

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

Configuration of the Poly-(dimethylsiloxane) Chain. I. The Temperature Coefficient of the Unperturbed Extension

BY J. E. MARK AND P. J. FLORY

RECEIVED AUGUST 13, 1963

The temperature coefficient $d \ln \langle r^2 \rangle_0 / dT$ of the unperturbed mean-square end-to-end distance for poly-(dimethylsiloxane) calculated from precise determinations of stress-temperature coefficients for cross-linked networks is $0.78 (\pm 0.06) \times 10^{-3} \text{ deg.}^{-1}$. According to the change of the intrinsic viscosity with temperature, determined on athermal solutions of the linear polymer in a low molecular weight dimethylsiloxane fluid, $d \ln \langle r^2 \rangle_0 / dT = 0.71 (\pm 0.13) \times 10^{-3} \text{ deg.}^{-1}$, in good agreement with the former value.

Introduction

The statistical configuration of a macromolecule in space is determined by its chain structure as specified by the lengths of bonds comprising the chain skeleton, by bond angles, and by potentials affecting rotations about these bonds. The spatial configuration may be adequately characterized by the dimensionless ratio $\langle r^2 \rangle_0 / nl^2$ of the mean-square distance between ends of the chain in the random, unperturbed state, to the product of the number n of bonds and the square of the length l of each, this ratio being taken in the limit of very large n . Recent advances in theory on the one hand and refinement of experimental methods on the other offer the possibility of relating this ratio quantitatively to the structure of the chain.

These methods have been applied successfully to the polyethylene chain.¹⁻⁴ Experimental values for the characteristic ratio $\langle r^2 \rangle_0 / nl^2$ and for its temperature coefficient stand in good accord with results of theoretical calculations based on: (i) known bond dimensions and angles; (ii) a threefold potential consistent with bond rotational potentials ascribed to the normal paraffin hydrocarbons, and involving a *trans* and two *gauche* conformations, the latter having energies exceeding the former by about 500 cal. mole⁻¹; and (iii) suppression of successive *gauche* rotations of opposite sign in consideration of the severe steric conflicts thus generated. Earlier, Ptitsyn and Sharanov⁵ showed that the corresponding quantities for the polyisobutylene chain could be rationally interpreted in terms of a twofold potential consistent with the conformation of this chain in the crystalline state.

These initial successes have encouraged attempts to extend the same methods to other polymer chains. The present paper and the two which follow are concerned with the poly-(dimethylsiloxane), or PDMS, chain. This chain presents several distinctive features. Unlike those previously investigated, it consists of an alternating succession of chain atoms, oxygen and silicon, which, respectively, join pairs of bonds at angles that differ considerably; the length of the Si-O bond, the small van der Waals radius of the O atom (compared with CH₂, for example), and the large angle at the O atom conspire to reduce steric conflicts, but do not eliminate them for all combinations of rotational conformations; the Si-O bond is polar and more exposed to the influence of solvent media than is the C-C bond in vinyl polymers. The consequences of these features are discussed in detail in the third paper of this series.⁶

In this paper we present an experimental investigation of the temperature coefficient, $d \ln \langle r^2 \rangle_0 / dT$, of

the mean-square extension for the unperturbed PDMS chain. Ciferri⁷ found this coefficient to be positive with a value of $0.40 (\pm 0.12) \times 10^{-3} \text{ deg.}^{-1}$. Since the temperature coefficient assumes critical importance in the theoretical interpretation, its determination with the utmost accuracy was undertaken. Two methods have been employed. One of these involves measurement of the stress-temperature coefficient for cross-linked networks.¹ The other requires determination of the temperature coefficient of the intrinsic viscosity in an appropriately chosen medium.² These methods have been described in detail in conjunction with previous applications to polyethylene,^{1,2} polyisobutylene,¹ and to natural rubber.^{1,8} As has been pointed out previously,^{1,2} comparison of results by these two methods affords a test of the postulate of additivity of the contributions of individual chains to the network free energy. This postulate underlies the theory of rubber elasticity.

