Conformational Energies and Unperturbed Chain Dimensions of Polysilane and Poly(dimethylsilylene)

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ABSTRACT: Conformational energy calculations using molecular mechanics (MM) methods were carried out on segments of polysilane [$-SiH_2-$] and poly(dimethylsilylene) [$-Si(CH_3)_2-$], and the results were compared with the published full-relaxation calculations of Damewood and West. The three MM methods compared (designated NR for "no relaxation", PR for "partial relaxation", and FR for "full relaxation") differ in the extent to which they permit molecular relaxation (deformation) in order to achieve energy minimization. All three MM methods show polysilane to prefer $G^{\pm}G^{\pm}$ states over the corresponding TT state by 0.5–0.7 kcal mol^{-1}, in contrast to the analogous *n*-alkanes, which prefer TT over $G^{\pm}G^{\pm}$ by ca. 1.0 kcal mol^{-1}. Even $G^{\pm}G^{\mp}$ states, commonly found to be prohibitively repulsive for the *n*-alkanes and most other polymers, were preferred over the TT states by 0.4 kcal mol^{-1}. Nearly all regions of configurational space were within 2 kcal mol^{-1} of the minima, indicating considerable chain flexibility. For poly(dimethylsilylene) the three MM methods differ in terms of predicted conformational preferences. While the NR calculations predict preferences for TT and $TG^{\pm}$ states over the corresponding $G^{\pm}G^{\pm}$ states by ca. 4 kcal mol^{-1}, the FR calculations in contrast indicate preferences for $G^{\pm}G^{\pm}$ states over TT and $TG^{\pm}$ by ca. 0.9 kcal mol^{-1}, with the PR calculations yielding results intermediate between these two. Calculated values of the characteristic ratio $C_{n\to\infty}$ for polysilane are rather low (4.02 at 25 °C) but increase with increasing temperature, indicating low chain extensibility and high flexibility with increased occurrence of the higher energy, chain-extending trans states over the preferred gauche states as temperature is increased. Values of $C_{n\to\infty}$ for poly(dimethylsilylene) at 25 °C are 15.0, 13.2, and 12.5 based on the NR, PR, and FR results, respectively. These relatively large values reflect a more inflexible and extended chain. The close agreement in $C_{n\to\infty}$ values yielded by the three MM methods for poly(dimethylsilylene), despite the differences in conformational preferences predicted by each, is a consequence of compensating factors.

Introduction

Polysilanes, having chain backbones consisting entirely of silicon atoms, represent a fascinating new class of polymeric materials with potential applications in such diverse areas a ceramics and semiconductors. Polysilane copolymers containing alternating phenylmethylsilyl and dimethylsilyl units, commonly known as "polysilastyrene", are soluble polymers that can be melted, molded, cast into films, or drawn into fibers. When exposed to ultraviolet light they undergo cross-linking, becoming rigid and insoluble, while heating above 800 °C converts the polymers to silicon carbide.[1] Experimental studies[1] indicate that polysilastyrene appears to become semiconducting upon addition of chemical dopants; thus this and possibly other polysilanes add to the growing list of conducting and semiconducting polymers.[2-5] Investigations are also under way to measure some of the configuration-dependent properties of a series of substituted polysilanes.[6,7] These results can be compared with those obtained by theoretical methods, based on the rotational isomeric state approximation using conformational energies computed from empirical potential energy functions,[8] to provide information regarding the rotational flexibility and preferred conformations about individual backbone bonds. Damewood and West (DW), using full-relaxation (FR) empirical force-field techniques, have investigated the structure and conformational energies of molecular fragments of both polysilane [$H-(SiH_2)_x-H$] and poly(dimethylsilylene) [$Me-(SiMe_2)_x-Me$].[9] The present study focuses on using the calculated structures and conformational energies of DW along with conformational energies calculated with two other, more simplified force fields, to compute the unperturbed chain dimensions $\langle r^2\rangle_0$ of polysilane and poly(dimethylsilylene). Results are compared with those obtained by similar methods for some analogous hydrocarbon chains.

Table I
Structural Parameters for [$-SiH_2-$] and [$-Si(CH_3)_2-$] Used in the Present Calculations

	[$-SiH_2-$]	[$-Si(CH_3)_2-$]
bond lengths[a]		
Si–Si	2.34	2.35
Si–C		1.87
Si–H	1.48	
C–H		1.10
bond angles[b]		
Si–Si–Si	109.4	115.4
Si–Si–H	110.0	
Si–Si–C		108.5
Si–C–H		110.0

[a] In angstroms. [b] In degrees.

Methodology

Details of the methodology used by DW to calculate the structure and conformational energies of the two polymer chains are given in ref 9. Briefly, they employed the empirical force-field program known as MM2[10,11] after deriving several Si-related parameters. DW adopted the option available in MM2 for complete relaxation of all internal degrees of freedom (viz., bond lengths, bond angles, and torsional angles) to achieve conformational-energy minimization. Hence, we refer to their technique as FR (for "full relaxation") to distinguish it from the two other force-field techniques to be described herein.

