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closely spaced. Therefore they may meet better than the other helices the steric requirements of the β-branched substituents of the oligovalines. These results suggest that there might be a limit to the number of residues per turn that a β-helical stereocooligo- or polypeptide can attain, and that this number might be determined by the position (and bulkiness) of the branching in the side chains. For a polypeptide such as poly(γ-benzyl glutamate), where branching is far removed from the backbone, this number might be as high as 9.0.[21]

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Registry No. II, 94202-58-1; ^{2}H^{2}(1)-II, 94202-59-2; ^{2}H^{2}(2)-II, 94202-60-5; III, 94202-61-6; ^{2}H^{2}(1)-III, 94202-62-7; IV, 94202-63-8; V, 94202-64-9; VI, 94202-65-0; VII, 94202-66-1; ^{2}H^{2}(1)-VII, 94202-67-2; ^{2}H^{2}(3)-VII, 94202-68-3; ^{2}H^{2}(5)-VII, 94202-69-4; ^{2}H^{2}(6)-VII, 94234-85-2; ^{2}H^{2}(7)-VII, 94202-70-7; VIII, 85459-45-6; IX, 94202-71-8; X, 94202-72-9; XV, 94202-73-0; Boc-L-Phe-OH, 13734-34-4; H-L-Phe-OMe·HCl, 7524-50-7; Boc-yd-Phe-OH, 18942-49-9; Boc-L-Phe-(D-Phe-L-Phe)$_3$-OH, 94202-74-1; Boc-L-Phe-D-Phe-OH, 93397-22-9; Boc-(L-Phe-D-Phe)$_2$-OH, 94234-86-3; Boc-L-Phe-(D-Phe-L-Phe)$_2$-OH, 94202-75-2; Ac-α-^{2}H-DL-Phe-OH, 63570-52-5; Ac-α-^{2}H-D-Phe-OH, 81583-96-2.

References and Notes

(1) Heitz, F.; Lotz, B.; Colonna-Cesari, F.; Spach, G. In "Biomolecular Structure, Conformation, Function and Evolution"; Srinivasan, R., Ed.; Pergamon Press: Oxford, 1980; Vol. 2, p 59.
(2) Heitz, F.; Dêtriché, G.; Vovelle, F.; Spach, G. *Macromolecules* *14*, **1981**, 47.
(3) Tomasic, L.; Stefani, A.; Lorenzi, G. P. *Helv. Chim. Acta* **1980**, *63*, 2000.
(4) Lorenzi, G. P.; Jäckle, H.; Tomasic, L.; Rizzo, V.; Pedone, C. *J. Am. Chem. Soc.* **1982**, *104*, 1728.
(5) Lorenzi, G. P.; Jäckle, H.; Tomasic, L.; Pedone, C.; Di Blasio, B. *Helv. Chim. Acta* **1983**, *66*, 158.
(6) Lorenzi, G. P.; Jäckle, H.; Tomasic, L.; Pedone, C. *Biopolymers* **1983**, *22*, 157.
(7) Jäckle, H.; Tomasic, L.; Lorenzi, G. P. In "Physical Chemistry of Transmembrane Ion Motions"; Spach, G., Ed.; Elsevier: Amsterdam, 1983; p 385.
(8) Boissonnas, R. A.; Guttmann, St.; Jaquenoud, P. A.; Waller, J. P. *Helv. Chim. Acta* **1956**, *39*, 1421.
(9) Failli, A.; Nelson, V.; Immer, H.; Götz, M. *Can. J. Chem.* **1973**, *51*, 2769.
(10) Schnabel, E. *Ann. Chem.* **1967**, *702*, 188.
(11) Moroder, L.; Hallet, A.; Wünsch, E.; Keller, O.; Wersin, G. *Hoppe Seyler's Z. Physiol. Chem.* **1976**, *357*, 1651.
(12) Vaughan, J. R., Jr.; Osato, R. L. *J. Am. Chem. Soc.* **1952**, *74*, 676.
(13) Widmer, U.; Lorenzi, G. P.; Pino, P. *Biopolymers* **1979**, *18*, 239.
(14) Nitecki, D. E.; Halpern, B.; Westley, J. W. *J. Org. Chem.* **1968**, *33*, 864.
(15) Upson, D. A.; Hruby, V. J. *J. Org. Chem.* **1977**, *42*, 2329.
(16) Birnbaum, S. M.; Levnikov, L.; Kingsley, R. B.; Greenstein, J. P. *J. Biol. Chem.* **1952**, *194*, 455.
(17) Lorenzi, G. P.; Tomasic, L.; Bangerter, F.; Neuenschwander, P.; DiBlasio, B. *Helv. Chim. Acta* **1983**, *66*, 2129.
(18) Lorenzi, G. P.; Gerber, C.; Jäckle, H. *Biopolymers*, **1984**, *23*, 1905.
(19) Ramachandran, G. N.; Chandrasekaran, R. *Ind. J. Biochem. Biophys.* **1972**, *9*, 1.
(20) Venkataram Prasad, B. V.; Chandrasekaran, R. *Int. J. Pept. Protein Res.* **1977**, *10*, 129.
(21) Heitz, F.; Cary, P. D.; Crane-Robinson, C. *Macromolecules* **1977**, *10*, 526.

