(4) (a) Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111–117. (b) Menger, F. M.; Bonicamp, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 2140. (c) Menger, F. M.; Doll, D. W. *J. Am. Chem. Soc.* **1984**, *106*, 1109.

(5) (a) Dill, K. A.; Flory, P. J. *Proc. Natl. Acad. Sci., U.S.A.* **1981**, *77*, 3115. (b) Dill, K. A.; Flory, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 676. (c) Dill, K. A.; Cantor, R. S. *Macromolecules* **1984**, *17*, 380. (d) Cantor, R. S.; Dill, K. A. *Macromolecules* **1984**, *17*, 384.

(6) (a) Hartley, G. S. *Trans. Faraday Soc.* **1935**, *31*, 31–50. (b) Hartley, G. S. *Q. Rev. Chem. Soc.* **1948**, *2*, 152–183.

(7) Wennerström, H.; Lindman, B. *Phys. Rep.* **1979**, *52*, 1–86.

(8) Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc.*, Faraday *Trans.* **1981**, *77*, 601–629.

(9) Fendler, J. H. *Chem. Eng. News* **1984**, January 2, p 25.

(10) Ramesh, U.; Labes, M. M. *J. Am. Chem. Soc.* **1986**, *108*, 4643–4644.

(11) Uroka, R.; Moss, R. A.; Swarup, S.; Malsumoto, Y.; Strauss, G.; Murakomi, Y. *J. Am. Chem. Soc.* **1985**, *107*, 2185–2186.

(12) Lennox, R. B.; McClelland, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 3771–3781.

(13) One model is the so-called " interphase model", which is a statistical representation of the micelle based on a core filled with randomly distributed chain segments[5a–d] wherein the surfactant head group is located at the polar–hydrocarbon interface. This interface is well defined with no water penetration into the core of the aggregate. A second case is the "water penetration model", which views the micelle as possessing an ill-defined interface with extensive water–hydrocarbon chain contact.[4a–c]

(14) (a) Presented at the 1st Society Polymer Science, Japan, International Polymer Conference, Kyoto, Japan, Aug. 1984. (b) Presented at the 6th Biennial Carl S. Marvel Symposium, Tucson, AZ, March 19, 1985. (c) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J. (Tokyo)* **1985**, *17*, 117–132. (d) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *19*, 2466. (e) Tomalia, D. A.; Dewald, J. R. U.S. Patent 4 507 466, March 26, 1985; U.S. Patent 4 558 120, December 10, 1985; U.S. Patent 4 568 737, February 4, 1986; U.S. Patent 4 587 329, May 6, 1986; U.S. Patent 4 631 337, December 23, 1986.

(15) Newkome, G. R.; Yao, Z.-q; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2003–2004. (b) Newkome, G. R.; Yao, Z.-q; Baker, G. R.; Gupta, V. K.; Russo, P. S.; Saunders, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 849.

(16) (a) Elias, H. G.; Kammer, U. *Kolloid Z. Z. Polym.* **1972**, *250*, 344. (b) Nagai, V.; Elias, H. G. *Makromol. Chem.*, to be published.

(17) (a) Mielke, E.; Ringsdorf, H. *Makromol. Chem.* **1972**, *153*, 307. (b) Paleos, C. M.; Dais, P. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1495. (c) Tarrabee, C. E., Jr.; Sprague, E. D. *J. Polym. Sci. Polym. Lett. Ed.* **1979**, *17*, 749. (d) Paleos, C. M.; Voliotis, S.; Margomeneou-Leonidopoulou, G.; Dais, P. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3463. (e) Paleos, C. M.; Stassinopoulou, C. L.; Malliaris, A. *J. Phys. Chem.* **1983**, *87*, 251. (f) Paleos, C. M.; Dais, P.; Malliaris, A. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3383. (g) Elias, H. G., Ed. *Polymerization of Organized Systems*; Gordon and Breach: New York, 1977; Midland Macromolecular Monographs, Vol. 3, p 187.

(18) Fendler, J. H. *CHEMTECH* **1985**, 686.