The two other techniques used to calculate conformational energies shall be referred to as NR for "no relaxation" and PR for "partial relaxation". They differ from the FR technique of DW basically in the degree to which they allow relaxation of the molecule's internal degrees of freedom in order to achieve energy minimization. The NR calculations employed a force field which includes both steric (nonbonded) and torsional terms and,

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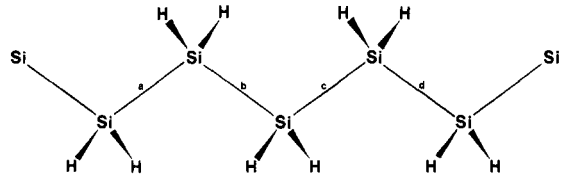

Figure 1. Illustration of the polysilane chain segment considered in the NR calculations.

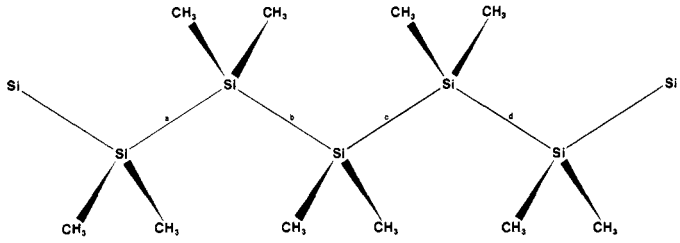

Figure 2. Illustration of the poly(dimethylsilylene) chain segment considered in the NR calculations.

for all conformations (i.e., torsional angles) considered, the energy was calculated without allowance for any molecular relaxation (deformation) as a means to achieve energy minimization. Hence, the molecule is modeled as being essentially stiff except for torsional rotations about the backbone bonds of the chain.

The PR force field differs from NR in that, for each conformation of poly(dimethylsilylene), the energy is minimized with respect to torsional rotations about the pendant Si–CH_3 bonds in the chain. In comparing the three force-field methods, we see a progression in the order NR, PR, FR of increased allowance for molecular deformation of the internal degrees of freedom so as to achieve energy minimization.

Conformational energies E calculated with the NR technique were obtained for the chain segments illustrated in Figures 1 and 2 as a function of the rotational angles ϕ_b and ϕ_c with bonds a and d held in the trans ($\phi = 0°$) conformation. The PR calculations on poly(dimethylsilylene) considered the segment $[Si(CH_3)_2]_5$ so as to be compared directly with the FR calculations of DW.[9] Each of the 10 methyl groups in this segment was permitted to rotate independent of one another about the Si–CH_3 bond.

Pertinent structural parameters used in the NR and PR calculations are summarized in Table I. The values chosen were taken from the FR calculations from DW[9] as averages for the most stable (minimum energy) conformations. Thus the corresponding C–C (1.53 Å) and C–H (1.10 Å) bond lengths in the structurally analogous n-alkanes[8,12] are substantially smaller, and the additional ~0.8-Å length of the Si–Si bond relative to the C–C bond would be expected to reduce considerably the severity of repulsive interactions in the polysilanes. At the same time, however, the additional length of 0.38 Å for the Si–H bond in polysilane over the C–H bond in the n-alkanes could act to offset this by rendering the pendant H atoms more proximate and hence the interactions more repulsive for certain conformations. Likewise, for some conformations $CH_3 \cdots CH_3$ interactions may be more repulsive in [–$Si(CH_3)_2$–] than in [–$C(CH_3)_2$–] owing to the greater length of the Si–CH_3 bond (1.87 Å) relative to the C–CH_3 bond (1.53 Å). The C–C–C and C–C–H bond angles in the n-alkanes are 112° and 109°,[8,12] respectively, and these are nearly identical with the corresponding angles used here for the polysilanes.

For the NR calculations, the nonbonded (NB) interactions were described by the exp–6 potential energy function[8]

$$E_{NB} = A \exp(-Br) - C/r^6 \quad (1)$$

where r is the interatomic distance for a given interaction and A, B, and C are the nonbonded potential energy parameters, as given in Table II. The parameter C characterizing the attractions was calculated from atomic polarizabilities[13] by application of the Slater–Kirkwood equation.[14] Values of B for a like-atom pair were taken from Scott and Scheraga[15] while values for an unlike pair were given by $B_{ij} = (B_{ii}B_{jj})^{1/2}$. The corresponding values of the parameter A were then determined by minimizing eq 1 at $r_{min} = r_1 + r_2$, where r_1 and r_2 are the "augmented"[8,16] van der Waals radii, taken from crystal structure data.[17]

For the PR calculations, E_{NB} was expressed in terms of the familiar Lennard-Jones (LJ) 12–6 function

$$E_{NB} = A'/r^{12} - C/r^6 \quad (2)$$

with the attractive parameter C the same as above and the repulsive parameter A', calculated in similar fashion as described for A above, given in Table II. These two equations, eq 1 and 2, yield virtually identical E_{NB} vs. r profiles for a given atom–atom interaction; however, use of the LJ 12–6 function obviates concern over the spurious maximum encountered in eq 1 for $r \ll r_{min}$.[18]

As a result of the larger size and greater polarizability of Si relative to C, the E_{NB} potential energy minimum for Si···Si is roughly 4 times as deep and located 0.50 Å more distant than that for the C···C interaction. Likewise, the E_{NB} minimum for the Si···H interaction is about twice as deep and 0.25 Å more distant than that for C···H.