Experimental

Preparation of Cross-Linked Samples.—Two unfractionated samples⁹ of PDMS having molecular weights of 1.4×10^6 and 0.50×10^6 , respectively, were used for the preparation of networks for the stress-temperature measurement. Sheets of the former polymer pressed at 100° to a uniform thickness of ca. 0.15 cm. were cross linked by ultraviolet radiation using a high-pressure quartz mercury vapor arc (Hanovia Model A, 550 w.) at a distance of 10 cm. Irradiations were performed under nitrogen at room temperature, without sensitizer for periods of 1.5 to 2.0 hr. The samples are designated Si-1, Si-2, and Si-3. The lower molecular weight polymer was allowed to flow to uniform thickness in a metal dish and then cross linked with high energy electrons from a G.E. resonant transformer. Sample Si-4 was cross linked in this manner using a dose of 8.0 megarads.

To ensure network uniformity, all samples were irradiated on opposite sides for equal exposure times. The efficacy of this procedure was demonstrated by the uniform swelling in carbon tetrachloride of cross-linked samples thus prepared.

The irradiated polymer samples were extracted with carbon tetrachloride for several hours. In no case did soluble constituents exceed 4% of the sample.

Tension Measurements.—The apparatus and procedure have been described previously.¹ The sample was mounted vertically between clamps, the lower one being attached to the bottom of the sample chamber and the upper one to a strain gage situated above the chamber. The length of the sample was adjusted by vertical movement of the strain gage mount. The gage was surrounded with polystyrene foam, and water was circulated through the metal block on which it was mounted in order to insulate it from the heated sample chamber. The gage and upper clamp were connected by a rod of low thermal conductivity. The sample chamber was Pyrex glass; all other parts of the apparatus were made of Invar, a metal having a low coefficient of thermal expansion. The temperature of the sample chamber was controlled to $\pm 0.05^\circ$. A stream of nitrogen through the chamber protected the sample against oxidative degradation at the higher temperatures.

The electronic system used in conjunction with the strain gage transducer (Statham Instrument Co., Model G1-24-350) consisted of a voltage-regulated power supply (Video Instrument Co., Model 200 EM) and millivolt recorder (Leeds and Northrup Co., Model Speedomax-G).

(1) A. Ciferri, C. A. J. Hoeve, and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 1015 (1961).

(2) P. J. Flory, A. Ciferri, and R. Chiang, *ibid.*, **83**, 1023 (1961).

(3) C. A. J. Hoeve, *J. Chem. Phys.*, **35**, 1266 (1961).

(4) K. Nagai and T. Ishikawa, *ibid.*, **37**, 496 (1962).

(5) O. B. Ptitsyn and I. A. Sharanov, *Zh. Tekh. Fiz.*, **27**, 2744, 2762 (1957).

(6) P. J. Flory, V. Crescenzi, and J. E. Mark, *J. Am. Chem. Soc.*, **86**, 146 (1964).

(7) A. Ciferri, *Trans. Faraday Soc.*, **57**, 846, 853 (1961).

(8) R. J. Roe and W. R. Krigbaum, *J. Polymer Sci.*, **61**, 167 (1962).

(9) These samples were generously provided by Drs. F. M. Lewis and C. G. Arcand, Jr., of the Silicones Department of the General Electric Co.

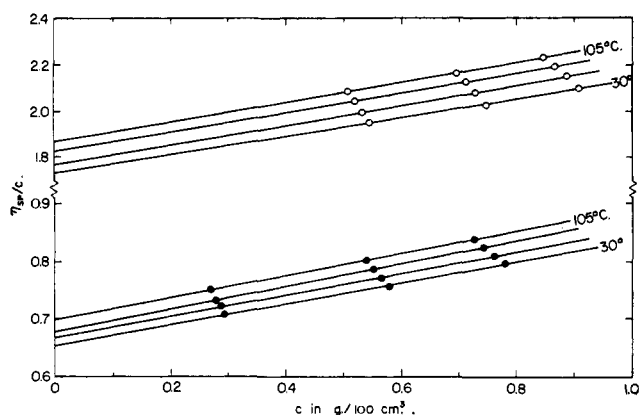


Fig. 1.—Dependence of the reduced specific viscosity on concentration at 25° intervals from 30 to 105°: O, $M = 2.5 \times 10^6$; ●, $M = 0.43 \times 10^6$.

