($\overline{M}_n$ 4600, MWD 1.95) was changed to block copolymer poly(SOC 1)$_x$-*block*-(SOC 2)$_y$ ($\overline{M}_n$ 10 600, MWD 1.66, x:y = 62:38). The block copolymer was soluble in *n*-hexane but insoluble in MeOH (yield 69%), while the initial poly(SOC 1) was insoluble in *n*-hexane (yield 87%). This change of solubility as well as the change of $\overline{M}_n$ confirms unambiguously the occurrence of the block copolymerization.

By the similar manner, the block copolymerization of the living poly(SOC 1) with *n*-BVE (*n*-butyl vinyl ether) was attempted to give block copolymer poly(SOC 1)$_x$-*block*-(*n*-BVE)$_y$ with complete consumption of *n*-BVE without any homopolymer.[12,13] Monodispersed GPC peaks of the crude polymers both before and after the copolymerization, either of which showed the same shape by both UV and RI detection, indicated an obvious shift of $\overline{M}_n$ to the high molecular weight region.[14] As expected, most of the block copolymer (80–90%) became soluble in *n*-hexane. This solubility change was consistent with the segment ratio (x:y = 37:63 by NMR).

The similar block copolymerization with *n*-BVE occurred with use of the heated poly(SOC 1) (for 2 h at 120 °C) as the initiator as mentioned above. However, the blocking efficiency was low and a homopolymer of *n*-BVE was produced according to the results of GPC. Moreover, poly[(SOC 1)(SOC 1)] formed by two-step polymerization was still living and could initiate the polymerization of *n*-BVE[12] to afford the block copolymer poly[(SOC 1)(SOC 1)]-*block*-(*n*-BVE) along with a small amount of poly(*n*-BVE).

Similar results were obtained with poly(SOC 1) formed in the polymerization with a thermally latent catalyst $PhCH_2\overline{S^+CH_2CH_2CH_2CH_2}SbF_6^-$ at 120 °C for 3 h. Fresh SOC 1 fed to the poly(SOC 1), which was kept at 120 °C for more than 10 h, was consumed very slowly. Meanwhile, *n*-BVE added to the polymer solution was polymerized at less than RT.[12] The polymer obtained as the *n*-hexane-insoluble part was also the block copolymer poly(SOC 1)$_x$-*block*-(*n*-BVE)$_y$ (20% yield, x:y = 80:20, $\overline{M}_n$ 5400, MWD 1.40; poly(SOC 1), $\overline{M}_n$ 4900, MWD 1.42). Thus, the poly(SOC 1) was still living even at such a high temperature, although its activity dropped obviously.

From the results mentioned thus far, the polymerization of SOC is not the ideal living polymerization but has a few of the characteristics of living polymerization.[15] Most interesting is the great stability of the growing end species. This living end is regarded as one of the most stable species,[2] as assumed from its structure. Recent ^{1}H, ^{13}C, and ^{19}F NMR studies on its structure suggest the trialkoxycarbenium ion as expected.[16] In addition, the formation of poly(SOC)-*block*-(*n*-BVE) would attract attention as a unique block copolymer between cyclic ether and vinyl monomers. We believe that this study should provide a new polymerization process involving stable propagating species as well as an attractive entry to synthesize a wide variety of new block copolymers of considerably controlled molecular weights.

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Registry No. SOC 1, 107711-17-1; PSOC 1, 107711-20-6; (SOC 1)(SOC 2) (block copolymer), 113180-82-8; (SOC 1)(*n*-BVE) (block copolymer), 113180-83-9.

Supplementary Material Available: Experimental procedures and a figure of GPC change (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part of this work has been presented: Endo, T.; Sato, H.; Takata, T. 8th International Symposium on Cationic Polymerization and Related Processes, Munchen, 1987; Abstract p 57.

(2) (a) Sawamoto, M.; Higashimura, T. *Makromol. Chem., Macromol. Symp.* **1986**, *3*, 83. (b) Higashimura, T.; Sawamoto, M. *Adv. Polym. Sci.* **1984**, *62*, 49. (c) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265, 2228. (d) Kennedy, J. P.; Kelen, T.; Tudos, F. *J. Makromol. Sci.-Chem.* **1982**, *A18* (9), 1189. (e) Faust, R.; Kennedy, J. P. *Polym. Bull.* **1986**, *16*, 317. (f) Zsuga, M.; Kelen, T. *Ibid.* **1986**, *16*, 285.

