[Contribution from the Department of Chemistry of Cornell University]

Molecular Dimensions of Polydimethylsiloxanes[1]

By P. J. Flory, L. Mandelkern, J. B. Kinsinger and W. B. Shultz

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Intrinsic viscosities of carefully fractionated polydimethylsiloxanes have been determined in methyl ethyl ketone and in phenetole at the limiting critical miscibility temperatures (Θ) for $M = \infty$, 20 and 83° for the two solvents, respectively. Molecular weights were established by osmotic pressure measurements. The intrinsic viscosity $[\eta]_\Theta$ in methyl ethyl ketone at 20° is accurately proportional to $M^{1/2}$ from $M = 52{,}500$ to $685{,}000$. The constant $K = [\eta]_\Theta/M^{1/2}$ has the value 0.80×10^{-3} at 20°. Less extensive measurements in phenetole at 83° indicate that K is nearly independent of the temperature. The root-mean-square end-to-end length ratio, $(\overline{r^2_0}/M)^{1/2}$, as calculated from K exceeds the free rotation value by 50%. This disparity is somewhat less than has been found for other polymers.

Introduction

The determination of the dimensions of polymer molecules from dilute solution viscosity measurements has been demonstrated in a series of recent papers.[2-5] This method depends in the first place on the specification of a solvent medium in which the osmotic forces acting on the polymer molecule are exactly zero. When this condition is fulfilled, the average configuration of the polymer molecule in solution and its average dimensions are "unperturbed" in the sense that they depend only on the bond structure of the polymer chain including the influence of hindrances to free rotation about these bonds. Since the intrinsic viscosity depends directly on the volume occupied by the chain, its determination in an "ideal" solvent as specified above affords a means for ascertaining the unperturbed dimensions of the chain.[2,6]

The intrinsic viscosities of polyisobutylene,[2] polystyrene,[2,5] natural rubber,[3] gutta percha,[3] cellulose tributyrate[4] and cellulose tricaprylate[4] have been shown to be in quantitative accord with the above interpretation, and their unperturbed dimensions have been deduced in this manner. This paper presents the results of similar studies on polydimethylsiloxane fractions.

Experimental

Materials.—Four polydimethylsiloxanes said to have been prepared under conditions which should avoid insofar as possible the introduction of units of functionality exceeding two were used in this study. Two of these, having viscosity-average molecular weights of about 100,000 and 125,000, designated A and B, respectively, were made available to us by the General Electric Laboratories, Silicone Division. The other two, designated C and E, were prepared by the Dow-Corning research group at the Mellon Institute.[7] Their average molecular weights according to intrinsic viscosity measurements were 2.2×10^6 and 0.66×10^6, respectively. All four samples dissolved completely in toluene and in methyl ethyl ketone without evidence of a gel component. This observation constitutes strong evidence for a preponderantly linear structure essentially uninterrupted by branching.

The solvents used for viscosity and osmotic measurements were reagent grade. They were carefully dried and distilled before use.

Fractionation.—Polymers A and B were fractionated from solutions in ethyl acetate at concentrations of 1 g./100 ml. by the addition of methanol. After a sufficient quantity of this precipitant had been added to produce a permanent turbidity at 30°, the solution was warmed until it became homogeneous, then placed in a constant temperature bath at 30.0°. After stirring gently for 30 minutes, the precipitate was allowed to settle for 24 hours, and the supernatant liquor was separated by decantation. The precipitated fraction was washed with methanol, dissolved in ethyl acetate, filtered to remove accumulated dirt, then transferred to a weighing bottle from which the solvent was removed by evaporation, the process being completed in vacuum at 60 to 80°. Washings were transferred to the main solution, and the next fraction was separated in the same manner.

Three fractions were separated similarly from polymer C, the third being retained for use in the precipitation measurements only. A lower concentration of about 0.3 g./100 ml. of ethyl acetate was used in order to effect adequate fractionation at the higher molecular weight. Polymer E was subjected to a rough preliminary fractionation. Three middle fractions consisting of about 30% of the original were combined and subjected to careful refractionation from an ethyl acetate solution containing about 0.15 g. of polymer per 100 ml. The third fraction thus obtained was used in the osmotic and viscosity studies (Table I).