Dumbbell-shaped samples were used in order to minimize rupture of the strips near the clamps. The section of the sample on which measurements were made was approximately $3.5 \times 0.60 \times 0.15$ cm. Reference marks were provided by two thin lengths of wire which had been inserted near the extremities of the test section while the strip was swollen (in order to minimize damage to the sample). The length was measured to ± 0.002 cm. with a cathetometer. The sample was elongated to the desired length at the highest temperature, 100°. After the tension became sensibly constant, which required up to 7 hr. at this temperature, it was recorded and the temperature was immediately lowered to 85°, the length being maintained constant within the stated limit of precision. A steady value of the force was quickly established at this temperature. The tension was similarly determined at the same length at 15° intervals of temperature down to 40°. The temperature sequence was then reversed over the same intervals and the tensions were compared with those observed over the preceding phase of the cycle. At the end of each run, the sample was permitted to recover under null force for at least 2 hr. The value of α at 100° was calculated using the recovered, unstressed length at this temperature.

Sample cross-sectional areas were determined by direct micrometer measurements. They were corrected to 100° by application of the thermal expansion coefficient (see Table I).

Material	Specific volume cm. ³ /g., 87.5°	$\beta \times 10^3$ deg. ⁻¹ , 87.5°
Dimethylsiloxane oligomer	1.112	0.947
PDMS	1.071	0.880 ± 0.004

Intrinsic Viscosities.—Two PDMS fractions prepared as described in the following paper¹⁰ were used. Their weight average molecular weights determined by light scattering were 2.5×10^6 and 0.43×10^6 . The solvent was a commercially available dimethylsiloxane fluid (General Electric, SF-96, 10 centipoise viscosity at 25°). The molecular weight of this material calculated from its bulk viscosity at 40° using the empirical relationship of Warrick, *et al.*,¹¹ is 1200. The specific volume and cubical thermal expansion coefficients of both the polymer and solvent (Table I) were measured using standard dilatometric and pycnometric techniques. Viscosities were measured with a Cannon-Ubbelohde viscometer (capillary size 1c) at 25° intervals over the temperature range 30 to 105°. Kinetic energy corrections were negligible.

All solutions were prepared by weighing solvent and solute. The concentration c , expressed in this paper in g./100 cm.³ in accord with convention in reference to intrinsic viscosities, was calculated at each temperature of measurement from the specific volumes and thermal expansion coefficients of the pure components (Table I). The hazards of cumulative error in the successive dilution procedure were avoided by preparing a separate solution for each concentration. Temperatures were controlled to $\pm 0.01^\circ$, and efflux times (110 to 520 sec.) were reproducible to $\pm 0.05\%$ or better. Reproducibility of the efflux times even at the highest temperature assured against the occurrence of degradation. Specific viscosities ranged from ca. 0.20 to 0.60. Intrinsic viscosities were obtained by extrapolation of η_{sp}/c to $c = 0$, as illustrated in Fig. 1. The Huggins constant¹² k' ,

