

SOLUTION PROPERTIES OF POLYPHENYLSILSESQUIOXANE

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ABSTRACT

The limiting viscosity number $[\eta]$ and translational diffusion coefficient D of polyphenylsilsequioxane (PPSQ) and their dependence on molecular weight M_w were studied by static and dynamic light scattering and viscometry techniques. NMR measurement was also performed to investigate PPSQ's structure. Results show that PPSQ molecules are not rigid rods and do not have fully regular ladder structure but with branches and uncondensed hydroxy groups, and their extensibility decreases with the increase of molecular weight.

INTRODUCTION

The structure of polyphenylsilsequioxane (PPSQ) was first proposed in 1960 by Brown^[1] who reported that PPSQ's chains are arranged in a *cis*-, syndiotactic, ladder-like order. Its intriguing structure has attracted much attention and several studies have been made on the rigidity of its double chains^[2-6].

The wormlike chain model was frequently used in these studies although many authors regarded PPSQ as a branched molecule. In order to find the influence of branching on the shape of the molecules, we examined the transport properties of PPSQ in dilute solution by measuring its viscosity and translational diffusion coefficient with a low angle laser light scattering spectrometer by which the influence of rotational motion, if there is any, can be diminished to the least. In this paper we report the study on the molecular structure and shape of PPSQ through the investigation of its dilution solution. A paper on simulation with various models will follow shortly.

EXPERIMENTAL

PPSQ samples were synthesized according to Brown's method and were fractionated using benzene as solvent and ethanol as nonsolvent. Five narrow fractions of medium molecular weight were used in this study. The concentrations of PPSQ-benzene solution used for the measurements of its solution properties were in the range of 10^{-4} — 10^{-2} g/ml. All solutions used in light scattering measurement were filtered through Millipore filters of 200nm pore size.

Figure 1 shows a schematic diagram of our light scattering spectrometer. The wavelength is 632.8 nm and the scattering angle, 3.8° . For static measurement the calibration coefficient of the instrument was determined based on Yin's method^[7], which consisted of the measurement of

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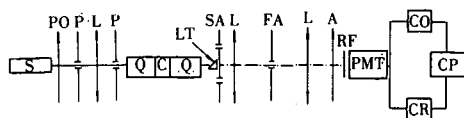


Fig. 1 Schematic diagram of the low angle light scattering apparatus

(A). analyzer; (C) cell; (CO) photocopier; (CP) computer; (CR) correlator; (FA) field aperture; (L) lens; (LT) light trap; (P) pin hole; (PMT) photomultiplier tube; (PO) polarizer; (Q) quartz block; (RF) ; red filter; (S) laser source; (SA) scattering aperture

several pure solvents with known Rayleigh ratio. The measured Rayleigh ratios $R_{\theta P}$ for polymer was analyzed with the relation

$$Kc/R_{\theta P} = 1/M_w P(\theta) + 2A_2c \quad (1)$$

where $K = 4\pi^2 n^2 (dn/dc)^2 / N_A \lambda^4$, N_A is the Avogadro number, n is the refractive index of solvent, dn/dc is the refractive index increment which is measured with a KMX-16 Laser Differential Refractometer and equal to 0.0792 ml/g. $P(\theta)$ is the scattering function. For small scattering angles it can be taken as unity. The second virial coefficient A_2 and the weight-average molecular weight M_w were obtained by measuring several solutions of different concentrations and then extrapolating to zero concentration as shown in Figure 2.