Structure Calculations for Silane Polymers: Polysilane and Poly(dimethylsilylene)

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ABSTRACT: The structure and conformational energies of polysilane, H–(SiH$_2$)$_n$–H, and poly(dimethylsilylene), Me–(SiMe$_2$)$_n$–Me, have been investigated by using full relaxation empirical force field (EFF) techniques. Gauche conformational states are calculated to be lowest in energy for both polymers. These results contrast with polyethylene hydrocarbon polymers which typically adopt trans conformations in the ground state. Both polysilane and poly(dimethylsilylene) are calculated to be conformationally more flexible than polyethylene.

Introduction

Though silane polymers have been known for some time,[1] it has only been recently that moderate and high molecular weight, soluble analogues have become available.[2,3] Interest in these compounds is active for a variety of reasons: they exhibit unusual spectral properties;[4] they serve as precursors to β-silicon carbide fibers;[5] they serve as impregnating agents for strengthening ceramics;[6] and they may become semiconducting upon doping.[2d] In addition, it has recently been discovered that silane polymers may have applications in photoresist technology[7] and as photoinitiators for vinyl monomer polymerization.[8] Despite this level of interest, relatively little is known about the structural details of such polymers. While acyclic catenanes[9] of more than two silicon atoms have been the subject of several theoretical[10] and experimental[11,12] studies, the focus of many of these investigations has been on relatively short-chain silanes and permethylsilanes. As our interests[2d–i,6–8] lie mainly with the higher molecular weight polymers of silicon, we have investigated, using empirical force field (EFF) methods,[13] the structure and conformational energies of oligomers which serve as models for these polymeric compounds.[14] This paper is concerned with the results obtained for the simplest members of this class of polymer, polysilane and poly(dimethylsilylene).

Methods

Calculations were performed by the empirical force field (EFF) method,[13] using the program MM2[16] and the full relaxation technique.[18] The silicon parameters developed for the program BIGSTRN[10b,19] for stretching and bending, which have been used previously in the program MM1,[10d,20] were employed in these calculations. Torsional parameters used in the present study are reported in ref 21. The H–Si–Si–H torsional parameter was obtained by adjusting V_3 until the rotation barrier[22] of 1.22 kcal/mol observed for disilane[23] was reproduced. The C$_{sp^3}$–Si–Si–C$_{sp^3}$ torsional parameter was set equal to this value[24] by analogy

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to the relationship between the $H-C_{sp^3}-C_{sp^3}-H$ and $C_{sp^3}-C_{sp^3}-C_{sp^3}-C_{sp^3}$ parameters.[10b,19,25] All other torsional parameters[21] were assigned reasonable values and were tested by comparing calculated structures of various silanes with known X-ray molecular structures.[26]

We have limited our choice of input structures to the all-trans (T), all-gauche (G), alternating gauche–trans (GT) and, for the silapentanes, the alternating gauche–gauche minus (G^+G^-) backbone conformations (for examples, see Figure 1). The T conformation is the zigzag structure normally associated with the ground state of polyethylene hydrocarbons[27] and the G and GT conformations are helical, with gauche torsion angles which are all of the same sign. The G^+G^- state is usually of relatively high energy for hydrocarbon polymers due to the repulsive four-bond steric interactions which result in this conformation (pentane effect).[28] In addition, while the G^+G^- state may exist as a kink in a polymer chain, it is not expected to be a repeat pattern since this would result in backbone atoms being superimposed.

We employ the convention discussed previously[27] for describing the magnitude and sign of the torsion angles in these compounds.

Polysilane ($H-(SiH_2)_n-H$)

The structure of trisilapropane ($n = 3$) and tetrasilabutane ($n = 4$) have been investigated previously by both experimental[12b] and theoretical methods.[10a,b] Tetrasilabutane exists in two conformationally isomeric forms (G and T) of approximately equal energy.[10b,12b] This contrasts with the conformational behavior of the carbon analogue, *n*-butane, in which the T form is more stable than the G by 0.8 kcal/mol.[29] The structure of the T form of polysilane has also been investigated by ab initio methods at the LP-31G and SSZ levels of sophistication,[30] but the relative energies of other pertinent conformations were not considered. With the recent synthesis of high molecular weight polysilane,[31] the structure and relative conformational energies of this polymer are now of considerable interest. In order to address this problem, and to see if the dissimilarities between silane and hydrocarbon structure as exemplified by tetrasilabutane persist in the higher homologues, we have investigated the structure of compounds which serve as models for high molecular weight polysilane.

Triacontasilatriacontane ($n = 30$) (**1**) was chosen as a reasonable model for polysilane. Calculations were also performed on decasiladecane ($n = 10$) (**2**) and pentasilapentane ($n = 5$) (**3**) in order to test the suitability of smaller fragment sizes in modeling this polymer. Decasiladecane represents a significant reduction in chain length relative to **1** and provides a measure of the effect such a reduction has on the computational results. The conformation of **3** is described by two internal torsion angles and therefore is the smallest chain length in which G, GT, T, and G^+G^- conformational states are possible. It is well-known[28] that information on the relative conformational energies of long-chain polyethylenes may be obtained from studies of the model compound *n*-pentane. Comparison of the results obtained for **1**–**3** will thus establish whether $n = 5$ fragments are also acceptable models for high polymers of silicon. For reasons mentioned in the methods section, the G^+G^- conformation was only investigated for **3**.

