Conformational Energies and Unperturbed Chain Dimensions of Poly(phenylmethylsilylene) and Poly(silastyrene)

William J. Welsh*

Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121

James R. Damewood, Jr.,[†] **and Robert C. West**

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

Received October 19, 1988

ABSTRACT: Molecular mechanics techniques were employed to calculate the molecular structure and conformational energies of model compounds for poly(phenylmethylsilylene) [–SiPhMe–] and poly(silastyrene) [–SiPhH–SiH_2–], in both isotactic and syndiotactic stereochemical forms. The structural and conformational energy data provided were used to calculate, by application of rotational isomeric state (RIS) theory, the unperturbed chain dimensions, given as the characteristic ratio $C_n = \langle r^2\rangle_0/nl^2$, and its temperature coefficient $d(\ln C_n)/dT_K$. Both iso and syn [–SiPhMe–] overwhelmingly prefer the trans, planar zigzag, conformations, at the exclusion of the corresponding gauche states. Corresponding $C_{n=400}$ values are 274 and 240 for iso and syn [–SiPhMe–], respectively, the large values being indicative of an essentially fully extended, rodlike chain. For [–SiPhH–SiH_2–], the iso form strongly prefers trans states over gauche states while the syn form conversely prefers gauche states over trans states. In both cases, the chains favor that conformational state providing maximal attractive overlap between the substituent phenyl groups. Values of $C_{n=400}$ are 19 and 79 for the iso and syn [–SiPhH–SiH_2–], respectively. Calculated C_n values qualitatively agree with experimental values published for related polymers.

Introduction

Substituted poly(organosilanes) [–SiRR′–] have recently become the focus of intense scientific[1–3] and commercial[4] interest, and synthetic efforts have been successful in obtaining high molecular weight organosilane polymers and copolymers containing both alkyl and aryl substituents.[1,4,5]

These materials are soluble in common organic solvents and can be processed into a variety of shapes, films, and fibers. They also exhibit strong UV absorption whose λ_{max} varies markedly with molecular weight and with the nature of the substituents R and R′. These materials are also highly radiation sensitive, being easily degraded by UV initiators or by heating to high temperatures.[1,4] As a consequence of these unusual properties, organosilane polymers have found commercial applications as UV photoresists in photolithography, as radical photoinitiators, as impregnating agents for strengthening ceramics, and as precursors for silicon carbide fibers. Examples have also shown promise as dopable electrical conductors and semiconductors.[1,4]

Much of the scientific interest in the polysilanes stems from the observation that the position of λ_{max} depends strongly on the nature and size of the substituents R and R′ and on the conformation of the chain backbone.[1–4] Specifically, UV spectroscopic data reveal a marked bathochromic shift in λ_{max} associated with an increase in the bulk of the substituents (R, R′). Both experimental and theoretical evidence[1–6] attributes this red shift to long-range conformational transitions of the silicon backbone from sequences of helical or random coil configurations to sequences corresponding to planar zigzag, all-trans conformations. The unusual conformational dependence of these electronic effects encourages a further theoretical analysis of the conformational characteristics of this family of polymers.

In the present study, empirical force-field (molecular mechanics) techniques with the inclusion of full geometry optimization were employed to calculate the molecular structure and conformational energies of model compounds for poly(phenylmethylsilylene) [–SiPhMe–] and poly(silastyrene) [–SiPhH–SiH_2–]. In each case the calculations considered both the isotactic and syndiotactic stereochemical isomeric forms of the model compounds.[7] The structures considered are illustrated in Figures 1 and 2.

The structural and conformational energy data thus provided were used to calculate, by application of rotational isomeric state (RIS) theory,[8] the unperturbed dimensions (mean-square end-to-end distance) $\langle r^2\rangle_0$ and its corresponding temperature coefficient $d(\ln \langle r^2\rangle_0)/dT_K$ for each chain. The results, given in terms of the characteristic ratio $C_n = \langle r^2\rangle_0/nl^2$ (where n is the number of skeletal bonds each of length l), can be interpreted in terms of the extensibility and conformational flexibility of the chains dissolved in a Θ solvent. In addition, the results are compared with experimental values of C_n obtained for a number of organopolysilanes from solution light-scattering measurements.[9]

Methodology

Energy Calculations. The model compounds used for representing the polymer chains in the calculations are CH_3[–SiPhMe–]$_5CH_3$ for [–SiPhMe–] and H[–SiPhH–SiH_2–]$_3SiH_3$ for [–SiPhH–SiH_2–], as illustrated in Figures 1 and 2 in both the iso and syn forms. Preliminary energy calculations on longer sequences gave negligible differences in terms of conformational preferences and structural parameters.