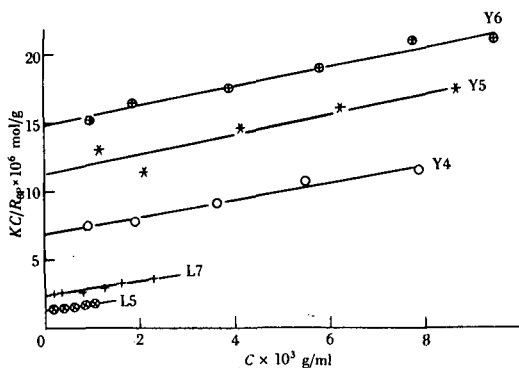


Fig. 2 Concentration dependence of $Kc/R_{\theta P}$

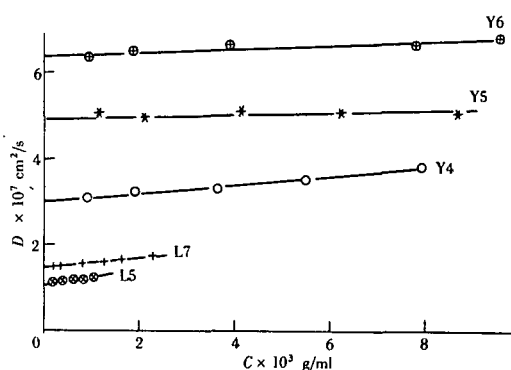


Fig. 3 Concentration dependence of D

For dynamic light scattering measurement a Langley-Ford correlator was used to generate the full autocorrelation function of the scattered intensity. The data were subsequently fitted using the method of cumulant to give the optical linewidth Γ . The translational diffusion coefficient were deduced according to equation

$$D = \Gamma q^{-2} \quad (2)$$

$$q = 4\pi n \sin(\theta/2) / \lambda$$

The translational diffusion coefficient at infinite dilution D_0 and constant k_D were obtained from Figure 3 by plotting D against concentration c , with the relation

$$D = D_0(1 + k_D c) \quad (3)$$

and extrapolating to zero concentration.

Viscometry measurements were made by using an Ubbelohde dilution viscometer with flow time of 175–350 seconds and negligible kinetic energy corrections. Data were plotted according to Huggins relation to determine the limiting viscosity number as shown in Figure 4.

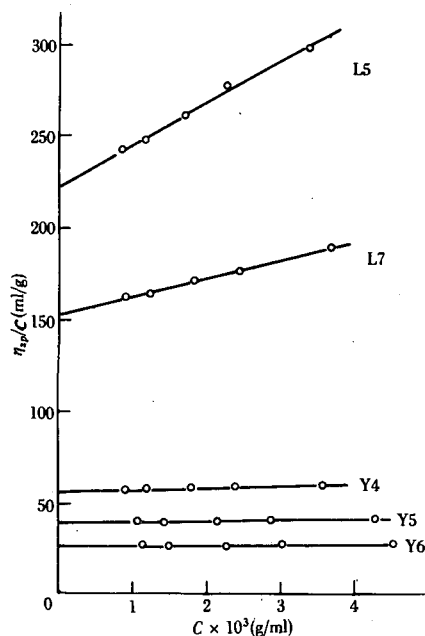


Fig. 4 Concentration dependence of viscosity

NMR measurements were performed on a WP80SY NMR spectrometer with CDCl_3 as solvent. Measurements were repeated after the samples were treated with D_2O .

All reagents used were analytical grade and all measurements were done at 25°C .

RESULTS AND DISCUSSION

Two samples, Y_4 and L_7 , were subjected to the depolarized light scattering measurement. If PPSQ molecules are anisotropic then the scattered intensity should obey the following relations

$$(R_{VV}/KMc)_{c \rightarrow 0} = 1 + (4/5)\delta^2 \quad (4)$$

$$(R_{HV}/KMc)_{c \rightarrow 0} = (3/5)\delta^2$$

However no scattered light at the direction of polarization perpendicular to that of the incident beam could be detected at all concentrations, which implies that PPSQ molecules are not rigid rods at all.

Results from static, dynamic light scattering measurements and viscosity measurements are listed in Table 1.

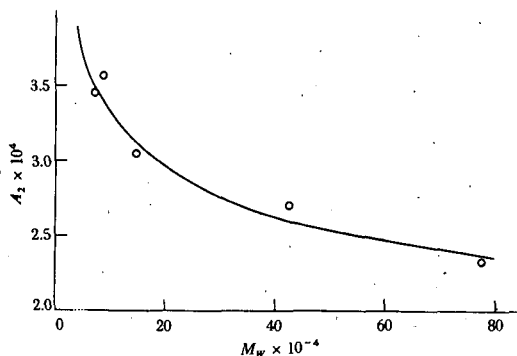
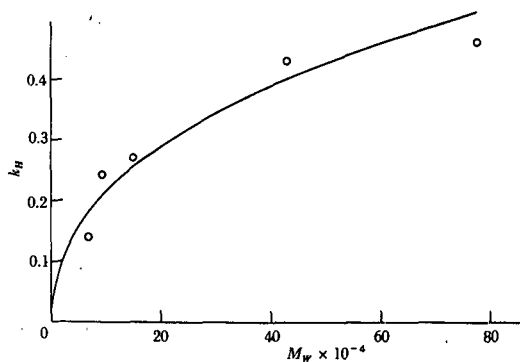
As a measure of the interaction between polymer segments and between solute and solvent molecules, the second virial coefficient also reflects the expansibility of PPSQ molecules in solution. Figure 5 clearly shows that, as the molecular weight increases, A_2 decreases. Their relation can be described by the equation

