

SOLUTION PROPERTIES OF LADDER-LIKE POLYMER POLYPHENYLSILSESQUOXANES

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ABSTRACT

Solution properties of ladder-like polymer polyphenylsilsesquioxane (PPS) were studied by measurement of intrinsic viscosity, small angle laser light scattering and gel permeation chromatography. It was found that PPS can be modeled with a wormlike continuous cylinder rather than a wormlike coil. A plot of $(M^2/[\eta])^{1/3}$ vs. $M^{1/2}$ was employed in obtaining the persistence length $(2\lambda)^{-1}$ and effective hydrodynamic diameter. When $MW \leq 5 \times 10^5$, Mark-Houwink equation is adequate in describing the relationship between MW and $[\eta]$ with α about unity. This implies that PPS chain is semi-stiff. For GPC experiments, it was shown that universal calibration can be applied in PPS. When molecular weights of PPS are sufficiently high, their molecular weight distributions are often very broad.

Polyphenylsilsesquioxane (PPS) is a double-chain ladder-like polymer with certain degree of stiffness. It is, however, soluble in many organic solvents in spite of its ladder structure. Since its first synthesis in 1960^[1], many papers^[2-6] have been published on its solution properties. Owing to the strong dependence of its structures on the method of preparation^[6] literature data are still diffused. In this work, two samples of PPS prepared by different methods were used to study their solution properties. One of the samples (PPS-2) has perfect ladder structure as confirmed by IR and NMR spectroscopy^[7,8]. These samples were fractionated by fractional precipitation into 8 and 13 fractions respectively. Eight fractions from each sample were then characterized by viscosity, small angle laser light scattering and high performance GPC. Mark-Houwink equation for PPS in THF was obtained and universal calibration of GPC data was shown to be applicable for this system. Data were also used to test the applicability of the theories based on wormlike model by Yamakawa-Fujii^[9] and by Hearst^[10].

EXPERIMENTAL

1. Preparation of PPS samples

Sample PPS-1 was prepared by a method similar to that of Brown^[11]. For sample PPS-2, PhSiCl_3 was hydrolyzed in ether and then the by-products were removed through azeotropic distillation^[7]. PPS-1 was fractionated in benzene-methanol system into 8 fractions while PPS-2 was fractionated in toluene-methanol system into 13 fractions, out of which 8 fractions were used for characterization.

2. Intrinsic viscosity measurement

Ubbelohde dilution viscometer and A.R. THF were used. Temperature was kept at $25 \pm 0.05^\circ\text{C}$ unless otherwise specified. Five concentrations of solutions were measured and intrinsic

viscosities were obtained by extrapolating η_{sp}/c and $\ln \eta_r/c$ to $c \rightarrow 0$.

3. Weight average molecular weight measurement

Chromatix KMX-6 light scattering photometer and Chromatix KMX-16 differential refractometer were used. dn/dc of PPS in THF at 25°C was found to be 0.135 at $\lambda = 6328 \text{ \AA}$, $\bar{M}_w$ and $[\eta]_{\text{THF}}$ measured are listed in Table 1.

Table 1 $\bar{M}_w$ and $[\eta]_{\text{THF}}$ of PPS fractions

Fraction	A-1*	A-2	A-3	A-4	A-5	A-6	A-7	A-8
$\bar{M}_w \times 10^{-5}$	12.5	9.62	4.55	3.16	2.44	1.52	0.50	0.20
$[\eta]_{\text{THF}}(\text{ml/g})$	370	324	191	148	88	40	14	6.6

Fraction	B-1**	B-2	B-3	B-4	B-5	B-6	B-7	B-8
$\bar{M}_w \times 10^{-5}$	5.58	3.63	3.33	1.72	1.50	1.36	1.16	0.75
$[\eta]_{\text{THF}}(\text{ml/g})$	146	103	107	67	43	39	31	23

* A series are fractions of PPS-1

** B series are fractions of PPS-2

4. Gel permeation chromatography

Gel permeation chromatograph of Waters model 244 with UV detector ($\lambda = 254 \text{ nm}$) was used. High performance columns of Shodex A-80M and J μ 101 + J μ 103 + J μ 105 three columns set were employed for PPS-1 and PPS-2 respectively. The molecular weight separation range of these columns is 10^2 to 4×10^6 . Monodispersed PS standards with molecular weights from 2,350 to 2.7×10^6 supplied by Waters Associates Inc. were used to calibrate the columns.