The energy calculations were carried out using the MM2 molecular mechanics program[10] with the inclusion of full geometry optimization. Force-field parameters used for the silicon-related interactions in [–SiPhMe–] were the same as described previously,[2] while those in [–SiPhH–SiH_2–] were taken from the MMP2 (1985) parameter set of Allinger.[11]

By analogy with previous theoretical studies of other polysilanes,[2,3,12] molecular structures and relative conformational energies were calculated as a function of rotation about two adjacent, backbone Si–Si bonds within the model molecules, described by the torsion angles ϕ_1 and ϕ_2. Particular attention was given to conformational states in the vicinity of the standard trans (T), gauche-plus (G^+), and gauche-minus (G^-) conformations corresponding to the

---

[†] Present address: Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716.

0024-9297/89/2222-2947$01.50/0

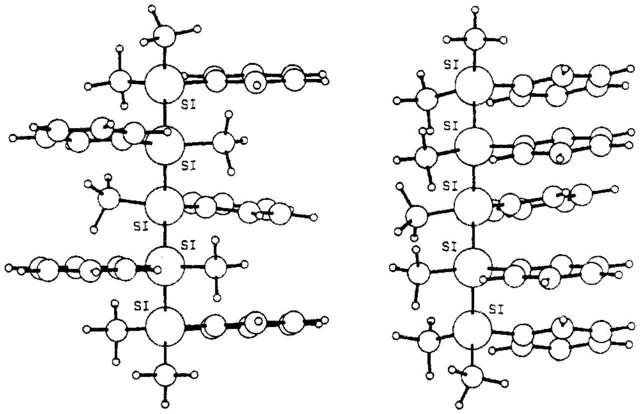


Figure 1. Ball-and-stick drawings of the isotactic (left) and syndiotactic (right) isomeric forms of the model compounds considered in the present study of the [-SiPhMe-] chain.[7] Both are depicted in their all-trans conformations viewed from atop and along the silicon backbone.

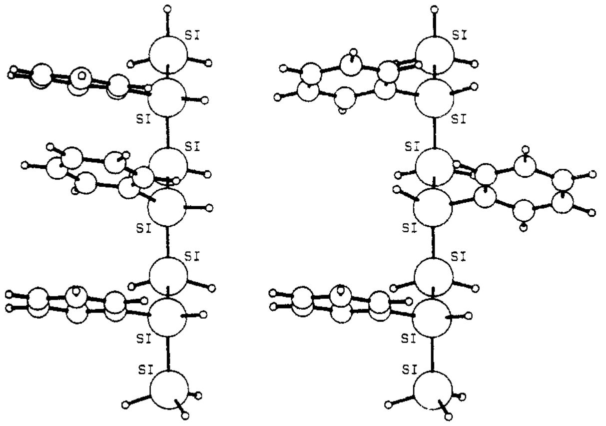


Figure 2. Ball-and-stick drawings of the isotactic (left) and syndiotactic (right) isomeric forms of the model compounds considered in the present study of the [-SiPhH-SiH$_2$-] chain. Both are depicted in their all-trans conformations viewed from atop and along the silicon backbone.

familiar three-state (i.e., T,G$^+$,G$^-$) rotational scheme found for the analogous carbon backbone polymers.[8] However, in all cases full conformational searches were carried out to locate other possible local minima. It is worth noting that for these polymers the substituents render the G$^+$ and G$^-$ states nonequivalent, and this feature, in addition to the stereoisomeric (i.e., iso or syn) nature of the corresponding chain, will dramatically influence the conformational features of these polymers. Given the three-state (T,G$^+$,G$^-$) scheme, the possible rotational states that a pair of Si-Si bonds can assume are TT, TG$^\pm$ (G$^\pm$T), G$^\pm$G$^\pm$, and G$^\pm$G$^\mp$. Hence, results of the MM2 energy calculations are presented in terms of the molecular structure and relative energies of these discrete states. These conformational energies also served as input for the RIS calculations of C_n and its temperature coefficient.[8]