(3) (a) Takeda, N.; Inoue, S. *Macromolecules* **1981**, *14*, 1162. (b) Aida, T.; Mizuta, R.; Yoshida, Y.; Inoue, S. *Makromol. Chem.* **1981**, *182*, 1073. (c) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1985**, *107*, 1358. (d) Asano, S.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1148. (e) Inoue, S.; Aida, T. In *Ring-Opening Polymerization*; Ivin, K. J.; Saegusa, T., Eds.; Elsevier: London, 1983; Vol. 1, Chapter 4.

(4) (a) Doi, Y.; Ueki, K.; Keii, T. *Macromolecules* **1979**, *12*, 814. (b) Doi, Y.; Keii, T. *Adv. Polym. Sci.* **1986**, *73/74*, 201. (c) Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holms, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942. (d) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1985**, 874. (e) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem.* **1985**, *97*, 507.

(5) Otsu, T.; Yoshida, M.; Kuriyama, A. *Polym. Bull.* **1982**, *7*, 45.

(6) (a) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Harnham, W. B.; RajanBau, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706. (b) Sogah, D. Y.; Webster, O. W. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 927.

(7) (a) Endo, T.; Bailey, W. J. *J. Polym. Sci., Polym. Symp.* **1978**, *64*, 17. (b) Endo, T.; Bailey, W. J. *Makromol. Chem.* **1975**, *76*, 2897. (c) Bailey, W. J.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1735. (d) Endo, T.; Katsuki, H.; Bailey, W. J. *Makromol. Chem.* **1976**, *177*, 3231. (e) Endo, T.; Arita, H. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 137.

(8) Olah, G. A.; Olah, J. A.; Svoboda, J. J. *Synthesis* **1973**, 490.

(9) Recently, we have reported synthesis and polymerization (120 °C) of SOC 1 as a moisture-resistant SOC: Endo, T.; Sato, H.; Takata, T. *Macromolecules* **1987**, *20*, 1416.

(10) Materials: SOC 1 (140 mg, 4 × 10^{-4} mol); $Ph_3C^+BF_4^-$ (6.8 mg, 5 mol %); chlorobenzene (417 mg, 3.7 × 10^{-3} mol).

(11) We believe that the deviation from the ideal behavior is due to (i) incomplete correspondence to the calibration based on standard polystyrene in GPC and (ii) small time lag in the initiation step because of lower solubility of $Ph_3C^+BF_4^-$ in chlorobenzene. Disappearance of the yellow color of the catalyst took several minutes.

(12) Experimental details are given in the Supplementary Material.

(13) Poly(SOC 1); $\overline{M}_n$ 2100 (M^* 3000), MWD 1.51. Poly(SOC 1)$_x$-*block*-(*n*-BVE)$_y$; $\overline{M}_n$ 5900 (M^* 6800), MWD 1.34, x:y = 59:41 (insoluble in *n*-hexane) and $\overline{M}_n$ 2700 (M^* 5700), MWD 2.12 (soluble in *n*-hexane).

(14) Figure of GPC change appears in Supplementary Material.

(15) Back-biting may be one of the factors which induce deviation from ideal behavior.

(16) In the experiments using CF_3SO_3H, $CF_3SO_3SiMe_3$, and CF_3SO_3Me, trialkoxycarbenium ion with counter anion $CF_3SO_3^-$ was detected by the NMRs: this work is under intensive investigation.

