Minireview

A new theory for rotational isomeric states: polysilanes lead the way

Robert West *

Organosilicon Research Center, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706, USA

Abstract

Conformational studies of polysilanes have led to a new model for rotational isomerism. The new model applies to most linear polymers and oligomers other than hydrocarbons, for which the familiar *anti* and *gauche* minima are valid. According to the model, the permitted rotational minima, their symbols and their approximate intrachain torsional angles ω are: *transoid*, *T*, $\pm 165°$; *deviant*, *D*, $\pm 150°$; *ortho*, *O*, $\pm 90°$; *gauche*, *G*, $\pm 55°$; and *cisoid*, *C*, $\pm 40°$.
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The potential energy diagram for *n*-butane shown in Fig. 1 is featured in almost every beginning of the organic chemistry textbook. From this, all students learn that the stable rotational states for hydrocarbons are *anti* [1] and *gauche*, with C–C torsional angles of 180° and 60°, respectively. But it is now clear that the hydrocarbons represent an exceptional, simplified case. For polymers, generally, rotational isomerism is much more complicated. Research with polysilane polymers and oligomers was the major driving force for the paradigm shift to this new model of rotational conformers [2,3].

One of the first cracks in the wall of the conventional model arose in 1986, when our group was studying the structures of cyclic permethylpolysilanes. Fig. 2 illustrates the molecular structures of the 16-membered ring hydrocarbon, 1,1,9,9-tetramethylcyclohexadecane [4] and the 16-membered silicon cycle, $(Me_2Si)_{16}$ [5]. The difference between these is striking. Underlying the contrasting structures are sharp differences in the inter-ring torsional angles in these molecules: the carbocyclic ring has eight torsional angles between 50.3° and 59.3°, *gauche*, and eight between 175.6° and 179.9°, clearly *anti*. Further, in the silicon ring the torsional angles also fall into two sets of eight, but the values are quite different: eight angles of 89.3°–93.9°,

and eight of 158.0°–169.5°. We speculated that these unexpected torsional angles in $(Me_2Si)_{16}$ result from repulsions between the methyl groups, but were unable to extend the model further at that time.

Meanwhile, the chemistry of polysilane-high polymers was undergoing rapid development. A crucial step was the discovery in 1985 that the UV absorption bands of polysilanes are thermochromic. Thermochromism was first observed for polysilanes in solution [6,7], and later for polysilane films [8]. The energy of the interband transition responsible for the UV absorption of polysilanes was soon shown to be strongly coupled to the chain conformation, with the energy decreasing (and wavelength increasing) as the polymer becomes more extended. Poly(di-*n*-hexylsilane) is a classic example; the low-temperature crystalline phase, described as all-*anti*, absorbs at 374 nm. Upon heating above 42 °C, it transforms reversibly into a disordered hexagonal mesophase, absorbing at 320 nm [8,9].

An intermediate conformation, described as 7/3 helical ($\omega = 154°$) was later established for two polysilanes, $(n\text{-butyl}_2Si)_n$ and $(n\text{-pentyl}_2Si)_n$ [10,11]. Crystalline phases of these polymers exhibit absorption bands at 315 nm. The usual approach until very recently has been to describe polysilane polymers in terms of the conventional A–G model, with addition of the helical form when necessary [12].

Careful thermal studies of polysilanes then began to show that polysilane conformational equilibria were

* Tel.: +1-608-262-1873; fax: +1-608-262-6143.
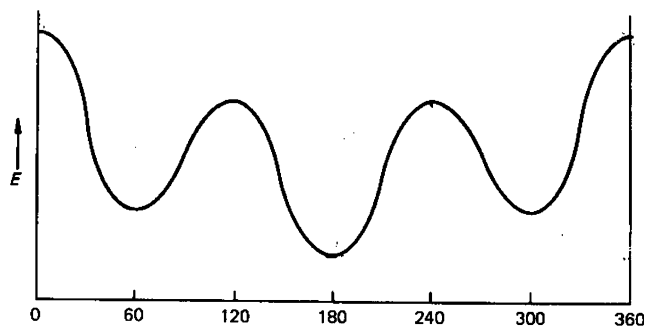*E-mail address:* rwest@wiscmail.wisc.edu (R. West).