Chain Statistics. With adoption of a three-state rotational scheme within the RIS theory, values of C_n were calculated by using standard RIS theory statistical mechanical techniques.[8] The corresponding statistical weight matrix **U**, inclusive of both first-order and second-order interactions (those interactions depending on rotations about one and two skeletal bonds, respectively), is represented in general by

$$\mathbf{U} = \begin{vmatrix} 1 & \sigma & \lambda \\ 1 & \sigma\psi & \lambda\omega' \\ 1 & \sigma\omega & \lambda\psi' \end{vmatrix} \tag{1}$$

Table I
Relative Energies E^a and Associated Torsion Angles ϕ for the Iso and Syn Isomeric Forms of the [-SiPhMe-] Model Compound

	iso		syn	
	E^a	ϕ, deg	E^a	ϕ, deg
TT	0.0	±2.2	0.0	±2.9
TG$^+$	5.5	116.3	3.8	116.3
TG$^-$	4.6	−115.6	3.9	−113.5
G$^+$*G*$^+$	6.2	119.8	5.6	107.3
G$^-$*G*$^-$	6.6	−112.2	7.5	−118.8
G$^-$*G*$^+$	>10	*b*	>10	*b*

[a] In kcal mol^{-1}, taken relative to E = 0.0 kcal mol^{-1} for the TT (ϕ = 0°) conformation. [b] No local minimum found.

Table II
Relative Energies E^a and Associated Torsion Angles ϕ for the Iso and Syn Isomeric Forms of the [-SiPhH-SiH$_2$-] Model Compound

	iso		syn	
	E^a	ϕ, deg	E^a	ϕ, deg
TT	0.0	±3.0	0.0	±3.5
TG$^+$	2.3	120.9	−1.4	107.9
TG$^-$	1.1	−116.4	−0.67	−101.6
G$^+$*G*$^+$	2.8	121.2	−2.3	120.6
G$^-$*G*$^-$	2.8	−121.95	−2.4	−119.8
G$^-$*G*$^+$	>10	+105.2	>10	+95.2

[a] In kcal mol^{-1}, taken relative to E = 0.0 kcal mol^{-1} for the TT (ϕ = 0°) conformation.

where the statistical weight parameters σ, λ, ψ, ψ', ω, and ω' are obtained as Boltzmann factors for the conformational energy associated with that rotational state, e.g., $\sigma = \exp[-E_\sigma/RT_K]$, where $E_\sigma = E_{TG^+} - E_{TT}$ and T_K is the temperature in kelvin. Note again that the torsional asymmetry with respect to the G$^+$ and G$^-$ conformations manifests itself with σ and λ (where $E_\lambda = E_{TG^-} - E_{TT}$) in general assuming different values. The parameters ψ, ψ', ω, and ω' are the second-order parameters whose values are calculated based on changes in the conformational energy when the bond preceding the subject bond is in a rotational state other than T.[8]

Using the MM2 calculated conformational energies to evaluate each of the statistical weight parameters in eq 1, characteristic ratios C_n were then calculated by using RIS theory.[8] Associated values of the temperature coefficient of C_n given by $d(\ln C_n)/dT_K$ were obtained in a straightforward fashion by evaluating the slope of the plot of RIS-calculated C_n values versus temperature near T_K = 298.15 K.

Results and Discussion

Conformational Energy Calculations. Values of the MM2 calculated conformational energies and associated torsion angles are summarized in Tables I and II for the iso and syn forms of the [-SiPhMe-] and [-SiPhH-SiH$_2$-] model compounds, respectively.

On the basis of the results given in Table I, both iso and syn [-SiPhMe-] show an overwhelmingly strong preference for the trans (planar zigzag) conformation. In fact, given their high relative energy, gauche states of any type or in any sequence would be virtually excluded at room temperature. This result reflects the influence of the steric bulk of the substituents. Steric congestion renders all but the all-trans conformation highly unfavorable. As expected, G$^\pm$G$^\mp$ states gave rise to the now-familiar "pentane effect"[8] and, as such, represent extraordinarily repulsive conformational energy domains. Thus both the iso and syn [-SiPhMe-] model compounds prefer the TT state almost exclusively.

