Conformational Features of Poly(silastyrene)

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Introduction

Studies on the conformational features of poly(organosilanes) are of interest due to the commercial prospects for these polymers as well as due to the physical behavior exhibited by them which have been interpreted in terms of conformational preferences of the skeletal and side-group bonds.[1] Due to their chemical structure resembling that of the vinyl chains that are the carbon polymer analogues, the methodologies that have been developed for the treatment of the statistical conformations of vinyl polymers can generally be applied to the analysis of poly(organosilanes).[2-6] Following the nomenclature set forth for the vinyl chains, the stereoconfiguration can be defined in terms of meso, racemic, or hetero diads and triads and isotactic, syndiotactic, or atactic polymer.

However, the tacticity definition for chains such as poly(methylphenylsilane) (PMPS) differs from that for common vinyl polymers due to the asymmetric substitution on the Si_i atom (see Figure 1). In the analogous carbon chain polymer, poly(α-methylstyrene), the carbon at the ith position is symmetrically substituted with hydrogens and hence the tacticity is defined in terms of the stereoconfigurations of the substitutions at the C_{i-1} and C_{i+1} atoms. However, the tacticity definition of PMPS should explicitly include the stereoconfiguration of the substitution at the Si_i atom relative to those of the substitutions at the Si_{i-1} and Si_{i+1} atoms. Thus, the treatment of the chain conformations in terms of only the meso and racemic diads is inadequate. Depending on the stereoconfiguration at the Si_i atom, three types of triads—meso, racemic, and hetero—should be considered. This has been discussed in detail in our previous paper[5] on PMPS. The previous calculations[5] showed that such heterotactic sequences influence the value of the characteristic ratio significantly. In addition, the elements of the statistical weight matrices also would be different for the meso, racemic, and hetero triads.

In this paper, the results of conformational modeling of poly(silastyrene) (see Figure 1) are presented and the features are compared with those of polystyrene. Recently, Welsh et al.[7] reported the conformational analysis of this polymer.

Statistical Weight Matrices for Poly(silastyrene)

The statistical conformations of the poly(silastyrene) chain can be treated in the rotational isomeric state scheme following the procedures developed for chains such as polystyrene. Accordingly, three statistical weight matrices are required: the matrix **U**′ for the pair of bonds $i-1$ and i, $\mathbf{U}_m''$ for the bond pair i and $i+1$ in a meso diad, and $\mathbf{U}_r''$ for such a bond pair in a racemic diad. These are given by

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix} \qquad (1)$$

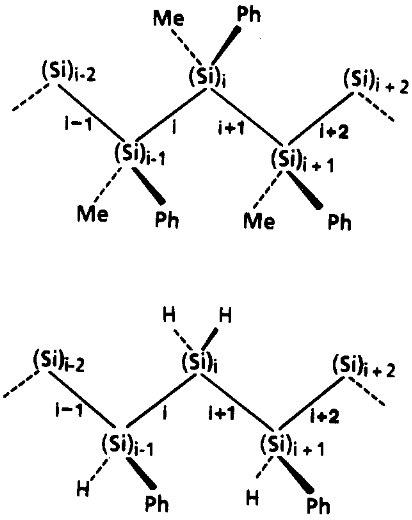

Figure 1. Schematic of segments of poly(methylphenylsilane) (top) and poly(silastyrene).

$$\mathbf{U}_m'' = \begin{bmatrix} \omega'' & 1/\eta & \tau\omega'/\eta \\ 1/\eta & \omega/\eta^2 & \tau\omega'/\eta^2 \\ \tau\omega'/\eta & \tau\omega'/\eta^2 & \tau^2\omega''\omega/\eta^2 \end{bmatrix} \qquad (2)$$

$$\mathbf{U}_r'' = \begin{bmatrix} 1 & \omega'/\eta & \tau\omega''/\eta \\ \omega'/\eta & 1/\eta^2 & \tau\omega/\eta^2 \\ \tau\omega''/\eta & \tau\omega/\eta^2 & \tau^2\omega'^2/\eta^2 \end{bmatrix} \qquad (3)$$

The first-order interactions in the t and $\bar{g}$ conformations of the skeletal bonds are taken into account by the statistical weights η and τ, respectively. The statistical weights ω, ω', and ω'' correspond to SiH_2---SiH_2, SiH_2---phenyl, and phenyl---phenyl interactions, respectively, which are of second order. The gg and $\bar{g}\bar{g}$ states of the bond pair($i-1$, i) in the **U**′ matrix have been assigned a weight of zero, as for the vinyl chains.

