

paper.¹⁰ A value of 0.2 was estimated for ψ_1 . For the purpose of testing the sensitivity of $d \ln \langle r^2 \rangle_0 / dT$ to ψ_1 , calculations were also performed with $\psi_1 = 0.5$. Results are summarized in Table III. It is apparent that the precise values chosen for ψ_1 and for $(\langle r^2 \rangle_0 / M)^{1/2}$ have little effect on the final results.

TABLE III

INTRINSIC VISCOSITY-TEMPERATURE COEFFICIENTS FOR PDMS;
SUMMARY OF CALCULATIONS

	$M = 2.5 \times 10^5$	$M = 0.43 \times 10^6$
$[\eta]_{30^\circ}$	1.730	0.653
$d \ln [\eta] / dT$	1.04×10^{-3}	0.858×10^{-3}
α_{calcd}	1.39, 1.59 ^a	1.24, 1.39 ^a
$(d \ln \langle r^2 \rangle_0 / dT) \times 10^3$	0.79, 0.83 ^a	0.59, 0.60 ^a

^a First values given calculated for $\psi_1 = 0.2$ (estimated); second values for $\psi_1 = 0.5$ (illustrative).

Modifications^{17,18} of eq. 3 and 4 which have been suggested turn out to be inconsequential in their effect on $d \ln \langle r^2 \rangle_0 / dT$ owing to compensating changes in the two terms of eq. 5 for values of the parameters applicable to these experiments. According to the viscosity method the best value for this quantity is therefore $0.71 (\pm 0.13) \times 10^{-3} \text{ deg.}^{-1}$. Ciferri⁷ found 0.28 to $0.38 \times 10^{-3} \text{ deg.}^{-1}$ by application of the same method.

Discussion

The two methods for evaluating the temperature coefficient of the unperturbed dimensions give results in remarkably good agreement. As a rounded mean of these results we adopt the value $0.75 \times 10^{-3} \text{ deg.}^{-1}$, which will be used in the theoretical interpretation⁶ of the configuration of the PDMS chain.

The agreement between the results on polymer chains in the very different environments consisting of the un-

(17) Stockmayer [*J. Polymer Sci.*, **15**, 595 (1955); *Makromol. Chem.*, **35**, 54 (1960)] has proposed an expression for α identical with that given by eq. 8 except that the numerical constant is reduced by one-half. Utilization of this modification would increase $d \ln \langle r^2 \rangle_0 / dT$ by approximately 3%.

(18) Kurata and co-workers [*J. Chem. Phys.*, **29**, 311 (1958); M. Kurata, H. Yamakawa, and H. Utiyama, *Makromol. Chem.*, **34**, 139 (1959)] have derived an expression similar to eq. 7 but with the following differences: the constant Φ is increased from 2.5×10^{21} to 2.9×10^{21} and the exponent of the expansion coefficient α is decreased from 3.00 to 2.43. If these revisions are adopted, the values of $d \ln \langle r^2 \rangle_0 / dT$ are decreased by approximately 3%.

diluted network in the one case and the dilute solution in the other lends additional support to the contention^{1,2} that the elastic free energies of polymer chains comprising a network are additive, and that the chain configuration in the amorphous state is not measurably influenced by intermolecular interactions.

Values of $d \ln \langle r^2 \rangle_0 / dT$ and f_e / f for polymers investigated by these methods are presented in Table IV. Poly-(dimethylsiloxane) is similar to natural rubber and atactic poly-(butene-1) in that it exhibits a positive energy contribution f_e to the total tension f . On a molecular basis, this indicates that extended configurations of these polymers must be associated with higher energies. In contrast, polyethylene and GR-S rubber show a negative energy contribution to the tension, whereas f_e / f for polyisobutylene and isotactic poly-(butene-1) is nearly zero.

TABLE IV

VALUES OF $d \ln \langle r^2 \rangle_0 / dT$ FOR VARIOUS POLYMERS

Polymer	Method	f_e / f	$\frac{d \ln \langle r^2 \rangle_0}{dT} \times 10^3$
Polydimethylsiloxane	$f, [\eta]$	0.27 ± 0.02	0.75 ± 0.15
Polyethylene ^{1,2}	$f, [\eta]$	$-.45 \pm .07$	$-1.2 \pm .15$
Polyisobutylene ¹	f	$-.03 \pm .02$	$-0.08 \pm .06$
Natural rubber ^{1,8,19}	f	$.13 \pm .02$	$.41 \pm .04$
GR-S ⁸ rubber ^{1,20}	f	$-.13 \pm .06$	$-.42 \pm .02$
Isotactic poly-(butene-1) ²¹	f	$.04 \pm .03$	$.10 \pm .07$
Atactic poly-(butene-1) ²¹	f	$.21 \pm .02$	$.48 \pm .05$

^a A copolymer of butadiene and styrene.

Acknowledgment.—Support of the United States Air Force under Grant AFOSR-62-131 is gratefully acknowledged. The authors are indebted to Dr. T. L. Smith of the Stanford Research Institute, Menlo Park, Calif., and the General Electric Co., Waterford, N. Y., for supplying samples of polymer. Thanks are due also to Dr. E. Stivers of the Raychem Corporation of Redwood City, Calif., for performing electron irradiations of various samples.

(19) L. A. Wood and F. L. Roth, *J. Appl. Phys.*, **15**, 781 (1944).

(20) F. L. Roth and L. A. Wood, *ibid.*, **15**, 749 (1944).