Table 1 Dilute solution parameters of PPSQ in benzene

No	$10^{-4}M_w$ (g·mol ⁻¹)	10^4A_2 (ml·mol·g ⁻²)	$[\eta]$ (ml·g ⁻¹)	k_H	10^7D_0 (cm ² ·s ⁻¹)	k_D	k'_f	k_f
Y ₆	6.8	3.44	26.5	0.14	6.37	6	40	5.8
Y ₅	8.9	3.56	39.5	0.24	4.96	1	62	5.6
Y ₄	14.6	3.05	56.6	0.27	2.97	33	56	1.8
L ₇	42.7	2.70	153	0.43	1.46	85	146	1.6
L ₅	77.1	2.32	222	0.46	1.05	185	172	1.3

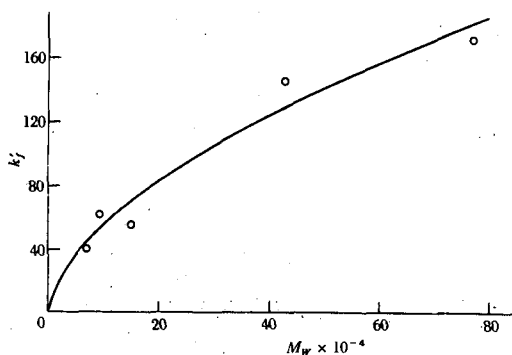
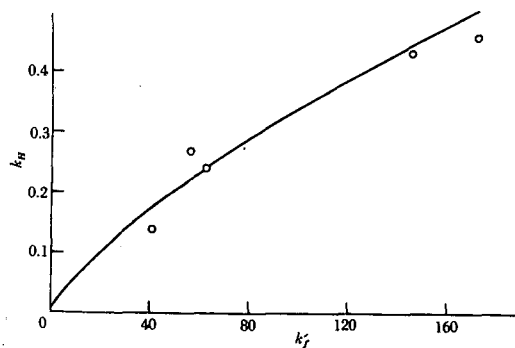
$$A_2 = 2.3 \times 10^{-4} M_w^{-0.17}$$

which indicates that when molecular weight increases, the interaction between PPSQ molecules and benzene molecules decreases, in other words, PPSQ molecules tend to contract.

Fig. 5 Molecular weight dependence of A_2 Fig. 6 Molecular weight dependence of K_H

As a general rule, Huggins constant k_H differs little with different molecular weights. But, in PPSQ-benzene system, the value of k_H increases remarkably with the increase of molecular weight (Figure 6), which has the relation

$$k_H = 1.4 \times 10^{-3} M_w^{0.44}$$

Fig. 7 Molecular weight dependence of k_f Fig. 8 The relationship between k_H and k_f

This phenomenon can be attributed to the fact that the molecular expansion factor α_f varies with molecular weight. In many cases, k_H is proportional to $\alpha_f^{-3[8]}$, thus

$$\alpha_f \propto k_H^{-1/3} \propto M_w^{-0.15}$$

i.e., α_f decreases with the increase of M_w .

The constant k_D in equation (3) consisted of two terms as shown in equation (5)^[9]. One is from thermodynamic contribution, the other from hydrodynamic contribution.

$$k_D = 2A_2M - k'_f \quad (5)$$

The values of k'_f calculated from k_D and A_2 are also listed in Table 1. Plot k'_f against M_w (Figure 7), one can obtain the relation

$$k'_f = 5.9 \times 10^{-2} M_w^{0.59}$$

Therefore

$$k_D = 4.6 \times 10^{-4} M_w^{0.83} - 5.9 \times 10^{-2} M_w^{0.59}$$

k'_f is controlled by two factors, one relates to hydrodynamic interaction between solute chain segments and solvent molecules, the other to molecular weight. Pyun and Fixman^[10] have derived an expression to describe the molecular weight dependence of k'_f .