(19) Hydrodynamic dimensions compared in this study were derived from intrinsic viscosity measurements reported in ref 14c. The Mark–Houwink coefficients were low (i.e., 0.19–0.20), thus supporting tight spheroidal structures. Dimensions calculated according to the Hester–Mitchell relationship (i.e., Hester, R. D.; Mitchell, P. H. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1727) were used to determine hydrodynamic surface areas and volumes for the respective dendrimer generations.

(20) de Gennes, P.-G.; Hervet, H. *J. Phys. Lett.* **1983**, *44*, 351.

(21) Maciejewski, M. *J. Macromol. Sci., Chem.* **1982**, *A17*(4), 689.

(22) Tomalia, D. A.; Hedstrand, D.; Hall, M. *J. Am. Chem. Soc.* **1987**, *109*, 1601.

(23) Given a starburst dendrimer with repeating units of constant length, it is evident that exponential accumulation of terminal groups (Z) as a function of generation will eventually congest the surface to a point where ideality of the starburst branching will be diminished. This generation is referred to as the "starburst limit" (see ref 20). An account of this dendrimer behavior is forthcoming; Tomalia, D. A.; Hedstrand, D.; Meier, D., unpublished results.

(24) Menger, F. M.; Jerkunica, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 688.

(25) This strongly supports the proposed micelle-like topology: Kiefer, G.; Tomalia, D. A., unpublished results.

(26) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Donald A. Tomalia,* V. Berry, M. Hall, and D. M. Hedstrand

Functional Polymers/Processes
and the Analytical Laboratory
Dow Chemical U.S.A.
Midland, Michigan 48640

Received December 29, 1986

Conformational Calculations on Poly(di-*n*-hexylsilane)

Substituted poly(di-*n*-alkylsilanes) have recently been the object of considerable attention[1–11] because of the applications potential embodied in their UV absorption characteristics. Alkyl-substituted polysilanes absorb at about 300–325 nm in solution,[1,2] the transition being attributed to a σ-bonded transition of the backbone silicon atoms. Films of poly(di-*n*-hexylsilane) (PDHS), on the other hand, show an absorption at 370–380 nm at room temperature.[2] Above 41 °C, the films absorb at the more typical 316-nm wavelength. Spectroscopic and X-ray diffraction studies[2,3,6,7] indicate that PDHS at room temperature is highly crystalline and that the backbone is in an all-trans, planar zigzag conformation. The long-wavelength absorption was attributed to the all-trans conformation, and the shift to shorter wavelength absorption was associated with a change in conformation, to either a conformationally disordered backbone structure or to an alternative regular conformation.[2,3,6,7]

X-ray diffraction studies[2,3,6,7] at room and elevated temperatures indicate that the structural transition is reversible on the time scale of the diffraction exposures (about 3 h). At room temperature, the structure is unusually well developed for a polymer, having sharp reflections out to 1.5 Å. Above the transition at 41 °C, the pattern consists of a single sharp diffraction maximum at about 13.5 Å. In fiber patterns, this reflection occurs on the zero layer and shows no significant broadening or elongation, even after prolonged periods above the transition temperature. Upon cooling to room temperature, the sample regains its remarkably well-ordered structure and remains highly oriented. These observations suggest a conformational change far less extensive than those typically associated with a melting phenomenon. Consideration of the severe steric crowding of the polymer due to the hexyl substituents on every backbone silicon atom further suggests a chain stiffness not readily amenable to major changes in the torsion angles. In order to elucidate the nature of the observed conformational transition, and thereby to provide information about the polymer conformation above the transition, semiempirical conformational energy calculations were undertaken for PDHS.

Full relaxation empirical force field calculations, as contained in the MM2 program, have recently been reported[10] for PDHS. Only all-trans, all-gauche, and trans–gauche backbone conformations were examined. A methylene group potential was used to describe the side chains, which were fixed in an all-trans conformation. The

0024-9297/87/2220-1167$01.50/0 © 1987 American Chemical Society

results showed the all-trans backbone conformation to be lowest in energy and to have an average Si–Si–Si bond angle of 110.4° and a Si–Si bond length of 2.355 Å.