(21) J. E. Mark and P. J. Flory, *J. Phys. Chem.*, **67**, 1396 (1963).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

Configuration of the Poly-(dimethylsiloxane) Chain. II. Unperturbed Dimensions and Specific Solvent Effects

By V. CRESCENZI¹ AND P. J. FLORY

RECEIVED AUGUST 13, 1963

Intrinsic viscosities of poly-(dimethylsiloxane) fractions, $M = 0.55$ to 1.2×10^6 , have been determined at the Θ -point in two solvents: (i) methyl ethyl ketone at 20° and (ii) a 1:2 mixture of C_6F_{18} and $CCl_2F \cdot CCl_2F$ at 22.5° . In (i), $[\eta]_\Theta / M^{1/2} = 7.8 \times 10^{-4}$ (with $[\eta]_\Theta$ in dl. g.⁻¹) in close agreement with previous results in other solvents which, like (i), have cohesive energy densities (CED) exceeding that of the polymer. In (ii), for which the CED is less than for the polymer, $[\eta]_\Theta / M^{1/2} = 10.6 \times 10^{-4}$. The ratios $\langle r^2 \rangle_0 / nl^2$ deduced from these results are 6.3 and 7.7 compared with 3.3 calculated for free rotation.

Introduction

The mean-square end-to-end length $\langle r^2 \rangle$ for a polymer chain molecule, a quantity widely used as a measure of its spatial configuration, varies considerably from one solvent medium to another. Interactions between segments in close conjunction in space, but distantly related in sequence along the chain, are largely responsible

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for the variations noted. The influence of these interactions on the chain molecule are usually treated in terms of the so-called volume exclusion effect which takes account of the elimination of those configurations in which two remotely connected segments would otherwise be superposed in space. The resulting expansion of the average configuration depends on the magnitude of the effective covolume of the polymer segment, and this in turn depends on the solvent medium.

If, through a suitable choice of solvent, the covolume is reduced effectively to zero, the volume exclusion effect is cancelled, and the mean-square dimension assumes its unperturbed value designated by $\langle r^2 \rangle_0$. In a good solvent, on the other hand, the covolume of the polymer segment is necessarily positive and large, hence $\langle r^2 \rangle$ for a chain of great length is substantially greater than the unperturbed mean-square length $\langle r^2 \rangle_0$. The combination of solvent composition and temperature for null covolume is termed the Θ -point, which is fully analogous to the Boyle point of a gas. Media meeting this condition are designated Θ -solvents.

Early studies²⁻⁴ indicated $\langle r^2 \rangle_0$ to be approximately the same in different Θ -solvents in the same temperature range. The most reliable relative measure of chain dimensions is provided by the intrinsic viscosity $[\eta]$, and the experimental basis for the generalization cited consists in the observation that the intrinsic viscosity $[\eta]_\Theta$ at the Θ -point for a given polymer is approximately independent of the solvent medium at a chosen temperature. These studies did not, however, establish precise coincidence of the values of $[\eta]_\Theta$ for the same macromolecule in different media. Specific solvent effects should certainly be expected, although they may often be quite small. The basis for this expectation is apparent from the obvious dependence of $\langle r^2 \rangle_0$ on hindrance potentials of the chain skeleton. While variations in $[\eta]_\Theta$ for a given polymer in different Θ -solvents are generally small—very much smaller than variations in $[\eta]$ among solvents chosen indiscriminately without imposing the Θ -condition—identity of values for $[\eta]_\Theta$ in different media should not be assumed.

Recent studies by Orofino and Mickey⁸ on polystyrene demonstrate that $[\eta]_\Theta$ and therefore $\langle r^2 \rangle_0$ also depend perceptibly on the solvent medium. Their results in conjunction with earlier work of Shultz and Flory⁴ and of Bianchi and Magnasco⁶ establish a variation of about 10% in $[\eta]_\Theta$ among the various Θ -solvents investigated in the neighborhood of 34°. Larger variations would be anticipated for polar polymers. This expectation has in fact been demonstrated in the work of Ivin, Ende, and Meyerhoff⁷ on poly-(hexene-1 sulfone). For a given fraction in *n*-hexyl chloride at $T = \Theta = 13^\circ$ they observed $[\eta]_\Theta$ to be some 25 to 30% greater than for the mixture methyl ethyl ketone (37)–isopropyl alcohol (63) at $T = \Theta = 27^\circ$.

The present investigation has been concerned primarily with the influence of the solvent medium on the distribution of bond rotational conformations in the poly-(dimethylsiloxane) chain, as reflected in its unperturbed mean-square dimension $\langle r^2 \rangle_0$. Features peculiar to the siloxane chain structure render it especially appropriate for the purpose cited. The oxygen atoms which alternate along the chain, being unshielded by bulky substituents, must be especially vulnerable to interactions with the solvent. The length and polarity of the Si–O bond also should be expected to enhance its susceptibility to the nature of the medium.

Experimental

Polymer Samples.—Three poly-(dimethylsiloxane) (PDMS) samples⁸ having average molecular weights approximating 1×10^6 , 5×10^6 , and 1×10^6 , respectively, were separated into fractions in the molecular weight ranges desired for subsequent

experiments by fractional precipitation from 0.1–0.2% solutions in ethyl acetate at 30.0° using methanol as the precipitant. Following each addition of methanol, the solution was warmed (ca. 5°) to effect homogeneity, then cooled to 30° with gentle stirring over a period of 0.5 hr. The polymer-rich phase was allowed to settle for 24 hr., the temperature being held at 30° throughout this period. After decantation of the supernatant solution, the precipitated phase was diluted with ethyl acetate and the polymer fraction recovered by addition of excess methanol. Four fractions were thus separated from each of the three original samples. Each of these fractions was further separated into three subfractions by the same procedure outlined above, starting, however, with polymer concentrations less than 0.1% in the ethyl acetate solution.

