Macromolecules

Volume 38, Number 6 March 22, 2005

© Copyright 2005 by the American Chemical Society

Communications to the Editor

Synthesis and Lithographic Patterning of Polycarbosilanes with Pendant Cobalt Carbonyl Clusters

Sharonna Greenberg, Scott B. Clendenning, Kun Liu, and Ian Manners*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada

Stéphane Aouba and Harry E. Ruda

Centre for Advanced Nanotechnology, University of Toronto, Toronto, Ontario M5S 3E4, Canada

Received August 8, 2004 Revised Manuscript Received December 16, 2004

Polycarbosilanes (PCS)¹⁻¹² represent structural hybrids between polysilanes and polyolefins which have found applications as lithographic resists,² liquid crystals,^{3,4} and pyrolytic precursors to silicon carbide-based ceramic fibers and monoliths.^{1,5} Ring-opening polymerization (ROP) provides the most convenient route to these materials: poly(silylenemethylene)s [RR'SiCH₂]_n, poly(silylenepropylene)s $[RR'SiCH_2CH_2CH_2]_n$ and other related polycarbosilanes can be synthesized by thermal or transition-metal-catalyzed ROP of 1,3-disilacyclobutanes or 1-silacyclobutanes, respectively.^{6,9,10,12b} Anionic ROP routes can also be used for 1-silacyclobutanes to afford moderate molecular weight polymers with narrow polydispersities.^{7,8,11,12a} The introduction of metal atoms into polymers is of interest as a means of creating functional macromolecular and supramolecular materials which combine processability with interesting redox, optical, electronic, preceramic, and catalytic properties.^{13–16} However, relatively few examples of metalfunctionalized linear polycarbosilanes have been reported.¹ In this communication we report the synthesis and characterization of a novel cobalt-clusterized poly-

 \ast To whom correspondence should be addressed: e-mail imanners@chem.utoronto.ca; Ph (416)-978-6157; Fax (416)-978-6157.

carbosilane, demonstrate a convenient method for molecular weight control, and illustrate the application of this material as a direct-write resist for electron beam lithography (EBL) to create metal-rich microscopic features with potential preceramic and catalytic applications.

To prepare cobalt-clusterized polycarbosilanes, we attempted a similar strategy to that used to prepare polyferrocenylsilane analogues (Co-PFS),^{17,18} which function as processable precursors to magnetic ceramics containing Fe/Co alloy nanoparticles. This involved clusterization of pendent acetylide groups on a polymer precursor.^{19,20}

The acetylide-substituted silacyclobutane **2** was prepared by the reaction of Li[C \equiv CPh] with the commercially available 1-chloro-1-methylsilacyclobutane (1), which resulted in selective substitution of the Cl atom for a phenylacetylene group (Scheme 1). A very slight excess of the silane was used to avoid anionic initiation of ring-opening polymerization by the lithium acetylide. Upon workup, the desired product (**2**) was obtained in good yield (64%) as a slightly yellow, highly viscous oil.

The ¹H, ¹³C{¹H}, and ²⁹Si{¹H} NMR spectra of **2** were consistent with the assigned structure. For example, the ¹³C{¹H} NMR spectrum showed resonances at 108.3 and 93.2 ppm, attributed to the acetylenic carbon atoms bound to the phenyl group and the silicon atom, respectively. This assignment was made in accord with the analogous acetylide-substituted [1]silaferrocenophane.²¹ The methylene carbon atoms on the silacyclobutyl ring were detected at $\delta = 19.2$ and 16.1 ppm (cf. $\delta = 21.1$ and 16.4 ppm for 1). A single resonance was observed in the ²⁹Si NMR spectrum at a chemical shift of $\delta = -6.8$ ppm, shifted upfield compared to 1 ($\delta = 33.2$ ppm).

