short chains versus that of the long ones for the different blends in the time scale where eq 1 should hold. The orientation of the short chains is clearly correlated with that of the long species for the different matrix molecular weights. The experimental data seem to indicate a linear relationship between the orientation of the long and short species from which the parameter $\epsilon$ can be calculated. We find $\epsilon = 0.26 \pm 0.03$.

This value is rather close to that obtained by Kornfield et al.[16] on hydrogenated polyisoprene melts (0.3–0.4). It is, however, much less than what is found in elastomeric networks where $\epsilon$ is close to one[7] or even higher.[6] The difference between the behavior in melts and networks seems to be an open question at the present time.

## Conclusion

The experiments reported here show that the relaxation of polymer melts cannot be solely accounted for by reptation and constraint release concepts. The orientation of the chain segments is influenced, in addition to the contribution of their own dynamics, by an orientational coupling with the surroundings. Binary blends of long and short chains are ideal candidates to reveal this interaction. The experimental data are in agreement with the theoretical treatment of this orientational coupling proposed by Doi et al.

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# Molecular Orbital Studies on Model Compounds of Simple Silane and Germane Polymers

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## Introduction

Poly(organosilanes) [–SiRR′–], where R and R′ represent in general various alkyl and aryl groups, are the focus of intense scientific and technological interest. In particular, their fascinating physical and chemical properties lend themselves toward numerous applications, including as UV photoresists in microlithography, as radical photoinitiators, as impregnating agents for strengthening ceramics, as precursors for silicon carbide fibers, and even as dopable electrical conductors and semiconductors.[1-5] More recently, Miller et al.[6] have synthesized a series of poly(organogermanes) [–GeRR′–] which exhibit many physical and electronic properties similar to the analogous polysilanes.

Among their more unusual properties, polysilanes and, more recently, polygermanes exhibit a marked bathochromic shift in $\lambda_{\max}$ of their electronic spectra associated with an increase in the bulk of the R and R′ substituents.[1-9] In addition, the electronic spectra of di-*n*-hexylsilane and higher alkyl homologues are highly and reversibly thermochromic: below approximately 40 °C they adsorb red-shifted near $\lambda_{\max} = 370–380$ nm whereas above 40 °C bands near $\lambda_{\max} = 320–325$ nm dominate.[7,8]

These phenomena have been attributed by some to a combination of side-chain crystallization and the occurrence of trans–gauche conformational transitions along the silicon backbone.[1-4,10] Specifically, melting of the side chains occurring at temperatures above 41 °C allows for conformational transitions away from the trans state, which in general is the one preferred, from the standpoint of side-chain packing efficiency and conformational energy considerations, to the conformationally higher energy gauche states. As temperatures increase, the gauche states become more populated relative to the alternative trans state; hence the chain experiences a gradual and characteristic blue shift in $\lambda_{\max}$ associated with these rod-to-coil transformations.

Several theoretical studies,[8-18] using both molecular mechanics (MM)[8-15] and, more recently, molecular orbital

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**Table I**
**Results of Conformational Energies[a] Taken from Various Computational Studies on Model Systems of [–$SiH_2$–]**

| | present work | | | other work | | | | |
|---|---|---|---|---|---|---|---|---|
| conformation[b] | MNDO/2 | 3-21G | 3-21G* | MM[c] | MNDO/2[d] | 3-21G*[e] | 6-31G*[e] | MP2/6-31G*[e] |
| tt | 0.00 | 0.000 | 0.000 | 0.0 | 0.00–0.421 | 0.00 | 0.00 | 0.00 |
| tg | 0.54 | 0.093 | 0.150 | –0.3 | 0.59[f] | 0.17 | 0.19 | –0.04 |
| te | 0.38 | | | | | 0.75 | 0.62 | 0.58 |
| tc | 0.80 | | | | | 1.26 | 1.65 | 1.25 |
| $g^{\pm}g^{\pm}$ | 0.86 | | | –0.7 | | 0.17 | | |
| $g^{\pm}g^{\mp}$ | 1.56 | | | –0.3 | | | | |

[a] Energies are given in units of kcal/mol, all relative to the tt state. [b] Abbreviations: t, trans; g, gauche; e, eclipsed; c, cis. [c] Molecular mechanics results taken from refs 12 and 15. [d] Taken from ref 17, the variation for the tt state being due to whether tt is defined as "rigid" (0.00 kcal/mol) or "skewed" (0.421 kcal/mol). [e] Taken from ref 18. [f] Value represents 1.764 kcal/mol (Table IV of ref 17) divided by 3 assumed as number of tg states contained in $Si_{10}H_{22}$ model compound.