RESULTS AND DISCUSSIONS

1. Viscosity behavior

According to the wormlike continuous cylinder model of polymer chain put forth by Yamakawa-Fujii^[9], the following equation should hold:

$$[\eta] = \Phi L_r^{3/2} / \lambda^3 M \quad (1)$$

where Φ is the viscosity function depending on the effective hydrodynamic diameter d and contour length L , $L_r = L/\lambda^{-1}$, λ^{-1} is Kuhn's statistical segment length and M is the molecular weight. Since $L = M/M_L$ where M_L is the relative molecular mass per unit contour length, Eq. (1) can be transformed into

$$(M^2/[\eta])^{1/3} = \Phi^{-1/3} (M_L \lambda)^{1/2} M^{1/2} \quad (2)$$

Using Φ values at different L_r and d_r (where $d_r = d/\lambda^{-1}$) given by Yamakawa and Fujii, $(M^2/[\eta])^{1/3}$ vs $M^{1/2}$ plots give straight lines as illustrated in Fig. 1 a.

For the modified equation of Hearst's wormlike coil model, we have

$$[\eta] = 2.19 \times 10^{23} [1 + 0.891\sigma(\lambda L)^{-1/2} + O(\lambda L)^{-1}]^{-1} (L\lambda^{-1})^{3/2} / M \quad (3)$$

$$\text{where} \quad \sigma = -\ln(b/\lambda^{-1}) - 2.43 + b/a \quad (4)$$

b being the distance between beads on the coil and a the diameter of frictional unit. Assume $b = a$

and substitute it into (4), we have

$$\sigma = -\ln d_r - 1.431 \quad (4')$$

$d_r = b/\lambda^{-1} = a/\lambda^{-1}$ is the reduced diameter. Substitute (4') into (3), we have

$$(M^2/[\eta])^{1/3} = KM^{1/2} \quad (5)$$

where

$$K = [1 - 0.891(\ln d_r + 1.431)(\lambda M/M_L)^{-1/2}]^{1/3} (\lambda M_L)^{1/2} \times (2.19 \times 10^{23})^{-1/3} \quad (6)$$

Similarly, in a broad range of molecular weight, $(M^2/[\eta])^{1/3}$ vs. $M^{1/2}$ plots give straight lines (Fig. 1b). The slope K is generally higher than that of Yamakawa-Fujii theory.

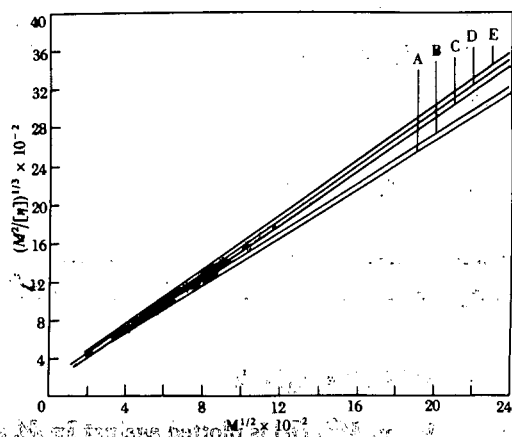


Fig. 1a $(M^2/[\eta])^{1/3}$ vs $M^{1/2}$ plots

(Yamakawa-Fujii theory)

A: $\lambda^{-1} = 159$ $d_r = 0.06$ B: $\lambda^{-1} = 159$ $d_r = 0.03$

C: $\lambda^{-1} = 127$ $d_r = 0.10$

D: $\lambda^{-1} = 127$ $d_r = 0.06$ E: $\lambda^{-1} = 127$ $d_r = 0.03$

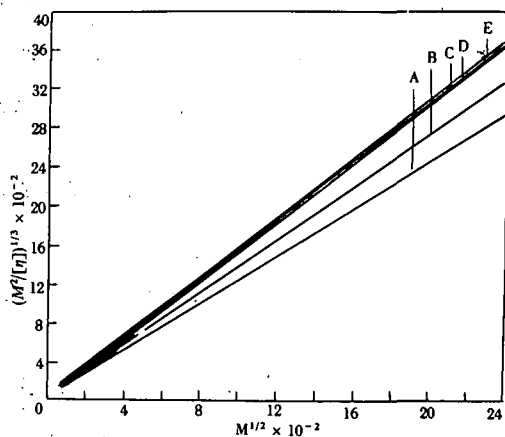


Fig. 1b $(M^2/[\eta])^{1/3}$ vs $M^{1/2}$ plots (Hearst theory)