Intrinsic Viscosities.—Dilute solution viscosities were measured according to procedures described previously,[2] and the extrapolation of the specific viscosity–concentration ratio, η_{sp}/c (in 100 ml./g.), to infinite dilution was carried out by established methods. The constant k in the Huggins[8] relationship

$$\eta_{sp}/c = [\eta] + k[\eta]^2c \qquad (1)$$

assumed abnormally high values of 0.7 to 0.8 in the poor solvents methyl ethyl ketone (MEK) and phenetole. Normal values of about 0.35 were observed in toluene, a good solvent.

Osmotic Pressure.—Osmometers of the Bureau of Standards design[9] were used.[3,4] Membranes were of gel cellophane. All measurements were carried out in methyl ethyl ketone at 30°. The surface tension of solutions in this solvent containing up to 0.5 g./100 ml. of polysiloxane did not differ detectably from that of the pure solvent, according to the capillary rise method. Thus, the procedure adopted by Scott,[10] involving the use of polysiloxane solutions differing in concentration on either side of the membrane proved to be unnecessary. Thorough cleaning of the capillaries with strong aqueous caustic solution after each measurement was essential, however; results obtained otherwise displayed anomalous irregularities.

The final osmotic pressure was recorded only after the

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[2] (a) T. G. Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.*, **53**, 197 (1949); This Journal, **73**, 1909 (1951); (b) *ibid.*, **73**, 1915 (1951); (c) *J. Polymer Sci.*, **5**, 745 (1950).

[3] H. L. Wagner and P. J. Flory, This Journal, **74**, 195 (1952).

[4] L. Mandelkern and P. J. Flory, *ibid.*, **74**, 2517 (1952).

[5] L. H. Cragg, T. E. Dumitru and J. E. Simkins, *ibid.*, **74**, 1977 (1952).

[6] P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949); P. J. Flory and T. G. Fox, Jr., This Journal, **73**, 1904 (1951).

[7] We are indebted to Dr. R. O. Sauer of the Silicone Products Dept., General Electric Company and to Dr. E. L. Warrick of the Mellon Institute for generously furnishing us with the various samples.

[8] M. L. Huggins, This Journal, **64**, 2716 (1942).

[9] S. G. Weissberg and G. A. Hanks, unpublished.

[10] D. W. Scott, This Journal, **68**, 1877 (1946).

TABLE I

POLYDIMETHYLSILOXANE FRACTIONS; PRINCIPAL DATA

Polymer fraction	Original polymer, %	[η] MEK at 30°	$M \times 10^{-3}$ osmotic	$M \times 10^{-3}$ calculated from [η] in MEK at 30°	T_c in MEK, °C.	T_c phenetole	[η] MEK at 20°	$K_{20°} \times 10^3$
C-3	14	2.24		4670	17.0			
E-3	9	0.766	685 (±25)	664			0.674	0.815 (±0.02)
B-2	16	.485	278 (±10)	290	7.8	74.7	.427	.815 (± .02)
A-5	15	.350		160	5.5	70.7	.314	.785[a]
A-6	13	.290	112 (±3)	113			.274	.820 (± .01)
A-7	8	.259	93 (±3)	92.3	−1.2	66.8		
A-8	11	.237		78.7				
A-9	7	.192		53.6			.180	.785[a]

[a] Based on molecular weights interpolated from intrinsic viscosities measured at 30° in MEK.

difference in height remained constant within ±0.2 mm. for 12 hours. After completion of a run the osmometer was removed from the solvent, the solution capillary was disconnected and the solution was removed. The cell was filled with MEK and allowed to stand overnight. It was rinsed twice with portions of the next solution to be run, then filled and reassembled using a clean capillary.