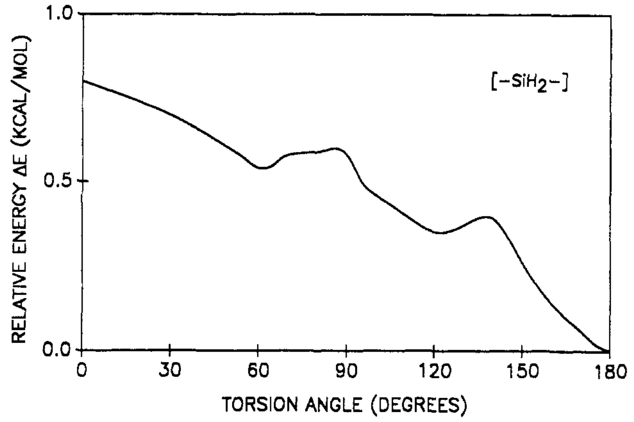

**Figure 1.** MNDO/2-calculated conformational energy $\Delta E$ vs torsion angle $\phi$ for a central Si–Si bond in the [–$SiH_2$–] model compound.

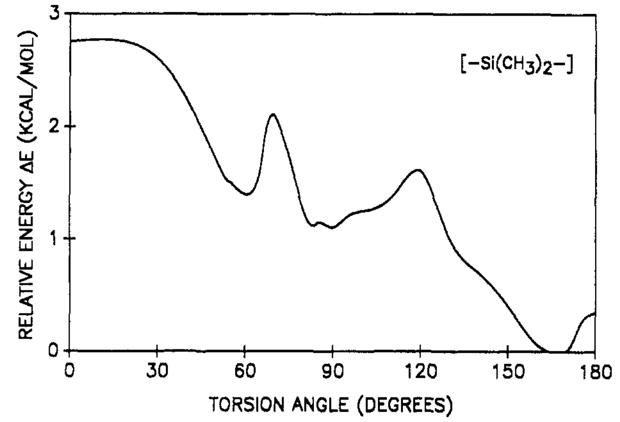

**Figure 2.** MNDO/2-calculated conformational energy $\Delta E$ vs torsion angle $\phi$ for a central Si–Si bond in the [–$Si(CH_3)_2$–] model compounds.

(MO)[16–18] approaches, have already revealed important information regarding the structural, electronic, and conformational properties of the polysilanes. Regarding conformational properties, the MM studies have modeled the simple polysilanes such as [–$SiH_2$–] and [–$Si(CH_3)_2$–].[12,15] More recently, they have been extended to include as R and R′ substituents the higher alkyl homologues (e.g., *n*-pentyl) and even aryl groups.[8–11,13,14] On the other hand, to date the MO approaches[16–18] have confined themselves to study model compounds for only the simplest member of the polysilanes [–$SiH_2$–]. Furthermore, the polygermanes remain virtually untouched from the standpoint of theoretical studies.

In the present study, MNDO/2[19,20] MO calculations have been carried out on model compounds for [–$SiH_2$–] and the simplest poly(organosilane) [–$Si(CH_3)_2$–]. Also included here are results applicable to the analogous [–$Ge(CH_3)_2$–] chain. The present study was undertaken to provide a computationally feasible yet rigorous tool for studying the structural, electronic, and conformational properties of the poly(organosilanes) and poly(organogermanes). The goal was thus to bridge the gap between the computationally economic but highly empirical MM approach and the computationally rigorous but CPU-time-consuming ab initio MO approaches. Finally, our study was initiated to validate the MNDO/2 method along with its present parameter set for further applications to the polysilanes and polygermanes.

## Methodology

The MNDO/2[20] calculations were carried out by using the MOPAC program (QCPE 455),[21] and computer graphics display and analysis of molecular structures was achieved by using the molecular modeling program Chem-X.[22] The MNDO/2 parameter set for both silicon and germanium atom types in the current version of MOPAC is without explicit inclusion of d orbitals.

In each case the model compound consisted of seven backbone atoms, e.g., $Si_7H_{16}$ representing [–$SiH_2$–]. The MNDO/2 molecular energies $E$ were calculated versus rotation about a central Si–Si bond given in terms of torsion angle $\phi$ (where $\phi = 180°$ corresponds to the trans, planar zigzag conformation). Energies were calculated over the range $0° < \phi < 360°$ in increments of 30° overall and 10° near energy extrema. The results are presented as profiles of conformational energy $\Delta E$ versus $\phi$, where $\Delta E$ is computed as the difference in molecular energy between the specified conformation and the energetically preferred conformation.