Solvents.—The solvents benzene, toluene, and methyl ethyl ketone (MEK) used for light scattering and viscosity measurements were of reagent grade. They were dried thoroughly and distilled before use. Inasmuch as the Θ -point is sensitive to impurities, it was essential to establish equivalence of the MEK to that used in an earlier investigation with which present results are correlated. Critical consolute temperatures were therefore determined for several PDMS fractions in MEK from precipitation temperatures. The results indicated a Θ -point of $21 \pm 2^\circ$, in satisfactory agreement with the previous result,⁹ $\Theta = 20^\circ$.

The "mixture" of low cohesive energy density chosen for measurement at the Θ -point consisted of 33.17% by weight of perfluorinated isomeric octanes,¹⁰ designated FC 75 (fully fluorinated, boiling range 95% between 99 and 107°, density 1.77 ± 0.02 at 25°, $n_D^{25} 1.274$), and 66.83% of *sym*-tetrachlorodifluoroethane¹¹ (Freon 112, m.p. 26°, b.p. 92.8°, density 1.634 at 30°, $n_D^{25} 1.413$). This mixture yielded a Θ -point for PDMS conveniently near room temperature (*cf.* following).

Dilute Solution Viscosities.—Measurements were carried out with Cannon–Ubbelohde viscometers. Each solution was prepared by weight and filtered directly into the viscometer; the hazards of compounded errors in dilution procedures were avoided. Efflux times were taken at 20° for MEK solutions and for benzene solutions, and at 20, 22.5, and 25° for the solutions in the FC–Freon 112 mixture. The temperature was controlled to $\pm 0.01^\circ$ in each case. Measurements at three concentrations chosen to yield relative viscosities in the range 1.1 to 1.5 were extrapolated to infinite dilution in the customary manner.

Liquid–Liquid Phase Separation.—Precipitation points in the FC–Freon 112 mixture of composition specified above were determined at a series of polymer concentrations from 1 to 6% by visual observation of the onset of turbidity as the temperature was decreased, followed by observation of its disappearance upon warming.^{4,12} A small sample of each solution contained in a 2-ml. test tube was agitated by magnetic stirring as the temperature was varied slowly. Precipitation temperatures T_p observed during the heating and cooling phases of the cycle agreed within $\pm 0.2^\circ$.

Light Scattering.—A SOFICA PGD light scattering instrument was used. The incident light beam (Phillips SP 500 high pressure mercury vapor lamp used in conjunction with a Wratten No. 61 filter) was unpolarized. The cylindrical cell and light probe (consisting of slit and total reflecting prism) for transmittal of scattered radiation to the photomultiplier tube (RCA IP-28) were immersed in benzene in a cylindrical container concentric with the scattering cell. The temperature was controlled within $\pm 0.1^\circ$ by water circulated from a thermostat external to the instrument. The optical alignment was checked by determining the scattering envelope for solutions of fluorescein in methanol and for carefully purified benzene.

Solutions of PDMS in benzene were filtered directly into light scattering cells, using ultrafine porcelain candle filters. After establishing constant temperature, scattered intensities were determined at various angles θ from 45 to 135°. The constancy of response of the apparatus was monitored at intervals by observing the 90° scattering for benzene. Molecular weights were calculated from the usual relationship

$$(2\pi^2/\lambda^4 N_A)(ndn/dc)^2(c/R_\theta)_{\theta=90} = 1/M_w \quad (1)$$

where n is the refractive index of the solution, N_A is the Avogadro number, c is its concentration in g. cm.⁻³, and R_θ is the Rayleigh ratio (corrected for scattering by the pure solvent) divided by the factor $1 + \cos^2 \theta$ appropriate for unpolarized incident radiation, *i.e.*

$$R_\theta = R_b \sin \theta (1 + \cos^2 \theta)^{-1} I_\theta / I_b$$

where I_θ is the galvanometer deflection for the solution at angle

(9) P. J. Flory, L. Mandelkern, J. B. Kinsinger, and W. B. Shultz, *J. Am. Chem. Soc.*, **74**, 3364 (1952).

(10) Samples were made available to us by the Minnesota Mining and Manufacturing Co.

(11) Fluorochlorocarbons were generously supplied by E. I. du Pont de Nemours and Co.

(12) A. R. Shultz and P. J. Flory, *J. Am. Chem. Soc.*, **75**, 5681 (1953).

(2) T. G. Fox and P. J. Flory, *J. Am. Chem. Soc.*, **73**, 1909, 1915 (1951).

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

(4) A. R. Shultz and P. J. Flory, *J. Polymer Sci.*, **15**, 231 (1955).

(5) T. A. Orofino and J. W. Mickey, *J. Chem. Phys.*, **38**, 2512 (1963).

(6) U. Bianchi and V. Magnasco, *J. Polymer Sci.*, **41**, 177 (1959).

(7) K. J. Ivin, H. A. Ende, and G. Meyerhoff, *Polymer*, **3**, 129 (1962).

(8) These specially prepared samples were kindly placed at our disposal by the General Electric Co., Silicone Products Department, Waterford N. Y.

