaces and interfaces,[2] as precursors to silicates,[3] and as polymerizable reagents.[4] This report describes the preparation of POSS monomers and corresponding linear polymers derived from methacrylate-functionalized polyhedral oligomeric silsesquioxanes (POSSMA).

Experimental Section. Precipitated powder samples were used for X-ray diffraction and differential scanning calorimetry (DSC) experiments. Samples were pressed into pellets for thermomechanical analysis (TMA). DSC experiments were run at 10 °C/min under nitrogen on a TA Instruments module 910, and TMA experiments were run at 3 °C/min under nitrogen on a TA Instruments module 2940. NMR spectra were obtained on a Bruker AMX 300 spectrometer operating at 300 MHz (^{1}H) and 59.6 MHz (^{29}Si). Molecular weight determinations were made by size exclusion chromatography with DAWN light scattering and refractive index detectors. Elemental analyses were performed by Galbraith Laboratories, Inc.

POSSMA Macromers. POSS reagents containing not more than one or two points of functionalization are desirable for the design of linear polymeric POSS systems. An efficient method for preparing such reagents involves the corner-capping of incompletely condensed POSS trisilanols $R_7T_7(OH)_3$ (Figure 1). Corner-capping of the POSS trisilanol can be carried out using a variety of trichlorosilane coupling agents[5] to produce a fully condensed T_8-POSS silicon–oxygen framework.[6] We have used this method to prepare octameric T_8-POSS reagents in which only one corner is functionalized with a graftable or polymerizable group (Scheme 1).[7] Families of functionalized POSS R_7T_8-acrylic, -α-olefin, and -silane reagents suitable for the preparation of linear POSS polymers have been prepared in this manner.

POSS reagents are unique in both their chemical composition and physical nature. The rigid, thermally stable silicon–oxygen framework[8] contains an oxygen to silicon ratio of 1.5, which is intermediate between that for siloxanes and silica. This inorganic framework is in turn covered by a hydrocarbon outer layer enabling solubilization and derivatization of these systems.

Macromers **3** and **4** (Scheme 1) are highly soluble in common solvents such as THF, hexane, and chloroform and are readily characterized by solution NMR spectroscopy.[7] The ^{1}H spectra for **3** and **4** show nearly identical sets of resonances for the vinyl protons, the methyl of the methacrylate group, and the first methylene of the propyl ester linkage. Resonances for the remaining two propyl ester methylenes partially overlap with the three broad cyclohexyl and cyclopentyl resonances of **3** and **4**. The ^{29}Si spectra for **3** and **4** are uncomplicated and show two resonances in a 1:7 ratio in which those for equivalently substituted silicons are overlapping.

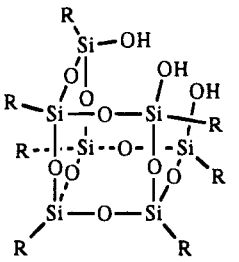
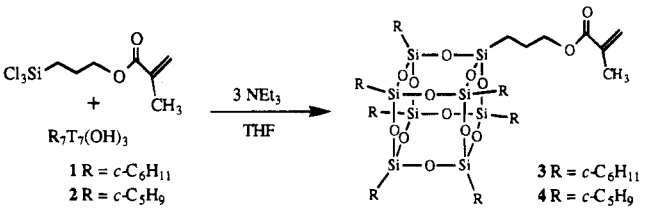


Figure 1. Structural representation of $R_7T_7(OH)_3$ trisilanol.

Scheme 1



Once appropriately functionalized, POSS macromers, like organic reagents, can participate in a variety of common transformations, polymerizations, and grafting reactions. For example, monofunctionalized T_8-POSS-α-olefins can be converted into α-epoxides using standard organic techniques.[9] In addition, the silane-functionalized compounds R_7T_8H readily participate in hydrosilylation reactions to afford a graftable source of POSS useful in the modification of various vinyl-containing reagents and polymers.[10]

POSSMA Polymers. The amenability of new monomers and polymers to standard reaction chemistry and processing techniques is highly desirable for manufacturing and engineering purposes. The methacrylate group on **3** and **4** enables these macromers to be polymerized under common free-radical conditions (Scheme 2).