Takeshi Endo,* Hiroyuki Sato, and Toshikazu Takata

Research Laboratory of Resources Utilization
Tokyo Institute of Technology
Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

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New Organometallic Polymers Containing Tungsten Carbene Complexes[1]

Inorganic and organometallic polymers containing transition metals, lanthanides, or main-group elements (P, Si, Sn, Li, or Pb) are a very intriguing group of materials and are currently receiving considerable attention.[2] These polymers have many useful applications as chemically

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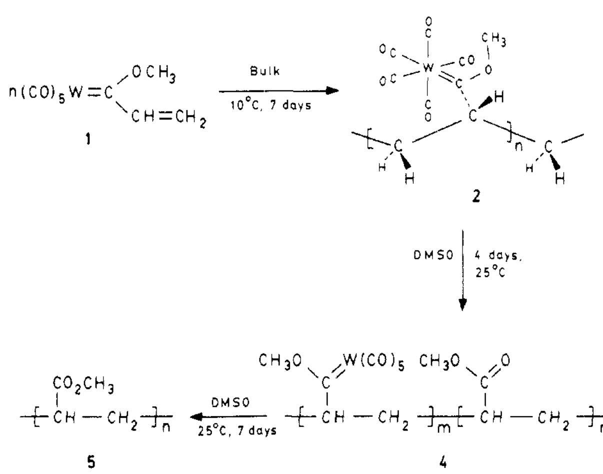
Scheme I



resistant elastomers,[3] reagents for organic synthesis,[4] catalysts,[5] antifouling agents,[6] electroactive films,[7] metal–polymer composites,[8] positive resists in microlithography,[9] or precursors to ceramics.[10] Most transition-metal organometallic polymers have been prepared by three methods: (1) chain polymerization of vinyl monomers,[2g] (2) step-growth polymerization of bifunctional monomers,[2g,11] or (3) modification of preformed polystyrene resins.[5] Among the various transition-metal-containing vinyl monomers prepared and polymerized[2a,f,g] are derivatives of cyclopentadienyl–metal complexes, styryl–metal systems, or diene–metal complexes in which the vinyl groups are connected to cyclopentadienyl ligands, arene rings, or diene ligands, respectively. To our knowledge, there is only one other account of polymeric materials that contain transition-metal carbene complexes.[12,13] We now report on the polymerization of the tungsten–carbene vinyl monomer **1**, which affords the first polymeric material **2** to contain repeating transition-metal carbene fragments, the characterization of this new polymer, and some initial findings dealing with its reactivity.

Upon preparing the α,β-unsaturated tungsten carbene complex **1**,[15] an insoluble orange solid was frequently observed. Nevertheless, this orange solid could be avoided if complex **1** was purified immediately after preparation and then stored at −30 °C. Purification involved chromatography on silica gel at −20 °C with the resulting pentane eluent collected at 0 °C. Removal of the pentane under high vacuum at 0 °C produced pure **1** as beautiful dark red crystals in yields between 25% and 35%.[16] It was subsequently found that if complex **1** was allowed to melt (ca. 10 °C) and then stand at this temperature in a nitrogen atmosphere for 7 days, a dark red polymeric glass formed (Scheme I).[18] After scraping this material from the sides of the flask, washing exhaustively with methylene chloride/ethyl acetate, and drying under high vacuum, the organotungsten polymer **2** was obtained in 80% yield.[20] Polymer **2**, formed in this manner, is insoluble in all organic solvents, is nonvolatile (at least down to 10^{-9} Torr), and decomposes at 80 °C to a dark solid and $W(CO)_6$.

The diffuse reflectance FT infrared spectrum of **2** exhibits characteristic metal carbonyl stretching bands at 2071 (w) and 1925 (s) cm^{-1} for Fischer-type tungsten carbene complexes. For example, $(CO)_5W[C(OCH_3)CH_3]$ exhibits metal carbonyl stretching bands at 2075 (w), 1953 (m), and 1939 (s) cm^{-1} in hexane. Solid-state CP-MAS ^{13}C NMR spectra[21] of polymer **2** show broad resonances at δ 338.8 (W=*C*), 197.9 (W*C*O), 71.5 (O*C*H$_3$), 68.5 (*C*H), and 36.8 (*C*H$_2$). In addition to these major resonances, small peaks were observed at δ 192.1, 58.3, and 26.5, which may be due to solid-state conformational effects in the polymer sample.[22] Most importantly, the carbene–carbon resonance at δ 338.8 could be distinguished from spinning side bands by changing the sample spinning rate; moreover, its chemical shift value is similar to those of other Fischer-type tungsten carbene complexes. For example, $(CO)_5W[C(OCH_3)CH_3]$ exhibits the following ^{13}C NMR spectrum in $CDCl_3$: δ 332.67 (W=*C*), 203.57 (W*C*O, trans), 197.51 (W*C*O, cis), 69.75 (O*C*H$_3$), 51.94 (*C*H$_3$). The lack of observable vinylic resonances in the solid-state CP-MAS ^{13}C NMR spectrum of **2** suggested that no unreacted vinyl monomer **1** was present in the polymer sample.[23]