In both the NR and PR calculations the torsional term was given by $E_{TOR} = (E_0/2)(1 - \cos 3\phi)$, with ϕ the rotational angle and E_0 the intrinsic torsional barrier height. The value of E_0 for the Si–Si bond was set at 1.2 kcal mol^{-1}, which is considerably smaller than the corresponding value (2.8 kcal mol^{-1}) used in most calculations for the C–C bond found in the n-alkanes.[8,12,19] This feature will tend to flatten the potential energy surface of silanes relative to the analogous alkanes. In the PR calculations E_0 for the Si–CH_3 bond was taken as 0.40 kcal mol^{-1}. These E_0 values correspond closely to those used in the FR calculations of DW.[9] Thus, the polysilanes and the n-alkanes differ markedly in terms of both their structure (i.e., bond lengths) and their energy parameters, and these differences manifest themselves in the potential energy surfaces calculated for the two types of chains.

While the PR methodology and more so the NR methodology represent simplications relative to that employed by DW, they do offer several benefits in that (1) the computational speed and affordability of these calculations permit use of fine grids and (2) in scanning the full range of conformational space (rather than seeking energy minima only), these methods traverse the entire conformational terrain and quantify domain sizes and rotational barriers needed for an analysis of dynamic flexibility and configuration-dependent properties. Such methods are thus complementary to the computationally more rigorous full-relaxation methods such as that employed by DW, which are designed to locate energy minima (global or local) within conformational-energy space. The current literature contains numerous examples of configuration-dependent properties calculated for a variety of polymers on the basis of conformational energies derived from methodologies of the NR and PR type.[8,12,19,20-24]

Conformational energy maps based on the NR and PR

Table II
Nonbonded Potential Energy Parameters

interaction	r_{min}[a]	$10^{24}\alpha$[b]	N_{eff}[c]	A'[d]	B[d]	C[d]	A[d]
Si···Si	4.10	2.8	13	4.59×10^6	4.10	3060	7.26×10^6
Si···H				1.97×10^5	4.30	371.4	2.62×10^5
Si···Cl				2.10×10^6	4.34	1050.0	1.71×10^6
C···C	3.60	0.93	5.0	9.08×10^5	4.59	363.0	3.95×10^5
H···H	2.60	0.42	0.9	1.037×10^4	4.54	47.1	7.22×10^3
C···H				8.61×10^4	4.57	127.0	5.63×10^4

[a] Adjusted sum of van der Waals radii for the two interacting atoms, in Å. [b] Polarizability, in cm^3. [c] Effective number of electrons. [d] Units are such as to give the energy E_{NB} in kcal mol^{-1} for r in Å.

calculations were generated by using energies calculated by scanning the entire 0–360° conformational energy space for both ϕ_b and ϕ_c in increments of 5° for the NR calculations and 20° for the PR calculations. These calculated E vs. (ϕ_b, ϕ_c) data sets were used to evaluate the conformational partition function z, the average energy $\langle E \rangle$, and the average torsional angles $\langle \phi_b, \phi_c \rangle$ for each state s of interest (e.g., TT, GT, GG), using[20]

$$z_s = \sum_{\phi_b} \sum_{\phi_c} \exp(-E_k/RT) \tag{3}$$

$$\langle E \rangle_s = z_s^{-1} \sum_{\phi_b} \sum_{\phi_c} E_k \exp(-E_k/RT) \tag{4}$$

$$\langle \phi_j \rangle_s = z_s^{-1} \sum_{\phi_b} \sum_{\phi_c} \phi_j \exp(-E_k/RT) \tag{5}$$

where the subscript k refers to each conformation (ϕ_b, ϕ_c) and j is b or c. Inspection of the generated potential energy maps revealed that adoption of the familiar three-state (T, G^+, G^-) scheme would suffice in the application of the rotational isomeric state theory to these chains.[7,8] The corresponding statistical weight matrix **U**, inclusive of both first-order and second-order interactions (those interactions depending on, respectively, one and two skeletal-bond rotations), is represented by[8]

$$\mathbf{U} = \begin{bmatrix} 1 & \sigma\psi & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix} \tag{6}$$