Fig. 1. Potential energy diagram for rotation of *n*-butane, showing *anti* (180°) and *gauche* (60° and 300°) minima.

Fig. 3. UV spectrum of di-*n*-decylpolysilane, cooled slowly from 25 to −20 °C.

more complicated. An early example was [*n*-butyl(*n*-hexyl)Si]$_n$. When cooled slowly from room temperature to −45 °C under near-equilibrium conditions, this polymer progresses through four different phases absorbing at 320, 339, 316 and, finally, 349 nm [13]. Another example is (*n*-decyl$_2$Si)$_n$. Fig. 3 shows the electronic absorption upon slow, near-equilibrium cooling from +25 to −20 °C. The polymer absorbs at 320 nm at room temperature; as the temperature decreases, two bands grow in at 365 and 375 nm. Later in the process, a band at 350 nm appears, and eventually overtakes the long-wavelength absorptions [14]. A recent study of (*n*-octyl$_2$Si)$_n$ and (*n*-decyl$_2$Si)$_n$, quenched from room temperature to −78 °C and then slowly warmed, provides evidence for a bewildering array of phases, each with a distinct X-ray diffraction pattern and UV spectrum [15].

These examples, along with others [16], indicated that solid polysilanes may exist in a variety of stable chain conformations. However, the nature of these intermediate phases remained obscure until the recent experimental and theoretical studies of polysilane oligomers
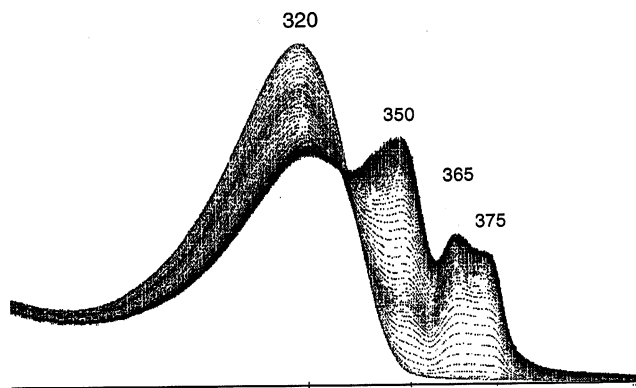
by Michl and coworkers, which are leading to a resolution of these problems [17–21].

Consider a linear polymer, (MX$_2$)$_n$. If the substituents X are small compared to the distance M–M between the atoms in the polymer chain, the conventional *anti-gauche* model applies. Such is the case for hydrocarbons, and presumably for other (MH$_2$)$_n$ polymers [22]. But when the van der Waals radius of X, R^X, becomes larger relative to the M–M distance, R^{M-M}, repulsions arise between X atoms on M atoms in 1,3 positions along the chain. The critical value for such interactions is $R^X/R^{M-M} \sim 0.8$. Beyond this value the anti conformer is no longer a minimum but becomes a transition state between two minima with $\omega \sim 165°$ [17]. These conformations are now termed *transoid*, with symbol *T*. Deviations from exact *anti* conformations in polymers have been noted before, for instance in (CF$_2$)$_n$, which occurs in two forms with $\omega = 166°$ and 168° [23].