Results

The individual fractions used in this work are characterized by the data given in the first five columns of Table I. Molecular weights of four of the fractions were measured osmotically. The osmotic results are shown in Fig. 1 where the experimental data are plotted as log (π/c) against log c. The curves correspond to the equation[11,12]

$$\pi/c = (\pi/c_0)\,[1 + \Gamma_2 c + (5/8)\,\Gamma_2^2 c^2] \qquad (2)$$

c being expressed in g./100 ml. and π in g./cm.^{2}. The theoretical curves have been matched to the experimental points by rectilinearly shifting a standard plot of log $[1 + \Gamma_2 c + (5/8)\Gamma_2^2\, c^2]$ *vs.* log $(\Gamma_2 c)$ in the manner previously described.[11]

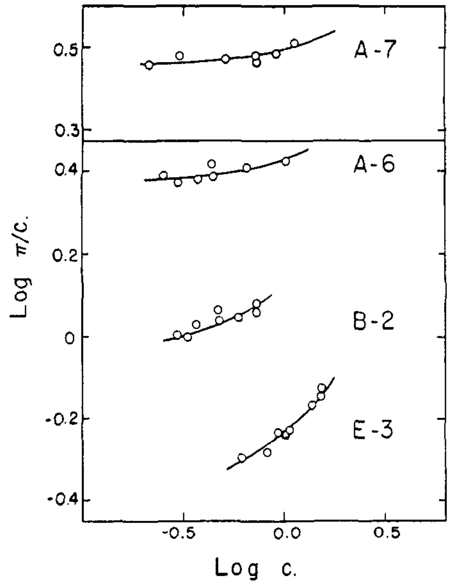

Fig. 1.—Osmotic pressure measurements: log π/c *vs.* c, with π in g./cm.^{2} and c in g./100 ml. Curves are best fitted according to equation (2). Note difference in ordinate scale for fraction A-7.

The vertical displacement gives log $(\pi/c)_0$, from which the molecular weights given in the fourth column of Table I have been computed according to van't Hoff's law.

In Fig. 2 log $[\eta]_{\text{MEK},30°}$ is plotted against the logarithm of the osmotic molecular weight. From the straight line drawn through the points we obtain the empirical relationship

$$\log\,[\eta]_{\text{MEK},30°} = -3.318 + 0.55 \log M \qquad (3)$$

which has been used to calculate the molecular weights given in column five of Table I. The extrapolation to fraction A-9, having a molecular weight only a little more than half that of the lowest osmotically measured fraction, is unquestionably justified by the behavior of other linear polymers; the much longer extrapolation involved in assigning a molecular weight for the highest fraction, C-3, is subject to greater uncertainty. This fraction was used, however, only for the measurement of T_c in a region where the maximum conceivable error in its molecular weight would be inconsequential.

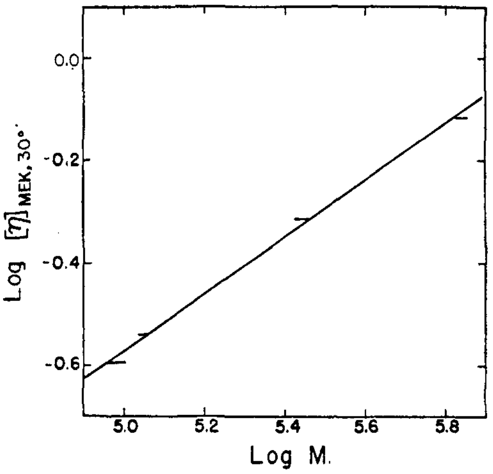

Fig. 2.—log $[\eta]_{\text{MEK},30°}$ *vs.* log M. Length of bar indicating each point corresponds to the uncertainty log M in each case.

Precipitation temperatures were measured on solutions of several of the fractions in MEK and in phenetole at suitable concentrations. These were chosen to cover in each case the region of the critical point, which occurred at about 1 g./100 ml. for the highest fraction, C-3, in MEK, and increased to about 8 g./100 ml. for the lowest fraction measured.