In the case of the NR and PR calculations, the statistical weights σ, ψ, and ω were determined from the respective values of z derived from the potential energy maps; for example

$$z_{TG}/z_{TT} = \sigma_0 \exp(-E_\sigma/RT) \tag{7}$$

Values of the statistical weight parameters determined in this manner take explicit consideration of the relative size of the domains for each state, as denoted by the so-called "entropy factor" σ_0 in eq 7. In the case of the FR calculations,[9] for which the absence of potential energy maps precludes computation of z values, the statistical weight parameters are given as simple Boltzmann factors in the conformational energy, for example, $\sigma = \exp(-E_\sigma/RT)$, with the tacit assumption of equal domain sizes (i.e., $\sigma_0 = \psi_0 = \omega_0 = 1.0$). Characteristic ratios $C_{n\to\infty} = \lim_{n\to\infty} \langle r^2 \rangle_0 / nl^2$, where $\langle r^2 \rangle_0$ represents the mean-square end-to-end distance, n the number of backbone bonds, and l the backbone bond length, were then calculated according to established methods described in the literature.[8]

Results and Discussion

The results of both the NR and PR conformational energy calculations are conveniently given in terms of potential energy maps depicting the conformational energy generated as a function of the torsional angles ϕ_b and ϕ_c.

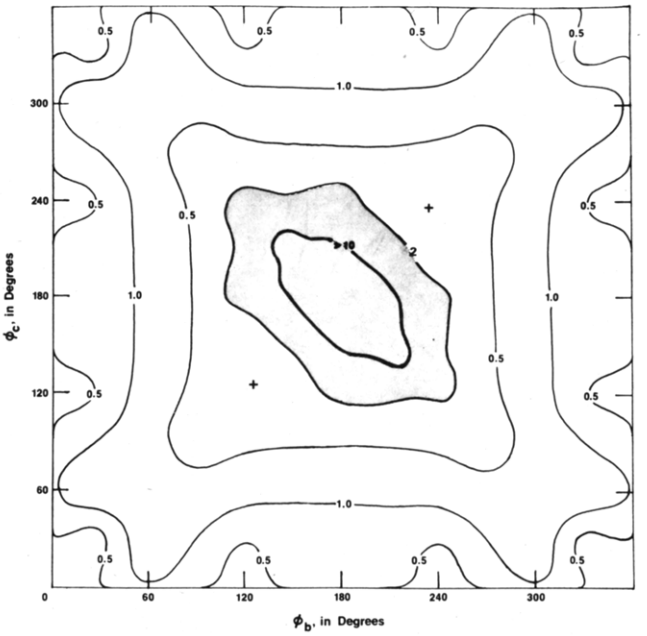

Figure 3. Conformational energy map for the polysilane [$-SiH_2-$] segment as determined by the NR and PR calculations. The energy, given in kcal mol^{-1} relative to the conformational energy minima designated by "+" on the map, is shown as contour lines.

Table III
Pertinent Conformational Parameters Determined by the NR Energy Calculations for the [$-SiH_2-$] Chain Segment

	TT	TG (GT)	$G^\pm G^\pm$	$G^\pm G^\mp$
z_s[a]	1.00	1.22	0.63	0.31
$\langle E_s \rangle$[b]	−0.204	−0.408	−0.711	−0.612
$\langle \phi_b, \phi_c \rangle_{min}$[c]	(0°, 0°)	(0°, 125°)	(±125°, ±125°)	(±120°, ∓120°)

[a] Expressed relative to $z_s = 1.00$ for the TT state. [b] In kcal mol^{-1}. [c] In which (0°, 0°) corresponds to the all-trans, planar zigzag conformation.

A general feature of all polysilanes when compared with their analogous hydrocarbon chains is the former's considerably greater conformational flexibility in terms of more energetically accessible areas of conformational space and lower barriers between energy minima. This is due primarily to the greater length of the Si–Si bond (2.34 Å) compared with the C–C bond (1.53 Å), which results in less severe repulsions for most conformations.

Polysilane. The NR and PR force fields yield virtually identical conformational energy maps for polysilane (Figure 3). Associated values of $\langle E \rangle$, z, and $\langle \phi_b, \phi_c \rangle$, calculated from the energy map for states TT, TG (GT), $G^\pm G^\pm$, and $G^\pm G^\mp$, are listed in Table III. It is seen that TG is preferred over TT by ca. 0.2 kcal mol^{-1} and that $G^\pm G^\pm$ states are preferred over the alternative TT states by ca. 0.5 kcal mol^{-1}. Even the $G^\pm G^\mp$ states, typically found prohibitively repulsive for many chains, including the alkanes,[8] are preferred over the TT state by ca. 0.4 kcal mol^{-1}. However, the relative size of each domain, as de-

Table IV
Relative Energies[a] and Torsional Angles[b] of Various Conformers of Polysilane As Calculated by the NR and FR[9] Methods

	NR[c]		FR	
	$\langle E\rangle^a$	$\langle\phi\rangle^b$	E^a	ϕ^b
TT	0.51	0.0	0.7	0.0
TG	0.21	125	0.4	121.4
GG	0.00	125	0.0	125.3
G^+G^-	0.41	−120	0.4	−111.2