While the results of these previous calculations[10] are in agreement with the observed solid-state conformation of PDHS, their limitation to only three possible conformations makes then insufficient for the present purposes. In addition, the lowest energy structure appears to have a significant distortion in the dispositions of the hexyl side chains, suggesting perhaps the influence of end effects in the computational model that are not representative of the true polymer molecule. X-ray fiber diffraction results also indicate a substantially larger Si–Si–Si bond angle (120°, assuming a standard Si–Si bond length of 2.35 Å) than indicated by the MM2 calculations. Finally, the use of a group interaction parameter for methylene units may be especially problematical for molecules subject to such severe steric constraints.

The present conformational calculations were undertaken with a program that has been described previously.[12] The program only examines conformational changes achievable by rotations about bonds in the backbone or side chains. It does not allow changes in the bonding geometry of the molecule and therefore does not allow distortions that are not repesentative of an actual polymer molecule. Standard bond lengths and bond angles were used, except for the Si–Si–Si angle, which was taken as the experimentally observed value of 120°, and the C–Si–C angle, which was taken as 98°. This latter value was chosen because it allowed hydrogen atoms attached to adjacent hexyl side chains to be slightly more than 1.0 Å apart when both the polymer backbone and side chains were in the all-trans conformation. When the more typical C–Si–C bond angle of 110° was used, such separation distances were only about 0.5 Å, a value too small for the interactions to be evaluated with the current potential functions. The effects of variations in these bond angles are currently under investigation.

All atoms constituting the polymer chain were included explicitly. No group interactions (e.g., methylene moiety) were used. The parameters for the exponential 6 potential energy function were taken without modification from calculations reported[13] for polysilane and poly(dimethylsilane). The polymer conformational repeat unit was taken to be defined by the rotations about two consecutive Si–Si bonds. Interactions were calculated between the first conformational repeat unit and the remainder of the polymer chain. No dependence on length was found as long as the polymer chain was represented by at least four conformational repeat units. No automatic minimization procedure was employed. Conformational space was searched in fairly large angular increments, with regions of potential interest being subsequently examined by using finer increments.

The primary calculation reported here was a full scan of four independent variables in 30-deg increments. Two consecutive backbone torsion angles and two Si–C side-chain torsion angles at adjacent silicon atoms and on the same side of the plane of the backbone were varied independently. Both Si–C bonds attached to the same silicon atom were assigned the same torsion angle value. The unique low-energy conformations thus identified were used as the starting points for further refinement using a grid-search method with 5-deg rotational increments. Interdependencies of rotations between adjacent side chains as well as between backbone and side-chain rotations were examined. The minimum energy conformations are shown in Table I. Conformations having the lowest energies are those having the same value for both Si–Si torsion angles and having the same value for both Si–C torsion angles. The conformational energies are dominated by interactions between side-chain atoms near the backbone of the polymer.

Table I
Energies of Preferred Conformations of PDHS

Si_1–Si_2, deg	Si_2–Si_3, deg	Si_1–C, deg	Si_2–C, deg	energy, kcal/mol
30	30	245	245	−49.7
35	35	15	10	−45.9
20	20	245	5	−45.6
25	25	5	235	−44.0
0	0	30	330	−6.0
110	0	340	340	+29.8

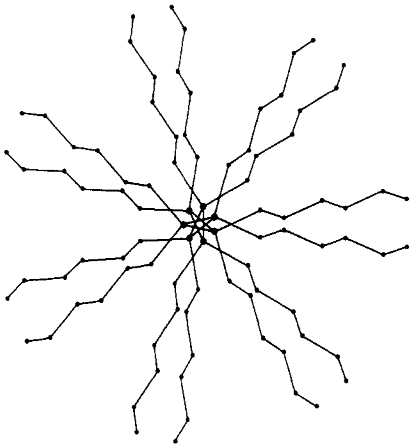

Figure 1. Projection of the 7/3 helical conformation of PDHS onto a plane normal to the helical axis. Silicon atoms are represented by the larger filled circles and carbon atoms by the smaller. Hydrogens atoms have been omitted for clarity.