Table III
Selected Values of the MM2 Geometry-Optimized Bond Lengths[a] and Bond Angles[b] for the Iso and Syn Forms of the [-SiPhMe-] Model Compound

	TT		TG^+		TG^-		G^+G^+		G^-G^-	
	iso	syn	iso	syn	iso	syn	iso	syn	iso	syn
bond lengths[a]										
Si-Si	2.354	2.357	2.356	2.353	2.354	2.353	2.361	2.353	2.359	2.366
Si-C_{Me}	1.867	1.868	1.868	1.867	1.867	1.868	1.867	1.867	1.867	1.867
Si-C_{Ar}	1.851	1.850	1.849	1.850	1.851	1.849	1.852	1.850	1.852	1.853
bond angles[b]										
Si-Si-Si	113.9	111.6	117.7	116.6	116.2	116.5	119.7	120.2	120.0	116.2
Si-Si-C_{Me}	107.8	109.6	106.4	107.6	108.7	107.8	108.4	106.5	107.3	107.6
Si-Si-C_{Ar}	110.2	108.9	109.2	109.7	107.9	107.6	110.6	108.1	108.8	110.9
C_{Me}-Si-C_{Ar}	111.2	111.3	111.3	111.6	111.9	111.8	108.9	110.8	109.5	107.5

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

Table IV
Selected Values of the MM2 Geometry-Optimized Bond Lengths[a] and Bond Angles[b] for the Iso and Syn Forms of the [-SiPhH-SiH_2-] Model Compound

	TT		TG^+		TG^-		G^+G^+		G^-G^-	
	iso	syn	iso	syn	iso	syn	iso	syn	iso	syn
bond lengths[a]										
Si-Si	2.340	2.340	2.341	2.340	2.337	2.342	2.338	2.346	2.337	2.341
Si-H[c]	1.490	1.489	1.489	1.489	1.489	1.489	1.489	1.489	1.489	1.488
Si-C_{Ar}	1.877	1.878	1.877	1.877	1.877	1.878	1.877	1.881	1.876	1.879
bond angles[b]										
Si-SiPhH-Si	109.3	110.2	109.1	110.2	111.2	110.1	110.9	107.9	110.9	109.7
Si-SiH_2-Si	108.6	107.9	108.4	108.4	110.1	107.6	109.3	109.5	109.8	109.3
Si-Si-C_{Ar}	109.0	108.1	109.5	110.0	108.6	109.8	109.3	108.5	109.6	107.6
C_{Ar}-Si-H	109.2	109.3	109.4	108.2	108.4	109.4	108.8	108.4	108.4	108.2

[a] In units of angstroms. [b] In units of degrees. [c] Values of Si-H bond lengths are nearly equal in -SiH_2- and -SiPhH- segments.

The calculated torsion angles are as expected for a highly congested molecule. Specifically, the trans conformations deviate slightly (ca. 2-5°) from the idealized value of $\phi = 0°$. Again, the gauche states are in all cases at least slightly less severe (i.e., less twisted) than the idealized $\phi = \pm 120°$.

For the [-SiPhH-SiH_2-] model compounds, the results in Table II reveal sharp differences between the iso and syn forms in terms of conformational preferences. In particular, the iso isomer shows a strong preference for T states over G states in general and for the TT state in particular. This preference for T states is comparably smaller than that described above for [-SiPhMe-] since in the case of [-SiPhH-SiH_2-] we are dealing with a much less sterically congested and hence a considerably more flexible molecule. In contrast to the iso form, syn [-SiPhH-SiH_2-] indicates a strong preference for G states in general and the G^+G^+ over TT by roughly the same amount of conformational energy (ca. 2.5 kcal/mol) as the iso form prefers TT over G^+G^+.