$$k'_f = k_f^\Phi \frac{4\pi N_A}{3M} \left(\frac{k_B T}{6\pi\eta_s D_0} \right)^3 \quad (6)$$

Where k_B , T , and η_s are the Boltzmann's constant, temperature and the viscosity of the solvent respectively. k_f^Φ corresponds to k'_f in terms of solute volume fraction and relates to the hydrodynamic interaction per segment. The calculated values of k_f^Φ are listed in Table 1. Since the effect of chain length on friction has been eliminated, k_f^Φ should be independent of molecular weight provided the shape of PPSQ molecules is independent of molecular weight. However, in this study, k_f^Φ decreases as M_w increases, showing the lessening of hydrodynamic interactions. This phenomenon can also be attributed to the contraction of PPSQ molecules at higher molecular weight.

k'_f and k_H are two different constants, but they both reflect the hydrodynamic interaction between solute and solvent. So it is reasonable that there is a correlation between these two constants. Plot k'_f versus k_H , they do correspond well as shown in Figure 8 and have the relation

$$k_H = 1.2 \times 10^{-2} k'_f^{0.72}$$

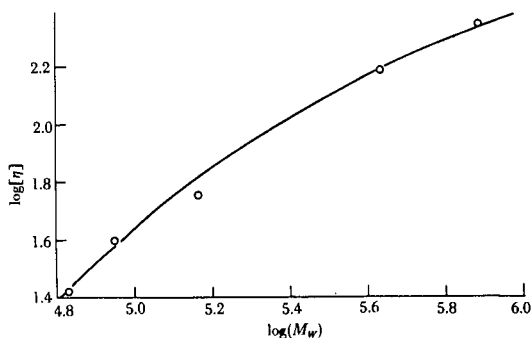
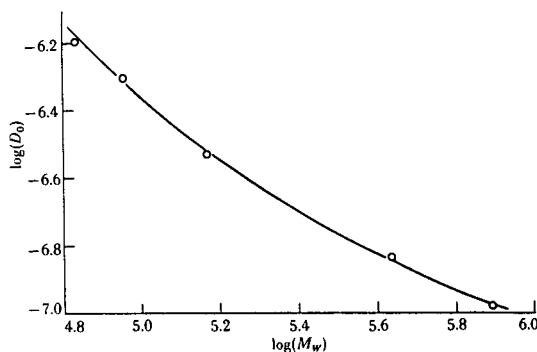
The molecular weight dependence of the limiting viscosity number and the translational diffusion coefficient is shown in double logarithmic forms in Figures 9 and 10, and may be represented by equations

$$[\eta] = K_\eta M_w^\alpha \quad (7)$$

$$D_0 = K_D M_w^{-\beta} \quad (8)$$

K_η , α , K_D and β calculated over the molecular weight range investigated are 2.2×10^{-3} , 0.86, 2.0×10^{-3} and 0.73, respectively. However, if one has a closer look at those lines in Figure 9 and Figure 10, one can see that they are not straight lines but have curvature, which indicates that

exponents α and β are not constant but change gradually with molecular weight. The values of α and β at different molecular weight were obtained by plotting tangent lines along the curves and are listed in Table 2.

Fig. 9 Molecular weight dependence of $[\eta]$ Fig. 10 Molecular weight dependence of D_0 **Table 2** Values of exponents α and β for different M_w

$10^{-4} M_w$	α	β
6.8	1.12	0.99
8.9	1.05	0.97
14.6	0.95	0.81
42.7	0.74	0.57
77.1	0.60	0.51

Exponents α and β qualitatively reflect the degree of the molecular expansion. The more extended the molecule is, the more rapidly the friction to molecular motion increases with M_w , and the larger the values of α and β are. In this study it is found that α and β values become smaller as M_w increases, showing that PPSQ molecule has a tendency of contract with the increase of M_w . This is consistent with the results obtained from the investigations of A_2 , k_H and k_f^Φ .

The extensibility of molecules is linked with its interior structures and mainly determined by the following two factors provided the external conditions, such as temperature and solvent, are kept unchanged.