Homopolymers **5** and **6** differ compositionally by the nonreactive alkyl substituent (R) on the POSS cage (**5**, R = *c*-C_6H_{11}; **6**, R = *c*-C_5H_9). Polymer **7** is a 50/50 copolymer containing both cyclohexyl- and cyclopentyl-substituted POSS cages. The nature of the alkyl substituent on the POSS cage significantly affects the solubilities of these systems. Homopolymer **5** and copolymer **7** are soluble in common solvents, while homopolymer **6** is insoluble in all common hydrocarbon and halogenated hydrocarbons. The disparity in solubilities between polymers **5** and **6** is not easily understood given the relatively minor differences between the cyclohexyl and cyclopentyl groups, nor is the behavior predictable given the observed solubility for copolymer **7**. Solubility differences between the POSSMA macromers **3** and **4** however were observed in THF, toluene, and benzene where the cyclohexyl-substituted **3** shows approximately twice the solubility of **4**. For the POSS triols (**1**, **2**), **2** cannot be appreciably solubilized without the addition of small amounts of a Lewis base (such as

Scheme 2

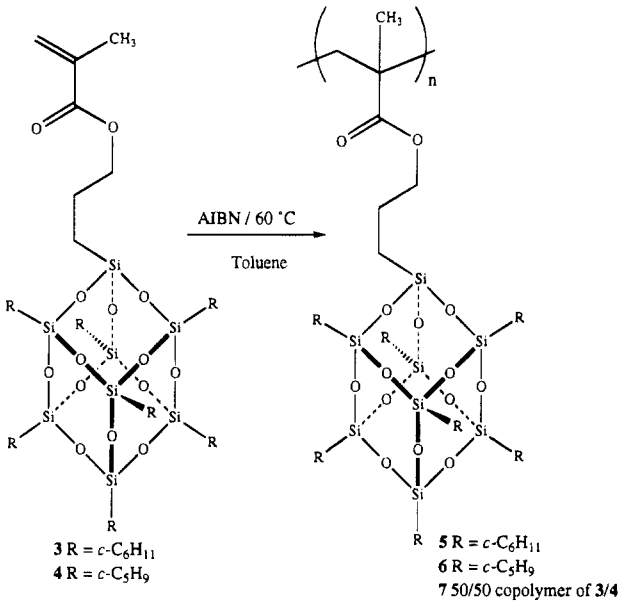


Table 1. Molecular Weights and Thermal Properties of POSSMA Reagents and Polymers

compound	mol wt (amu)	transition (°C)[c]	T_{dec} (°C)[f]
1 (c-$C_6H_{11})_7T_7(OH)_3$	973.69	244–287[d]	383
2 (c-$C_5H_9)_7T_7(OH)_3$	875.50	246–276[d]	310
3 macromer	1125.92	186–257, 387–416[e]	410
4 macromer	1027.73	192–242, 279–298[e]	351
5 homopolymer	222[a]/117[b]	none	388
6 homopolymer		none	389
7 copolymer 50/50	376[a]/147[b]	none	389

[a] $M_w \times 10^3$. [b] $M_n \times 10^3$. [c] By TMA with a penetration probe and 10 g weight. [d] Melt/polymerization. [e] Melt/polymerization/decomposition onset. [f] Defined by a 10% mass loss at a 10 °C/min heating rate under nitrogen.

pyridine or other amine). In this case, Lewis bases are needed in order to disrupt the hydrogen bonding between the silanols of the POSS cages.[11]

It was originally thought that the bulkiness of the POSSMA macromers **3** and **4** might prevent their polymerization. Despite this preconsideration, these systems easily polymerized and molecular weights were determined for polymers **5** and **7**. Homopolymer **5** had M_n = 117K and M_w = 222K, which corresponds to about 104 monomer units per chain. Copolymer **7** had M_n = 147K, and M_w = 376K, which corresponds to about 137 monomer units per chain if we assume that macromers **3** and **4** had similar reactivity ratios and were equally consumed in the polymerization. The sequence composition, tacticity, and macromer reactivity ratio favored under these and other conditions will be discussed in subsequent work.