It was found that the lowest energy conformation for the PDHS chain is one having every Si–Si bond rotated 30° and every Si–C bond rotated 245° from trans. This backbone conformation is surprisingly similar to the helical conformation adopted by poly(tetrafluoroethylene)[14,15] where fluorine atoms on every carbon atom provide steric interactions analogous to (but less serious than) those present between side chains in PDHS. This low-energy region extends from about 15° to 30° rotation about the Si–Si bonds and encompasses the 7/3 helical structure observed[11] in poly(di-*n*-pentylsilane) (PDPS), which also has a silicon–silicon torsion angle of about 30°. A projection of this 7/3 helix onto a plane normal to the helical axis is shown in Figure 1, where the C–C bonds of the side chains have been shown in the trans conformation and hydrogen atoms have been omitted for clarity. For this backbone conformation, other side-chain positions also have reasonably low energies with respect to both Si–C and C–C torsions. Most likely, the side chains do not exist exclusively in the all-trans conformation depicted in the figure.

Also shown in Table I are the side-chain torsion angles having the lowest energy for all-trans and trans–gauche backbone conformations. These were refined in the same manner as the lower energy conformations and therefore represent distinct local energy minima. The proximity of the distinct minima for the all-trans and the helical backbone conformations is illustrative of the dependence of the conformational results on the chosen starting conformation. The all-trans conformation is always higher in energy than the 7/3 helical conformation, but appropriate rotations about the Si–C bonds allow the side chains to position themselves so as to eliminate their most severe steric interactions. Inclusion of an appropriate torsional energy potential to account for the rotation required for the helical structure would make the helix and all-trans conformations somewhat closer in energy while the trans–gauche conformation would still remain higher in energy. While bond-angle and bond-length distortions in the latter could perhaps lower the energy significantly by reducing severe steric interactions, it is unlikely that such deformations (each carrying its own energy cost) could make the conformation comparable to the lowest energy conformations available to PDHS. It should be noted that rotations about all of the C–C bonds have not yet been fully examined for their influence on the energies for these backbone conformations, nor have all possible combinations of torsion angles for the Si–C and the first C–C bond been explored. Such additional calculations are currently in progress.

In spite of the somewhat preliminary nature of the calculations, the results are in good agreement with the structures observed in X-ray diffraction studies. The lowest energy conformation, the 7/3 helix, is actually observed[11] in the crystalline structure of PDPS. At the same time, the all-trans conformation observed[6,7] in the crystalline state of PDHS is also found to have a reasonable, though somewhat higher, energy. Other spectroscopic data for PDHS also indicate[6] that the side chains are not normal to the plane of the backbone, in accord with the indicated rotations about the Si–C bonds needed to give a low energy.

The present results are not in agreement with results of earlier calculations.[10] These discrepancies are attributable to the limitations of the previous calculations cited earlier.

Perhaps the most significant finding from the energy calculations thus far is that the all-trans conformation is not the lowest energy structure for the symmetrically alkyl-substituted silane polymers. In fact, a helical structure is preferred for the isolated molecule. The calculations, in conjunction with X-ray data[6,7,11] from PDHS and PDPS, indicate that it is intermolecular interactions in the crystal that lead to the all-trans conformation. Furthermore, these results suggest that there is a critical side-chain length (about six carbon atoms) needed to provide sufficient intermolecular interaction in the solid state to force the silicon backbone out of the preferred helical conformation into the all-trans conformation in order to optimize those intermolecular side-chain interactions. This result, taken in the context of experimental data reported elsewhere, provides a framework wherein the UV absorption characteristics of these polymers can be understood.

Registry No. PDHS, 97036-67-4.