Input structures for calculations on the various conformations of **1**–**3** were of ideal symmetry with G and T angles equal to 60° and 180°, respectively. Structures obtained after complete geometry optimization were relatively close to the input orientations, indicating that these conformational states are potential energy minima on the polysilane hypersurface.

Relative conformational energies for **1**, **2**, and **3** are reported in Table I[32] and selected bonding parameters are reported in Table II. Views of the calculated G, GT, T, and G^+G^- structures for **3** are shown in Figure 1.

Table I
Relative Energies of Isomers of 1, 2, and 3[a]

	1	2	3
G	0.0	0.0	0.0
GT	8.0	2.3	0.4
T	13.0	3.7	0.7
G^+G^-			0.4

[a] In kcal/mol.

Table II
Selected Bonding Parameters for Isomers of 1, 2, and 3

	1	2	3
	Average Si–Si Bond Lengths[a]		
G	234.1	234.2	234.2
GT	234.3	234.2	234.2
T	234.4	234.2	234.2
G^+G^-			234.3
	Average Si–Si–Si Bond Angles[b]		
G	108.3	108.5	109.1
GT	110.0	109.2	109.5
T	110.8	110.0	109.7
G^+G^-			112.2
	Si–Si–Si–Si Torsion Angles[b]		
G[c]	57.7	51.4	54.7
GT (G)	59.6[c]	59.1[c]	58.6
GT (T)	177.9[d]	178.4[d]	179.6
T[d]	180.0	179.8	180.0
G^+G^- [d]			68.8

[a] In picometer units. [b] In degrees. [c] Reported as the average of these angles. [d] Reported as the average of the absolute value of these angles.

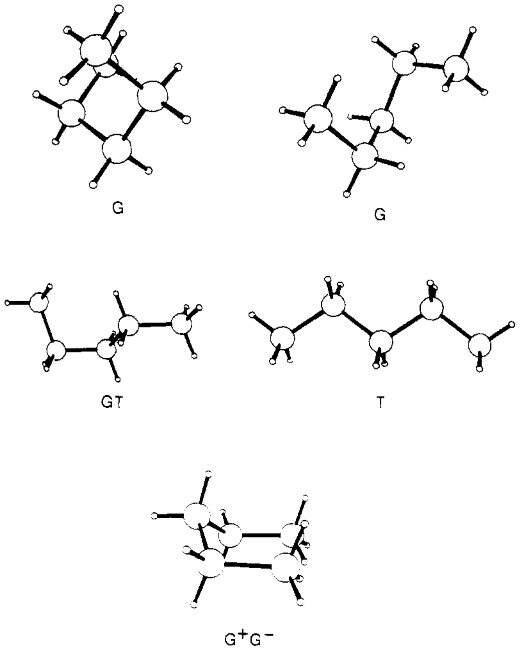

Figure 1. Views of the G, GT, T, and G^+G^- conformations of **3**. Top: the G conformation. Left: viewed down the helical axis. Right: viewed perpendicular to the helical axis. Middle left: The GT conformation viewed perpendicular to the helical axis. Middle right: The T conformation viewed perpendicular to the least-squares plane of the silicon atoms. Bottom: Side view of the G^+G^- conformation.

Inspection of Table I reveals that, in contradistinction to polyethylene hydrocarbons which in general prefer T conformational states,[27] the lowest energy conformers for **1**, **2**, and **3** are G. The GT conformations have relative conformational energies of 8.0, 2.3, and 0.4 kcal/mol and T is the highest energy conformer in each case with relative energies of 13.0, 3.7, and 0.7 kcal/mol for **1**, **2**, and **3**, respectively.[33] The relative energy calculated for the G^+G^- conformation of **3** is 0.4 kcal/mol. While energy differences between conformers increase as n, the polymer chain length, increases (Table I), the relative energies per GT and TT unit are comparable and are 0.6, 0.7, 0.4, and 1.0, 1.1, and 0.7 kcal/mol for **1**, **2**, and **3**, respectively. Although **3** may slightly underestimate these relative energies by comparison to **1** and **2**, the results obtained by this measure are in very reasonable[34] agreement. Thus calculations on **1**–**3** uniformly predict the G conformational state to be lowest in energy and obtain similar quantitative results.

Differences in the conformational behavior of silanes and hydrocarbons have been attributed to[10b,11] the disparity in typical Si–Si and C–C bond lengths (ca. 234 and 153 pm, respectively[35]). This structural difference often results in diminished steric interactions in silanes relative to hydrocarbons. In addition, the longer Si–Si bonds can lead to significant van der Waals attractions between molecular fragments which would typically be considered sterically repulsive in hydrocarbon chemistry.[10b] It is therefore interesting to note that, although partitioning of the component strain energies in EFF calculations is of doubtful physical significance,[13c] within the context of the present model of the molecules the van der Waals terms for **1**–**3** are attractive and substantially larger than any of the other strain energy terms. Of special interest in this regard are the 1,4 and 1,5 distances between silicon atoms in the G conformations. With separations of ca. 430 and 500 pm, respectively, these backbone atom pairs reside within nonbonded attractive regions. It seems likely that the G conformational state is favored due to the dominance of the nonbonded attractive terms for these molecules which are at a maximum in the G conformation. The attenuation of the pentane effect in silanes relative to hydrocarbons, as revealed by the energy of the G^+G^- state relative to the other conformations of **3** (Table I), is further evidence of the difference in steric requirements of silanes and hydrocarbons.