A: $\lambda^{-1} = 159$ $d_r = 0.06$ B: $\lambda^{-1} = 159$ $d_r = 0.03$

C: $\lambda^{-1} = 127$ $d_r = 0.10$

D: $\lambda^{-1} = 127$ $d_r = 0.06$ E: $\lambda^{-1} = 127$ $d_r = 0.03$

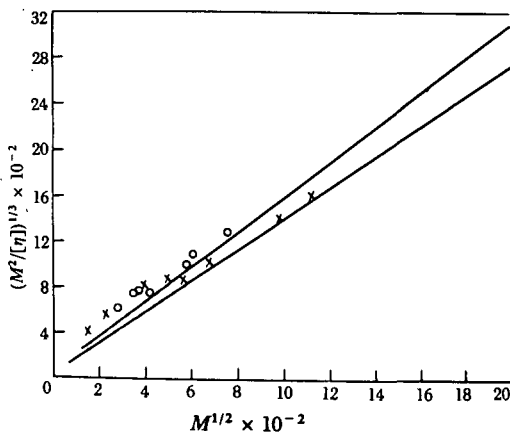
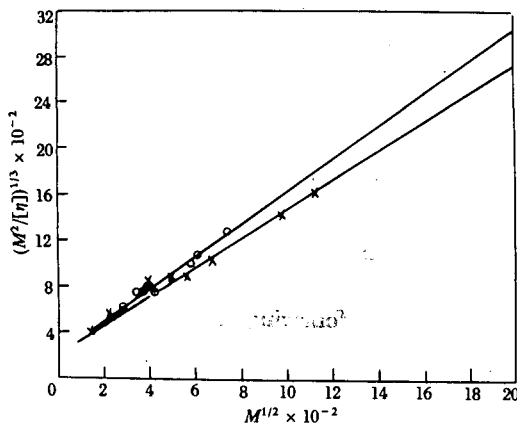


Fig. 2 $(M^2/[\eta])^{1/3}$ vs. $M^{1/2}$ plots (Hearst theory the right side one)

○ for PPS × for PS

The above-mentioned two graphic methods are applied to PPS, the results of which are shown in Fig. 2. The experimental data of both PPS-1 and PPS-2 fit very well the graphic method deduced from wormlike continuous cylinder theory of Yamakawa and Fujii. In the case of using Hearst's wormlike coil theoretical graphic method, the slope obtained is comparatively larger and the experimental points do not fit very well.

From the graphic method based on Yamakawa-Fujii's theory, we obtained persistence length $(2\lambda)_{\text{PPS-1}}^{-1} = 80 \text{ \AA}$ and $(2\lambda)_{\text{PPS-2}}^{-1} = 64 \text{ \AA}$, effective hydrodynamic diameter $d_{\text{PPS-1}} = 4.77 \text{ \AA}$ and $d_{\text{PPS-2}} = 3.81 \text{ \AA}$. Relatively large values of persistence length of PPS molecules indicate certain degree of chain stiffness.

For the wormlike model, the following relation holds

$$\langle s^2 \rangle / M = s(L_r/2)\lambda^{-1}/6M_L \quad (7)$$

where $\langle s^2 \rangle$ is the radius of gyration. As $L_r \rightarrow \infty$, $s(L_r/2) \rightarrow 0$,

therefore $\lim_{M \rightarrow \infty} \langle s^2 \rangle / M = 2.57 \times 10^{-17}$ (for PPS-1)

$$\lim_{M \rightarrow \infty} \langle s^2 \rangle / M = 2.06 \times 10^{-17} \text{ (for PPS-2)}$$

Higher values of PPS also indicate that PPS chains possess certain degree of stiffness.

When the molecular chain is of the extended rigid cylinder, the following equation should hold

$$M^2/[\eta] = (90M_L^3/\pi N_A)(a_1 - a_2 \ln(M_L d) + a_2 \ln M) \quad (8)$$

where N_A is Avogadro constant, a_1 and a_2 are constants. When $M^2/[\eta]$ is plotted against $\ln M$, a straight line should be obtained. Fig. 3 is such a plot for PPS. Instead of a straight line, a concave curve was obtained indicating that the molecular chain is not of the shape of a rigid rod.