The reason for this reversal in conformational preferences can be traced to the observation that both the iso and syn chains appear to prefer conformations in which the phenyl substituents are nearly overlapping. For the iso form this situation is achieved in the TT state, while for the syn form this occurs more nearly in the alternative G states. The phenyl···phenyl interplanar distance is about 3.8 Å for both the iso form at TT and the syn form at G^+G^+, and this distance represents a near minimum in the potential energy for $C_{Ar} \cdots C_{Ar}$ interactions. Hence, in the case of [-SiPhH-SiH_2-], for the iso form an all-trans, planar zigzag conformation is predicted to dominate while for the syn form a more helical conformation corresponding to sequences of G^+G^+ and TG^+ states is indicated by the calculations.

Considering the calculated torsion angles for [-SiPhH-SiH_2-], the TT state is again represented by a pair of nearby minimum energy conformations straddling $\phi = 0°$. For the iso form the gauche minima (except of course the highly repulsive $G^{\pm}G^{\mp}$ states) are located very near the standard $\phi = \pm 120°$ values. For the syn form, $G^{\pm}G^{\pm}$ states are located very near $\phi = 120°$, while $TG^{\pm}$ states are receded from this value.

Calculated Geometrical Parameters. Values of the MM2 geometry optimized bond lengths and bond angles for each conformational state are given in Tables III and IV, respectively, for the [-SiPhMe-] and [-SiPhH-SiH_2-] model compounds. Values of the bond lengths vary only slightly with conformation for both systems. Average values taken from Tables III and IV are 2.35, 1.87, and 1.49 Å for the Si-Si, Si-C_{Me}, and Si-H bonds, respectively. For Si-C_{Ar} bond lengths, the average value is 1.85 Å in Table III and 1.88 Å in Table IV. This difference is attributable to the differences in the Si-related force-field parameters used for the [-SiPhMe-][2] (Table III) and [-SiPhH-SiH_2-][11] (Table IV) model compounds.

Calculated bond angles in general vary with conformation more so than do bond lengths due to the "softer" nature of their deformation energy functions. This is reflected in Tables III and IV where, for instance, the Si-Si-Si bond angle ranges from 111.6° to 120.2° for [-SiPhMe-]. On the other hand the values listed for [-SiPhH-SiH_2-] (Table IV) are surprisingly uniform over all conformations, with deviations ranging only about 1-2°. These smaller deviations reflect the lesser steric congestion found in [-SiPhH-SiH_2-] relative to [-SiPhMe-].

Chain Statistics Calculations. The structural information given in Tables III and IV for the [-SiPhMe-] and [-SiPhH-SiH_2-] model compounds, in conjunction with the conformational energy and torsion angle data given in Tables I and II, were used to calculate the characteristic ratio C_n for $n = 200$, 300, and 400 backbone bonds. The number 400 would correspond to a chain of molecular weight of about 48 000 for [-SiPhMe-] and 27 200 for [-SiPhH-SiH_2-]. The associated statistical

Table V
Values of the Statistical Weight Parameters Computed at 25 °C for Iso and Syn Forms of [-SiPhMe-] and [-SiPhH-SiH$_2$-]

	[-SiPhMe-]		[-SiPhH-SiH$_2$-]	
	iso	syn	iso	syn
σ	0.00	0.00	0.17	10.10
λ	0.00	0.00	0.02	3.10
ψ	0.31	0.05	0.48	4.65
ψ'	0.03	0.00	0.05	12.58
$\omega = \omega'$	0.00	0.00	0.00	0.00

Table VI
Calculated Values of the Characteristic Ratios $C_{n=200}$, $C_{n=300}$, and $C_{n=400}$ and Associated Temperature Coefficient d(ln $C_{n=400}$)/dT at 25 °C for [-SiPhMe-] and [-SiPhH-SiH$_2$-]

	$C_{n=200}$	$C_{n=300}$	$C_{n=400}$	d(ln $C_{n=400}$)/dT^a
[-SiPhMe-]				
iso	140	209	274	-7.8×10^{-4}
syn	130	188	240	-3.4×10^{-3}
[-SiPhH-SiH$_2$-]				
iso	17.9	18.4	18.6	-4.5×10^{-3}
syn	50.4	67.0	78.8	-7.9×10^{-3}

[a] In units of degree^{-1}.

weight parameters σ, λ, ψ, ψ', ω, and ω' calculated at 25 °C for each polymer are listed in Table V.

