

STUDY ON POLYPHENYLSILSESQUOXANE'S SHAPE IN DILUTE SOLUTION

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ABSTRACT

Based on relations between the limiting viscosity number, the translational diffusion coefficient and the molecular weight, the shape of polyphenylsilsesquioxane (PPSQ) in dilute solution was simulated with different models. It is found that the oblate ellipsoid of revolution and free-draining random coil are two suitable models, showing that PPSQ is a polymer with rigid chains, and its shape is closer to sphere due to chain branching rather than flexibility.

INTRODUCTION

As a ladder polymer, the conformation of polyphenylsilsesquioxane (PPSQ) in dilute solution has been studied by several authors^[1-5]. The wormlike chain model is often adopted and the assumption that the mass per unit contour length equals the molar mass per contour length of a chain repeat unit is frequently made. However the assumption seems not very appropriate for polymers with branches. In the previous paper^[6], we reported studies on molecular structure and shape of PPSQ through the investigation of its dilute solution properties. In this study some models were used to simulate PPSQ's conformation in dilute solution on the basis of relations between translational diffusion coefficient and M_w , and between limiting viscosity number and M_w . Results from simulation were also informative for the elucidation of PPSQ's structure.

THEORY

Many different models were proposed to link polymer solution properties and the molecular weight, size and shape. Brief notes to models used in this study are given below.

For ellipsoid model, the whole molecule is taken as an ellipsoid regardless of its microstructure. Simha^[7] and Perrin^[8] derived expressions for its limiting viscosity number, $[\eta]$, and translational diffusion coefficient, D , respectively.

$$[\eta] = (4\pi N_A A^3 / 3M\rho^2) V(\rho) \quad (1)$$

$$D = (k_B T / 6\pi\eta_s A) G(\rho) \quad (2)$$

where N_A , k_B , M and T are in turn the Avogadro constant, Boltzmann constant, molecular weight and temperature. A is the halflength of the rotation axis. The other two axes have the same halflength of axis, B . ρ is the axes ratio and equals to B/A . Combining equations (1) and (2) yields

$$M[\eta]D^3 = (4\pi N_A / 3\rho^2) V(\rho) [k_B T G(\rho) / 6\pi\eta_s]^3 \quad (3)$$

where $V(\rho)$ and $G(\rho)$ are both functions of the axes ratio. Obviously, for spherical molecules, $\rho = 1$, $V(\rho) = 1$, $G(\rho) = 1$. For oblate ellipsoids, $\rho > 1$, there are relations

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$$V(\rho) = 16\rho/15\tan^{-1}\rho \quad (4)$$

$$G(\rho) = (\rho^2 - 1)^{1/2}\rho\tan^{-1}[(\rho^2 - 1)^{1/2}] \quad (5)$$

For prolate ellipsoids, $\rho < 1$ and one has

$$V(\rho) = 14/15 + \{15\rho^2[-\ln(\rho/2) - 3/2]\}^{-1} \\ + \{5\rho^2[-\ln(\rho/2) - 1/2]\}^{-1} \quad (6)$$

$$G(\rho) = (1 - \rho^2)^{1/2}\ln\{[1 + (1 - \rho^2)^{1/2}]/\rho\} \quad (7)$$

M , $[\eta]$ and D are all measurable parameters so that A and ρ can thus be calculated. Then its radius of gyration can be finally obtained according to equation (8).

$$R_g = A[(2 + \rho^3)/5]^{1/2} \quad (8)$$

For the random coil model, Kirkwood and Riseman^[9] developed the theory of the limiting viscosity number and translational diffusion coefficients of flexible macromolecules on the basis of random coil with the hydrodynamic interaction of the monomer units of the molecule and of inhibited flow through the chain. The following expressions were given

$$[\eta] = (N_A \zeta b^2) z F(x) / 36 \eta_s M_0 \quad (9)$$

$$D = k_B T [1 + 8x/3] / z \zeta \quad (10)$$

where

$$\lambda_0 = \zeta / (6\pi^3)^{1/2} \eta_s b$$

$$z = M / M_0$$

$$x = \lambda_0 z^{1/2}$$

$$F(x) = \{6/\pi^2\} \sum_{k=1}^{\infty} [k^2(1 + k^{-1/2}x)]^{-1}$$

where η_s is the viscosity of the solvent. M_0 , b and ζ are mass, length and friction coefficient for an equivalent segment, respectively. Multiplication of equations (9) and (10) yields

$$M[\eta]D = N_A k_B T z b^2 (1 + 8x/3) F(x) / 36 \eta_s \quad (11)$$

thus

$$R_g = (z b^2 / 6)^{1/2} = [6 \eta_s (1 + 8x/3) F(x) M[\eta] D / N_A k_B T]^{1/2} \quad (12)$$