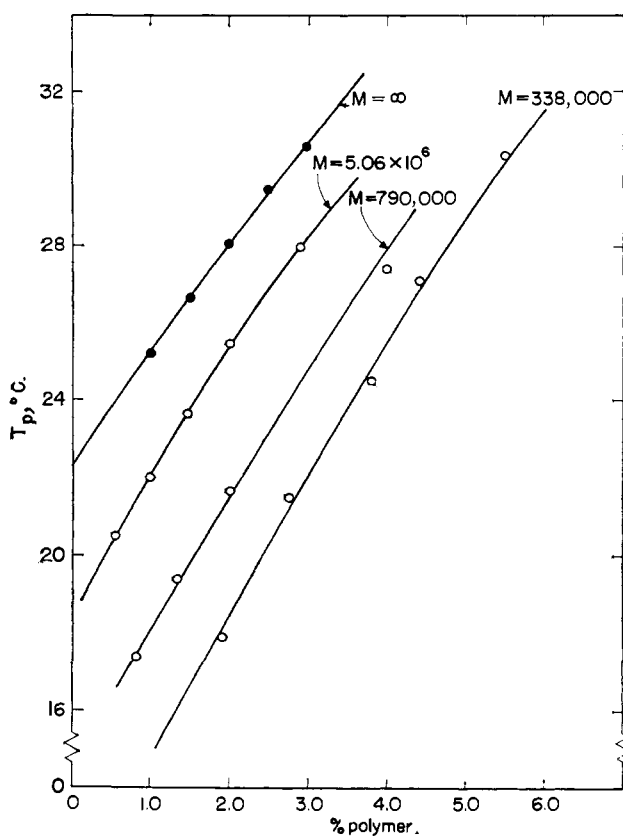


Fig. 1a.—Precipitation temperatures T_p for several PDMS fractions plotted against concentration in the mixture of C_8F_{18} and $C_2Cl_4F_2$. Experimental points for fractions of the molecular weights indicated on the graph are shown by open circles. Results of extrapolation to $M = \infty$ according to Fig. 1b are shown by filled circles.

θ (corrected for scattering by the pure solvent at the same angle), I_b is the deflection for pure benzene, and R_b is the Rayleigh ratio (16.2×10^{-6}) for pure benzene at an angle of 90° . The second virial coefficient A_2 and the z -average of the radius of gyration were calculated in the usual way from the concentration dependence of c/R_9 at zero angle and from the angle dependence of the same quantity at zero concentration, respectively.

The refractive increment for PDMS in benzene at 20° , and λ 546 $m\mu$, was determined using a Brice-Phoenix differential refractometer. The average value obtained was $dn/dc = 0.0993$ cm^3/g . The refractive increment for the FC-Freon 112 mixture was not measured. Light scattering measurements on this system served only to establish the Θ -point at which $A_2 = 0$; determination of other quantities in this solvent was not attempted.

Results

The Θ -Point.—In quest of a Θ -solvent having a Hildebrand solubility parameter below that for PDMS (solubility parameter¹³ *ca.* 7.3), lower paraffin hydrocarbons, various fluorochlorocarbons (C_2 and C_3), and two C_8 -perfluorocarbon mixtures were examined. PDMS is completely miscible in the first two classes of solvents down to 0° ; it failed to dissolve in the perfluorocarbon up to 40° . However, the mixture of the composition specified in the Experimental section, and consisting of one part by weight of perfluorinated isomeric octanes and approximately two parts of *sym*-tetrachlorodifluoroethane, proved to be a solvent for the polymer above about 20° . Solubility parameters for the C_8F_{18} and for $C_2Cl_4F_2$ are approximately 5.8 and 7.3, respectively¹⁴; that for the mixture should be

(13) F. P. Price, S. G. Martin, and J. P. Bianchi, *J. Polymer Sci.*, **22**, 49 (1956); R. C. Osthoff, *J. Am. Chem. Soc.*, **76**, 339 (1954).

(14) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962; p. 172; J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," Third Ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 438.

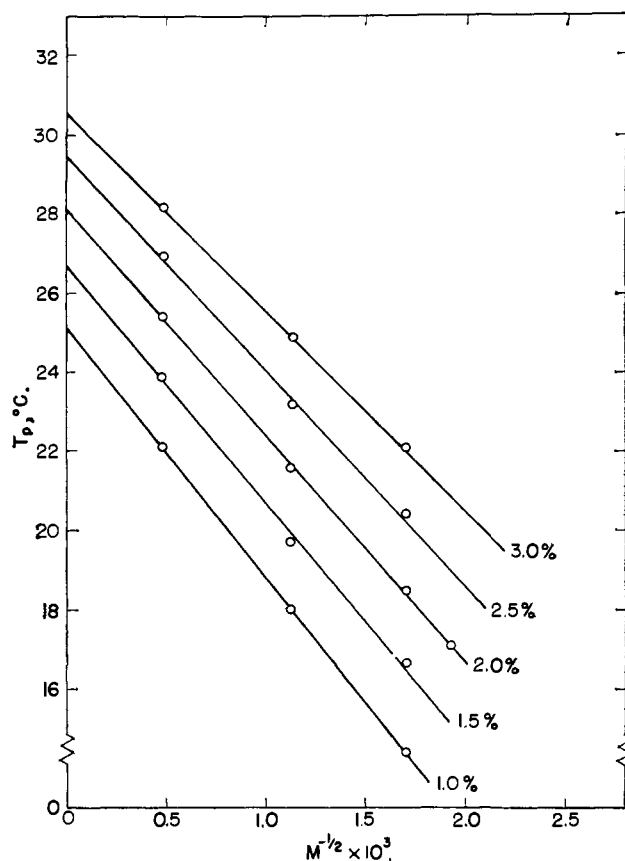


Fig. 1b.—Smoothed values of T_p taken from Fig. 1a at the concentrations indicated plotted against $M^{-1/2}$.

about 6.8. Hence the mixture afforded a Θ -solvent having a solubility parameter (and a cohesive energy density) below that for the polymer. Its Θ -point (see below) is close to that for MEK (20°), the latter having a solubility parameter, *ca.* 9.3, exceeding that of the polymer.