In the present analysis, values of the backbone Si-Si bond length and Si-Si-Si bond angle were fixed at 2.35 Å and 113.9°, respectively, for [-SiPhMe-] and at 2.34 Å and 109.2°, respectively, for [-SiPhH-SiH$_2$-]. These values were obtained by taking Boltzmann factor weighted averages of those corresponding values listed in Tables III and IV.

In a similar fashion, torsion angles associated with the T, G$^+$, and G$^-$ states were set at 0°, 116°, and -116° for both iso and syn [-SiPhMe-] and at 0°, ±116.4° and 0°, ±120.0° for iso and syn [-SiPhH-SiH$_2$-], respectively. These values were similarly chosen based on weighted averages taken from the results of the conformational energy calculations (Tables I and II). For [-SiPhMe-], it should be noted that all T states were set at 0°, as opposed to the actual values found in the energy calculations, largely as a mathematical convenience. Preliminary calculations showed that setting all T states to, for example, ±3° had negligible effect on the calculated C_n values.

The RIS-calculated values of C_n for n = 200, 300, and 400 and the associated temperature coefficient d(ln $C_{n=400}$)/dT at T_K = 298 K for the chains considered here are listed in Table VI. The essentially rodlike configurations adopted by the [-SiPhMe-] chains, as manifested in the conformational energy calculations yielding virtually exclusive preference for TT states, give rise to very large and nonconvergent values of C_n. In this context, these chains cannot be considered as random coils.

In contrast, the $C_{n=400}$ values for [-SiPhH-SiH$_2$-] are nearly convergent. In particular, the value $C_{n=400}$ = 18.6 for the iso form is fully converged and depicts a fairly extended chain but one that is just conformationally flexible enough to contain sequences such as TTTG$^+$TG$^-$T and TTTG$^+$TTG$^-$ that would tend to alter the direction of chain propagation away from the rodlike configurations associated with [-SiPhMe-]. In contrast, the C_n values for the syn form of [-SiPhH-SiH$_2$-] are substantially higher, and at n = 400 are still not yet convergent. These results depict chains having sequences almost exclusively G$^+$G$^+$G$^+$G$^+$ (noting that the associated G$^-$G$^-$G$^-$G$^-$ sequences would be energetically and hence statistically much less probable owing to the asymmetry of the substituents), thus revealing an inflexible and highly extended helical configuration.

Calculated values of d(ln $C_{n=400}$)/dT at 25 °C (Table VI) are all negative in sign and typically small. The negative sign is interpreted to mean that an increase in temperature causes conformational transitions from low-energy conformational states of high spatial extension to the alternative high-energy, more conformationally compact, states. Thus for each polymer an increase in temperature results in a decrease in the dimensions (i.e., $\langle r^2 \rangle_0$) of the chains. The small magnitude of the d(ln $C_{n=400}$)/dT values listed in Table VI indicates that each polymer shows a strong preference for a particular conformational state and hence that each is quite inflexible.

Comparison with Experiment. These calculated C_n values are qualitatively in agreement with preliminary experimental values of Cotts et al.,[9] obtained from dilute solution light-scattering measurements. They found a value $C_{n=\infty}$ = 64 ± 20 for a probably atactic [-SiPhMe-] sample having a weight average of 400 ± 75 backbone chain atoms. While this experimental value is substantially smaller than our calculated values of 240-270, the basic picture of a nearly fully extended chain persists. By comparison, the $C_{n=\infty}$ values reported by Cotts et al.,[9] for a number of probably atactic dialkyl polysilanes fall in the 14-30 range. Given these experimental values, the calculated values of 19 and 79 obtained, respectively, for iso and syn [-SiPhH-SiH$_2$-] seem reasonable.[13]

Acknowledgment. We thank John Eksterowiez (UD) for assistance in generating the figures.

Registry No. *iso*-H$_3$C[SiPhMe]$_5$CH$_3$, 119945-13-0; *iso*-H[SiPhHSiH$_2$]$_3$SiH$_3$, 119878-75-0; *syn*-H[SiPhHSiH$_2$]$_3$SiH$_3$, 119944-21-7; *syn*-H$_3$C[SiPhMe]$_5$CH$_3$, 119878-74-9; poly(silastyrene), 119878-77-2; poly(phenylmethylsilylene) (homopolymer), 31324-77-3; poly(phenylmethylsilylene) (SRU), 111404-81-0.