Inspection of Table II reveals that the average Si–Si bond lengths in **1**–**3** in the G, GT, T, and G^+G^- conformations do not deviate significantly from the strain-free value of 234.5 pm. In addition, the individual bond lengths calculated for each conformation of **1**–**3** differ by no more than 0.2 pm, a value which is within the error limits of the EFF method.[13] Thus, unlike hydrocarbons which have expanded C–C bond lengths in the interior of T chains,[36] Si–Si bond lengths in silanes are calculated to remain relatively constant within a given conformation.

The Si–Si–Si bond angles, which adopt values between 108.3° and 112.2°, are in general somewhat compressed from the strain-free value of 111.7°. The G conformations of **1**, **2**, and **3** have the smallest average Si–Si–Si angles of 108.3°, 108.5°, and 109.1°, respectively. The GT conformations have somewhat larger average angles of 110.0°, 109.2°, and 109.5° while in the T conformations the averages are still larger with values of 110.8°, 110.0°, and 109.7°. The difference in angles between the G and GT (GT and T) conformations are 1.7° (0.8°), 0.7° (0.8°), and 0.4° (0.2°) for **1**, **2**, and **3**, respectively. Thus while the relative magnitude of the difference in average angles is greatest for **1**, the trend in this structural feature (i.e., G < GT < T) is present in all three compounds. The G^+G^- conformation of **3** has the largest Si–Si–Si angles of any of the structures with an average value of 112.2°.

The Si–Si bond lengths and Si–Si–Si angles calculated in this work for the T conformation are ca. 8 pm longer and ca. 8° smaller than the 226.4 pm and 118.97° obtained at the LP-31G level[30] and ca. 11 pm shorter and ca. 4.5° smaller than the 245.3 pm and 114.5° obtained by SSZ calculations.[30,37] While we are unable to account for these differences[37] the present calculations are in very good agreement with EFF calculations on trisilapropane and tetrasilabutane which obtained bond lengths of ca. 234.3 pm and bond angles of ca. 110°.

Table III
Relative Energies of Isomers of 4[a]

G	0.0
GT	0.8
T	0.9
G^+G^-	38.4

[a] In kcal/mol.

The average torsion angles for the G conformations are 57.7°, 51.4°, and 54.7° for **1**, **2**, and **3** and are somewhat smaller than the average gauche values of 59.6°, 59.1°, and 58.6° calculated for the GT conformations. With gauche torsion angles which are less than 60°, the axial advancement per helical turn in these conformers is reduced relative to that expected for ideal G or GT structures. The trans torsion angles in the GT and T conformations are all within ca. 2° of 180° and for the GT conformations are all of the same sign. The average torsion angle in the G^+G^- conformation is 68.8°.

As was previously mentioned it is well established[28] that information on the relative conformational energies of long-chain polyethylenes may be obtained from studies of the model compound n-pentane. In addition, certain structural trends are shared by n-pentane and its higher homologues.[36] On the basis of the above comparison, we similarly conclude that **3** may serve as a reasonable model compound for higher order silanes.

Comparison of the conformation energies calculated for **3** with those previously reported for n-pentane[28] allows for an estimation of the relative conformational flexibilities of polysilane and polyethylene. The relative energies for the T, GT, G, and G^+G^- conformations of n-pentane are 0, 2, 3, and >5 kcal/mol,[28] respectively, i.e., much larger than the 0.0–0.7 kcal/mol range calculated for **3**. Thus polysilane is predicted to exhibit considerably more conformational flexibility than its carbon analogue. In addition, while the G^+G^- state is highly disfavored in polyethylene, the comparable energies calculated for the GT and G^+G^- conformation of **3** (Table I) indicate that near-equivalent populations of these two conformational states are expected in polysilane.

If it is permissible to extrapolate the suitability of the fragment size chosen to model polysilanes to alkyl-substituted silanes, pentasilapentane (i.e., $n = 5$) fragments of such polymers should also be acceptable conformational models. In the calculations which follow we focus on a pentasilapentane fragment of the alkyl-substituted silane, poly(dimethylsilylene). As for the silanes, the energetic and structural information obtained will be discussed in terms of their relevance to the structure of the corresponding polymer.

Poly(dimethylsilylene) ($Me-(SiMe_2)_n-Me$)

Dodecamethylpentasilapentane ($n = 5$) (**4**) was chosen as the model compound for the polymer poly(dimethylsilylene). The calculated relative conformational energies for **4** are reported in Table III and selected bonding parameters are reported in Table IV. Views of the G, GT, and T conformations are shown in Figure 2.