Precipitation temperatures T_p determined for several PDMS fractions at concentrations from 1 to 6% by weight in this mixture are presented in Fig. 1a. Approximate molecular weights of these fractions were calculated from their intrinsic viscosities in MEK at 30° using the empirical relationship⁹

$$\log M = 6.0 + 1.8 \log [\eta]_{\text{MEK}, 30^\circ}$$

The monotonic increase in T_p with polymer concentration shown in Fig. 1a is characteristic of a ternary system consisting of a polymer in a mixed solvent^{12,15a}; maxima such as occur in the dilute range for binary systems are not in evidence.

Smoothed values of T_p taken from the curves in Fig. 1a at selected concentrations are plotted in Fig. 1b against $1/M^{1/2}$ as prescribed by theory.^{12,15} Extrapolation to the ordinate yields T_p for $M = \infty$ at each concentration. These ordinate intercepts are plotted against the concentration in Fig. 1a (filled circles). Extrapolation of this set of points gives T_p in the limit $M = \infty$ and $c = 0$. As is well known,¹⁵ this limit represents a critical point for the system comprising polymer of $M = \infty$ and solvent components present in the arbitrarily fixed ratio. The second virial coefficient must here equal zero, and hence the condition for a Θ -point is fulfilled. We thus obtain $\Theta = 22.5 \pm 0.5^\circ$ for PDMS in the solvent mixture.

The Θ -point for the mixture was independently determined by measuring light scattering intensities at

(15) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953; (a) pp. 548-559; (b) pp. 280, 301.

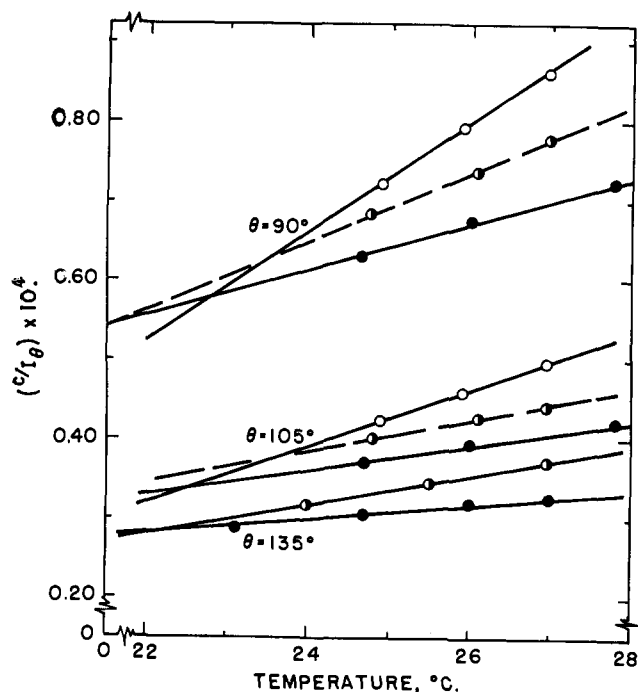


Fig. 2.—Reciprocal scattering ratios plotted against temperature for the angles θ indicated on the graph. Points for the several lines for each angle θ represent different concentrations; e.g., at $\theta = 90^\circ$, $c = 0.45, 0.35$, and 0.26 wt. %. All data for $M = 1.2 \times 10^6$ in the FC-Freon 112 mixture.

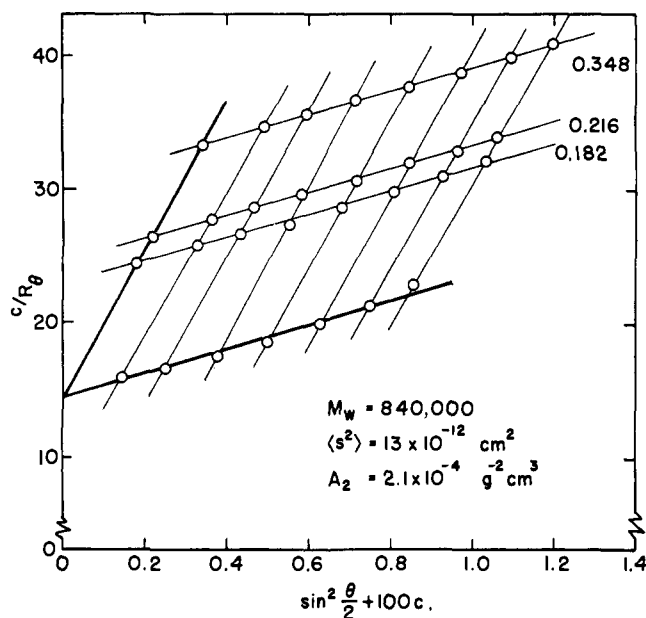


Fig. 3.—Zimm plots of c/R_θ vs. concentration and angle for highest fraction recorded in Table I. Numerals with each angle plot denote $c \times 100$.

angle θ over a range of temperatures in the vicinity of the Θ -point using solutions differing in polymer concentration. The usual difficulties attending determination of molecular weights from light scattering in mixed solvents are inoperative with respect to the stated objective of our measurements, for it is required merely to establish the temperature at which the second virial coefficient vanishes, *i.e.*, at which c/R_θ is independent of the concentration c .