One is the chain flexibility. Although the double-chain backbone of PPSQ limits its chain mobility and hence displays some rigidity, it is still possible for bending or distortion of the ladder structure to occur due to the relatively high mobility of Si—O—Si links and the incompactness of the big repeat unit, a ring of 8 elements. Furthermore, this flexibility develops as the chain length increases. The other factor is chain branching. Kovar et al.^[3] have studied PPSQ's solution properties and asserted that PPSQ is a ladder polymer with certain chain branches. During the condensation polymerization, besides the formation of energetically preferable ladder structure, it is conceivable that some hydroxy groups stray off from the right partners to react with others and results in the formation of chain branches owing to stereo hindrance or "trapping" effect in viscous surrounding. This is confirmed by our NMR measurement. Figures 11 and 12 show the NMR spectra of sample Y₆ and L₇. The relative intensity of the peak of Y₆ at chemical shift equal to 1.76

ppm is much higher than that of L_7 . After treated with D_2O , this intensity of Y_6 decreases remarkably, whereas L_7 's remains almost unchanged. In consideration of the synthesis procedure this peak can be attributed to hydroxy groups, which implies that there are uncondensed hydroxy groups in samples. Moreover, Y_6 , a sample of low molecular weight, has more uncondensed hydroxy groups and L_7 , a sample of higher molecular weight, has less uncondensed hydroxy groups but more chain branches.

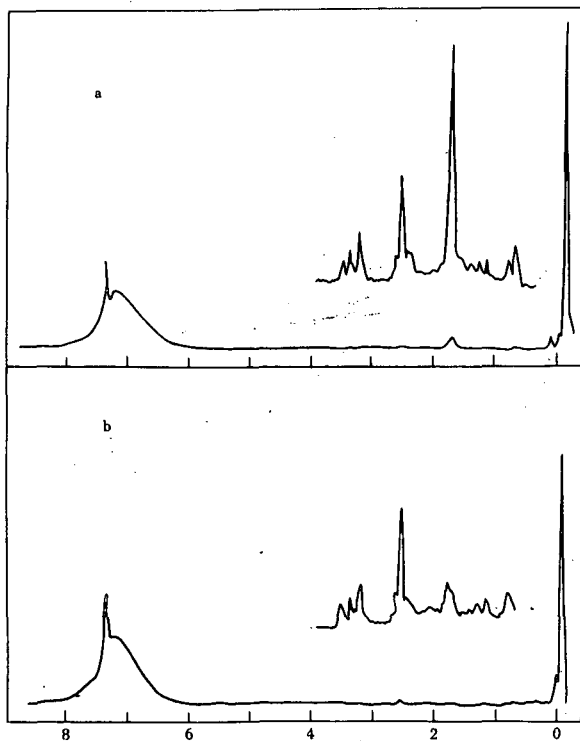


Fig.11 H^1 NMR spectra of PPSQ(Y_6)

(a) the original sample

(b) the sample treated with: D_2O

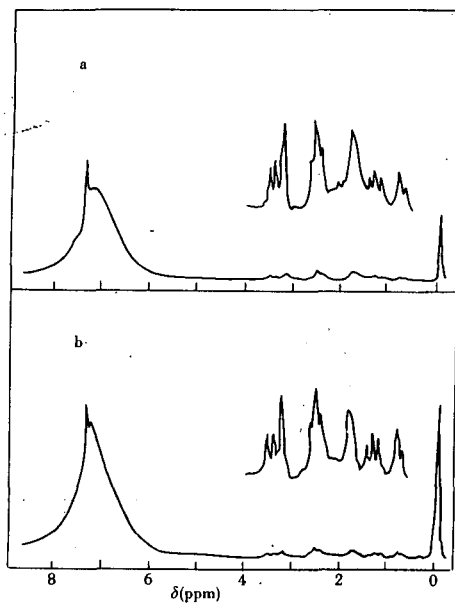


Fig.12 H^1 NMR spectra of PPSQ(L_7)

(a) the original sample

(b) the sample treated with D_2O

CONCLUSION

With the use of light scattering, viscometry and NMR techniques, and the study of the concentration and molecular weight dependence of translational diffusion coefficient and limiting viscosity number, the following conclusion can be reached.

PPSQ molecules do not have the conformation of rigid rods in dilute solution. Its extensibility decreases with the increase of M_w . It does not have a fully regular ladder structure. In its chains there are some hydroxy groups remaining uncondensed, and also some branches whose number increases gradually with M_w .

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