Treatment of 1-silacyclobutanes with a transitionmetal catalyst (e.g., Pt or Rh complexes) has been shown to afford high molecular weight polycarbosilanes.^{1,22} Ring-opening polymerization of **2** in the presence of Karstedt's catalyst (Pt-divinyltetramethyldisiloxane complex in xylenes) occurred after 6 h at 60 °C in Scheme 1. Synthesis of the Acetylide-Substituted Silacyclobutane 2 and Its ROP To Afford the Polycarbosilane (PCS) 3 Which Yields Co-PCS 4 Following Clusterization with Dicobalt Octacarbonyl



toluene to afford PCS **3**, as an off-white gummy material following precipitation into methanol (Scheme 1).

The ¹H, ¹³C{¹H}, and ²⁹Si{¹H} spectra of **3** were consistent with the assigned structure. Only two resonances corresponding to the methylene protons were observed at $\delta = \text{ca. } 1.95$ and 1.0 ppm, instead of four resonances observed for **2**, supporting a linear chain structure. These peaks were shifted upfield compared to **2**, which may be attributed to the steric or electronic effects of ring opening. In the ¹³C{¹H} NMR spectrum, resonances assigned to the acetylenic carbon atoms were observed at $\delta = 107.6$ and 93.7 ppm, which were very similar to the corresponding monomer **2**. The methylene carbon atoms bound to silicon exhibited a significant downfield shift compared to **2**, with a resonance at $\delta =$ 19.9 ppm (cf. 16.1 ppm for **2**). The ²⁹Si{¹H} NMR spectrum displayed a peak at $\delta = -14.8$ ppm (cf. -6.8 ppm for 2). The molecular weight of 3, as measured by GPC, was determined to be in the range $3.9 \times 10^4 < M_n < 6.8 \times 10^4$ over several trials. The polydispersities (PDI) and yields for these polymers were in the ranges of 1.8-2.0 and ca. 50-60%, respectively.

To provide a means of conveniently controlling the molecular weight of **3**, we adapted a method first used to control the chain length of low molecular weight oligocarbosilanes ($M_{\rm n}$ < 4800)⁹ and, in our group, high molecular weight polyferrocenylsilanes^{23,24} (5000 < \dot{M}_n < 50000) which involves the addition of Si-H functional silanes such as Et₃SiH to the metal-catalyzed polymerization mixture. It is believed that the Si-H bond competes with the strained monomer for oxidative addition at the catalytic metal center and subsequent reductive eliminations yield end-functionalized materials (e.g., with Et₃Si and Si-H end groups).^{23,25} The addition of Et₃SiH to the ROP of 2 in the presence of Karstedt's catalyst (toluene, 6 h, 60 °C) indeed permitted excellent molecular weight control over the range of $5.0 \times 10^2 < M_{\rm n} < 5.8 \times 10^4$, as determined by GPC (Figure 1). The isolated yields of end-capped PCS 3 were lower (ca. 40%) for ratios of $2:Et_3SiH = 2:1$ and 10:1but were fairly consistent around ca. 60% for larger ratios of **2**:Et₃SiH.

Apart from the main chain Si atoms, four ²⁹Si NMR resonances were observed for end-capped **3** at $\delta = -18.9$, -6.2, 1.7, and 6.5 ppm, which were assigned to the silicon atoms in the Si-H, Si-OH, Si-OMe, and Et₃Si-C end groups, respectively. Presumably, the Si-OMe end group resulted from the methanolysis of the initial Si-H end group upon precipitation of the polymer into methanol. The presence Si-OH group could be attributed to hydrolysis of the initial Si-H end group and/or the Si-OMe group. In the ¹H NMR spectrum, the methyl protons of the Et₃Si-C end group resonated at $\delta = 1.0$ ppm, but the methylene protons of the Et₃Si-C end group could not be observed, presumably because they overlap with the relatively broad peaks of the polymer backbone. Two weak singlets at $\delta = 3.00$ and 3.02 ppm were ascribed to the two possible diastereotopic environments for the Si–OMe end groups.

To clusterize PCS 3, the polymer was reacted with excess dicobalt octacarbonyl $[Co_2(CO)_8]$. This resulted in the generation of polymer 4, by selective clusteriza-



Figure 1. Plot of M_n vs mole ratio of 2:Et₃SiH, demonstrating molecular weight control for the synthesis of PCS 3.

tion of the triple bond with a dicobalt hexcarbonyl moiety (Scheme 1). A powdery, brown, air- and moisture-stable polymer was obtained after precipitation from THF into methanol in 67% yield.