For the G, T, and G^+G^- conformational states, geometry optimized structures were relatively close to the ideal input structures. For the GT conformation, however, uncon-

Table IV
Selected Bonding Parameters for Isomers of 4

Average Si–Si Bond Lengths[a]	
G	234.9
GT	234.9
T	235.0
G^+G^-	235.1
Average Si–Si–Si Bond Angles[b]	
G	116.6
GT	115.4
T	114.2
G^+G^-	117.6
Si–Si–Si–Si Torsion Angles[b]	
G[c]	54.7
GT (G)	59.7
GT (T)	180.0
T[c]	180.0
G^+G^-[d]	72.3

[a] In picometer units. [b] In degrees. [c] Reported as the average of these angles. [d] Reported as the average of the absolute value of these angles.

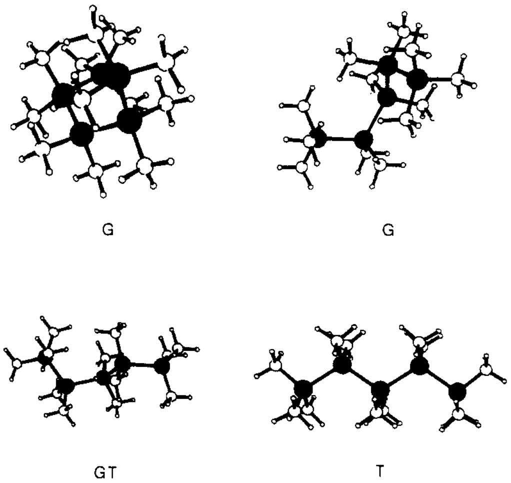

Figure 2. Views of the G, GT, and T conformations of **4**. Top: The G conformation. Left: viewed down the helical axis. Right: viewed perpendicular to the helical axis. Bottom left: The GT conformation viewed perpendicular to the helical axis. Bottom right: The T conformation viewed perpendicular to the least-squares plane of the silicon atoms. Silicon atoms have been shaded for clarity.

strained geometry optimization leads to a structure which may not properly be described as GT. In order to obtain the energy of the GT state to allow for a comparison to polysilane, the T torsion angle was constrained to remain at 180° and all other geometric parameters were optimized.[18]

Inspection of Table III reveals that the G conformational state is calculated to be lowest in energy for **4**. The relative energies for the GT and T conformations are 0.8 and 0.9 kcal/mol, respectively,[38] and the relative energy of the G^+G^- conformation is 38.4 kcal/mol. Although increasing the steric bulk at silicon by replacing the hydrogens of polysilane with methyl groups does not alter the relative energy ordering of the G, GT, and T conformations (see tables), two significant changes associated with this substitution are noteworthy. The relative energies obtained for the GT and T conformations of **4** are somewhat higher than those obtained for **3** and the energy of the G^+G^- conformation is now significantly larger than that calculated for any other conformation of **4**. While differences in the conformational behavior of **3** and **4** are thus apparent, both polysilane and poly(dimethylsilylene) are predicted to adopt G conformations in the ground state.

Previous EFF calculations[10b] on decamethyltetrasilabutane ($n = 4$) predicted that the T conformation is lower in energy than the G but only by 0.13 kcal/mol. In quantitative agreement, later experimental studies[11] concluded that the two conformations are present in comparable quantities at room temperature. The longer chain length of **4** ($n = 5$) includes the second-order (four bond) interactions required for an adequate model of a polymer chain[39] as well as the first-order (three bond) interactions found in decamethyltetrasilabutane. The present calculations thus reveal that, as for polysilanes (see above), when these second-order interactions are considered for permethylpolysilanes, the G conformational state is energetically favored.

On the basis of the conformational energies calculated for **4**, we conclude that poly(dimethylsilylene), like polysilane, is conformationally very flexible. The large relative energy of the G^+G^- form of **4** of 38.4 kcal/mol indicates that the pentane effect[28] has a significant influence on the conformational energies of alkyl-substituted silanes. Accordingly, the flexibility of poly(dimethylsilylene) is diminished relative to polysilane since an appreciable population of the G^+G^- state is not expected. In the structural discussion which follows we therefore focus only on the G, T, and GT conformations of **4**.

The Si–Si bond lengths in **4** are on average 0.7 pm longer than those calculated for **1**–**3** and are 234.9 pm for the G and GT and 235.0 pm for the T conformation. The average Si–Si–Si bond angles are all larger than those calculated for **1**–**3** and are 116.6°, 115.4°, and 114.2° for the G, GT, and T conformations, respectively. It is interesting to note that the average angles in **4** follow a trend which is opposite to that calculated for **1**–**3** with T having the smallest, GT intermediate, and G the largest average angles (i.e., $T < GT < G$). The difference between the average angles for the G and GT and the GT and T conformations is 1.2°, a value which is significantly larger than the differences of 0.4° and 0.2° calculated for **3**.

Compensating for this increased angle strain relative to **1**–**3** are additional methyl–methyl and silicon–methyl van der Waals attractive interactions in **4**. As for **1**–**3** the van der Waals attractive terms for conformations of **4** are larger than any of the other strain energy terms and are maximized in the G conformation. Thus while increasing the steric bulk at silicon by methyl substitution does have a significant effect on certain aspects of backbone structure, the preference for the G conformation is maintained.

