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.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for support of this research. We also wish to acknowledge Professor P. M. A. Sherwood for assistance in obtaining ESCA spectra and Professor W. G. Fateley for assistance in obtaining diffuse reflectance FT infrared spectra. We also acknowledge the Colorado State University Regional NMR Center, funded by the National Science Foundation Grant CHE-8208821. Finally, we thank one of the referees for making us aware of the related research described in ref 12.

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 $K\alpha$ 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

Received November 24, 1987

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-

0024-9297/88/2221-1189$01.50/0

substituted polysilanes, in particular poly(di-*n*-hexylsilane) and other poly(di-*n*-alkylsilanes), have recently been reported to exhibit[4-6] a red shift of λ_{max} of up to about 40 nm (corresponding to an energy shift of 0.4–0.5 eV) with decreasing temperature and a concomitant narrowing of the absorption line shape occurring at roughly −35 °C. These bathochromic shifts have been attributed to a transition of the polysilane skeletal framework as the temperature is decreased to a highly ordered system having a nearly all anti (or planar zigzag) conformation of the silicon backbone from that of a disordered system with an entropic mix of anti and gauche conformers along the silicon backbone and in the alkyl chain substituents. This explanation is supported by the observed trend for λ_{max} to increase with increasing substituent size, which is expected if increased steric effects resulting from increased substituent size are assumed to stabilize the anti conformers relative to the gauche conformers.

Such an order–disorder transition would imply small energy differences (less than roughly 1 kcal/mol per available silicon backbone bond rotation) between conformers which differ by rotations about bonds in the silicon backbone. Experimental valence photoelectron spectra indicate that the measured ionization potentials of silane oligomers in the series Si_nH_{2n+2} can only be explained in terms of a nearly equal mix of rotamers for tetrasilane and pentasilane.[7,8] Based on these spectra, Ensslin et al. estimate that the anti conformer of tetrasilane is lower in energy by 0.4 kcal/mol relative to the gauche conformer.[7] Similarly, NMR and vibrational spectroscopy measurements on the methyl-substituted oligomer decamethyltetrasilane, $Si_4(CH_3)_{10}$, indicate that the anti conformer lies roughly 0.5 kcal/mol lower than the gauche conformer.[9]

Theoretical results have, in general, predicted such small energy differences between conformers. Empirical force-field calculations suggest stabilizations of the all-gauche conformers relative to the all-anti conformers of 0.09 and 0.7 kcal/mol for tetrasilane[10] and pentasilane,[11] respectively, with similar trends reported for n-$Si_{30}H_{62}$ and n-$Si_{10}H_{22}$. In contrast, semiempirical methods for n-$Si_{10}H_{22}$ predict that the all-anti conformer should be lower in energy by ~2.5 kcal/mol relative to the all-gauche conformer.[12] No ab initio theoretical work for systems larger than trisilane (Si_3H_8) or definitive experimental work has been published which can serve as a reference for these empirical and semiempirical approaches. A need, therefore, exists for accurate theoretical benchmarks of the total energy of polysilane oligomers as a function of bond rotations.

As one part of a broader theoretical study of the electronic structure and properties of organopolysilanes, we have carried out an ab initio study of a series of polysilane oligomers, Si_nH_{2n+2} (n = 1–5), as a model study of the behavior of the more complicated polysilane chains. First, we carried out full geometry optimizations within a restricted Hartree–Fock SCF scheme[13] using a 3-21G* basis set for four conformations of tetrasilane: an anti conformer with the Si–Si–Si dihedral bond angle fixed at 0°, a gauche conformer with the dihedral angle fixed at 60°, and two eclipsed conformers with dihedral angles of 0° and 120°. The anti and gauche conformers represent the local minima in the total energy curve as a function of bond twist; the two eclipsed conformers represent the local maxima for the gauche-gauche and gauche-anti barriers. Geometry optimizations were also performed for the all-anti and helical all-gauche (G^+G^+ in the nomenclature of ref 12) conformers of pentasilane. The total energies of the tetrasilane conformers were recalculated at the 3-21G* equilibrium geometry by using a 6-31G* basis set with the inclusion of second-order Møller–Plesset (MP2) perturbation theory energy terms.[14] Although full details of these calculations will appear elsewhere,[15] we should briefly comment on the choice of basis set. Basis set studies on singly bonded silicon compounds[16] suggest that inclusion of *d*-functions in the basis set is important for a good description of the silicon–silicon bond distances. Similar studies on disilane[17] as well as our own calculations indicate that no major improvement results from the use of larger basis sets. We did use the slightly more complete 6-31G* basis sets for both the MP2 total energy calculations and the calculation of electron binding energies described below.