The Co-PCS 4 was characterized by ${}^{1}H$, ${}^{13}C{}^{1}H$, and $^{29}\mathrm{Si}$ NMR spectroscopy. The resonances for 4 were shifted downfield compared to those for 3. The ¹H NMR and ¹³C{¹H} NMR spectra of **4** showed broadened peaks; however, the observed resonances were consistent with the assigned structure. In the ¹H NMR spectrum, the broad peaks tended to overlap with regions at which resonances for 3 are located, and as a result, it was difficult to estimate the degree of clusterization of 4. Nonetheless, the region from 1.9 to 2.0 ppm, where some of the methylene protons of 3 are expected, did not display any peaks, suggesting that clusterization with dicobalt hexacarbonyl was quantitative. The resonances at $\delta = 1.55$ and 1.05 ppm were assigned to the protons of the methylene groups. In the ¹³C{¹H} NMR spectrum, the carbonyl groups were detected at $\delta = 200.9$ ppm, while the acetylenic carbon atoms were observed at δ = 107.6 and 78.9 ppm. Peaks corresponding to the methylene carbon atoms were located at $\delta = 21.8$ and 19.9 ppm. Solid-state ²⁹Si NMR spectroscopy revealed a broad singlet for 4 at $\delta = 1.3$ ppm.

Three stretches corresponding to terminal carbonyl groups were found in the IR spectrum of 4, located at 2086, 2049, and 2023 cm⁻¹. In addition, the C=C stretch at 2157 cm^{-1} present in the PCS precursor 3 was notably absent in the IR spectrum of 4, suggesting that clusterization was quantitative. We assume that clusterization of 3 proceeds without significant chain cleavage,²⁶ and molecular weight analysis of **4** by GPC was not attempted due to potential adsorption to the column material. The $T_{\rm g}$ of polymer 4 was observed at 48 °C by differential scanning calorimetry (DSC). This thermal transition was fully reversible, indicating that the transition did not correspond to the endothermic loss of labile carbonyl ligands. This value is higher than for the unclusterized polymer **3** ($T_g = -9$ °C) as expected for a material with bulkier substituents and therefore lower skeletal flexibility. Thermogravimetric analysis of 4 under an atmosphere of N_2 to 1000 °C resulted in the formation of a black ceramic material in 45% vield.

Co-PCS (4) is an attractive lithographic resist for the formation of patterned, functional, metal-containing ceramics due to its excellent film-forming ability and high concentration (25 wt %) of a transition metal exhibiting bulk ferromagnetism. Direct-write patterning of Co-PFS using EBL to give features rich in Fe and Co was recently reported,²⁷ and Co-PCS (4) should allow access to highly metallized cobalt-rich features.

Co–PCS 4 was indeed found to operate as a negative tone resist for EBL. This behavior may be the result of chain cross-linking induced by homolytic cleavage of σ -bonds and radical dimerization caused by exposure to the electron beam.²⁷ Regions of the film that were exposed to the electron beam were firmly attached to the substrate, while the unexposed material could be washed away. Using a thin film (175 nm) of Co–PCS 4 as a resist, arrays of bars ca. 0.5 μ m × 4.0 μ m were fabricated using a dose of 5.0 mC cm⁻² followed by development with THF. An optical micrograph of a large array of bars is shown in Figure 2a. Sectional analysis of an atomic force micrograph of the bars (Figure 2b) revealed an average height of 175 ± 3 nm.



Figure 2. Microbars of Co-PCS (4) patterned by electron beam lithography visualized by (A) optical microscopy and (B) tapping mode AFM with sectional analysis.