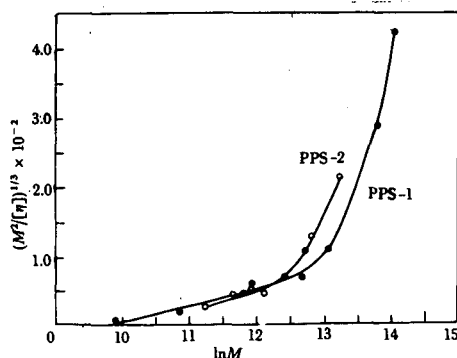


Fig. 3 $(M^2/[\eta])^{1/3}$ vs. $\ln M$ plots

In Eq. 1, Φ is functions of L_r and d_r , and it has the following form

$$\Phi = \Phi_{\infty}(1 + A_0 L_r^{-1/2})^{-1} \quad (9)$$

where [5]

$$A_0 = f(d_r) \quad (10)$$

Substitute (9) into (1), the following equation is obtained.

$$[\eta] = [(\Phi'_{\infty} L_r^{1/2}) / (L_r^{1/2} + A_0)] (L_r^{3/2} / \lambda^3 M) \quad (11)$$

Take logarithm for both sides of equation (11) and then take derivative with respect to $\ln M$, we have

$$d \ln [\eta] / d \ln M = 1 - d \ln (L_r^{1/2} + A_0) / d \ln M \quad (12)$$

From Mark-Houwink equation we have

$$\alpha = d \ln [\eta] / d \ln M \quad (13)$$

Compare (12) with (13), we obtain

$$\alpha = 1 - d \ln (L_r^{1/2} + A_0) / d \ln M \quad (14)$$

$\ln (L_r^{1/2} + A_0)$ is an increasing function of $\ln M$ and the second term at the right side of equation (14) is bigger than zero. When L_r is very small, $\alpha \rightarrow 1$; when $L_r \rightarrow \infty$, $\alpha \rightarrow \frac{1}{2}$. This means for wormlike continuous cylinder chain, α decreases with increase of molecular weight. The experimental data were plotted in Fig. 4, confirming the result of theoretical prediction. It is obvious that wormlike cylinder theory is very useful in characterizing the solution properties of PPS. From Fig. 4, we obtained Mark-Houwink equations of PPS as follows:

$$[\eta]_{\text{THF}} = 2.26 = 10^{-4} M^{1.03} \quad (\text{PPS-1})$$

$$[\eta]_{\text{THF}} = 2.33 = 10^{-4} M^{1.02} \quad (\text{PPS-2})$$

The high values of α for PPS are also an indication of chain stiffness.

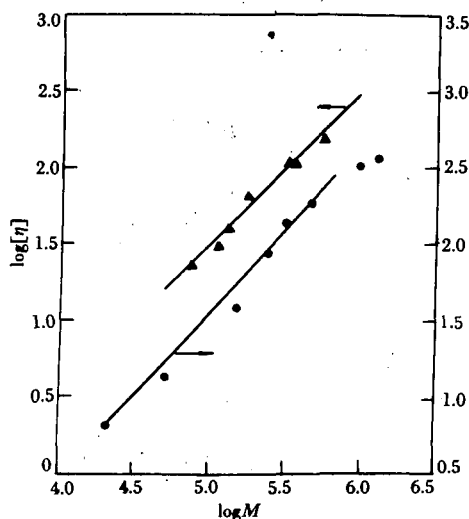


Fig. 4 $\log[\eta]$ vs. $\log M$ plot

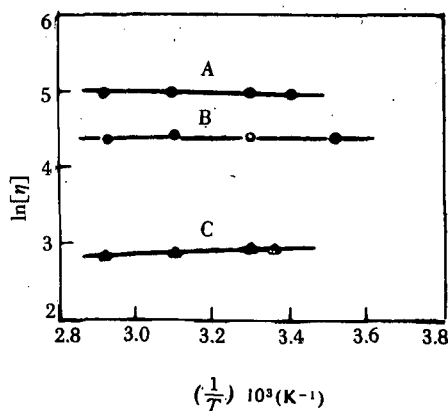


Fig. 5 Temperature dependence of intrinsic viscosities

Temperature dependence of $[\eta]$ of PPS as well as of two kinds of flexible polysiloxanes, polyphenylmethylsiloxane and polydimethylsiloxane, were compared in Fig. 5. All of their $[\eta]$ have very low temperature dependence. Since polydimethylsiloxane chain is very flexible, low temperature dependence of $[\eta]$ of PPS cannot be attributed to the stiffness of chain of PPS.