Table I
Relative Energies of HF/3-21G* Structures (kcal/mol)

	RHF		MP2
	3-21G*	6-31G*	6-31G*
	Si_4H_{10}		
anti	0.00	0.00	0.00
eclipsed (120°)	+0.75	+0.62	+0.58
gauche	+0.17	+0.19	−0.04
eclipsed (0°)	+1.26	+1.65	+1.25
	Si_5H_{12}		
anti-anti	0.00		
gauche-gauche	+0.17		

For the anti and gauche rotamers of tetrasilane and the all-anti and all-gauche rotamers of pentasilane we obtained respectively average Si–Si bond lengths of 2.345, 2.347, 2.346, and 2.346 Å and average Si–Si–Si bond angles of 111.7°, 111.5°, 111.9°, and 110.8°. These results are in substantial agreement with results from earlier empirical model studies of these systems.[10,11] Our results for the total energies of tetrasilane and pentasilane are presented in Table I. We find no significant difference in energy between the anti and gauche conformations of either species. As can be seen from the table, the inclusion of second-order perturbation theory corrections (MP2) is sufficient to change the relative ordering of the two energies. A modest difference in the heights of the gauche-gauche and gauche-anti rotational barriers (1.3–1.7 versus 0.6–0.8 kcal/mol) is observed, however. This difference is consistent with earlier experimental evidence for a higher barrier for the gauche-gauche interconversion based on NMR broadening effects observed in the decamethyltetrasilane system.[9] We also note that our predicted barrier for anti-gauche conversion of 0.6–0.8 kcal/mol is roughly half the experimentally determined barrier of disilane[18] of 1.22 kcal/mol; most of this decrease probably arises from the Coulombic attraction between the end silicon nuclei and the relatively electronegative hydrogen nuclei eclipsing them.

Electron binding energies were calculated for the tetrasilane conformers by using electron propagator theory[19] (EPT) in the quasi-particle approximation[20] and the 6-31G* basis. The poles of the electron propagator (representing the electron binding energies) are located by using a second-order expression; this energy is then inserted into the third-order self-energy expression. Higher order corrections to the electron binding energy are introduced by the outer valence approximation (OVA).[21] This theoretical model tends to agree with experiment to within 0.2 eV as basis set effects are exhausted. In Figure 1, EPT-(OVA)/6-31G* vertical ionization energies are plotted as a function of dihedral angle from 0° to 60° (gauche) to 120° to 180° (anti). The three lowest ionization energies pertain to Si–Si bonding molecular orbitals with *a*, *b*, and *a* (C_2 point group) symmetry. The 1–4 interaction between the terminal silicons decreases as the dihedral angle increases.

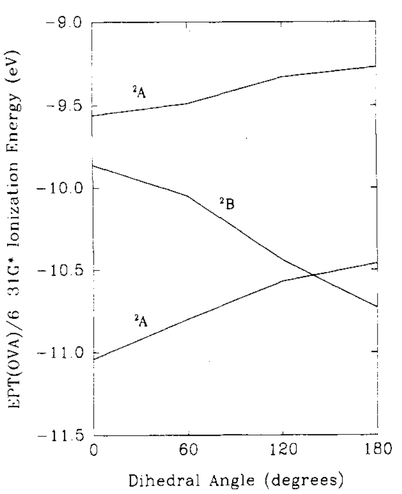


Figure 1. Electron propagator theory vertical ionization energies for tetrasilane versus dihedral angle. Labels denote final states of molecular species.

The nonadjacent Si–Si bond regions in the *a* symmetry MO's are in-phase; these regions in the *b* symmetry MO's are out-of-phase. Thus the *a* levels are destabilized and the *b* levels are stabilized as the dihedral angle increases. The ionization energies for the anti (9.27, 10.46, and 10.73 eV) and gauche (9.49, 10.05, and 10.81 eV) conformers are in close agreement with the broad experimental maxima[8] at 9.62, 10.3, and 10.85 eV. The width of each of these peaks is compatible with the concept that both conformers are contributing to the spectrum. Vertical ionization energies have a much greater conformational dependence than ground-state total energies.

Pentasilane ionization energies studied at the 3-21G* Koopmans' theorem level display similar conformation dependent trends. (Koopmans' theorem results on tetrasilane with the 3-21G* basis are not as accurate as those of Fig. 1 but give curves of similar shape.) The highest occupied MO is bonding between Si neighbors but has nodes between successive Si–Si bond regions. In going from the anti-anti to the gauche-gauche conformer, this *b* MO is stabilized by 0.35 eV because the Si_1–Si_2 and Si_3–Si_4 bond regions are in phase. The four Si–Si bonds also generate another *b* MO plus two *a* symmetry MO's. The 1–4 interaction also controls the conformational dependence of these orbital energies.[15] From these results, we infer that the highest occupied level of larger chains will consist of nearest-neighbor Si–Si bonding regions with alternating phases, as has been suggested earlier from semiempirical calculations.[12,22] The 1–4 interaction will be in phase and the energy of the level will rise as the conformation changes from gauche to anti.