Further characterization of polymer **2** involved X-ray photoelectron spectroscopy (ESCA), which indicated only one type of tungsten species present on the surface (and presumably also in bulk).[24] A high-resolution ESCA spectrum of **2** exhibited binding energies for $W(4f_{7/2})$ = 31.2 and $W(4f_{5/2})$ = 33.3 ± 0.1 eV. To our knowledge, no comparative ESCA data were available for low-valent tungsten carbene complexes.[25] This compelled us to prepare $(CO)_5W[C(OCH_3)(4\text{-}n\text{-}C_{15}H_{31})C_6H_4]$ (**3**)[26] and measure its ESCA spectrum. Compound **3** showed binding energies for tungsten of 31.5 and 33.7 eV [$W(4f_{7/2})$ and $W(4f_{5/2})$, respectively]. Both polymer **2** and complex **3**, which are formally W(0), exhibit considerably lower binding energies than Schrock's alkylidene complex $W(O)(CHCMe_3)Cl_2(PEt_3)_2$ [$W(4f_{7/2})$ = 34.1, $W(4f_{5/2})$ = 36.3 eV],[25] which is formally W(IV).

Treating polymer **2** with dimethyl sulfoxide for long periods (4 days) produced a soluble copolymer **4** consisting of monomer **1** and poly(methyl acrylate) (Scheme I).[28] The yellow-orange copolymer **4** is soluble in polar organic solvents, from which transparent films can be cast. The copolymer composition was determined by using ^1H NMR spectroscopy by integrating the broad three-proton methoxy resonances of the tungsten carbene fragment (δ 4.6) and ester group (δ 3.6). The infrared spectrum of **4** ($n \cong n - m$) in chloroform exhibited two metal carbonyl bands at 2075 (w) and 1935 (s) cm^{-1} and an organic carbonyl band at 1730 (w) cm^{-1}. The ^{13}C NMR spectrum of **4** ($n \cong n - m$) in $CDCl_3$ at 25 °C exhibited the following resonances: δ 338.7 (W=*C*) 200.5 (W*C*O, trans), 197.1 (W*C*O, cis), 174.9 (*C*=O), 71.1 (W=C*C*HCH$_2$), 66.5 (W=CO*C*H$_3$), 51.7 (O=CO*C*H$_3$), 41.3 (O=C*C*HCH$_2$), 35.0 (CH*C*H$_2$), which are consistent with the assigned structure. A high-resolution ESCA spectrum of **4** ($n \cong n - m$) exhibited binding energies for $W(4f_{7/2})$ = 31.4 and $W(4f_{5/2})$ = 33.5 ± 0.1 eV. These values are similar to those found in the other W(0) carbene fragments of polymer **2** and complex **3**, described above. Furthermore, tungsten species with higher binding energies were not observed in the spectrum of **4**, which indicates that DMSO cleanly removes the $(CO)_5W$ fragments from the surface of polymer **2**.

Although direct molecular weight measurements on polymer **2** were impossible due to its complete insolubility, we were able to determine the intrinsic viscosity of copolymer **4** ($[\eta] = 7.3 \times 10^{-2}$ dL/g, $CHCl_3$, 13 °C, $n \cong n - m$). Further oxidation of **4** using DMSO (7 days, 25 °C) provided poly(methyl acrylate) (**5**) in 45% yield (Scheme I). Polymer **5**, prepared in this manner, exhibited an ^1H NMR spectrum which was virtually superimposable on the spectra of standard poly(methyl acrylate) samples. A value of 9000 was obtained for the viscosity average molecular weight ($\bar{M}_v$) of **5** by using the Mark–Houwink–Sakurada equation and the intrinsic viscosity ($[\eta] = 6.1 \times 10^{-2}$ dL/g, acetone, 24 °C).