References and Notes

(1) For a review, see: West, R. J. *J. Organomet. Chem.* **1986**, *300*, 327, and references therein.

(2) Damewood, J. R., Jr.; West, R. *Macromolecules* **1985**, *18*, 159.

(3) Damewood, J. R., Jr. *Macromolecules* **1985**, *18*, 1793. For a reinvestigation of poly(di-*n*-hexylsilylene) using less sophisticated methods see: Farmer, B. L.; Rabolt, J. F.; Miller, R. D. *Macromolecules* **1987**, *20*, 1169.

(4) Miller, R. D.; et al. In *Polymers for High Technology: Electronics and Photonics*; Bowden, M. J., Turner, S. R., Eds.; ACS Symposium Series 346; American Chemical Society: Washington, DC, 1987; pp 170-187, and references therein.

(5) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 2039, and references therein.

(6) Ortiz, J. V.; Mintmire, J. W. *J. Am. Chem. Soc.* **1987**, *110*, 4522.

(7) In accordance with the terminology associated with vinyl chains noting, however, that [-SiPhMe-] is not a vinyl polymer.

(8) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.

(9) Cotts, P. M.; Miller, R. D.; Trefonas, P. T., III; West, R.; Fickes, G. N. *Macromolecules* **1987**, *20*, 1046. Cotts, P. M. *Proc. ACS Div. Polym. Mater., Sci. Eng. (PMSE)* **1985**, *53*, 336.

(10) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph Series 177; American Chemical Society: Washington, DC, 1982.

(11) Allinger, N. L.; Flanagan, H. L. *J. Comput. Chem.* **1983**, *4*, 399. An update of the MMP2 (1985) force-field parameter set was obtained by W.J.W. through the courtesy of Prof. N. L. Allinger, Department of Chemistry, University of Georgia.

(12) Welsh, W. J.; Debolt, L.; Mark, J. E. *Macromolecules* **1986**, *19*, 2987. Welsh, W. J.; Beshah, K.; Ackerman, J. L.; Mark, J. E. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1983**, *24*, 131.

Macromolecules **1989**, *22*, 2951–2957

(13) Note added in proof: Experimental results pertinent to and supportive of the conclusions drawn here for poly(phenylmethylsilylene) are found in: (a) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 2037. (b) Harrah, L. A.; Zeigler, J. M. In *Photophysics of Polymers*; Hoyle, C. E., Torkelson, J. M., Eds.; ACS Symposium Series 358; American Chemical Society: Washington, DC, 1987; p 482. Also, another conformational analysis of poly(phenylmethylsilylene) has recently been published: Sundararajan, P. R. *Macromolecules* **1988**, *21*, 1256.

Structure and Surface Energy Characteristics of a Series of Pseudo-Perfluoroalkyl Polysiloxanes

Marca M. Doeff[*,†] **and Elek Lindner**[‡]

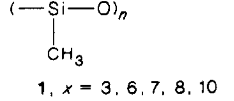
Naval Ocean Systems Center, Code 521, San Diego, California 92152, and Computer Sciences Corporation, 4045 Hancock Street, San Diego, California 92110.
Received September 6, 1988; Revised Manuscript Received December 27, 1988

ABSTRACT: A series of pseudo-perfluoroalkyl-substituted polysiloxanes were synthesized and characterized by contact-angle measurements and polarization specular reflectance infrared spectroscopy. It was found that the dispersive surface energies for the siloxanes are comparable to the values found for carbon-based polymers such as poly(1*H*,1*H*-perfluorooctyl acrylate) and poly(1*H*,1*H*-perfluorooctyl methacrylate) and only slightly higher than that for adsorbed monolayers of perfluorolauric acid, the substance with the lowest known dispersion energy. This result as well as polarization specular reflectance infrared spectra indicates that the side chains in the siloxane polymers are oriented so that the perfluoroalkyl groups are approximately parallel to one another and normal to the substrate surface. Also, several of the free polymers have a fibrous appearance, and polarized light microscopy shows a high degree of orientation in some of the thicker fibers. However, X-ray diffraction does not indicate crystallinity. There is no straightforward variation of dispersive surface energy with the length of the perfluoroalkyl side chains in the polysiloxanes as there is in the carbon-based materials.