The value of the parameter x depends on the hydrodynamic interaction between the solute and the solvent. For free-draining random coils, the velocities of the motion of solvent molecules inside and outside the random coil are the same, i.e., independent of the velocity of the random coil, namely, ζ approaches to zero. Therefore, both x and $x F(x)$ approach to zero and $F(x)$ to unity. Equation (12) becomes

$$R_g = (6 \eta_s M[\eta] D / N_A k_B T)^{1/2} \quad (13)$$

For non-draining random coils, the solvent molecules inside the random coil move in the same velocity as their neighbouring polymer segments, namely ζ comes near to infinite. Therefore x comes near to infinite, $F(x)$ equals zero and $x F(x)$ approaches to 1.588. Then equation (12) becomes

$$R_g = (25.4 \eta_s M[\eta] D / N_A k_B T)^{1/2} \quad (14)$$

Partial-draining mode is in between the above two extreme ones, and its α value may be evaluated by the relation between $[\eta]$ and M . Comparing equation (9) with $[\eta] = K_\eta M^\alpha$ and with some simple mathematical operations, equation (15) can be derived

$$\alpha = 1 + 0.5(d \log F(x)) / (d \log x) \quad (15)$$

From this relation, the value of x can be estimated and finally R_g can be calculated.

The third model used in this study is the wormlike cylinder. Based on the wormlike chain model, Yamakawa-Fujii^[10] developed a model of wormlike cylinder. This model regards a molecular chain as a continuous, wormlike cylinder. The diameter of its section is d . The contour length is L . The mass per contour length, M_L , equals M/L . The persistence length is $(2\lambda)^{-1}$.

They obtained the following equations for the translational diffusion coefficient and the limiting viscosity number

for $L_r > \sigma$

$$D = k_B T (3\pi\eta_s L)^{-1} (A_1 L_r^{1/2} + A_2 + A_3 L_r^{-1/2} + A_4 L_r^{-1} + A_5 L_r^{-3/2}) \quad (17)$$

$$[\eta] = 2.87 \times 10^{23} M^{-1} (L/\lambda)^{3/2} \left(1 - \sum_{i=1}^4 B_i L_r^{-i/2} \right)^{-1} \quad (18)$$

for $L_r < \sigma$

$$D = k_B T (3\pi\eta_s L)^{-1} [C_1 \ln(L_r/d_r) + C_2 + C_3 L_r + C_4 L_r^2 + C_5 L_r^3 + C_6 (d_r/L_r) \ln(L_r/d_r) + C_7 (d_r/L_r) + C_8 (d_r/L_r)^2 + \dots] \quad (19)$$

$$[\eta] = 3\pi N_A L^3 L_r^{-4} [(48M \ln(L_r/d_r))]^{-1} (e^{-2L_r} - 1 + 2L_r - 2L_r^2 + 4L_r^3/3) \left\{ 1 + \sum_{i=1}^4 D_i [\ln(d_r/L_r)]^{-i} \right\}^{-1} \quad (20)$$

where $d_r = \lambda d$, and $L_r = \lambda L$, are reduced diameter and reduced contour length. A_i , B_i , C_i , and D_i , are constants which solely depend on d_r . σ equals 2.278 and is a parameter introduced during the deduction of above equations.

The unknown parameters in equations (17), (18), (19) and (20) are d , M_L , and $(2\lambda)^{-1}$, which are parameters relating to molecular shapes, can be obtained by measuring functions of D - M and $[\eta]$ - M , and then by fitting those curves to above relations.

RESULTS AND DISCUSSION

The molecular weight, translational diffusion coefficient and limiting viscosity number measured with static and dynamic laser light scattering and viscometry are listed in Table 1. Models of wormlike cylinder, ellipsoid and random coil were used to simulate the shape of PPSQ.

1. Wormlike chain model

In papers on PPSQ's solution property reported so far, Eizner-Ptitsyn's wormlike chain model^[11] and Yamakawa-Fujii's wormlike cylinder model were two most frequently used models in simulation.