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[11] T. G. Fox, Jr., P. J. Flory and A. M. Bueche, THIS JOURNAL, **73**, 285 (1951).

[12] P. J. Flory, *J. Chem. Phys.*, **17**, 1347 (1949); P. J. Flory and W. R. Krigbaum, *ibid.*, **18**, 1086 (1950).

The critical, or consolute, temperature T_c was taken as the maximum in the plot of the precipitation temperature against concentration. Results are tabulated in columns six and seven of Table I. In accordance with prevous procedure,[2-4] these are plotted against $M^{-1/2}$ in Fig. 3. The critical miscibility temperatures Θ in the limit of infinite molecular weight, obtained from the extrapolation of these plots to $M^{-1/2} = 0$, are 293 and 356°K. for MEK and phenetole, respectively. At these temperatures in the respective solvents *ideal behavior should prevail at all molecular weights*[1,2] *and the osmotic forces acting on a polymer molecule should be zero.*[2,6]

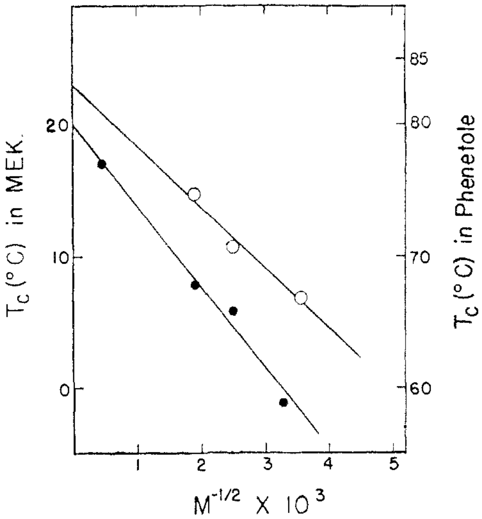

Fig. 3.—Consolute temperature *vs.* $M^{-1/2}$. In methyl ethyl ketone (●), left ordinate scale; in phenetole (O), right ordinate scale.

According to the theory developed previously[8] which has been found to hold without exception in related investigations on other linear polymer[2-5]

$$[\eta] = KM^{1/2}\alpha^3 \tag{4}$$

where

$$K = \Phi(\overline{r_0^2}/M)^{3/2} \tag{5}$$

and

$$\alpha^5 - \alpha^3 = 2C_M\Psi_1(1 - \Theta/T)M^{1/2} \tag{6}$$

The linear distortion of the average polymer configuration owing to solvent–polymer interaction is represented by α, and $\overline{r_0^2}$ is the mean-square end-to-end length for the unperturbed chain; the parameter Φ is believed to be a universal constant; C_M is a constant for a given solvent–polymer system, and Ψ_1 is an entropy of dilution parameter. At $T = \Theta$ equation (6) gives $\alpha = 1$ as the physically valid solution, as is required by the fact that the osmotic forces are then zero. It follows that

$$[\eta]_\Theta = KM^{1/2} \tag{4'}$$

Results of intrinsic viscosity measurements made in MEK at $T = \Theta$, *i.e.*, at 20°, given in the next to the last column of Table I, are shown graphically in Fig. 4. A straight line has been drawn through the points in accordance with equation (4′). Given in the last column of Table I are the values obtained for $K_{20°}$ taken as ratios of $[\eta]_{MEK,20°}$ to $M^{1/2}$ for each fraction. The directly determined osmotic molecular weights have been used in the three instances in which these are available; molecular weights calculated empirically from $[\eta]_{MEK,30°}$ (column five) have been used for the other two fractions. The results given in the last column of Table I show K to be constant within experimental error over a range exceeding tenfold in molecular weight. The basic assumption on which Eq. (4) rests,[2] namely, that the effective hydrodynamic volume increases as the cube of a linear dimension of the molecule in solution, finds further support in the behavior of the polysiloxanes, therefore.