[a] In kcal mol^{-1}, given relative to E = 0.0 kcal mol^{-1} for the minimum-energy conformation. [b] In degrees, given relative to ϕ = (0°, 0°) for the all-trans, planar zigzag conformation. [c] Values of E and ϕ represent Boltzmann-weighted averages taken from the generated potential-energy maps.

termined by the relative magnitudes of z, follows the more typical order TG > TT ≫ $G^{\pm}G^{\pm}$ ≫ $G^{\pm}G^{\mp}$. By comparison, in the analogous n-alkanes TT states are preferred over $G^{\pm}G^{\pm}$ states by ca. 1.0 kcal mol^{-1}, and $G^{\pm}G^{\mp}$ states are almost prohibitively high in energy.[8,12] Given the preferences for successive gauche conformations and based on the assumption that *inter*molecular energies generally have only a small effect on conformation,[8] the crystalline-state configuration of polysilane is predicted to be more likely helical rather than similar to the polyethylene [CH_2CH_2–] planar zigzag conformation. For polysilane nearly all regions of the conformational-energy space are within 2.0 kcal mol^{-1} of the energy minima; this is in sharp contrast to the relatively high barriers (>6 kcal mol^{-1}) and large regions of prohibitively high energy found in the case of the n-alkanes.[8]

Values of the relative energies and associated conformations ϕ for polysilane, calculated by both the FR method of DW[9] and the methods employed herein, are compared in Table IV. Agreement is satisfactory, as one would expect for such a structurally simple and conformationally flexible molecule as polysilane.

Poly(dimethylsilylene). The potential energy map for poly(dimethylsilylene) based on the PR calculations is given in Figure 4. Associated values of $\langle E\rangle$, z, and $\langle\phi_b, \phi_c\rangle$ are listed in Table V along with those derived from the NR calculations. A summary of the relative energies and their associated conformations for poly(dimethylsilylene) as calculated by the NR, PR, and FR methods is given in Table VI. In this case, substantial qualitative differences are noted among the results given by the three methods. Specifically, the most striking difference is that, whereas the GG state is found prohibitively high in energy by the NR calculation, it is the preferred state for the FR calculation. Since values of the bond lengths and backbone bond angles used in both methods are nearly identical, the discrepancy is largely attributable to torsional relaxation of the pendant Si–CH_3 groups afforded by the FR method. That the influence of torsional relaxation of pendant groups is dominant is corroborated by the results of the PR calculations, which, while allowing torsional relaxation only with respect to the Si–CH_3 bonds, show a marked reduction of the relative energy for the GG conformation, although not sufficient to render it the preferred conformation. Of course, other forms of structural relaxation (e.g., deformation of the Si–C–H and Si–Si–C bond angles, which the PR program as written does not include) would be expected to contribute but less so.

Notwithstanding this discrepancy, the three methods do yield some similarities in modeling the conformational characteristics of poly(dimethylsilylene). Specifically, all three find the $G^{\pm}G^{\mp}$ states prohibitively high in energy, and the relative conformational energy preferences of TT and TG states are in reasonable agreement. While corresponding values of ϕ given by the NR and FR methods are close, the PR calculations located gauche states quite smaller in magnitude (and thus correspondingly less compact) than conventional values (i.e., ±120°).

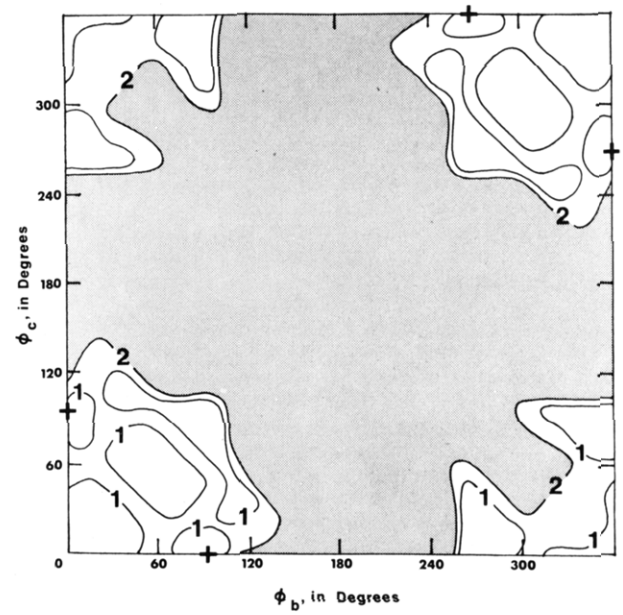

Figure 4. Conformational energy map for poly(dimethylsilylene) as determined by the PR calculations.