Results for the fraction of molecular weight 1.2×10^6 are shown in Fig. 2. Lines drawn through sets of points representing c/R_θ for the same angle at different concentrations should intersect at the Θ -temper-

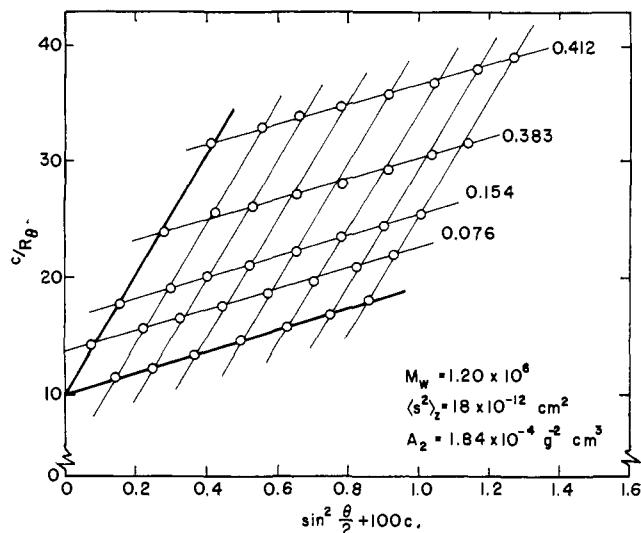


Fig. 4.—Zimm plot for second fraction in Table I. Numerals with each angle plot denote $c \times 100$.

ature. Scattering intensities for solutions at three concentrations were measured at the angles indicated in the figure over the temperature range from 23 to 28° . Discounting intersections of the line for solutions of the intermediate concentration in consideration of inaccuracies resulting from the small differences in concentration, we arrive at $\Theta = 22.5 \pm 1^\circ$, in agreement with the result from precipitation temperatures.

Molecular Weights.—Zimm plots for two fractions in benzene are shown in Fig. 3 and 4. Measurements were recorded at angle intervals of 15° from 45 to 135° . Weight average molecular weights calculated according to eq. 1 from the limiting intercepts are listed in Fig. 3 and 4. Mean-square radii of gyration $\langle s^2 \rangle_z$ and second virial coefficients A_2 , as deduced from the slope with $\sin^2(\theta/2)$ at $c = 0$ and from the slope with c at $\theta = 0$, respectively, are also given on each graph. The data were also treated according to the alternative procedure^{15b} involving plots of $(c/R_\theta)^{1/2}$ against c at each angle, with subsequent extrapolation to $\theta = 0$. Results thus obtained are equivalent to those recorded in the figures.

Light scattering molecular weights of the several fractions investigated are listed in the first column of Table I. Intrinsic viscosities of the first and third fractions

TABLE I
MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES^a

M_w $\times 10^{-6}$	Benzene, 20°	—MEK, 20°—		—Mixture, 22.5°—	
	$[\eta]$	$[\eta]_\Theta$	$[\eta]_\Theta M^{-1/2}$ $\times 10^4$	$[\eta]_\Theta$	$[\eta]_\Theta M^{-1/2}$ $\times 10^4$
1.20	1.63	0.835	7.63	1.155	10.55
0.84	1.29	.720	7.86	0.985	10.74
.74	1.17	.685	7.96	.865	10.05
.553	0.965	.585	7.87	.815	10.96
			Av. 7.83		Av. 10.57

^a Expressed in dl. g.⁻¹.

($M = 1.2 \times 10^6$ and 0.74×10^6) in toluene at 25° were 2.07 and 1.42, respectively. Molecular weights calculated using the relationship of Haug and Meyerhoff,¹⁶ are 1.28×10^6 and 0.76×10^6 for these frac-

$$[\eta]_{\text{toluene}, 25^\circ} = 0.828 \times 10^{-4} M^{0.72}$$

tions. Although higher than our results, the difference is not beyond the uncertainty in light scattering intensity calibrations. Osmotic molecular weights found by Flory, Mandelkern, Kinsinger, and Shultz⁹

(16) V. A. Haug and G. Meyerhoff, *Makromol. Chem.*, **53**, 91 (1962).

for fractions of PDMS are about 8% lower than our values, comparisons being interpolated to the same intrinsic viscosity in MEK at 20°. The difference accords with expectation based on the ratio of the number (osmotic) to the weight average (light scattering) molecular weights.

The intrinsic viscosities in benzene are well represented by

$$[\eta]_{\text{benzene, 20}^\circ} = 1.2 \times 10^{-4} M^{0.68} \quad (2)$$

The range of the data is small, hence accuracy cannot be claimed for this empirical relationship.

Intrinsic Viscosities at the θ Point.—The ratio $[\eta]_\theta/M^{1/2}$ recorded in Table I for MEK ($\theta = 20^\circ$) and the low cohesive energy density mixture ($\theta = 22.5^\circ$) show no discernible trend with M , in accord with an abundance of data on solution of other linear chain homologs at their θ -points. The disparity between the mean values for $[\eta]_\theta/M^{1/2}$ in the two media is striking. That uncertainties in the exact θ -temperatures cannot have contributed to this unusually large dependence of $[\eta]_\theta$ on the solvent medium is made evident by examination of the temperature coefficients of the intrinsic viscosities in the neighborhood of the θ -point. Thus, for the second fraction in the mixture, $d \ln [\eta]/dT = 0.016 \text{ deg.}^{-1}$ in the vicinity of the θ -point, according to measurements not included here. A similar coefficient was found previously for a comparable fraction in MEK near its θ -point.⁹ The 35% difference between the two $[\eta]_\theta/M^{1/2}$ ratios greatly exceeds any conceivable error from this source.