A major assumption was made, that is the mass per unit contour length equals to the molar

Table 1 Dilute solution parameters for solutions of PPSQ in benzene (25°C)

No	$10^{-4}M_w$ (g.mol ⁻¹)	10^7D_0 (cm ² .s ⁻¹)	$[\eta]$ (ml.g ⁻¹)
Y ₆	6.8	6.37	26.5
Y ₅	8.9	4.96	39.5
Y ₄	14.6	2.97	56.6
Y ₇	42.7	1.46	153
Y ₅	77.1	1.05	222

mass per contour length of a chain repeat unit, i.e., $M_L = 1032$ daltons/nm. However this assumption seems only adequate to molecules with perfect ladder structure.

In this study we first calculated the persistence length by combining relations of D - M and $[\eta]$ - M without making any assumption on M_L . But no solution could be obtained. Then we assumed $M_L = 1032$ daltons/nm, as others did, to work out persistence length and the diameter of wormlike cylinder via two different approaches, i.e., D - M relation with equation (17) and $[\eta]$ - M relation with equation (18). Results are listed below, which are far from identical.

$$\begin{aligned} (2\lambda)^{-1} &= 28.0\text{nm}, & d &= 0.65\text{nm} & (\text{from } D-M) \\ (2\lambda)^{-1} &= 7.5\text{nm}, & d &= 0.40\text{nm} & (\text{from } [\eta]-M) \end{aligned}$$

It is also noted that in many author's simulation, calculations are only based on the relation between the limiting viscosity number and the molecular weight without taking account of the translational diffusion coefficient or equivalently the sedimentation constant. Based on data D and M available in their papers we calculated the persistence length and then compare them with reported ones which were calculated according to the relation of $[\eta]$ - M . It is found that they also differ remarkable.

The above calculation manifests that no definite and reliable results can be obtained from this model. This is consistent with Yamakawa-Fujii's conclusion that the wormlike cylinder model is not a suitable model for PPSQ^[10].

2. Ellipsoid

Table 2 Parameters calculated from the model of oblate ellipsoid

No	$A(\text{nm})$	$B(\text{nm})$	ρ	$R_{g(E)}(\text{nm})$	$R_{g(LS)}(\text{nm})$
Y ₆	10.2	16.4	1.60	11.3	7.7
Y ₅	12.8	20.4	1.59	14.1	13.6
Y ₄	16.5	24.5	1.48	16.9	24.7
L ₇	32.6	48.1	1.47	33.3	42.6
L ₅	45.0	66.2	1.47	45.8	52.9

In consideration of that ladder polymer PPSQ may curve in the direction perpendicular to the ladder plane, a model of oblate ellipsoid of revolution was used.

The halflength of axes A , B and the axes ratio ρ can be easily calculated by replacing M_w , D_0 and $[\eta]$ in equations (3), (4) and (5) with data from Table 1. $R_{g(E)}$ can then be calculated from equation (8). Results are listed in Table 2. The last column labeled as $R_{g(LS)}$ are experimental data from the wide angle light scattering measurement with a BI2030 light scattering spectrometer.

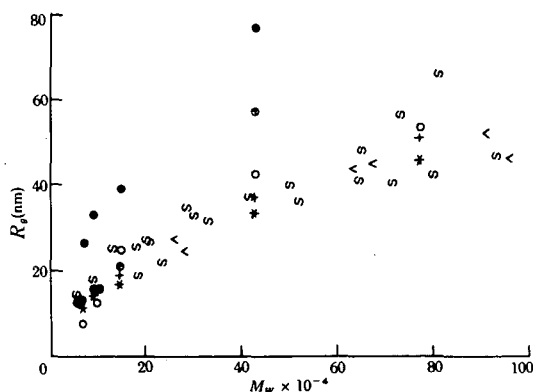


Fig. 1 The relationship between R_g and M_w .