Description of the Calculations

The calculations of the conformational energies were performed for the meso and racemic diads of poly(silastyrene) in terms of the skeletal and side-group rotations ϕ_i, ϕ_{i+1}, χ_{i-1}, and χ_{i+1}. The lengths of the Si-Si, Si-H, Si-C^{ar}, C^{ar}-C^{ar}, and C^{ar}-H bonds were taken to be 2.34, 1.49, 1.87, 1.39, and 1.1 Å, respectively. The skeletal bond angles at both Si_{i-1} and Si_{i+1} were assigned a value of 109.5°. These are similar to the values obtained by Welsh et al.[7] following the optimization of the geometry by the MM2 method. The Lennard-Jones 6-12 potential was used to evaluate the nonbonded interactions, with parameters given before.[5,6] A close agreement was noted between the results obtained with these parameters and the MM2 results in the previous study.[6] A torsional barrier of 1.2 kcal·mol^{-1} was used for the rotations around the Si-Si bonds. The rotations χ_{i-1} and χ_{i+1} of the phenyl side groups about the Si-C^{ar} axis were varied from −40 to +40° in each of the skeletal rotational states ϕ_i and ϕ_{i+1} so as to place the atoms of the phenyl groups in their minimum-energy positions. In addition, since invariably the minima for the bond conformations are shifted from perfect staggering, the terminal $(SiH_3)_{i-2}$ and $(SiH_3)_{i+2}$ groups were allowed a variation of up to 20° about the $i-1$ and $i+2$ bonds, respectively, to locate these hydrogens in their minimum-energy positions.

As described previously,[5,6,8] the average energies $\langle E_i \rangle$ of the various states and the average skeletal torsional

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Table I
Results of the Energy Calculations

state	$(\Delta E)_{\min}$, kcal·mol^{-1}	$\langle E \rangle$, kcal·mol^{-1}	$\langle \phi_i, \phi_{i+1} \rangle$, deg	$(\phi_i, \phi_{i+1})_{\min}$, deg	Z
$(\mathrm{tt})_m$	−0.8	−0.252	11.7, 11.7	(0, 20), (20, 0)	42.5
$(\mathrm{tg})_m$	−0.8	−0.176	9.4, 94.5	(20, 80)	40.04
$(\mathrm{t\bar{g}})_m$	2.1	2.53	14.2, −133.0	(40, −130)	0.61
$(\mathrm{gg})_m$	−1.1	−0.75	118.8, 118.8	(130, 110), (110, 130)	31.26
$(\mathrm{g\bar{g}})_m$	1.5	2.0	116.5, −108.5	(110, −110)	1.78
$(\mathrm{\bar{g}\bar{g}})_m$	2.9	3.41	−114.5, −114.5	(−130, −100) (−100, −130)	0.2
$(\mathrm{tt})_r$	0.0	0.52	31.3, 31.3		10.92
$(\mathrm{tg})_r$	−1.7	−1.1	3.0, 112.7	(0, 110)	157.0
$(\mathrm{t\bar{g}})_r$	1.2	1.80	1.4, −126.3	(0, −130)	1.67
$(\mathrm{gg})_r$	−1.6	−1.05	109, 109	(110, 110)	40.1
$(\mathrm{g\bar{g}})_r$	1.6	2.06	109.9, −110.4	(100, −120)	1.05
$(\mathrm{\bar{g}\bar{g}})_r$	2.7	3.25	−125.1, −125.1	(−130, −140) (−140, −130)	0.22

angles $\langle \phi_i, \phi_{i+1} \rangle$ were calculated by Boltzmann averaging over the energy surface surrounding each of the minima. The results are shown in Table I. The locations of the minima and the energies of the various minima with respect to the racemic tt state are also given.

Results and Discussion

Relative Energies of the Conformations. In Table I, the energies are given relative to the racemic tt state. This is necessary if one wants to calculate properties such as the characteristic ratio for stereo*irregular* chains. The conformational energies, partition functions, etc. should be normalized with respect to one of the states of one of the isomers (e.g., the tt state of the racemic diad) for such analyses.

The relative energies for the meso diad conformations given in Table I show that the energies at the minima for the tt and tg states are equal. This is similar to the case of the meso diad of polystyrene.[9,10] The gg state is ~0.3 kcal·mol^{-1} lower in energy than both of the above. In the case of polystyrene, however, the gg state is substantially higher in energy than the tt state. For the racemic diad, the tg and gg states are of lower energy than the tt state. The t$\bar{\mathrm{g}}$ and $\bar{\mathrm{g}}\bar{\mathrm{g}}$ states are 1.2 and 2.7 kcal·mol^{-1}, respectively, higher in energy than the tt state. It had been shown in a number of cases of vinyl chains with planar substituents such as phenyl or carbazole moieties that the conformations involving the $\bar{\mathrm{g}}$ state are of high energy.[9,11,12] The same feature is exhibited in the poly(silastyrene) conformations, although the energy of the t$\bar{\mathrm{g}}$ state relative to tt is not as high as that in the case of polystyrene.