Values of the ratio $[\eta]_\theta/M^{1/2}$ for PDMS in various media, based largely on the recent work of Schulz and Haug,¹⁷ are presented in Table II. These authors concluded that $[\eta]_\theta$ depends very little either on solvent or temperature. Their values for $[\eta]_\theta/M^{1/2}$ are somewhat lower than ours for MEK, but the difference probably is not beyond the limit of experimental error in the light scattering calibration.

TABLE II

Solvent	$\theta, ^\circ\text{C.}$	$[\eta]_\theta \times 10^4/M^{1/2}$
Methyl ethyl ketone	20	7.8, ^a 8.15 ^b
Low CED mixture	22.5	10.6 ^a
Ethyl iodide	2	7.0 ^c
Bromocyclohexane	29	7.4, ^c 7.8 ^d
Bromocyclohexane-phenetole (6:7)	36	7.5 ^c
Chlorobenzene-dimethyl phthalate (45:6)	57.5	7.6 ^c
Bromobenzene	78.5	7.6 ^c
Phenetole	89.5	7.3, ^c 7.7 ^b

^a Present investigation. ^b Flory, Mandelkern, Kinsinger, and Shultz, ref. 9. ^c Schulz and Haug, ref. 17. ^d Haug and Meyerhoff, ref. 16.

Kuwahara, Miyake, Kaneko, and Furuichi¹⁸ arrived at a value of 8.9×10^{-4} for $[\eta]_\theta/M^{1/2}$ from measurements in benzene on a PDMS fraction having an osmotic molecular weight of 0.107×10^6 . They converted the observed intrinsic viscosity to the unperturbed state using the method of Orofino and Flory.¹⁹ If their result is further corrected for heterogeneity, a value in the vicinity of that for MEK is indicated for PDMS in benzene.

The "mixture" used in the present work represents the only solvent medium so far investigated in which the cohesive energy density is less than that of PDMS. It alone exhibits a markedly different value for the ratio $[\eta]_\theta/M^{1/2}$.

(17) G. V. Schulz and A. Haug, *Z. physik. Chem. (Frankfurt)*, **34**, 328 (1962).

(18) N. Kuwahara, Y. Miyake, M. Kaneko, and J. Furuichi, *Chem. High Polymers (Tokyo)*, **19**, 25 (1962); *J. Phys. Soc. Japan*, **17**, 568 (1962).

(19) T. A. Orofino and P. J. Flory, *J. Chem. Phys.*, **26**, 1067 (1957).

The Unperturbed Dimensions.—The mean-square radii of gyration $\langle s^2 \rangle$ obtained from the angular dependence of the scattered light intensity recorded in Fig. 3 and 4 for the two higher fractions permit calculations of the constant Φ in the relationship

$$[\eta] = \Phi \langle r^2 \rangle^{3/2}/M \cong \Phi (6 \langle s^2 \rangle)^{3/2}/M \quad (3)$$

Through the use of the z -average values of $\langle s^2 \rangle$ without correction we thus obtain 1.75×10^{21} and 1.58×10^{21} for Φ . Correction for the probable molecular heterogeneity of the fractions would increase these values by 10 to 20% in fair agreement with the Φ values of 2.0 to 2.2×10^{21} generally found for other polymers in good solvents.²⁰⁻²²

At the θ -point $\langle r^2 \rangle = \langle r^2 \rangle_\theta$, and eq. 3 can be rearranged to

$$\langle r^2 \rangle_\theta/nl^2 = (M_b/l^2 \Phi^2)^{2/3} ([\eta]_\theta/M^{1/2})^{2/3} \quad (4)$$

where n is the number of bonds in the chain, l is the bond length, and $M_b = M/n$ is the molecular weight per bond. For the PDMS chain, $M_b = 37.05$ and $l = 1.64 \times 10^{-8} \text{ cm.}$ ²³ Values for the characteristic (unperturbed) ratio $\langle r^2 \rangle_\theta/nl^2$, calculated according to eq. 4 from the $[\eta]_\theta/M^{1/2}$ found in this investigation, are given in the first two rows of Table III. For this purpose, we have assigned to Φ its empirical value 2.5×10^{21} for unperturbed random coils.²⁰⁻²² This value is somewhat smaller than the theoretical²⁴ $\Phi = 2.86 \times 10^{21}$. Characteristic ratios have not been calculated from the results given for other solvents in Table II inasmuch as departures from that for MEK appear not to be significant.

The free rotation entry in the last row of Table III has been calculated assuming bond angles of 110 and 143°, respectively, at the silicon and at the oxygen atoms (see following paper²⁵).

TABLE III

Medium	$\langle r^2 \rangle_\theta/nl^2$
MEK, 20°	6.3
Low CED mixture, 22.5°	7.7
Calcd. for free rotation	3.32

The main source of error in the absolute values deduced for $\langle r^2 \rangle_\theta/nl^2$ arises from an uncertainty of about 10% in the value of Φ . The experimental $[\eta]_\theta/M^{1/2}$ ratios are believed to be accurate within $\pm 5\%$. Taking account of the fractional powers in eq. 4, we arrive at an estimated uncertainty of $\pm 10\%$ in the absolute values of $\langle r^2 \rangle_\theta/nl^2$ given in Table III. The relative accuracy for these ratios in the two solvent media is of course much greater; the maximum relative error is estimated at $\pm 5\%$. The difference between values of $\langle r^2 \rangle_\theta$ in the two media exceeds this limit several-fold.

