

## **An experimental study of the unperturbed chain dimensions of poly(tetramethyl-*p*-silphenylene-siloxane)**

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### **Summary**

Experimental values of the characteristic ratio of the unperturbed dimensions of poly(tetramethyl-*p*-silphenylene-siloxane) were obtained from intrinsic viscosities and osmotic pressures. It was found that the characteristic ratio of this polymer is  $1.55 \pm 0.30$  when the phenylene group is treated as a virtual bond, and  $4.51 \pm 0.40$  when the individual bonds in the phenylene group are taken into account separately. This value is unexpectedly low, considering the usual stiffening effect of the *p*-phenylene group. Apparently this group can also have a "buffering" effect which decreases stiffness, by reducing interactions among the atoms or groups preceding it and succeeding it along the chain backbone.

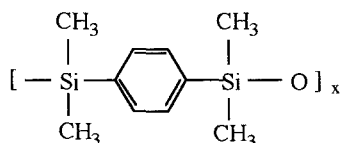
**Key words:** Intrinsic viscosities, osmotic pressures, unperturbed dimensions, characteristic ratio, chain stiffness, poly(tetramethyl-*p*-silphenylene-siloxane).

### **Introduction**

The unperturbed mean-square end-to-end length  $\langle r^2 \rangle_0$  of a polymer chain is a convenient index of its domain in space. It is usually expressed as the characteristic ratio (CR)  $\langle r^2 \rangle_0/nl^2$ , which is the ratio of this unperturbed mean-square length to the product of the number  $n$  of skeletal bonds and the square of their average bond length  $l$ . The ratio converges to a limit for large  $n$ , and this limiting value is widely used as a measure of equilibrium chain stiffness. It depends on (i) bond geometry, specifically bond lengths, bond angles, and locations of rotational states, and (ii) conformational preferences, arising from intrinsic rotational potentials and intramolecular attractions and repulsions. A great deal of work has been done in this area, both theoretically and experimentally (1,2), for a variety of polymer chains (3-5).

Experimentally, the unperturbed dimension  $\langle r^2 \rangle_0$  can be measured in two ways. The first is the direct measurement of  $\langle r^2 \rangle_0$  by light scattering or solution viscometry under  $\Theta$  conditions, where the attractive forces between polymer segments exactly nullify the excluded volume expansion (1,2). Another way is to measure  $\langle r^2 \rangle$  under non- $\Theta$  conditions and then convert it to  $\langle r^2 \rangle_0$  from knowledge of the polymer-solvent interactions (1,2). In the present investigation, the second approach was employed.

The siloxane-type polymer, poly(tetramethyl-*p*-silphenylene-siloxane) [poly(TMPS)]



has received considerable attention recently (6-8). This polymer has greater thermal stability than poly(dimethylsiloxane), with repeat unit  $[-\text{Si}(\text{CH}_3)_2\text{O}-]$ , and has a much higher melting point (148 °C).

The main purpose of the present study was to determine values of the unperturbed dimensions of these chains, thereby gauging the effects of the *p*-phenylene groups on equilibrium chain stiffness.

### Details of the Experimental Approach

The determination of chain dimensions by means of solution viscometry is based on the well-known relationship (2,5)

$$[\eta] = \Phi \langle r^2 \rangle^{3/2} / M \quad (1)$$

where  $[\eta]$  is the intrinsic viscosity of the polymer in a convenient solvent,  $M$  the molecular weight of the polymer,  $\Phi$  a hydrodynamic constant (equal to  $2.1 \times 10^{21}$  dl cm<sup>-3</sup> mol<sup>-1</sup> in a good solvent), and  $\langle r^2 \rangle$  the chain dimension as perturbed by the long-range interactions. The unperturbed chain dimension  $\langle r^2 \rangle_0$  is related to  $\langle r^2 \rangle$  by the expansion factor  $\alpha = [\langle r^2 \rangle / \langle r^2 \rangle_0]^{1/2}$ . Thus,

$$[\eta] = \Phi [\langle r^2 \rangle_0 / M]^{3/2} M^{1/2} \alpha^3 \quad (2)$$

The required values of  $\alpha$  can be obtained from the Flory-Orofino expression (9),

$$A_2 M / [\eta] = (2^{5/2} \pi N / 3^3 \Phi) \ln [1 + (\pi^{1/2} / 2) (\alpha^2 - 1)] \quad (3)$$

where  $N$  is Avogadro's number, and  $A_2$  the second virial coefficient (which is a measure of the extent of departure from the unperturbed or  $\Theta$  system) (1,2). The required values of  $A_2$  and  $M$  can be obtained from membrane osmometry.