Characterization and Properties. While detailed structure–property relationships have only begun to be determined for polymeric POSS-based systems,[12] it was anticipated that POSS segments may behave as a hard, reinforcing component in elastomers or as a crystalline/glassy segment/phase or filler in linear thermoplastics.[13] Can POSS segments behave like conventional organic hard blocks in thermoplastic systems? This assumption is in part supported by the thermal transitions for the macromers and polymers listed in Table 1.

The POSS triols and POSSMA macromers **1**–**4** were confirmed by X-ray powder diffraction to be crystalline. The POSS-triol systems displayed lower melt transitions than the corresponding macromers **3** and **4**. Interestingly, macromer **3** shows a broad two-step thermal transition beginning at 186 °C that involves melting, polymerization, and decomposition. The cyclopentyl-substituted macromer **4** underwent a similar transition beginning at 192 °C. Differences between the POSS alkyl substituents (R) did not influence the relative thermal stabilities of the macromers or polymers.

No thermal transitions were observed by DSC or TMA (from 0 to 400 °C) for the polymeric POSS methacrylates **5**–**7**. This result contrasts with the observed glass transitions (T_g) for atactic (105 °C), syndiotactic (160 °C), and isotactic (43 °C) PMMA and for atactic (104 °C), syndiotactic (163 °C), and isotactic (51 °C) PCyMA.[14b] It was our preconception that incorporation of the POSS group into linear polymers would result in a reduction of segmental mobility. This is due to the physical size of **3** and **4**, which is on the order of 15 Å with approximate equivalent weights of 1000 amu. The dependency of T_g in methacrylate polymers on the nature and motions of the ester group is known.[14] The apparent absence of a glass transition in the poly-POSSMA systems perhaps reflects an overall rigid nature of the methacrylate polymer backbone resulting from the dominant T_8-POSS pendant groups. The magnitude of such effects should be tailorable via copolymerization.[15]

Polymers **5**–**7** are best described as transparent, brittle plastics. X-ray diffraction studies on reprecipitated powder samples of **5**–**7** showed them to be amorphous, a surprising result given the highly crystalline structure of the pendant POSS group and the observation of crystallinity and liquid crystallinity for acrylates containing long and/or mesogenic ester groups.[16] The lack of crystallinity in these systems may reflect the propyl ester linkage being too short to decouple the T_8-POSS group from motions of the amorphous backbone. Alternatively, the macromeric nature of the POSS group may prohibit or retard kinetic processes that could ultimately lead to the formation of crystalline regions in these materials. Attempts to anneal these materials have been unsuccessful.

The thermal stability of polymers **5**–**7** (and for **1**–**4**) was observed to be very high, with **5**–**7** decomposing at 388 °C without melting. This decomposition is higher than that observed for poly(methyl methacrylate) (PMMA). PMMA begins its depolymerization to methyl methacrylate above 200 °C and quantitatively yields monomer at 350–450 °C.[17]

The synthesis of functionalized polyhedra such as the T_8-POSSMA in this work is an effort to advance materials chemistry by providing new classes of monomers, polymers, and additives. Monomethacrylate-functionalized POSS reagents are capable of being polymerized into novel linear silsesquioxane-based materials. Efforts to copolymerize these POSSMA with other acrylic comonomers have been successful, and reports will be forthcoming.

Acknowledgment. This research was supported by the Air Force Office of Scientific Research, Directorate of Chemistry and Life Sciences. We thank Mr. Paul Jones for thermal analysis assistance and Dr. Kevin Chaffee for X-ray powder diffraction experiments.

References and Notes

(1) Feher, F. J.; Tajima, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 2145 and references therein. Field, L. D.; Lindall, C. M.;

Maschmeyer, T.; Masters, A. F. *Aust. J. Chem.* **1994**, *47*, 1127. Herrmann, W. A.; Anwander, R.; Dufaud, V.; Scherer, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1285. Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 586.

(2) Banaszak Holl, M. M.; Lee, S.; McFeely, F. R. *Appl. Phys. Lett.* **1994**, *65*, 1097. Lee, S.; Makan, S.; Banaszak Holl, M. M.; McFeely, F. R. *J. Am. Chem. Soc.*, in press. Banaszak Holl, M. M.; McFeely, F. R. *Phys. Rev. Lett.* **1993**, *71*, 2441. Bürgy, H.; Calzaferri, G.; Kamber, I. *Mikrochim. Acta* **1988**, *1*, 401. Beer, R.; Bürgy, H.; Calzaferri, G.; Kamber, I. *J. Electron Spectrosc. Relat. Phenom.* **1987**, *44*, 121.