Discussion of the basis for this striking departure of the unperturbed dimension of the chain low CED medium is reserved for the paper which follows. We note, however, that Ivin, Ende, and Meyerhoff⁷ also found $[\eta]_\theta$ for poly-(hexene-1-sulfone) to be greater in the less polar θ -solvent n -hexyl chloride than in the mixture of MEK-isopropyl alcohol at its θ -point. Al-

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though this correspondence between the two sets of results may be coincidental, the fact that both polymers are polar in nature possibly is significant. These effects of the medium, amounting to 22% in $\langle r^2 \rangle_0$ for PDMS and 15 to 20% for the sulfone, far exceed specific solvent effects observed to date for nonpolar polymers.

The disparity between $\langle r^2 \rangle_0$ and the result calculated for free rotation is considerably smaller than for other polymer chains. The effects of hindrances to free rotation are by no means insignificant, however. They are discussed in detail in the following paper.

Acknowledgment.—Support of the United States Air Force under Grant 62-131 is gratefully acknowledged.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY, STANFORD, CALIF.]

Configuration of the Poly-(dimethylsiloxane) Chain. III. Correlation of Theory and Experiment

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RECEIVED AUGUST 13, 1963

The characteristic ratio $\langle r^2 \rangle_0/nl^2$ for poly-(dimethylsiloxane) has been calculated by Ising lattice methods using the *trans-gauche* rotational isomeric state model as a convenient device for introducing various bond conformations with appropriate statistical weights. Steric interactions between nonbonded atoms must exclude successive *gauche* rotations of opposite sign for the pair of bonds on either side of a silicon atom; coulombic repulsions of O atoms may largely suppress the similar conformation about O. Bond rotations cannot, therefore, be treated as independent. These inferences from the structure of the siloxane chain are confirmed by experimental values of the characteristic ratio. Owing to the inequality of the bond angles ($\angle \text{OSiO} = 110^\circ$ and $\angle \text{SiOSi} = 143^\circ$), a decrease in the *trans* population increases $\langle r^2 \rangle_0/nl^2$. Hence, the positive temperature coefficient for this ratio denotes a lower energy for the *trans* state by ca. 800 cal. mole⁻¹. This energy is attributed to favorable interaction between CH₃ pairs separated by 3.8 Å. in the planar (*i.e.*, *trans*) conformation. The larger value observed for the ratio in a less polar medium is in the direction predicted for enhanced electrostatic interaction within a chain of partially ionic Si-O bonds.

Bond angles at the oxygen and silicon atoms of the poly-(dimethylsiloxane) chain differ considerably, as we have had occasion to point out in a preceding paper.² Whereas $\angle \text{OSiO}$ is approximately tetrahedral, $\angle \text{SiOSi}$ is much larger, being in the neighborhood of 143° .³ It is this alternation in bond angles which marks the point of departure in the analysis of the spatial configuration of the siloxane chain⁴ from that of other macromolecules for which successive bond angles are identical, or virtually so.

The significance of this difference is rendered apparent by considering the all-*trans* conformation of the siloxane chain shown by solid lines in Fig. 1 and 2. Owing to the inequality $\theta' < \theta''$, these being the supplements of the bond angles at oxygen and silicon, respectively, the planar conformation generated by assigning all bonds to *trans* rotational "states" consists of a succession of closed figures approximating polygons (the impossibility of superposition of successive polygons being ignored). This is in sharp contrast to chains for which $\theta' = \theta''$; their planar conformations are highly extended, the units being disposed about a rectilinear axis. Rigid adherence to a unique conformation obviously will not prevail except under special circumstances such as those imposed by the crystalline state. Comparison of the two cases considered serves, however, to indicate the profound difference to be expected in the dependence of the chain configuration on $\Delta\epsilon/kT$, where $\Delta\epsilon$ is the difference in energy between the nonplanar and the planar bond conformations. Thus the ratio $(\langle r^2 \rangle_0/nl^2)_{n \rightarrow \infty}$ of the unperturbed mean-square end-to-end length of the chain to the product of the number n of bonds and the square of the bond length l , taken in the limit $n = \infty$, increases without limit with $\Delta\epsilon/kT$ for chains having $\theta' = \theta''$. But for $\theta' \neq \theta''$ this ratio must vanish in the limit $\Delta\epsilon/kT = \infty$.

Birshtein, Ptitsyn, and Sokolova⁴ stressed the importance of bond angle alternation on the configurational characteristics of the siloxane chain. Through misinterpretation of the experimental value of $\langle r^2 \rangle_0/nl^2$, however, they were led to conclude that a satisfactory account of experimental results could be achieved assuming: (a) a threefold rotational hindrance potential symmetric about the *trans* form ($\varphi = 0$), this form being assigned a slightly lower energy than that of the *gauche* forms ($\varphi = \pm 120^\circ$); and (b) mutual independence of the hindrance potentials for neighboring bonds. Experimental results gathered in the two preceding papers are irreconcilable with predictions based on the latter assumption, as we shall have occasion to point out. Moreover, examination of structural models of the chain shows this assumption to be untenable. Certain combinations of rotations about two successive bonds give rise to severe interactions; hence, the potential hindering rotation about a given bond must depend on the rotations of its neighbors. The more elaborate mathematical methods appropriate to this latter case must therefore be employed for interpretation of the siloxane chain configuration.

In this paper we undertake to interpret the experimental values of the characteristic ratio $\langle r^2 \rangle_0/nl^2$ and its temperature coefficient for the poly-(dimethylsiloxane) (PDMS) chain in terms of the rotational isomeric chain model.⁵⁻⁸ Specifically, a threefold potential is assumed, with allowance for interdependence of neighboring bond rotations as indicated by analysis of the molecular geometry.

Theoretical Treatment

The Rotational Isomeric State Approximation.—The barrier height for the potential hindering rotation about the C-O bond of methanol is 1.07 kcal. mole⁻¹,⁹⁻¹¹ com-

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