The locations of the minima listed in Table I are generally shifted by 10–20° from perfect staggering. However, the shift is significant for the meso tg state, with the minimum occurring at $(\phi_i, \phi_{i+1}) = (20°, 80°)$. The energy surface in this area is shallow and the energy difference between this conformation and the one with $(\phi_i, \phi_{i+1}) = (0, 120°)$ is 0.7 kcal·mol^{-1}. The shift is also pronounced in the racemic tt state, with the minimum occurring at $(\phi_i\ \phi_{i+1}) = (30°, 30°)$. This conformation is again surrounded by a low-energy region and the minimum is not sharp.

It is well-known that, in the common crystalline form, the isotactic polystyrene chain adopts a threefold helical structure with a pitch of 6.65 Å. With the longer Si–Si bond length in the case of poly(silastyrene), the conformation of the isotactic chain with $(\phi_i, \phi_{i+1}) = (20°\ 80°)$ corresponds to a helix with 4.78 residues in a pitch of 12.21 Å. With the conventional value of $(\phi_i, \phi_{i+1}) = (0, 120°)$, the chain would be a threefold helix with a pitch of 9.36 Å, which is significantly larger than that of isotactic polystyrene in the threefold helical conformation.

Table II
Statistical Weight Parameters Derived from Energy Calculations

statistical weight	energy, kcal·mol^{-1}	prefactor
η	0.63	1.52
τ	2.8	2.22
ω''	−0.98	1.0
ω'	−0.63	1.15
ω	−0.15	1.04

Table III
Calculated Values of the Characteristic Ratios of Poly(silastyrene) Chains of Various Tacticities

isotactic frac	C_∞
1.0	2.14
0.8	3.27
0.6	4.49
0.5	5.10
0.4	5.88
0.2	8.42
0.0	12.73

Statistical Weights and Characteristic Ratios

The statistical weights and prefactors were evaluated by using the results given in Table I and the overdetermined set of equations, as described before,[13] and are given in Table II. The characteristic ratios ($C_\infty = \langle r^2 \rangle_0 / nl^2$) calculated as a function of the isotacticity of the poly(silastyrene) chain containing 500 units are given in Table III. For stereoirregular chains, the average of 10 such chains was taken.

From Table III, the value of C_∞ for the isotactic chain is 2.14 and it is 12.73 for the syndiotactic chain. Between an isotacticity of 0.0 and 0.4, the characteristic ratio decreases sharply. The characteristic ratio for the isotactic chain is significantly lower than that for isotactic polystyrene ($C_\infty = 11$).[14,15] For an atactic polystyrene chain with an isotactic fraction of 0.3–0.5, Yoon et al.[9] quote a value of $C_\infty = 10$. For the poly(silastyrene) chain with an isotactic fraction of 0.5, the calculated value of C_∞ is 5.1. Because of the substantially low energy of the gg state and because its partition function is comparable to that of the tt and tg states, the value of C_∞ for the isotactic chain is small. For the syndiotactic chain, the minimum for the tt state occurs at (30°, 30°), which gives rise to large looping chain segments. The tg state is highly preferred compared to the tt state. In Table I, although the racemic tg and gg states are of comparable energy, the partition function for the tg state is about 4 times that of the gg state. This is due to the fact that the area surrounding the tg minimum is shallow whereas in the gg state, the energy increases sharply for the conformations away from the minimum. Thus, in terms of the statistical properties, the contribution of the gg state is significantly reduced, in spite of the low energy at the minimum position. This illustrates the importance of averaging over the domains rather than using minimum energies alone in the calculations of average properties.

There are at present no experimental data on C_∞ for poly(silastyrene) to compare with the theoretical calculations. Although Cotts et al.[16] have reported the experimental values of the characteristic ratios for a number of arylsilane polymers, the conformational behavior of poly(silastyrene) can be expected to be substantially different from those of diaryl- or dialkylsilane polymers since the basic chemistry is different, which leads to additional stereoisomers as discussed above. The longer Si–Si bond length in poly(silastyrene) would cause the energy difference between conformers to be softer than in the case of polystyrene. This is reflected in the results of the present calculations, and the value of C_∞ for poly(silastyrene) is calculated to be lower than that of polystyrene.

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Registry No. $(SiCl_2H_2)(SiCl_2HPh)$ (copolymer), 119878-77-2.