### Experimental Details

*Fractionation.* The samples, which were obtained from Dow Corning Corporation, were fractionated to decrease their polydispersity. This was done by fractional precipitation, which depends on the decrease in solubility with increase in molecular weight. Specifically, the polymer was dissolved in benzene to a concentration of approximately 2 wt %, and a mixture of 99 % methanol and 1% water was chosen as non-solvent. The percent water employed was found to be critical in ensuring the separation of an amorphous polymer-solvent phase, rather than one in which the polymer is crystalline (6). The non-solvent was added slowly until a slight cloudiness developed. The mixture was warmed until the turbidity disappeared, and then cooled slowly back to the original temperature ( $30 \pm 0.1$  °C). A total of fifteen fractions were thus collected. Portions of the fractions were characterized by gel permeation chromatography (Waters Model 599), using tetrahydrofuran as solvent, and polystyrene as the calibration material. The average value thus obtained for the polydispersity ratio  $M_w/M_n$  (of weight-average to number-average molecular weights) was 1.033.

*Viscometry Measurements.* The intrinsic viscosities of the poly(TMPS) fractions in toluene at several temperatures were measured using an Ubbelohde viscometer in the usual manner (10). The concentrations were prepared individually by weight and the solutions were filtered directly into the viscometer. In this way, problems of compounded errors in dilution procedures were avoided.

*Membrane Osmometry Measurements.* Portions of the fractions were used here as well, and degassed toluene was used as solvent. Values of the number-average molecular weight and second virial coefficient were obtained by means of membrane osmometry in the usual manner (10). Measurements were carried out with a Hewlett-Packard Model 501 High Speed Membrane Osmometer, operated at several temperatures.

### Results and Discussion

The intrinsic viscosities of the polymer in toluene at different temperatures were obtained by extrapolating the viscosity data to infinite dilution, as shown in Figure 1. Values of  $[\eta]$  for the fractions

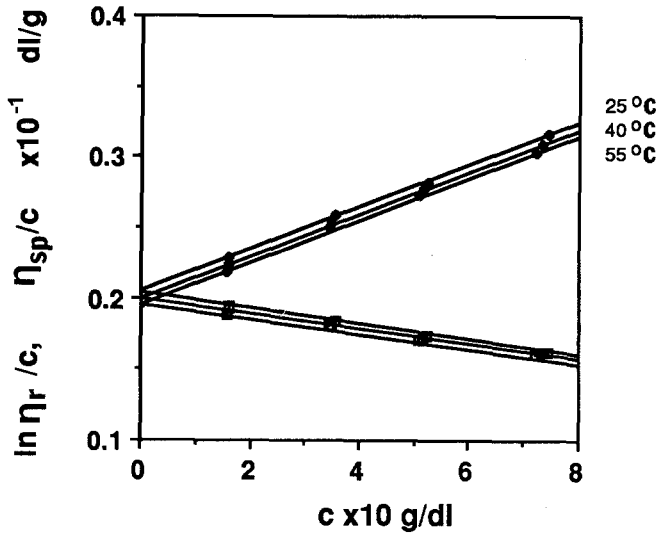


Figure 1. Intrinsic viscosities of poly(tetramethyl-*p*-silphenylene-siloxane) at several temperatures.

at various temperatures are given in the third column of Table 1.

The number-average molecular weights and second virial coefficients were obtained from the membrane osmometry data, using the equation

$$\pi/c = RT(1/M + A_2c) \quad (4)$$

where  $\pi = \rho g \Delta h$  is the osmotic pressure,  $\rho$  is the density,  $\Delta h$  is the hydrostatic pressure head,  $T$  is the absolute temperature, and  $c$  is the concentration. A typical plot is shown in Figure 2. By extrapolation to infinite dilution, values of  $A_2$  and  $M$  were obtained for the fractions used in this part of the study. The results are listed in the fourth and the fifth columns of Table 1.