References and Notes

(1) Trefonas, P., III; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1986**, *21*, 823.
(2) Miller, R. D.; Hofer, D.; Rabolt, J.; Fickes, G. N. *J. Am. Chem. Soc.* **1985**, *107*, 2172.
(3) Rabolt, J. F.; Hofer, D.; Miller, R. D.; Fickes, G. N. *Macromolecules* **1986**, *19*, 611.
(4) Trefonas, P., III; Damewood, J. R., Jr.; West, R.; Miller, R. D. *Organometallics* **1985**, *4*, 1318.
(5) Harrah, L. A.; Zeigler, J. M. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 209.
(6) Kuzmany, H.; Rabolt, J. F.; Farmer, B. L.; Miller, R. D. *J. Chem. Phys.* **1986**, *85*, 7413.
(7) Lovinger, A. J.; Schilling, F. C.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* **1986**, *19*, 2657.
(8) Schilling, F. C.; Bovey, F. A.; Lovinger, A. J.; Zeigler, J. M. *Macromolecules* **1986**, *19*, 2260.
(9) Gobbi, G. C.; Fleming, W. W.; Sooriyakumaran, R.; Miller, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 5624.
(10) Damewood, J. R., Jr. *Macromolecules* **1985**, *18*, 1793.
(11) Miller, R. D.; Farmer, B. L.; Fleming, W.; Sooriyakumaran, R.; Rabolt, J. *J. Am. Chem. Soc.* **1987**, *109*, 2509.
(12) Farmer, B. L., M. S. Thesis, Case Institute of Technology, 1972.
(13) Welsh, W. J.; Mark, J. E. *Macromolecules*, in press.
(14) Weeks, J. J.; Clark, E. S.; Eby, R. K. *Polymer* **1981**, *22*, 1480.
(15) Clark, E. S.; Muus, L. T. *Z. Kristallogr.* **1962**, *117*, 119.

B. L. Farmer*

Department of Mechanical and Materials Engineering
Washington State University
Pullman, Washington 99164-2720

J. F. Rabolt and R. D. Miller

IBM Almaden Research Center
San Jose, California 95120-6099

Received December 8, 1986

Ring-Opening Polymerization of Norbornene by a Living Tungsten Alkylidene Complex

Careful design of isolable, well-characterized catalysts is the key to the preparation of living polymers and ultimately well-defined block copolymers by ring-opening metathesis polymerization of cyclic olefins.[3] This has been demonstrated recently in the ring-opening polymerization of norbornene by a titanacyclobutane/titanium carbene complex[4a] and by a related tantalum catalyst.[4b] These living polymer systems produce monodispersed polymer. The utility of the Ti polymerization catalyst in polymer synthesis has been demonstrated by the production of A–B–A triblock polymers.[5] Tungsten metathesis catalysts have recently been reported that are much more active than the titanium catalysts and show a greater tolerance of polar functional groups.[6-9] One of these has been shown to produce a growing alkylidene in the polymerization of norbornene.[7] Since a variety of ligand combinations is now available, we should be able to fine tune catalyst activity precisely to the point required for controlled polymer synthesis. The complex $W(CH^tBu)(NAr)[OCMe(CF_3)_2]_2$ (Ar = 2,6-diisopropylphenyl)[6] will react rapidly with ordinary olefins to give isolable tungstacyclobutane complexes or alkylidene complexes (depending on the degree of substitution of the tungstacyclobutane ring) and will metathesize an internal olefin such as *cis*-2-pentene at a rate whose lower limit is 1000 turnovers per minute at 25 °C. Here we show that the activity of this system is dramatically altered by the choice of the alkoxide, and we can prepare a catalyst that shows all the characteristics for a living ring-opening polymerization of norbornene.

In an initial experiment $W(CH^tBu)(NAr)[OCMe(CF_3)_2]_2$ was allowed to react with 288 equiv of norbornene in toluene at −40 to −20 °C over several hours. Aliquots were withdrawn at intervals and the isolated polymers analyzed by GPC.[10] *All* of the samples had the same high molecular weight values ($M_n \approx 400\,000$; $M_w \approx 650\,000$; vs. polystyrene standards), indicating slow initiation followed by very rapid propagation and finally termination.[11] Analysis by ^{13}C NMR indicated ≥95% cis double bonds.[12]

The polymerization was investigated further in a series of sealed NMR-tube experiments in toluene-d_8. The initial ^{1}H NMR spectrum obtained at −80 °C showed no catalyst or catalyst-derived signals (only monomer and polymer were observed). A constant rate of polymer formation (zero order in monomer) was observed when the polymerizations were followed at −60 °C.[13] As the reaction proceeded signals attributable to decomposed catalyst slowly in-

0024-9297/87/2220-1169$01.50/0