Table V
Pertinent Conformational Parameters for the Poly(dimethylsilylene) Chain Segment As Determined by the NR and PR Energy Calculations

	NR			PR		
	z_s^a	$\langle E_s\rangle^b$	$\langle\phi\rangle^c$	z_s^a	$\langle E\rangle^b$	$\langle\phi\rangle^c$
T(T)	1.00	−5.99	0	1.00	−16.7	0
T(G)	0.26	−6.04	125	0.82	−17.1	98
G(G)	∼0.0	(∼−2)	125	0.38	−17.0	89
$G^+(G^-)$	∼0.0	≫6	−115	∼0.0		

[a] Expressed relative to z = 1.00 for the TT state. [b] In kcal mol^{-1}, given as the Boltzmann-weighted averages derived from the conformational energy maps. [c] In degrees, in which 0° corresponds to the all-trans, planar zigzag conformation.

Table VI
Relative Energies[a] and Associated Torsional Angles[b] of Various Conformers of the Poly(dimethylsilylene) Segment As Calculated by the NR, PR, and FR[9] Force-Field Methods

	NR[c]		PR[c]		FR	
	$\langle E\rangle^a$	$\langle\phi\rangle^b$	$\langle E\rangle^a$	$\langle\phi\rangle^b$	E^a	ϕ^b
T(T)	0.1	0.0	0.42	0	0.9	0.0
T(G)	0.0	125	0.00	98	0.8	120.3
G(G)	∼4	125	0.08	89	0.0	125.3
$G^+(G^-)$	>12	−115	*d*		38.4	−107.7

[a] In kcal mol^{-1}, given relative to the energy of the minimum-energy conformation. [b] In degrees, given relative to ϕ = 0°, corresponding to the trans conformation. [c] Values $\langle E\rangle$ and $\langle\phi\rangle$ correspond to Boltzmann-weighted averages derived from the respective potential energy maps. [d] Calculated energy was prohibitively high.

Values of z obtained from both the NR and PR calculations indicate that the size of the domain associated with TT is larger than that for TG or GG. Figure 4 is noted for its large regions of prohibitively high energy, in contrast to that (Figure 3) for polysilane itself, for which nearly all regions are within 2 kcal mol^{-1} of the energy minima. The difference is attributable to the steric bulk of the methyl groups in poly(dimethylsilylene) relative to that of the H atoms in polysilane.

Table VII
Values of the Statistical Weight Parameters Computed at 25 °C Derived from Results of the NR, PR, and FR Conformational Energy Calculations

	polysilane			poly(dimethylsilylene)		
	NR	PR	FR	NR	PR	FR
σ	1.6	...	1.6	0.27	0.82	1.2
ψ	1.5	...	2.0	0.00	0.56	3.8
ω	0.52	...	1.0	0.00	0.00	0.0

Chain Statistics. The structural information given in Table I and the dihedral angles listed in Tables IV and V for polysilane and poly(dimethylsilylene), respectively, were used in conjunction with eq 6 and 7 to calculate the characteristic ratio $C_{n\to\infty}$ for the two chains. The statistical weight parameters σ, ψ, and ω computed at 25 °C for the two chains based on the NR, PR, and FR calculations are listed in Table VII. For polysilane, the corresponding $C_{n\to\infty}$ values are 4.1 and 3.9 based on the NR and FR calculations, respectively. The nearly identical values reflect the similarity in conformational characteristics obtained by the two different force fields for this chain. The relatively small value of $C_{n\to\infty}$ for polysilane is indicative of rather low chain extensibility, a feature consistent with the chain's overall conformational flexibility (i.e., no overwhelming preference for any one particular conformational state), its identifiable preferences for the more compact TG and $G^{\pm}G^{\pm}$ states over the alternative and more chain-extending TT states, and, moreover, its allowance for $G^{\pm}G^{\mp}$ states, whose occurrence typically leads to reversals in chain direction. For comparison, values of $C_{n\to\infty}$ at 25 °C for two other flexible polymers, polyethylene and poly(dimethylsiloxane), are 6.7[25] and 6.4,[26] respectively.

Values of $C_{n\to\infty}$ at 25 °C for poly(dimethylsilylene) were 15.0, 13.2, and 12.5 based on the NR, PR, and FR calculations, respectively. Given the differences in conformational preferences predicted by the three force-field methods, the closeness in the values is surprising. Specifically, the value $C_{n\to\infty}$ = 12.5 obtained based on the FR calculations is only slightly smaller than the corresponding value of 15.0 based on the NR results, yet the FR results indicated clear preferences for GG states over the alternative TT and TG states where, in contrast, the NR results yielded precisely the opposite preferences (i.e., TT and TG states over GG). These substantial quantitative and qualitative differences are obviously not strongly reflected when comparing the corresponding $C_{n\to\infty}$ values.