The MNDO/2 calculations were implemented by using the default Davidon–Fletcher–Powell method[23] for energy minimization and the PRECISE option, as recommended,[24] for augmenting the convergence criteria. The SYMMETRY option was also employed to identify equivalent structural parameters within the model compound. For example, terminal Si–Si bond lengths were defined as equivalent. The purpose here was to help minimize so-called "end effects" and thus render structural parameters associated with the central Si atoms in the model compounds more like those expected for the analogous polymer chain.

## Results and Discussion

**The [–$SiH_2$–] Model Compounds.** The calculated conformational energies $\Delta E$ are plotted vs $\phi$ in Figure 1. The results indicate a preference for the trans state (tt) over the alternative gauche states (tg±) by 0.54 kcal mol$^{-1}$, and the trans state appears to be associated with the global energy minimum with respect to this rotation. The chain is found to exhibit high rotational flexibility with a maximum energy barrier of only 0.80 kcal $mol^{-1}$ occurring at $\phi = 0°$ (cis).

Extended calculations were carried out for conformations associated with $g^{\pm}g^{\pm}$ and $g^{\pm}g^{\mp}$ states for purposes of application of rotational isomeric state (RIS) theory to compute the configuration dependent properties of these chains.[12,25] The calculated energies for $g^{\pm}g^{\pm}$ and $g^{\pm}g^{\mp}$ are only 0.86 and 1.56 kcal $mol^{-1}$, respectively, higher than the tt state, as indicative of a highly flexible chain.

The results calculated here are consistent with the earlier MNDO/2 calculations of Bigelow and McGrane[17] although our trans–gauche energy differences appear slightly smaller. They are also qualitatively consistent with the results of recent ab initio calculations[18] which prefer trans over gauche by ~0.17 kcal $mol^{-1}$ at the 3-21G* and 6-31G* levels but which prefer gauche by a slight 0.04 kcal $mol^{-1}$ when correlation is included in the calculations (Table I: MP2/6-31G*). The present MNDO/2 results disagree however with the published MM results[12] which consistently indicate a preference for gauche over trans for [$-SiH_2-$] model compounds. Values of conformational energies obtained from various theoretical studies are compared in Table I, which also includes some ab initio results calculated by the authors at the 3-21G and 3-21G* levels.

**The [$-Si(CH_3)_2-$] Model Compound.** The MNDO/2 results corresponding to this chain are plotted in Figure 2. The results indicate a preference for trans over gauche by 1.4 kcal $mol^{-1}$. Another, local energy minimum was located near $\phi = 90°$ about 1.1 kcal $mol^{-1}$ above the trans energy minimum. A similar skewed gauche state was found in earlier MM calculations on these model compounds.[12] The energy minimum associated with the trans state is also skewed, in this case toward values near $\phi = 170°$. The maximum energy barrier was located at $\phi = 0°$ (cis), some 2.75 kcal $mol^{-1}$ higher in energy than trans. Hence this chain is predicted to be considerably less flexible rotationally than the corresponding [$-SiH_2-$] chain.

The picture that emerges is of a chain possessing distinct trans and gauche energy minima but whose locations vary considerably from the typical values of $\phi = 180°$ and $\phi = 60°$, respectively. In particular, at $\phi = 90°$ the "gauche" minimum is found here to be skewed some 30° (toward the more extended trans conformation) relative to the location of the typical gauche state (i.e., 60°). The present results agree with the conclusions of earlier MM calculations[12] indicating a preference for trans over gauche, although the present results yield an energy difference about 1.5 times as high (1.4 vs ~0.9 kcal $mol^{-1}$).

**The [$-Ge(CH_3)_2-$] Model Compound.** Overall, its MNDO/2 conformational energy profile is remarkably similar in shape to that obtained for the analogous [$-Si(CH_3)_2-$] model compound except that the energy barriers to rotation are uniformly lower. This is reasonable since the Ge–Ge bonds along the chain backbone are longer than the corresponding Si–Si bonds by about 0.3 Å (MNDO/2 gives average bond lengths for Si–Si and Ge–Ge of 2.35 and 2.65 Å, respectively), and the additional length results in a considerably decrease in steric congestion and a concomitant increase in rotational flexibility.

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**Registry No.** $Si_7H_{16}$, 14693-65-3; $H_3C(Si(CH_3)_2)_7CH_3$, 13452-88-5; $H_3C(Si(CH_3)_2)_7CH_3$, 12112-81-1.