The gauche torsion angles calculated for **4** are similar in magnitude to those obtained for **1**–**3** and are all less than 60°. The gauche torsion angle for the GT structure is 59.7° and, as found for **1**–**3**, this angle is somewhat larger than the average of 54.7° calculated for the G conformation. The trans torsion angles average 180° in the T conformation.

Summary

Full relaxation, EFF calculations on polysilane and poly(dimethylsilylene) indicate that the gauche conformational states are lowest in energy for both polymers.[40] Comparison of the relative conformational energy differences calculated for the G, GT, T, and G^+G^- conformations reveal that both polysilane and poly(dimethylsilylene) are more conformationally flexible than the hydrocarbon polymer, polyethylene. For polysilane, the pentane effect is attenuated relative to hydrocarbon chemistry as indicated by the comparable energies calculated for the GT and G^+G^- conformational states. While the preference for the G conformation is maintained in poly(dimethyl-

silylene), the energy of the G^+G^- conformation is much higher than that calculated for the other conformations demonstrating that the pentane effect has a significant influence on the conformational behavior of alkyl substituted silane polymers. Accordingly, the flexibility of poly(dimethylsilylene) is diminished relative to polysilane since an appreciable population of the G^+G^- state is not expected.

Efforts are presently under way to investigate the structure and conformational properties of other silane polymers.

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References and Notes

(1) For examples, see: (a) Kipping, F. S. *J. Chem. Soc.* **1924**, *125*, 2291. (b) Burkhard, C. A., *J. Am. Chem. Soc.* **1949**, *71*, 963. (c) Wesson, J. P.; Williams, T. C. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2833.

(2) (a) Wesson, J. P.; Williams, T. C. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 959. (b) Trujillo, R. E. *J. Organomet. Chem.* **1980**, *198*, C27. (c) Wesson, J. P.; Williams, T. C. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 65. (d) West, R.; David, L. D.; Djurovich, P. I.; Stearley, K. L.; Srinivasan, K. S. V.; Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 7352. (e) Trefonas, P., III; Djurovich, P. I.; Zhang, X. H.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 819. (f) Trefonas, P., III; West, R.; Miller, R. D.; Hofer, D. *Ibid.* **1983**, *21*, 823. (g) Zhang, X. H.; West, R. *Ibid.* **1984**, *22*, 159. (h) *Ibid.* **1984**, *22*, 225. (i) Zhang, X. H.; West, R. *Polym. Commun.* (*Beijing*), submitted.

(3) Poly(dimethylsilylene) is soluble in various solvents at elevated temperatures.[1c]

(4) For a review, see: Pitt, C. G. In "Homoatomic Rings, Chains and Macromolecules of Main-Group Elements"; Rheingold, A. L. Ed.; Elsevier Scientific: New York, 1977.

(5) Yajima, S.; Hasegawa, Y.; Hayashi, J.; Iimura, M. *J. Mater. Sci.* **1978**, *13*, 2569. Hasegawa, Y.; Iimura, M.; Yajima, S. *Ibid.* **1980**, *15*, 720 and references therein.

(6) Mazdiyasni, K. S.; West, R.; David, L. D. *J. Am. Ceram. Soc.* **1978**, *61*, 504. West, R.; David, L. D.; Djurovich, P. I.; Yu, H.; Sinclair, R. *Ceram. Bull.* **1983**, *62*, 899.

(7) Trefonas, P., III; West, R. "Abstracts of Papers", XVII Organosilicon Symposium, 1983.

(8) Wolff, A. R.; West, R.; Peterson, D. G. "Abstracts of Papers", XVIII Organosilicon Symposium, 1984.

(9) For reviews of the chemistry of main-group catenanes, see: "Homoatomic Rings, Chains and Macromolecules of Main-Group Elements"; Rheingold, A. L., Ed.; Elsevier Scientific: New York, 1977.

(10) (a) Dewar, M. J. S.; Lo, D. H.; Ramsend, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 1311. (b) Hummel, J. P.; Stackhouse, J.; Mislow, K. *Tetrahedron* **1977**, *33*, 1925. (c) Cowley, A. in ref 8 and references therein. This reference reports the results of rigid rotor CNDO calculations on n-Si_5H_{12} which obtain conformational energies for the staggered C_{2v}, C_1, C_2, and C_s conformers of 0.0, 0.4, 0.8, and 0.8 kcal/mol, respectively. (d) Hönig, H.; Hassler, K. *Monatsh. Chem.* **1982**, *113*, 129. (e) Verwoerd, W. S. *J. Comput. Chem.* **1982**, *3*, 445.

(11) Ernst, C. A.; Allred, A. L.; Ratner, M. A. *J. Organomet. Chem.* **1979**, *178*, 119 and references therein. See also: Allred, A. L.; Ernst, C. A.; Ratner, M. A. In ref 9.

(12) (a) Bock, H.; Ensslin, W.; Fehér, F.; Freund, R. *J. Am. Chem. Soc.* **1976**, *98*, 668. (b) Ensslin, W.; Bergmann, H.; Elbel, S. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 913. (c) See also ref 10c. (d) Molecular motion in polysilastyrene has been investigated: McGarvey, B. R.; Schlick, S. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2145.