(3) (a) Feher, F. J.; Weller, K. J. *Chem. Mater.* **1994**, *6*, 7. (b) Agaskar, P. A. *Colloids Surf.* **1992**, *63*, 131. (c) Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 8262.

(4) Lichtenhan, J. D. *Comments Inorg. Chem.* **1995**, *17*, 115. Haddad, T. S.; Lichtenhan, J. D. *J. Inorg. Organomet. Polym.* **1995**, *5*, 237. Feher, F. J.; Weller, K. J.; Schwab, J. J. *Organometallics* **1995**, *14*, 2009. Sellinger, A.; Laine, R. M.; Chu, V.; Viney, C. *J. Polym. Sci., A.* **1994**, *32*, 3069. Weidner, R.; Zeller, N.; Deubzer, B.; Frey, V. U.S. Patent 5 047 492, 1991.

(5) Otonari, Y. A.; Lichtenhan, J. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 513. Haddad, T. S.; Lichtenhan, J. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 511. Feher, F. J.; Weller, K. J.; Schwab, J. J. *Organometallics* **1995**, *14*, 2009. Shockey, E.; Lichtenhan, J. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 525.

(6) The symbols M_x, D_x, T_x, and Q_x denote the type and number (x) of silicon atoms bound to 1, 2, 3, and 4 oxygen atoms within a silicon–oxygen framework. See: Barton, T. J.; Boudjouk, P. In *Silicon-Based Polymer Science: A Comprehensive Resource*; Zeigler, J. M., Gordon Fearon, F. W., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990; p 6.

(7) The POSS triols (c-$C_6H_{11})_7Si_7O_9(OH)_3$ (**1**) and (c-$C_5H_9)_7$-$Si_7O_9(OH)_3$ (**2**) were prepared according to literature methods.[11] Macromer **3** was prepared by dissolving **1** (2.508 g, 2.58 mmol) and triethylamine (1.15 mL, 8.25 mmol) in 25 mL of THF. The solution was cooled in an ice bath, and a THF solution of ((3-(methacryloxy)propyl)trichlorosilane (0.675 g, 2.58 mmol, 0.516 M) was added dropwise over a 5 min period to the stirred solution. The mixture was allowed to warm to room temperature and reacted for 12 h. The reaction was filtered to remove $Et_3N{\cdot}HCl$, and the filter cake was washed with THF (1 × 30 mL). Removal of volatiles under reduced pressure and ambient temperature afforded a yellow solid that was subsequently dissolved in a minimum amount of benzene and precipitated into acetonitrile (5-fold excess). After filtration and drying under vacuum, the yield of white powder was 94% (2.73 g) **3**. ^{1}H-NMR ($CDCl_3$): 6.11 (dq, 1 H), 5.54 (dq, 1 H), 4.13 (t, J_{H-H} = 13 Hz, 2 H), 1.95 (dd, 3 H), 1.73 (m, 37 H), 1.23 (m, 35 H), 0.76 (m, 9 H) ppm. ^{29}Si-NMR ($CDCl_3$): −66.77 (1 Si), −68.62 (7 Si) ppm. Elemental anal. (calcd) for **3**: C, 52.39 (52.27); H, 8.00 (7.88). Macromer **4** was prepared and recovered under similar conditions except that **2** (25.0 g, 28.56 mmol) was dissolved in 400 mL of THF to which 10 mL of pyridine was additionally added for improved dissolution. Yield of reprecipitated white solids was 71% (20.86 g) **4**. ^{1}H-NMR ($CDCl_3$): 6.11 (dq, 1 H), 5.54 (dq, 1 H), 4.12 (t, J_{H-H} = 13 Hz, 2 H), 1.95 (dd, 3 H), 1.75 (b, 14 H), 1.52 (m, 44 H), 0.97 (m, 7 H), 0.67 (m, 2 H). ^{29}Si-NMR ($CDCl_3$): −66.49 (7 Si), −66.91 (1 Si). Elemental anal. (calcd) for **4**: C, 49.09 (49.09); H, 7.48 (7.26). In a typical polymer synthesis, a 0.5 M toluene solution of macromer **3** or **4** was prepared to which 1 mol % of azobis(isobutyronitrile) (based on macromer) was added from a stock solution. The clear solution was heated at 60 °C for 24 h and then precipitated into methanol. Further purification was performed by reprecipitation from toluene into methanol (100 fold excess). Yield of white powder was nearly quantitative. Polymer **5**: ^{1}H-NMR ($CDCl_3$): 3.85 (b, 2 H), 1.73 (b, 42 H), 1.24 (b, 35 H), 0.76 (b, 9 H). ^{29}Si-NMR ($CDCl_3$): −67.05 (1 Si), −68.69 (7 Si). Elemental anal. (calcd) for polymer **5**: C, 51.99 (52.27); H, 8.23 (7.88). Elemental anal. (calcd) for polymer **6**: C, 48.76 (49.09); H, 7.28 (7.26). Polymer **7**: ^{29}Si-NMR ($CDCl_3$): −66.46 (7 Si), −67.02 (2 Si), −68.57 (7 Si). Elemental anal. (calcd) for polymer **7**: C, 50.50 (50.75); H, 7.69 (7.58).