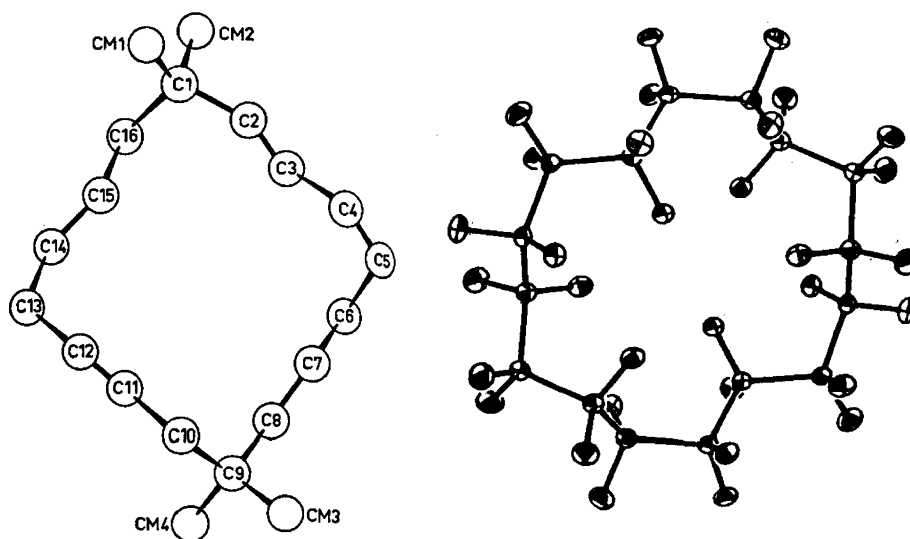In addition, interactions between X substituents on M atoms in 1,4 positions lead to a splitting of the *G*

Fig. 2. Structure diagrams for 1,1,9,9-tetramethylcyclohexadecane (left) and (Me$_2$Si)$_{16}$ (right). Hydrogen atoms are omitted.
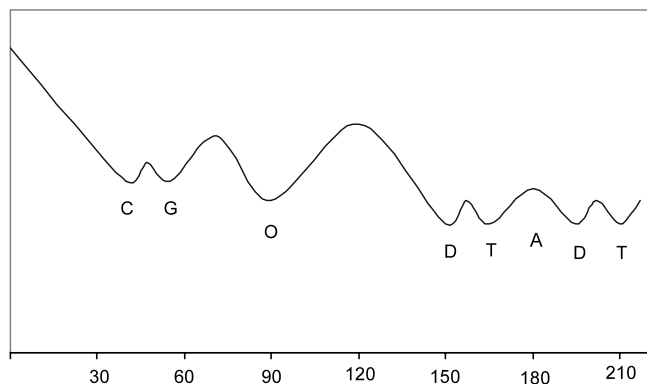
Fig. 4. Qualitative potential energy diagram for rotation in polysilanes with side groups C_2H_5 and larger, showing possible minima.

conformation into two states with $\omega \sim 55°$ (*gauche*) and $\omega \sim 90°$ (*ortho*), O. The unexpected structure of $(Me_2Si)_{16}$ is now understandable; the ring contains eight T and eight O conformations. As yet there is little evidence for O conformations in linear polymers, although they have been directly observed in the oligomers C_4F_{10} [24], Si_4Cl_{10} [21], and Si_4Me_{10} [25].

For longer substituents X, additional interactions may arise. Calculations on the ethyl-containing oligomers $Me_3Si–SiMeEt–SiMeEt–SiMe_3$ and $Me_3Si–SiEt_2–SiEt_2–SiMe_3$ indicate that depending on the conformations of the ethyl side chains, the T and G minima may be replaced by new conformations with torsional angles of $\sim 150°$ (*deviant*, D) and $\sim 40°$ (*cisoid*, C) [20,21]. The helical phases of $(n\text{-butyl}_2Si)_n$ and $(n\text{-pentyl}_2Si)_n$ can now be classified as *deviant*. As yet no experimental evidence for *cisoid* conformations exists, but it seems likely that they will be observed in future studies.

Fig. 4 displays a qualitative potential energy diagram for a polymer with sizeable side groups, of the sort being considered here. The energy differences between the minima are small, and may easily be overcome by packing forces in the crystalline phases.

Polysilanes with near-*anti* conformation absorb near 375 nm, while the all-D polymers absorb at 315 nm. For the many crystalline polysilanes with intermediate values of the absorption maximum, a number of possibilities can now be considered: T_+T_-, and regular arrays: AT_+AT_-, $T_+D_+D_-T_-$, etc.

The model for rotational conformers presented here is described more fully in a commentary [2] and in a review [3]. This new model should be general for $(MX_2)_n$ oligomers and polymers, including polysilanes, polygermanes, polystannanes, and many carbon-based polymers, though not for polyethylene.

Acknowledgements

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