- * — Values calculated with oblate ellipsoid model.
- + — Values calculated with free-draining random coil model.
- — Values calculated with non-draining random coil model.
- ⊕ — Values calculated with partial-draining random coil model.
- — Data from the wide angle light scattering measurement.
- ∞ — Data from Kovar et al.^[12] (toluene at 25°C).
- > — Data from Helminiak-Berry^[11] (THF at 25°C or CHCl₃ at 20°C)

The values of calculated R_g are in reasonable good agreement with the measured ones. In comparison with the radius of gyration measured by Kovar et al.^[12] and Helminiak-Berry^[11], it is found that the calculated data is also in good agreement with their experimentally determined relation of R_g and M_w as shown in Figure 1. The solvents used in our experiment and Kovar's were benzene and toluene, respectively. However, to PPSQ, both solvents are good solvents and have the similar effect on chain expansion, so that this comparison is valid. This shows that the model of oblate ellipsoid of revolution is a suitable model to describe the shape of PPSQ in dilute solution.

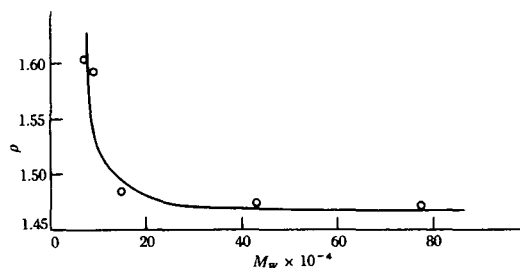


Fig. 2. The relationship between ρ and M_w

Furthermore the relation between the radius of gyration and the molecular weight can be expressed as

$$R_{g(E)} = 0.048M_w^{1/2} \text{ (nm)}$$

The axes ratios of all samples are around 1.5, indicating that the shape of PPSQ is closer to a sphere rather than a disk. It can be seen from Figure 2 that ρ decreases with the increase of M_w . This can be explained with the conclusion that we derived in the previous paper^[6]. That is, as the molecular weight increases, PPSQ molecule tends to contract due to the increase of flexibility or the development of chain branching.

3. Random coil

Results obtained from the ellipsoid model shows that the axes ratio ρ is rather small so that it may also proper to simulate with a random coil model by taking account of the hydrodynamic interaction between solute and solvent.

For free-draining and non-draining, the two extreme cases, the radius of gyration can be calculated directly from molecular weight, limiting viscosity number and translational diffusion coefficient with equations (14) and (13). For partial draining, with equation (15) and the exponent α in Mark-Houwink equation (given in the previous paper^[6]), α and $F(x)$ can first be evaluated. Then with equation (12) and data of M_w , D_0 , and $[\eta]$, the radius of gyration can be estimated. All results are listed in Table 3.

Table 3 Parameters calculated from the model of random coil

No	α	x	$F(x)$	$R_{g(P)}$ (nm)	$R_{g(F)}$ (nm)	$R_{g(N)}$ (nm)	$R_{g(LS)}$ (nm)
Y ₆	1.12	0	1	12.9	12.9	26.5	7.7
Y ₅	1.05	0	1	16.0	16.0	32.9	13.6
Y ₄	0.95	0.14	0.90	21.0	18.9	39.0	24.7
L ₇	0.74	1.60	0.45	57.4	37.3	76.8	42.6
L ₅	0.60	8.27	0.16	98.4	51.2	105.4	52.9

To compare $R_{g(LS)}$ with the calculated ones it can be seen that $R_{g(F)}$ calculated from free-draining model is in good agreement with the measured ones. Data of $R_{g(F)}$, $R_{g(P)}$ and $R_{g(N)}$ are also plotted in Figure 1. The values of $R_{g(P)}$ and $R_{g(N)}$ deviate from the $R_g - M_w$ relation greatly, whereas $R_{g(F)}$ coincides it well. This shows that PPSQ molecules in benzene can be most suitably modeled by free-draining molecules. Usually only molecules with rigid chain segments are possible to meet the requirements for free-draining model in consideration of the hydrodynamic interaction between solute and solvent. This indicates that, in the molecular weight range studied, PPSQ molecules appear as rigid chain molecules. In addition the relation between $R_{g(F)}$ and M_w can be written as

$$R_{g(F)} = 0.056M_w^{1/2}$$

After the simulation with different models, several conclusions can be made. First, the shape of PPSQ molecules in benzene can be well simulated with the models of the oblate ellipsoid of

revolution and the free-draining random coil. Second, PPSQ is a polymer with rigid chain segments. By combining the results investigated with light scattering, viscometry and NMR^[6], a third conclusion can be deduced that it is the chain branching which is responsible for the contractness of molecular shape at higher molecular weight rather than the increase of chain flexibility.

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