An explanation for the closeness of $C_{n\to\infty}$ values in this case and the consequent lack of sensitivity to the MM method used can be found in a detailed analysis of the sequences of states allowable based on the conformational preferences elucidated by the MM calculations. In point, the helix associated with ...$G^{\pm}G^{\pm}G^{\pm}G^{\pm}G^{\pm}$... sequences, predicted by the FR calculations as having a high probability of occurrence, is more compact than either that associated with the ...TTTTT... or ...$TG^{\pm}TG^{\pm}T$... sequences predicted by the NR calculations. However, this is compensated somewhat by the fact that the NR calculations also indicate high probability for sequences such as ... $TG^{\pm}TG^{\mp}T$... and ...$TG^{\pm}TTG^{\mp}T$..., whose inclusion of nearby gauche states of opposite sign will tend to divert chain direction and thus foreshorten the dimensions of the chain. The FR calculations predict relatively low probability of occurrence of such sequences and, in general, of any sequences corresponding to reversal or redirection of chain propagation. Thus in different but nearly compensatory ways the NR and FR calculations allow for sequences of states more compact than the fully extended all-trans configuration. In fact, if the poly(dimethylsilylene) chain adopted an all-trans conformation, then as $n = \infty$ the calculated value of C_n would approach ∞ rather than the values (12.5–15.0) obtained here.

As would be expected from the intermediate nature of its calculated conformational energies, the PR method yielded $C_{n\to\infty}$ = 13.2, nearly midway between the values obtained from using the NR $C_{n\to\infty}$ and FR calculations. The value of $C_{n\to\infty}$ obtained from the PR results would have been somewhat closer to that (12.5) obtained from the FR results except that the locations (i.e., 90–100°) of the gauche states obtained in the PR calculations are more extended than those found in the NR and FR calculations (120–125°).

The NR results yield $C_{n\to\infty}$ values of 3.85, 4.02, 4.15, and 4.25 at 0, 25, 50, and 75 °C, respectively, for polysilane and 15.0 at all four temperatures for poly(dimethylsilylene). That the values for polysilane increase slightly as the temperature increases reflects the greater accessibility of the higher energy and chain-extending trans states. Values of $C_{n\to\infty}$ for poly(dimethylsilylene) are negligibly affected in this temperature range, as would be expected given the virtual exclusion of all states except TT and TG indicated by the NR calculations.

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Registry No. Polysilane, 32028-95-8; poly(dimethylsilylene), 28883-63-8.

References and Notes

(1) West, R.; David, L. D.; Djurovich, P. I.; Stearley, K. L.; Srinivisan, K. S. V.; Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 7352. Trefonas, P., III; Djurovich, P. I.; Zhang, X.-H.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci.* **1983**, *21*, 819. Trefonas, P., III; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci.* **1983**, *21*, 823. West, R. *J. Organomet. Chem.* **1986**, *300*(1–2), 327.
(2) Chiang, C. K.; Drey, M. A.; Gau, S. C.; Heeger, A. J.; MacDiarmid, A. G.; Park, Y. W.; Shirakawa, H. *J. Am. Chem. Soc.* **1978**, *100*, 1013. Chiang, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G. *J. Chem. Phys.* **1978**, *69*, 5098.
(3) Ivory, D. M.; Miller, G. G.; Sowa, J. M.; Shacklette, L. W.; Chance, R. R.; Baughman, R. H. *J. Chem. Phys.* **1979**, *71*, 1506.
(4) Rabolt, J. F.; Clarke, T. C.; Kanazawa, K. K.; Reynolds, J. R.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1980**, 347.
(5) Kanazawa, K. K.; Diaz, A. F.; Geiss, R. H.; Gill, W. D.; Kwak, J. F.; Logan, J. A.; Rabolt, J. F.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1979**, 854.
(6) Bhaumik, D.; Mark, J. E. *Polym. Prepr.*, (*Am. Chem. Soc., Div. Polym. Chem.*) **1982**, *23*, 105.
(7) Welsh, W. J.; Beshah, K.; Ackerman, J. L.; Mark, J. E.; David, L. D.; West, R. *Polym. Prepr.*, (*Am. Chem. Soc., Div. Polym. Chem.*) **1983**, *24*, 131.
(8) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.
(9) Damewood, J. R., Jr.; West, R. *Macromolecules* **1985**, *18*, 159.
(10) Allinger, N. L., et al. *QCPE* **1981**, *13*, 395.
(11) Hummel, J. P.; Stackhouse, J.; Mislow, K. *Tetrahedron* **1977**, *33*, 1925. Tribble, M. T.; Allinger, N. L. *Ibid.* **1972**, *28*, 2147.
(12) Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.
(13) Ketelaar, J. A. A. A. *Chemical Constitution*; Elsevier: New York, 1958.
(14) Pitzer, K. S. *Adv. Chem. Phys.* **1959**, *2*, 59.
(15) Scott, R. A.; Scheraga, H. A. *J. Chem. Phys.* **1965**, *42*, 2209; **1966**, *45*, 2091.