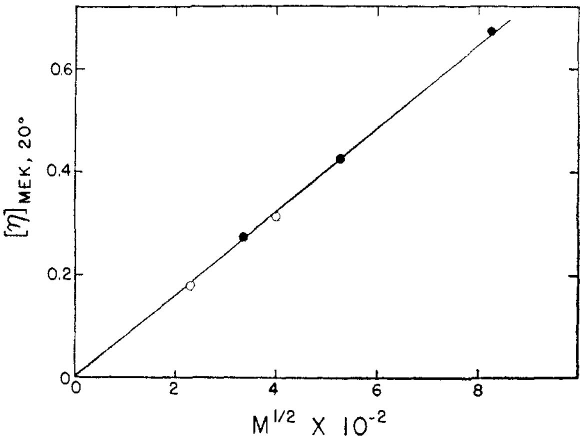

Fig. 4.—$[\eta]_{MEK,20°}$ *vs.* $M^{1/2}$. Osmotic molecular weight measured directly, ●; molecular weight calculated from $[\eta]_{MEK,30°}$, O.

Results pertaining to the similar evaluation of K from intrinsic viscosities measured in phenetole and interpolated to $T = \Theta = 356°K.$ are given in Table II. The mean value of K, 0.77×10^{-3}, at this temperature is less than the average, 0.805×10^{-3}, for the measurements at 20°, but the difference is not beyond the limit of experimental error. We conclude that K for the polydimethylsiloxane chain is approximately independent of temperature; it may decrease slightly with increase in temperature, however.

TABLE II

DETERMINATION OF K AT 83° USING PHENETOLE

Fraction	$[\eta]_{77°}$	$[\eta]_{87°}$	$[\eta]_{83°}$ interpolated	$K \times 10^3$
B-2	0.381	0.438	0.416	0.79(±0.02)
A-5	.283	.309	.298	.75
			Av.	0.77

Discussion

Comparisons of intrinsic viscosities of polyisobutylenes and polystyrenes[2] with the values of $\overline{r^2}$ obtained from the dissymmetry of light scattered by their solutions lead to $\Phi = 2.1 \times 10^{21}$ when $\sqrt{\overline{r^2}}$ is expressed in cm. and M in molecular weight units. Taking $K = 0.805 \times 10^{-3}$ for the polydimethylsiloxane chain, we obtain according to equation (5), $(\overline{r_0^2}/M)^{1/2} \times 10^{11} = 730$. This quantity is numerically equal to the root-mean-square unperturbed end-to-end length expressed in ångström units for $M = 10^6$. Values obtained similarly for other linear polymers are included in the second column of Table III.

TABLE III

ROOT-MEAN-SQUARE END-TO-END CHAIN LENGTHS COMPARED WITH THOSE CALCULATED FOR FREE ROTATION

Polymer	$(\overline{r_\theta^2}/M)^{1/2} \times 10^{11}$ Obsd.	Calcd.	$(\overline{r_0^2}/\overline{r_{0f}^2})^{1/2}$
Polydimethylsiloxane at 20°; free rotation values calcd. for θ_2 = 130°	730	456^a	1.60
Polydimethylsiloxane at 20°; free rotation value calcd. for θ_2 = 160°	730	530^a	1.38
Polyisobutylene[2a] at 25°	795	412^b	1.93
Polystyrene[2b] at 34°	725	302^b	2.4
Polymethyl methacrylate[2c] at 31°	680	310^b	2.2
Natural rubber[3] at 0 to 60°	830	485^c	1.7
Gutta percha[3] at 60°	1030	703^c	1.5
Cellulose tributyrate[4] at 45°	1090	408^c	2.7
Cellulose tricaprylate[4] at 48°	850	366^c	2.3

[a] l = 1.65 Å. and θ_1 = 110°. [b] l = 1.54 Å. and θ = 109.5°. [c] Calculated from appropriate bond lengths and angles assuming free rotation about single bonds.