(8) Lichtenhan, J. D.; Mantz, R. A.; Jones, P. F.; Gilman, J. W.; Chaffee, K. P.; Ismail, I. M. K.; Burmeister, M. J. *Chem. Mater.*, submitted.

(9) Shockey, E.; Bolf, A. B.; Lichtenhan, J. D., manuscript in preparation. Haddad, T. S.; Lichtenhan, J. D., manuscript in preparation. Lichtenhan, J. D.; Feher, F. J.; Schwab, J. J., work in progress.

(10) Shockey, E.; Bolf, A. B.; Lichtenhan, J. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 515.

(11) Feher, F. J.; Newman, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1931. Brown, J. F., Jr.; Vogt, L. H., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 4313. Feher, F. J.; Budzichowski, T. A.; Blanski, R. L.; Weller, K. J.; Ziller, J. W. *Organometallics* **1991**, *10*, 2526.

(12) Lichtenhan, J. D.; Vu, N. Q.; Carter, J. A.; Gilman, J. W.; Feher, F. J. *Macromolecules* **1993**, *26*, 2141. Lichtenhan, J. D.; Mantz, R. A.; Jones, P. F.; Carr, M. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 523. Shockey, E.; Lichtenhan, J. D.; Mantz, R. A.; Jones, P. F., manuscript in preparation.

(13) For example, see: Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice-Hall: Englewood Cliffs, NJ, 1992; pp 155–158. Sperling, L. H. *Introduction to Physical Polymer Science*; Wiley: New York, 1986; pp 346–348.

(14) (a) Schmidt-Rohr, K.; Kulik, A. S.; Beckham, H. W.; Ohlemacher, A.; Pawelzik, U.; Boeffel, C.; Spiess, H. W. *Macromolecules* **1994**, *27*, 4733. (b) Kine, B. B.; Novak, R. W. In *Concise Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; Wiley: New York, 1990; p 18. (c) Gargallo, L.; Hamidi, N.; Radic, D. *Thermochim. Acta* **1987**, *114*, 319. (d) Krause, S.; Gormley, J. J.; Roman, N.; Shetter, J. A.; Watanabe, W. H. *J. Polym. Sci., Part A* **1965**, *3*, 3573.

(15) Scholsky, K. M.; Lichtenhan, J. D., work in progress. Bolf, A. B.; Otonari, Y. A.; Lichtenhan, J. D., work in progress.

(16) For example, see: Craig, A. A.; Imrie, C. T. *Macromolecules* **1995**, *28*, 3617. Lorenz, R. *Liq. Cryst.* **1991**, *91*, 127. Finkelmann, H.; Ringsdorf, H.; Wendorff, J. H. *Makromol. Chem.* **1978**, *179*, 273.

(17) Saunders, K. J. *Organic Polymer Chemistry*; Chapman and Hall: London, 1973; p 131.

MA9509016