Introduction

Low surface energy polymer coatings have many characteristics that are useful industrially; for example, they may be used as mold release coatings in manufacturing processes. Poly(tetrafluoroethylene), widely used as a "nonstick" coating, has a dispersive surface energy of 18.5 dyn/cm.[1] Monolayers of perfluorolauric acid adsorbed onto platinum have an energy of about 10 dyn/cm,[2] the lowest value known. Various polymeric materials have been discovered that have dispersion energies nearly as low as that of the perfluoroacid monolayers. These polymers generally have a carbon-based backbone and long perfluoroalkyl side chains in a comblike arrangement. Extensive studies have been made on the effect of side-chain length, crystallizability, and type of backbone[3,4] upon the dispersion energy of these macromolecules. Less information is available for comb polymers that do not have a carbon-based backbone, although there have been a few reports on siloxanes.[5,6]

We are studying the variation of dispersive surface energy as a function of type of polymer backbone and length of perfluoroalkyl chain in "comb" polymers. The present paper concerns siloxane polymers substituted with pseudo-perfluoroalkyl chains (1).



$$(\!-\!\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2CH_2(n\text{-}C_xF_{2x+1})}{Si}}\!-\!O)_n$$

1, $x = 3, 6, 7, 8, 10$

Experimental Section

The pseudo-perfluoroalkyl-substituted polysiloxanes were made by reacting poly(methylhydrosiloxane) (MW = 2270, Alfa Products, Danvers, MA) with the appropriate perfluoroalkyl-substituted 1-olefin in a modification of a method described by Rim et al.[7] In this procedure, weighed amounts of the polysiloxane starting material, the 1-olefin, and once-distilled toluene were added to a three-neck round-bottom flask fitted with a water-cooled condensor, an argon-gas purge, and a rubber septum cap. The amounts were chosen so that the olefin was in about 15% molar excess over poly(methylhydrosiloxane) and the total volume was about 20–30 mL. Argon gas was bubbled through the mixture at room temperature for 15 min to remove adventitious oxygen. The argon gas was then allowed to flow over the reaction mixture as it was heated to 60 °C and stirred. At this point, 2 mL of a solution of about 5 mg of H_2PtCl_6 in ethanol was added quickly by syringe to the reaction mixture. Larger amounts of catalyst did not give better results and caused difficulty in purification of product. After 3 days of reaction time, the mixture was filtered hot through a glass frit, and the toluene and excess olefin were distilled from the filtrate under vacuum. The resulting opaque white polymers were allowed to air dry for several days to remove remaining solvent. The complete absence of the Si–H stretch at 2171 cm^{-1} in the IR spectrum of these materials confirmed complete reaction of the material.

3,3,4,4,5,5,5-Heptafluoro-1-pentene used in the above synthesis was supplied by SCM (Gainesville, FL). The other 1-olefins were made by dehydro-iodination of the corresponding 1-iodo-1*H*,1*H*,2*H*,2*H*-perfluoroalkanes, which were purchased from SCM or made by reacting ethylene gas with a perfluoroalkyl iodide obtained from SCM.[8]

Glass slides coated with the perfluoroalkyl-substituted polysiloxanes were used for the contact-angle measurements and for the FT-IR spectra. Duplicate samples were made for each polymer. The polymers were dissolved in mixtures of Freon 113 and hexane (approximately 1:100 w/w) and brushed onto clean glass slides. This process was repeated until coverage was complete, as judged by visual inspection. Then, slides were placed in an oven set at 60 °C for 24 h. After this time, most of the coatings had dried to a hard, translucent finish. Coating thicknesses are estimated to be about 4 μm, on the basis of the specular reflectance IR spectra.[9]

In addition to the samples coated with the perfluoroalkyl-substituted siloxanes, two slides were coated with poly(hydro-

---

[†] Computer Sciences Corp.
[‡] Naval Ocean Systems Center.

0024-9297/89/2222-2951$01.50/0 © 1989 American Chemical Society