(16) Allinger, N. L.; Miller, M. A.; Catledge, F. A.; Hirsch, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 4345.
(17) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(18) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954.
(19) Welsh, W. J.; Mark, J. E.; Riande, E. *Polym. J. (Tokyo)* **1980**, *12*, 467.
(20) Jorgensen, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 677; *J. Phys. Chem.* **1983**, *87*, 5304.
(21) Sundararajan, P. R. *Macromolecules* **1978**, *11*, 256.
(22) Suter, U. W. *J. Am. Chem. Soc.* **1979**, *101*, 6481.
(23) Suter, U. W.; Flory, P. J. *Macromolecules* **1975**, *8*, 765.
(24) Abe, A. *J. Am. Chem. Soc.* **1984**, *106*, 14.
(25) Sundararajan, P. R.; Flory, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 5025.
(26) Crescenzi, V.; Flory, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 141.

Translational Diffusion of Linear and 3-Arm-Star Polystyrenes in Semidilute Solutions of Linear Poly(vinyl methyl ether)

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ABSTRACT: The technique of dynamic light scattering from isorefractive ternary solutions has been used to investigate the translational diffusion behavior of linear and 3-arm-star polymers in linear polymer matrices. Diffusion coefficients have been obtained for four polystyrene (PS) samples present in trace amounts in solutions of poly(vinyl methyl ether) (PVME) in *o*-fluorotoluene over the range 0.001–0.1 g/mL in PVME concentration. The high molecular weight of the PVME sample, 1.3×10^6, guarantees that these concentrations extend well into the entangled regime. For PS with molecular weights around 4×10^5, a 3-arm star diffuses slightly more rapidly than its linear counterpart. However, when the PS molecular weight exceeds 1×10^6, a 3-arm star diffuses much less rapidly than its linear counterpart at the higher matrix concentrations. These data are interpreted as evidence for the importance of topology in determining diffusion rates for polymers in concentrated solutions. While this observation is consistent with the reptation mechanism, it is also apparent that reptation cannot dominate the diffusion process until the diffusing molecules are thoroughly entangled with the matrix.

Elucidation of the mechanisms by which polymer molecules in entangled solutions and melts diffuse, relax stress, or renew their conformations is an aim with great practical and theoretical importance. Over the past decade, a large number of experimental and theoretical studies have been undertaken to examine the validity and range of applicability of the reptation concept; the subject has recently been reviewed.[1] For polymer melts, diffusion coefficients measured by a wide variety of techniques are consistent with the M^{-2} power law, which can be considered the signature of reptation. However, the experimentally well-established $M^{3.4}$ power law for shear viscosity is not in agreement with the reptation prediction. It is not yet clear whether this discrepancy can be explained by modifications to the basic reptation hypothesis, which was originally proposed for linear chains in fixed obstacles,[2] or whether fundamentally different molecular-level processes need to be invoked. In polymer solutions above the coil overlap concentration, the situation is even less clear. Reptation-based predictions for the molecular weight, concentration, and solvent quality dependence of the translational diffusion coefficient have all been compared with experimental results, with distinctly differing degrees of agreement.[1,3]

The solution situation may be more complicated than that of the melt due to several factors including the enhanced mobility of the molecules surrounding a test polymer, the role of solvent quality, and the concentration dependence of the monomeric friction coefficient. Among the possible contributing mechanisms that have been suggested, in addition to reptation, are (1) constraint release, or tube renewal, in which a test chain moves laterally into a vacancy created by the departure of a neighboring chain;[4-6] (2) the "noodle effect", in which a diffusing chain drags other entangling chains for finite distances;[7] (3) Stokes–Einstein diffusion, in which the test chain moving as a hydrodynamic sphere experiences only the bulk solution viscosity;[4,8] and (4) diffusion through a field of obstacles that generate hydrodynamic screening.[9-13] To design experiments to distinguish among these possibilities, given that they are not mutually exclusive, is challenging. One promising approach is to compare the diffusion coefficients of model branched polymers with those of linear molecules under identical conditions.

In the framework of reptation, the presence of long-chain branches should severely impede translational diffusion;[14] studies of 3-arm-star diffusion in the melt support this picture.[15-17] However, apparently no similar studies in solution have been reported. The pioneering diffusion studies of von Meerwall et al.[18,19] on dilute solutions of 3-arm-star polystyrenes, polyisoprenes, and polybutadienes did extend into the semidilute regime in some cases, but not for sufficiently high molecular weights to expect entanglement. These NMR measurements were performed on binary solutions, i.e., identical test and matrix polymers, and thus represent a different physical situation from that examined here. Nevertheless, these authors' conclusion that 3-arm-star and linear polymer diffusion behaviors are qualitatively indistinguishable is interesting in light of the results presented below. The importance of pursuing diffusion measurements in entangled solutions is underscored by considering that, unlike reptation, none of the four mechanisms listed above explicitly considers the topology of the diffusing polymer. As a result, linear and 3-arm-star polymers with either equal numbers of entanglements per molecule (cases 1 and 2) or equivalent hydrodynamic radii (cases 3 and 4) should diffuse at comparable rates. To test this hypothesis, diffusion data are presented for two 3-arm and two linear polystyrenes (PS) in semidilute solutions of linear poly(vinyl methyl ether)

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