(13) For reviews of the EFF method, see: (a) Williams, J. D.; Stang, P. J.; Schleyer, P. v. R. *Annu. Rev. Phys. Chem.* **1968**, *19*, 531. (b) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (c) Altona, C.; Faber, D. H. *Fortschr. Chem. Forsch.* **1974**, *45*, 1. (d) Dunitz, J. D.; Bürgi, H.-B. *MTP Int. Rev. Sci.: Org. Chem., Ser. One* **1976**, 81. (e) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. (f) Ermer, O. *Struct. Bonding* (*Berlin*) **1976**, *27*, 161. (g) White, D. N. J. *Comput. Chem.* **1977**, *1*, 225. (h) Kitaigorodsky, A. I. *Chem. Soc. Rev.* **1978**, *7*, 133. (i) Mislow, K.; Dougherty, D. A.; Hounshell, W. D. *Bull. Soc. Chim. Belg.* **1978**, *87*, 555. (j) Burkert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, DC, 1981.

(14) An initial account of this work has been presented previously: Damewood, J. R., Jr.; West, R. "Abstracts of Papers", XVII Organosilicon Symposium, June 3–4, 1983.[15]

(15) After beginning this work, we learned that rigid rotor empirical potential energy calculations were being performed by another group:[18] Welsh, W. J.; Beshah, K.; Ackerman, J. L.; Mark, J. E. "Abstracts of Papers", Molecular Mechanics Symposium, June 23–24, 1983. We thank the authors for communicating their results.

(16) Allinger, N. L.; et al. *QCPE* **1981**, *13*, 395.[17]

(17) Converted to the Harris/7 version by Prof. H. Whitlock.

(18) All bond lengths, angles, and torsion angles are adjusted to minimum energy values for each conformation in the calculations reported in this paper unless otherwise indicated.

(19) Andose, J. D.; et al. *QCPE* **1978**, *11*, 348.

(20) Hönig, H.; Hassler, K. *Monatsh. Chem.* **1982**, *113*, 285.

(21) For H–Si–Si–H, C_{sp^3}–Si–Si–C_{sp^3}, H–Si–Si–Si, C_{sp^3}–Si–Si–Si, and Si–Si–Si–Si, $V_3 = 0.135$. For H–C_{sp^3}–Si–Si, $V_3 = 0.156$. KSB2 = KSB2H = 0.

(22) Calculated as the difference in energy between the D_{3d} and D_{3h} conformations.

(23) Pfeiffer, M.; Spangenberg, H.-J. *Z. Phys. Chem.* **1966**, *232*, 47.

(24) This results in a calculated hexamethyldisilane rotation barrier[22] of 1.29 kcal/mol, i.e., higher than the barrier observed for disilane.[23] This stands in contrast to the computational results obtained[10b,22] using the program BIGSTRN, which predicts a rotation barrier of 1.05 kcal/mol, and with the results of MM1 calculations[10d] which predict a barrier of 1.22 kcal/mol.[22] Slight differences in the force fields are, no doubt, responsible for this discrepancy.

(25) Allinger, N. L.; et al. *QCPE* **1976**, *11*, 318.

(26) For examples of available structures see ref 10b and 10d.

(27) Tadokoro, H. "Structure of Crystalline Polymers"; Wiley: New York, 1979.

(28) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience Publishers: New York, 1969.

(29) Pitzer, K. S. *J. Chem. Phys.* **1940**, *8*, 711. See also: Woller, P. B.; Garbisch, E. W., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 5310. Verma, A. L.; Murphy, W. F.; Bernstein, H. J. *J. Chem. Phys.* **1974**, *60*, 1540.

(30) Teramae, H.; Yamabe, T. *Theor. Chim. Acta* **1983**, *64*, 1.

(31) John, P.; Odeh, I. M.; Wood, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1496.

(32) In **1** and **2** there are an odd number of backbone torsion angles and hence the GT and TG conformational states are not equivalent. However, differences in energy and structure are not sufficient to change the conclusions reached in this work. The relative TG energies are 8.4 and 2.5 kcal/mol for **1** and **2**, respectively.

(33) This result is in qualitative agreement with that found by others[15] but differs from the rigid rotor CNDO calculations on **3**[10c] which obtains T as the lowest energy conformer.

(34) Differences between **1** and **3** are 0.2–0.3 kcal/mol.

(35) For examples, see: "Tables of Interatomic Distances and Configuration in Molecules and Ions, Special Publication No. 11"; The Chemical Society Burlington House: London, 1958.

(36) Scarsdale, J. N.; Sellers, H. L.; Schäfer, L.; Allinger, N. L. *J. Comput. Chem.* **1982**, *3*, 269 and references therein.

(37) We note that a Si–Si bond length of 226.4 pm is considerably shorter and 245.3 pm is considerably longer than bond lengths which have previously been observed for hydro or alkyl-substituted silanes. For examples, see: Dräger, von M.; Walter, K. G. *Z. Anorg. Allg. Chem.* **1981**, *479*, 65 and ref 35.

(38) To a first approximation it might be expected that the energy of the GT conformation would be somewhat closer to the average of the G and T energies (i.e., ca. 0.5 kcal/mol). Since such an approximation is strictly only valid within the framework of a rigid rotor model, when changes in geometry are allowed within individual conformations, departures from ideal behavior may be expected.[18] Thus the nonideal relative energy differences calculated for **4** may reflect changes in structure (and hence energy) which accompany geometry optimization (Table IV).