To date, the mechanism of formation of polymer **2** under bulk conditions (Scheme I) is not known, but both free radical and anionic pathways appear possible.[30] Further studies involving the formation, structure, and reactivity of polymers containing transition-metal carbene fragments are under way in our laboratory. By taking advantage of the extensive chemistry associated with transition-metal carbene complexes,[31] we hope to be able to prepare a wide variety of new materials with interesting properties.

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Registry No. 1 (homopolymer), 113218-88-5; **3**, 113218-89-6.

References and Notes

(1) Presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, March, 1987; paper INORG 337.

(2) (a) Carraher, C. E., Jr., Sheats, J. E., Pittman, C. U., Jr., Eds. *Organometallic Polymers*; Academic: New York, 1978. (b) Ray, N. H. *Inorganic Polymers*; Academic: New York, 1978. (c) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1981**, *41*, 151–179. (d) Carraher, C. E., Jr., Sheats, J. E., Pittman, C. U., Jr., Eds. *Advances in Organometallic and Inorganic Polymer Science*; Marcel Dekker: New York, 1982. (e) Cowley, A. H., Ed. *Rings, Clusters, and Polymers of the Main Group Elements*; ACS Symposium Series No. 232; American Chemical Society: Washington, DC, 1983. (f) Sheats, J. E., Carraher, C. E., Jr., Pittman, C. U., Jr., Eds. *Metal-Containing Polymeric Systems*; Plenum: New York, 1985. (g) Pittman, C. U., Jr.; Rausch, M. D. *Pure Appl. Chem.* **1986**, *58*, 617.

(3) Allcock, H. R. *Chem. Eng. News* **1985**, *63* (11), 22.

(4) (a) Reference 2f, pp 405–424. (b) Hodge, P. In *Polymer-Supported Reactions in Organic Synthesis*; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980; pp 83–155.

(5) (a) Reference 4b, pp 249–291. (b) Pittman, C. U., Jr., In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, pp 553–611.

(6) Reference 2a, pp 175–180.

(7) (a) Reference 2f, pp 137–147. (b) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441. (c) Thackeray, J. W.; White, H. S.; Wrighton, M. S. *Ibid.* **1985**, *89*, 5133. (d) Rosenthal, M. V.; Skotheim, T.; Warren, J. *J. Chem. Soc., Chem. Commun.* **1985**, 342. (e) Nishihara, H.; Aramaki, K. *Ibid.* **1985**, 709. (f) Okahata, Y.; Takenouchi, K. *Ibid.* **1986**, 558. (g) Nishihara, H.; Noguchi, M.; Aramaki, K. *Ibid.* **1987**, 628.

(8) (a) Reference 2d, pp 251–260. (b) Reference 2f, pp 303–339. (c) Kim, H.; Mason, J.; Miller, J. R. *J. Vac. Sci. Technol., A* **1983**, *2*, 890.

(9) (a) Haller, I.; Feder, R.; Hatzakis, M.; Spiller, E. *J. Electrochem. Soc.* **1979**, *126*, 154. (b) Webb, D. J.; Hatzakis, M. *J. Vac. Sci. Technol.* **1979**, *16*, 2008. (c) Labadie, J. W.; MacDonald, S. A.; Willson, C. G. *Macromolecules* **1987**, *20*, 10.

(10) Wynne, K. J.; Rice, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 297.

(11) Gonsalves, K.; Zhan-ru, L.; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3862 and references therein.

(12) Chen, L. B.; Jin, J. X.; Lin, J.; Huang, G. C.; Li, X. Y.; Chen, H. S.; Lin, X. X. *Tokyo Seminar on Macromolecule-Metal Complexes*; Preprints, Oct 1987; pp 37–38.

(13) In addition to the polymers described in ref 12, it has been reported recently that catalytically active transition-metal carbene complexes have been incorporated into polymers.[14] In these cases, however, the polymer chains consist of repeating organic monomer units terminated with *one* carbene fragment.

(14) (a) Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942. (b) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 899. (c) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169. (d) Murdzek, J. S.; Schrock, R. R. *Macromolecules* **1987**, *20*, 2640.