The known values of  $M$  and  $A_2$  were used in Equation (3) to calculate values of the expansion factor  $\alpha$ . Rearranging Equation (1), one obtains

$$\langle r^2 \rangle_o / nl^2 = \left[ \frac{[\eta]}{\Phi M^{1/2} \alpha^3} \right]^{2/3} M_o l^2 \quad (5)$$

**Table 1. Experimental Data and Results on Poly(tetramethyl-*p*-silphenylene-siloxane) Fractions**

Fraction	T °C	[ $\eta$ ] dl g <sup>-1</sup>	10 <sup>3</sup> A <sub>2</sub> cm <sup>3</sup> mol g <sup>-2</sup>	10 <sup>-5</sup> M <sub>n</sub> g mol <sup>-1</sup>	$\alpha$	CR	
						n <sub>r</sub> = 3*	n <sub>r</sub> = 7**
A	25.0	2.03	1.18	3.82	1.88	1.63	4.31
	40.0	2.00	1.18	3.82	1.90	1.58	4.18
	55.0	1.97	1.18	3.82	1.91	1.55	4.10
B	25.0	2.01	1.12	3.60	1.77	1.86	4.92
	32.5	2.00	1.13	3.60	1.79	1.81	4.79

\* Using a virtual bond for the phenylene group.

\*\* Using individual bonds for the phenylene group.

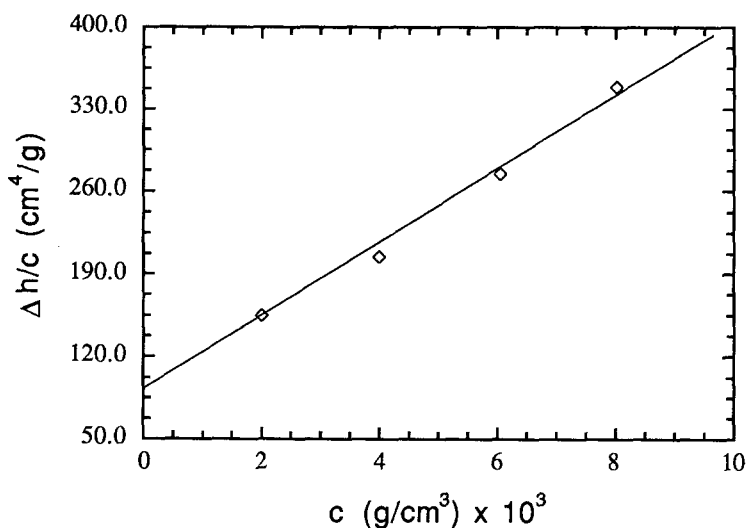


Figure 2. A typical plot of osmometry results.

where  $l$  is the average skeletal bond length, and  $M_0$  is the average molecular weight per backbone bond. The first of these two quantities is given by

$$l^2 = \sum l_i^2 / n_r \quad (6)$$

where  $l_i$  is a particular bond length, and  $n_r$  is the number of skeletal bonds in the repeat unit. Therefore

$$M_0 = M_i/n_r \quad (7)$$

where  $M_i$  is the molecular weight of the repeat unit. For the poly(TMPS) chain,  $n_r$  is 3 when the phenylene group is taken to be a virtual bond; in this case,  $M_0$  is 69.3 g/mol, and  $l^2$  is 16.23 Å<sup>2</sup>. Alternatively, every skeletal bond can be treated separately, including those in the phenylene group; in this case,  $n_r$  is 7,  $M_0$  is 29.7 g/mol, and  $l^2$  is 2.63 Å<sup>2</sup>.

The characteristic ratios thus calculated are given in the last two columns of Table 1. The values obtained range from 1.55 to 1.86 for  $n_r$  equal to 3, and from 4.10 to 4.92 for  $n_r$  equal to 7. It is not very reliable to estimate the temperature dependence of the unperturbed dimensions from data of this type, but it does appear to be negative.

The values obtained for the characteristic ratio are surprisingly low, considering the expected stiffening effect of the *p*-phenylene group. Apparently this group can also have a "buffering" effect which decreases stiffness, by reducing interactions among the atoms or groups preceding it and succeeding it along the chain backbone (11). The introduction of rings into the chain backbones of polymers can increase their rigidity (12), but apparently not necessarily when the rings are separated by a number of more flexible skeletal bonds. This conclusion seems to be supported by results reported for several polymers having this type of structural unit, including poly(phenylene oxide) (13), poly(ethylene terephthalate) (14), and 2,6-disubstituted phenylene oxide polymers (15).

### Acknowledgment

It is a pleasure to acknowledge the financial support provided by the National Science Foundation through Grant DMR 89-18002 (Polymers Program, Division of Materials Research).

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Accepted June 14, 1993 K