2. GPC behavior of PPS

It is quite interesting to see whether the universal calibration of GPC data of PPS is still applicable to this double chain polymer. As mentioned above, PPS molecule can be treated with the wormlike chain theory. We have

$$[\eta]M = \Phi L_r^{3/2} \lambda^{-3} = f(\Phi, \langle s^2 \rangle) \quad (15)$$

If there is no adsorption of solute and partition is at equilibrium, the distribution coefficient of GPC column, K_d , is equal to $(\sum_i n_i)/N_k$. Where n_i is the number of conformation of polymer molecule which can get into the micropore of the packing; N_k is the total number of conformations of the polymer molecules. K_d is a function of solvation term Φ as well as of the entropy term $\langle s^2 \rangle / r$ where r is the radius of micropore. Equation (15) describes the result of the joint effects of these two parameters. Therefore, universal calibration should be applicable for wormlike chain. In Fig. 6, $\log[\eta]M$ of fractions of two PPS samples and PS standards in THF are plotted against V_p , peak retention volume, for two different column sets. For each column set, points of $\log[\eta]M-V_p$ plot for PPS and PS lie on the same straight line, indicating that universal calibration is applicable for PPS.

The molecular weight and molecular weight distribution of PPS depend significantly on the method of preparation. High molecular weight samples usually have wide molecular weight distribution. In Fig. 7, a typical GPC chromatogram of a PPS sample with perfect ladder structure is shown. $\bar{M}_w$ and $\bar{M}_w / \bar{M}_n$ of this sample are 3.64×10^5 and 10.4 respectively, showing a rather broad distribution.

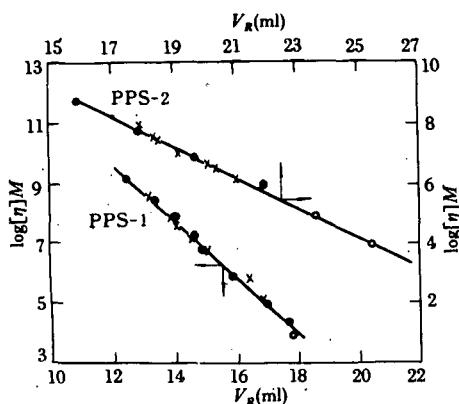


Fig. 6 Universal calibration plot

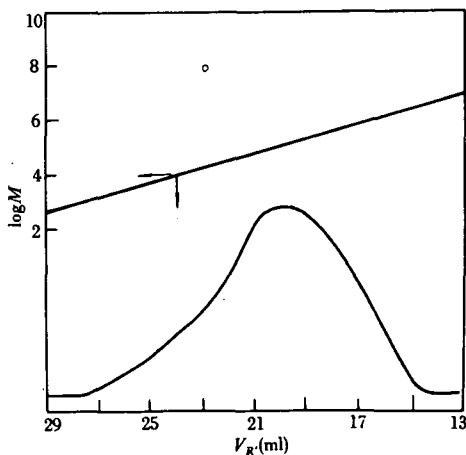


Fig. 7 GPC chromatogram of PPS

CONCLUSION

1. A graphic method of $(M^2/[\eta])^{1/3} - M^{1/2}$ plots based on wormlike chain theories of Yamakawa-Fujii and of Hearst can be used to characterize the hydrodynamic behavior of wormlike chain.
2. Viscosity behavior of PPS can be treated with Yamakawa-Fujii wormlike continuous cylinder theory. Parameters such as $(2\lambda)^{-1}$, d and $\langle s^2 \rangle / M$ can be obtained. It is found

that Hearst's wormlike coil theory would not give satisfactory result for PPS.

3. Even if the ladder structure of PPS is perfect, PPS chains possess a certain degree of stiffness. Extended rigid chain theory is not applicable.
4. Mark-Houwink equation was obtained for PPS in THF. α decreases as molecular weight exceeds 5×10^5 .
5. Temperature dependence of $[\eta]$ of PPS is very small. This is not due to chain stiffness.
6. GPC universal calibration is applicable for PPS as predicted by Yamakawa-Fujii theory. High molecular weight PPS samples usually have broad molecular weight distribution.

Keywords:

polymer solution, ladder polymer, wormlike cylinder, polyphenylsilsesquioxane

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