The polysiloxane chain consists of identical bonds of length l meeting at angles θ_1 and θ_2 which alternate along the chain as shown in Fig. 5. If free rotation is assumed about each Si–O bond, it is possible to show that the mean-square end-to-end distance is given by

$$\overline{r_{0f}^2} = nl^2(1 - \cos\theta_1)(1 + \cos\theta_2)/(1 - \cos\theta_1\cos\theta_2) \quad (7)$$

when n, the number of chain bonds, is assumed to be large.[13] (The added subscript "f" included with r_0 refers to the assumption of free rotation.) X-Ray[14] and electron diffraction studies[15] on lower cyclic dimethylsiloxane polymers give l = 1.65 ± 0.03 Å. (1.64 ± 0.03 Å. and 1.66 ± 0.04 Å., respectively), $\theta_1 \cong 110°$ and $\theta_2 \cong 130°$. It may be argued that these values for the angles are of little significance for the linear polymers inasmuch as they were obtained on six-membered rings which are known to be strained.[16] The silicon angle θ_1 is quite certainly nearly tetrahedral[15] in the absence of strain, hence the value 110° may be accepted as approximately correct. The Si–O–Si angle θ_2 probably is easily deformable,[17] and the unstrained θ_2 therefore probably exceeds 130°. Sauer and Mead's[17] value of 160 ± 15° for θ_2, based on dipole moments is considered too large, however.[15,18]

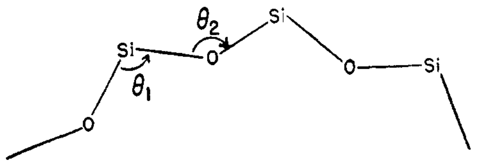

Fig. 5.—Structure of the siloxane chain.

Values of $(\overline{r_{0f}^2}/M)^{1/2}$ obtained from equation (7), with n replaced by $M/37$, are given in the third column of Table III for two values of θ_2, 130 and 160°, which almost certainly are extremes. The ratios of the observed root-mean-square unperturbed end-to-end lengths to those thus computed assuming free rotation are given in the last column of Table III. Also included are corresponding data obtained for other linear polymers. Although the average extension of the polysiloxane chain is considerably larger than that calculated assuming free rotation, the deviation is less than has been observed for most other polymers. This is in accord with the high degree of flexibility commonly attributed to the siloxane chain. It should be borne in mind, however, that ordinary hindrance to rotation about the chain bonds is not the only factor contributing to the increase of $\overline{r_0^2}$ over $\overline{r_{0f}^2}$; "short range" steric interactions between near neighboring units of the chain will increase the observed dimensions over those calculated by the over-simplified approximation of *independent* free rotation about each bond. This factor alone may be largely responsible for the disparity between $\overline{r_0^2}$ and $\overline{r_{0f}^2}$ (calcd.) for the siloxane chain.

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[13] The derivation of equation (7) parallels that employed to obtain the well known relation

$$\overline{r_{0f}^2} = nl^2(1 - \cos\theta)/(1 + \cos\theta)$$

for a simple chain of identical atoms. See H. Eyring, *Phys. Rev.*, **39**, 746 (1932), and F. T. Wall, *J. Chem. Phys.*, **11**, 67 (1943). When $\theta_1 = \theta_2$, equation (7) reduces to this expression.

[14] W. L. Roth, THIS JOURNAL, **69**, 474 (1947); *Acta Krist.*, **1**, 34 (1948).

[15] E. H. Aggarwal and S. H. Bauer, *J. Chem. Phys.*, **18**, 42 (1950).

[16] D. W. Scott, THIS JOURNAL, **68**, 2294 (1946).

[17] R. O. Sauer and D. J. Mead, *ibid.*, **68**, 1794 (1946).

[18] ADDED IN PROOF.—On the basis of X-ray studies on the cyclic octasiloxane and on frozen stretched silicone rubber, Dr. L. K. Frevel has selected the following as the best values: l = 1.70Å. and θ_2 = 130 ± 10°. The authors are indebted to Dr. Frevel for bringing these results to their attention in advance of publication.