In summary, we have synthesized a highly metallized (25 wt % Co) polycarbosilane by ROP of an acetylidesubstituted 1-silacyclobutane, followed by clusterization with $[Co_2(CO)_8]$. Furthermore, a convenient method for molecular weight control using a silane capping reagent has been thoroughly demonstrated, and this process is likely to be transferable to other monomers, allowing a general route for molecular weight control of high molecular weight polycarbosilanes which function as a desirable alternative to the painstaking anionic polymerization method. A preliminary study of materials science applications of Co-PCS 4 has revealed its potential use as a resist for EBL in the direct writing of cobalt-rich patterned films. These offer access to ordered arrays of magnetic ceramics containing cobalt nanoparticles on pyrolysis or plasma treatment²⁸ which are expected to be harder magnets compared to those obtained from iron or a mixture of iron and cobalt. These nanostructures may find applications in spintronics as an isolating magnetic layer in a nanogranular in-gap structure²⁹ or as catalysts, for example, for the synthesis of carbon nanotubes.^{30,31} The synthetic methodology utilized herein, involving macromolecular clusterization of an acetylide-substituted polycarbosilane precursor, may be extended to incorporate different metal clusters, and research in all of these areas is currently in progress.¹⁸

Acknowledgment. I.M. and H.E.R. thank NSERC for an AGENO grant. I.M. thanks the Canadian government for a Canadian Research Chair. S.B.C. acknowledges NSERC for a PDF. H.E.R and S.A. thank NSERC, MMO, CITO, ORDCF, and CIPI. We thank Dr. Tim Burrow and Dr. Sara Bourke for assistance with the HMBC pulse sequence, Dr. Andrew J. Baer for assistance with solid-state NMR spectroscopy, and Patrick Yang for assistance with AFM.

Supporting Information Available: Complete description of materials and equipment as well as experimental details for the synthesis and characterization of 2-4. This material is available free of charge via the Internet at http:// pubs.acs.org.

References and Notes

- (1) Interrante, L. V.; Shen, Q. In Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applica-tions; Jones, R. G., Ando, W., Chojnowski, J., Eds.; Kluwer Academic Publishers: Dordrecht, 2000; pp 247–321.
- (2) Babich, E. D. Am. Chem. Soc. Polym. Prepr. 1998, 39, 532.
- (3) Park, S. Y.; Zhang, T.; Interrante, L. V.; Farmer, B. L. Polymer 2002, 43, 5169.
- (4)Park, S. Y.; Zhang, T.; Interrante, L. V.; Farmer, B. L. Macromolecules 2002, 35, 2776.
- (a) Interrante, L. V.; Rushkin, I.; Shen, Q. Appl. Organomet. Chem. 1998, 12, 695. (b) Laine, R. M.; Babonneau, F. Chem. Mater. 1993, 5, 260.
- (6)Vdovin, V. M.; Pushchevaya, K. S.; Belivova, N. A.; Sultanov, R.; Plate, A. F.; Petrov, A. D. Dokl. Akad. Nauk SSSR 1961, 136, 96.
- (7) Liao, C. X.; Weber, W. P. Polym. Bull. (Berlin) 1992, 28, 281.
- (8)Knischka, R.; Frey, H.; Rapp, U.; Mayer-Posner, F. J. Macromol. Rapid Commun. **1998**, *19*, 455. Bamford, W. R.; Lovie, J. C.; Watt, J. A. C. J. Chem. Soc. C
- **1966**. 1137.
- Yamashita, H.; Tanaka, M.; Honda, K. J. Am. Chem. Soc. (10)1995, 117, 8873.
- Theurig, M.; Sargeant, S. J.; Manuel, G.; Weber, W. P. (11)Macromolecules 1992, 25, 3834.
- (a) Uenishi, K.; Imae, I.; Shirakawa, E.; Kawakami, Y. Chem. Lett. 2001, 30, 986.
 (b) Uenishi, K.; Imae, I.; Shirakawa, E.; Kawakami, Y. Macromolecules 2002, 35, (12)2455.