In summary, our ab initio results indicate no significant difference in total energy between the anti and gauche conformers in tetrasilane and the anti-anti and gauche-gauche conformers in pentasilane when basis set and electron correlation improvements are made. Our calculated EPT vertical ionization energies are in good agreement with experimental photoelectron spectra assuming an approximately equal mix of anti and gauche rotamers. Furthermore, these results support the idea that the highest occupied MO energy level of the larger silane oligomers will decrease as the backbone is transformed from an all-anti conformation to one with a larger gauche population.

Registry No. Si_4H_{10}, 7783-29-1; Si_5H_{12}, 14868-53-2.

References and Notes

(1) For a review, see: West, R. *J. Organomet. Chem.* **1986**, *300*, 327 and references therein.
(2) Trefonas, P., III; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 823.
(3) Zeigler, J. M.; Harrah, L. A.; Johnson, A. W. *SPIE Adv. Resist Technol. Proc. II* **1985**, *539*, 166.
(4) Harrah, L. A.; Zeigler, J. M. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 209.
(5) Miller, R. D.; Hofer, D.; Rabolt, J.; Fickes, G. N. *J. Am. Chem. Soc.* **1985**, *107*, 2172. Rabolt, J. F.; Hofer, D.; Miller, R. D.; Fickes, G. N. *Macromolecules* **1986**, *19*, 611.
(6) Trefonas, P., III; Damewood, J. R., Jr.; West, R.; Miller, R. D. *Organometallics* **1985**, *4*, 1318.
(7) Ensslin, W.; Bergmann, H.; Elbel, S. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 913.
(8) Bock, H.; Ensslin, W.; Fehêr, F.; Freund, R. *J. Am. Chem. Soc.* **1976**, *98*, 668.
(9) Ernst, C. A.; Allred, A. L.; Ratner, M. A. *J. Organomet. Chem.* **1979**, *178*, 119.
(10) Hummel, J. P.; Stackhouse, J.; Mislow, K. *Tetrahedron* **1977**, *33*, 1925.
(11) Damewood, J. R., Jr.; West, R. *Macromolecules* **1985**, *18*, 159.
(12) Bigelow, R. W.; McGrane, K. M. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1233. Bigelow, R. W. *Chem. Phys. Lett.* **1986**, *126*, 63.
(13) GAUSSIAN 82, Release A by: Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A. Carnegie Mellon University, Pittsburgh, PA.
(14) Bartlett, R. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359. Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.
(15) Ortiz, J. V.; Mintmire, J. W. *J. Am. Chem. Soc.*, in press.
(16) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 260.
(17) See, for example: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; pp 146–164 and references therein.
(18) Pfeiffer, M.; Spangenberg, H.-J. *Z. Phys. Chem.* **1966**, *232*, 47.
(19) Öhrn, Y.; Born, G. *Adv. Quantum Chem.* **1981**, *13*, 1.
(20) Ortiz, J. V. Ph.D. Dissertation, University of Florida, Gainesville, 1981.
(21) Cederbaum, L. S.; Domcke, N.; von Niessen, W. *J. Phys. B* **1977**, *10*, 2963.
(22) Takeda, K.; Teramae, H.; Matsumoto, N. *J. Am. Chem. Soc.* **1986**, *108*, 8186.

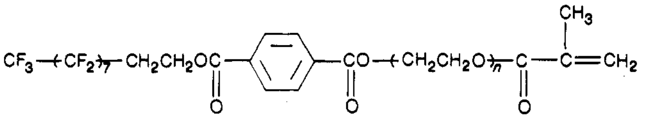
J. W. Mintmire*
Chemistry Division, Naval Research Laboratory
Washington, D.C. 20375

J. V. Ortiz
Department of Chemistry, University of New Mexico
Albuquerque, New Mexico 87131

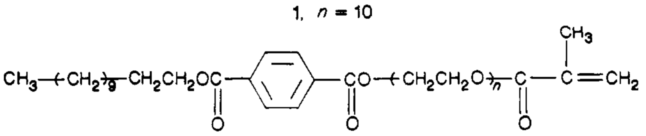
Received November 2, 1987

Specific Copolymerization Behavior of a Fluorocarbon Amphiphilic Macromonomer

In this paper we present a new type of macromonomer 1 and its specific behavior in copolymerization with styrene. The extremely higher copolymerizability of 1 that was assumed to be attributable to a characteristic property of the fluorocarbon chain was observed in comparison with methyl methacrylate as a model compound of 1. In contrast, a reversed trend was observable for the corre-



1, *n* = 10



2