(39) Bovey, F. A.; Winslow, F. H. "Macromolecules, An Introduction to Polymer Science"; Academic Press: New York, 1979; p 248.

(40) It is, of course, possible that different chemical environments may affect the ground-state structure and conformational energies of these polymers. Such effects are clearly illustrated by the difference in preferred structure of isotactic polystyrene in the crystalline state[41] and in stretched gels.[42] While it is not presently possible to predict the direction or magnitude of such

factors, barring significant crystal packing forces, etc., we are confident that our calculations accurately represent the conformational properties of polysilane and poly(dimethylsilylene).

(41) Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cimento, Suppl.* **1960**, *15*, 68. See also ref 27.
(42) Atkins, E. D. T.; Keller, A.; Shapiro, J. S.; Lemstra, P. J. *Polymer* **1981**, *22*, 1161 and references therein.

Assessment of Long Branches in Free Radical Polyethylene: Correlation between the Melt and Solid States

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ABSTRACT: A series of branched polyethylenes of the same apparent molecular weight have been characterized by gel permeation chromatography (GPC), viscometry, NMR, and SAXS. By use of these different techniques, the molecular weight distribution and the number of long branches have been determined. In these materials quenched from the melt, we show that the long period of the semicrystalline state and the dimensions of the coils in the melt before crystallization are correlated. These correlations permit verification of theories of Zimm and Stockmayer and Daoud and Joanny giving the conformations of the coils in the melt. Finally, we emphasize that the SAXS technique combined with GPC is an accurate method of assessment of the number of branches, comparable to the ^{13}C NMR technique and viscometry.

I. Introduction

In a series of papers it has been shown that in monodisperse fractions, mixture of fractions, and polydisperse polyethylene (PE), the quenched state and the melt state are correlated.[1-3] For these linear chains, the long period L of the semicrystalline state is a function of the weight average of the radius of gyration R_w. The relationship

$$L \cong R_w \sim \sum_i \omega_i M_i^{1/2} \tag{1a}$$

where ω_i is the mass concentration of chains of molecular weight M_i and has been verified for polyethylene and poly(ethylene terephthalate).[4]

In branched polymers, the dimensions of the coils vary with the molecular weight M and with the number of branches N_b per chain. These dimensions have been calculated by Zimm and Stockmayer[5] (ZS) and more recently by Daoud and Joanny[6] (DJ). Up to now neither the dimensions of the chains in the liquid state nor the long period in the solid state has been systematically studied for these randomly branched materials. By comparison with relation 1a we expect a long period dependence of the form

$$L \sim R \sim f(M)g(N_b) \tag{1b}$$

where $g(N_b)$ is a decreasing function of N_b. A knowledge of the functions f and g and a measurement of R or L would give an estimate of the number of branches N_b, if the molecular weight distribution is known.

The aim of this paper is to compare the assessment of long branches in radical PE by the three following methods coupled with gel permeation chromatography (GPC) on a series of well-defined high-pressure PE's: (a) viscometry, (b) NMR, and (c) small-angle X-ray scattering (SAXS) in the semicrystalline state obtained by quenching the melt.

The assessment of branching by methods a and b has been studied by several authors.[7-15,22] The last method, which is new, is based on the correlations existing between the solid and melt states of branched polymers expressed by relation 1b. Finally, we discuss our results in light of the scaling theory of Daoud and Joanny.

II. Characterization of Polyethylene Samples

1. GPC and Viscosity Measurements. We give in Table I the characteristics of branched (B) and linear (L) PE samples. For branched PE the GPC chromatogram at 135 °C in trichlorobenzene (TCB) permits us to define the apparent average molecular weights M_n^* and M_w^*, which are the number- and weight-average molecular weights of the equivalent linear PE having the same chromatogram. Samples B_1–B_8 have nearly the same chromatogram and, therefore, the same apparent molecular weight distribution ($M_n^* \sim 18\,000$, $M_w^* = 120\,000$).

Linear samples L_1–L_3 have been studied in ref 2 and 3. Sample L_1 is a mixture of equal weights of two monodisperse fractions of molecular weight 10 000 and 260 000. Samples L_2 and L_3 are two Pennings fractions.[3] L_1 and L_2 have different molecular weight distributions but the same weight- and number-average molecular weights as the apparent molecular weight of the branched PE samples B_1–B_8 (Figure 1).

Sample L_4 is a polydisperse, high-density commercial product (Manolene 6050). The indices of branching, b, of the materials have been determined from GPC and intrinsic viscosity measurements. Following the procedure given by Prechner et al.,[7] b is defined as the ratio of the intrinsic viscosity $[\eta]_l^*$ of the linear PE to the intrinsic viscosity of $[\eta]_b$, the branched PE having the same elution volume:

$$b = [\eta]_l^*/[\eta]_b \tag{2}$$

The parameter β can be calculated for each fraction; in Table I b is an average value, $[\eta]_l^*$ and $[\eta]_b$ being the weight average of the intrinsic viscosity of the linear and branched polymer, respectively.

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