(15) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726.

(16) The low yields of complex 1 are due to the formation of $(CO)_5W[C(OCH_3)(\eta^2\text{-}CH{=}CH_2)]W(CO)_5$ and methyl propionate at the expense of 1.[17]

(17) Macomber, D. W.; Liang, M.; Rogers, R. D., unpublished results.

(18) Wilson and Fischer reported a similar observation for the analogous α,β-unsaturated chromium carbene complex. They did not, however, characterize their material nor speculate on its structure.[19]

(19) Wilson, J. W.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *57*, C63.

(20) Anal. Calcd for $C_9H_6O_6W$: C, 27.43; H, 1.54. Found: C, 27.70; H, 1.72.

(21) Solid-state NMR spectra were obtained at the Colorado State University Regional NMR Facility with the spectrometer operating at 37.73 MHz. The chemical shifts were referenced to external TMS.

(22) Axelson, D. E. In *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; Komoroski, R. A., Ed.; VCH Publishers: Deerfield Beach, 1986; pp 227–245.

(23) The ^{13}C NMR spectrum of 1 exhibits the following resonances: δ 312.49 (W=C), 203.77 (WCO, trans), 197.44 (WCO, cis), 152.44 (CH=C), 119.30 ($C{=}CH_2$), 68.76 (OCH_3) in C_6D_6.[17]

(24) ESCA spectra were measured on a AEI ES200B spectrometer at −196 °C utilizing Mg Kα radiation. Samples were run on 3M (Y-966) double-sided tape and each sample was calibrated against the C(1s) binding energy (284.6 eV).

(25) Gassman, P. G.; Macomber, D. W.; Willging, S. M. *J. Am. Chem. Soc.* **1985**, *107*, 2380.

(26) Compound **3** was prepared from 1-(4-lithiophenyl)pentadecane[25] according to well-established literature procedures for Fischer-type carbene complexes.[27]

(27) Fischer, E. O.; Schubert, U.; Kleine, W.; Fischer, H. *Inorg. Synth.* **1979**, *19*, 164.

(28) In a typical experiment, 2.3 g of homopolymer **2** was stirred with 20 mL of DMSO for 4 days at 25 °C. After the addition of H_2O (100 mL), extracting with CH_2Cl_2, and drying over anhydrous $MgSO_4$, the copolymer **4** ($n \cong n - m$) (0.76 g, 54%) could be obtained by precipitation from hexane. ^1H NMR ($CDCl_3$) δ 4.6 (br s, 3 H), 4.1–3.5 (br m, 1 H), 3.6 (br s, 3 H), 2.7–1.4 (br m, 5 H). Oxidation of pentacarbonyltungsten carbene complexes to $(CO)_5W{\cdot}SMe_2$ and organic carbonyl compounds is a well-known process.[15,29]

(29) Fischer, H.; Schmid, J.; Zeuner, S. *Chem. Ber.* **1987**, *120*, 583. Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127.

(30) We have recently discovered that monomer 1 can be homopolymerized in moderate yields in benzene using AIBN. Likewise, monomer 1 can be homopolymerized in THF to afford excellent yields of 2 by using many anionic initiators, including TMEDA, PPh_3, diphos, $P(OMe)_3$, *t*-BuLi, KF, KCN, K_2CO_3, K_3PO_4, KO-*t*-Bu, and 1,1-diphenylhexyllithium. We are continuing to investigate the polymerization behavior of vinyl monomers, containing chromium and tungsten carbene complexes, using both free radical and anionic initiators. The results of these investigations will be reported in forthcoming publications.

(31) (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983. (b) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89.

David W. Macomber,* Mu-Huang Hung, Mong Liang, Akhilkumar G. Verma, and Puttannachetty Madhukar

Department of Chemistry, Kansas State University
Manhattan, Kansas 66506

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Ab Initio Conformation and Ionization Potentials of Polysilane Oligomers

Experimental work on organosilane polymers[1] has demonstrated the strong conformational dependence of ultraviolet (UV) absorption. The wavelength of maximum absorption, λ_{max}, of a range of disubstituted polysilanes increases with increasing length of the silicon backbone and with increasing substituent size.[2] Several dialkyl-

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