- (13) Manners, I. Synthetic Metal-Containing Polymers; Wiley-VCH: Weinheim, 2004.
- Archer, R. D. Inorganic and Organometallic Polymers; (14)Wiley-VCH: New York, 2001.
- (15) Manners, I. Science 2001, 294, 1664.
- (16) Macromolecular Symposia; Abd-El-Aziz, A. S., Ed.; Wiley-VCH: Ottawa, Canada, 2003; Vol. 196.
- (17) Berenbaum, A.; Ginzburg-Margau, M.; Coombs, N.; Lough, A. J.; Safa-Sefat, A.; Greedan, J. E.; Ozin, G. A.; Manners, I. Adv. Mater. 2003, 15, 51.
- (18) (a) Chan, W. Y.; Berenbaum, A.; Clendenning, S. B.; Lough, A. J.; Manners, I. Organometallics 2003, 22, 3796. (b) Chan, W. Y.; Clendenning, S. B.; Berenbaum, A.; Lough, A. J.; Aouba, S.; Ruda, H. E.; Manners, I. J. Am. Chem. Soc. 2005, 127, 1765.
- (19) For the use of alkyne clusterization to prepare organosilicon systems such as organosilane dendrimers and oligomeric [(diorganosilylene)diacetylene]s containing dicobalt hexacarbonyl clusters, see: (a) Seyferth, D.; Kugita, T.; Rheingold, A. L.; Yap, G. P. A. Organometallics 1995, 14, 5362.
 (b) Corriu, R. J. P.; Devylder, N.; Guerin, C.; Henner, B.; Jean, A. J. Organomet. Chem. 1996, 509, 249. (c) Allen, C. W.; Bahadur, M. J. Inorg. Organomet. Polym. 1998, 8, 23. (d) Kuhnen, T.; Stradiotto, M.; Ruffolo, R.; Ulbrich, D.; McGlinchey, M. J.; Brook, M. A. Organometallics 1997, 16, 5048
- (20) For a recent report of block copolymers with pendent Co clusters attached to one block using this strategy, see: Mîinea, L. A.; Sessions, L. B.; Ericson, K.; Glueck, D. S.; Grubbs, R. B. Macromolecules 2004, 37, 8967.
- (21) Berenbaum, A.; Lough, A. J.; Manners, I. Organometallics 2002, 21, 4415.
- (22) Cundy, C. S.; Eaborn, C.; Lappert, M. F. J. Organomet. Chem. 1972, 44, 291.
- Gómez-Elipe, P.; Resendes, R.; Macdonald, P. M.; Manners, (23)I. J. Am. Chem. Soc. 1998, 120, 8348.
- (24) Bartole-Scott, A.; Resendes, R.; Manners, I. Macromol. Chem. Phys. 2003, 204, 1259.
- (25) Temple, K.; Jäkle, F.; Sheridan, J. B.; Manners, I. J. Am. Chem. Soc. 2001, 123, 1355.
- (26)The analogous reaction with the monomer 2 proceeds cleanly.
- Clendenning, S. B.; Aouba, S.; Rayat, M. S.; Grozea, D.; Sorge, J. B.; Brodersen, P. M.; Sodhi, R. N. S.; Lu, Z.-H.; (27)Yip, C. M.; Freeman, M. R.; Ruda, H. R.; Manners, I. Adv. Mater. 2004, 16, 215.
- (28) (a) Clendenning, S. B.; Han, S.; Coombs, N.; Paquet, C.; Rayat, M. S.; Grozea, D.; Brodersen, P. M.; Sodhi, R. N. S.; Yip, C. M.; Lu, Z.-H.; Manners, I. *Adv. Mater.* **2004**, *16*, 291. (b) Clendenning, S. B.; Manners, I. J. Vac. Sci. Tech. B 2004, 22, 3493
- (29) Jalil, M. B. A. IEEE Trans. Magn. 2002, 38, 2613.
- (30) Rao, C. N. R.; Govindaraj, A. Acc. Chem. Res. 2002, 35, 998
- (a) Lastella, S.; Jung, Y. J.; Yang, H.; Vajtai, R.; Ajayan, P. M.; Ryu, C. Y.; Rider, D. A.; Manners, I. J. Mater. Chem. (31)2004, 14, 1791. (b) Hinderling, C.; Keles, Y.; Stöckli, T.; Knapp, H. F.; de los Arcos, T.; Oelhafen, P.; Korczagin, I.; Hempenius, M. A.; Vancso, G. J.; Pugin, R.; Heinzelmann, H. Adv. Mater. 2004, 16, 876.

MA048368U