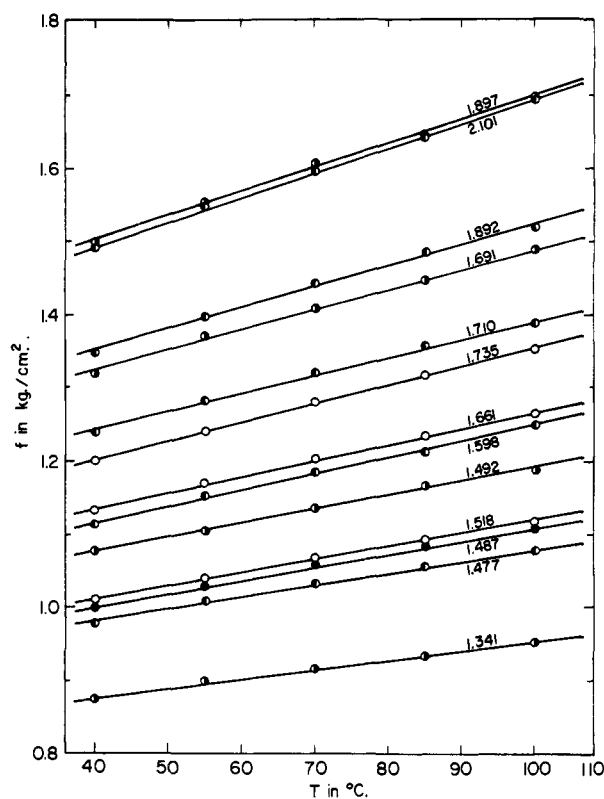


Fig. 2.—Tension f (referred to the unstrained cross section) vs. temperature at constant length: O, Si-1; ●, Si-2; ●, Si-3; ●, Si-4. Values of α at 100° are indicated.

representing the ratio of the slope to the square of the intercept ($[\eta]$), was found to be 0.47 ± 0.05 without evidence of trend with temperature.

Results

Determination of $d \ln \langle r^2 \rangle_0 / dT$ from Stress-Temperature Coefficients.—Tensions observed at various fixed lengths are plotted against temperature for the several cross-linked samples in Fig. 2. Indicated with each plot are the extension ratios α at 100°, where $\alpha = L/L_i$ is the ratio of the length L of the strained sample to its relaxed length at the same volume. To facilitate comparison between samples, the tension has been divided by the cross-sectional area of the undistorted sample at 100°. On this basis, values are quoted in kg. cm.⁻². Although the dimensions are those of stress, these quantities are obviously not true stresses. Slopes calculated by the method of least squares from the plot in Fig. 2 are given in the fourth column of Table II.

According to the theory of rubber elasticity,^{1,13} the temperature coefficient of $\langle r^2 \rangle_0$ is related as follows to the temperature coefficient of the tension f at constant V and L

$$d \ln \langle r^2 \rangle_0 / dT = -[\partial \ln (f/T) / \partial T]_{V,L} = f_e / fT \quad (1)$$

The relationship expressed by the second equality is thermodynamic, f_e being the contribution to f from the change in internal energy with length. The coefficient at constant V and L required by eq. 1 can be obtained from the corresponding coefficient measured at constant p and L only by resort to an equation of state for the elastic body.¹³ According to the theoretical equation of state for gaussian networks, the difference between these coefficients is given¹³ by $\beta(\alpha^3 - 1)^{-1}$, where β is the cubical coefficient of thermal expansion. Hence

$$d \ln \langle r^2 \rangle_0 / dT = -[\partial \ln (f/T) / \partial T]_{p,L} - \beta(\alpha^3 - 1)^{-1} \quad (2)$$

(10) V. Crescenzi and P. J. Flory, *J. Am. Chem. Soc.*, **86**, 141 (1964).

(11) E. L. Warrick, W. A. Piccoli, and F. O. Stark, *ibid.*, **77**, 5017 (1955).

(12) M. L. Huggins, *ibid.*, **64**, 2716 (1942).

(13) P. J. Flory, A. Ciferri, and C. A. J. Hoeve, *J. Polymer Sci.*, **45**, 235 (1960); P. J. Flory, *Trans. Faraday Soc.*, **57**, 829 (1961).

TABLE II
 STRESS-TEMPERATURE RESULTS

Sample	α	f , kg. cm. ⁻²	$(\partial f/\partial T)_{p,L}$ $\times 10^3$	$-\left[\frac{\partial \ln(f/T)}{\partial T}\right]_{p,L}$ $\times 10^3$	$\frac{\beta}{\alpha^2 - 1} \times 10^4$	f_e/f	$\frac{d \ln \langle r^2 \rangle_0}{dT} \times 10^3$
Si-1	1.518	1.07	1.76	1.26	0.35	0.31	0.91
	1.661	1.20	2.23	1.05	.25	.27	.80
	1.735	1.28	2.56	0.91	.21	.24	.70
Si-2	1.477	1.03	1.68	1.28	.40	.30	.88
	1.598	1.18	2.26	1.02	.29	.25	.73
	1.710	1.32	2.51	1.01	.22	.27	.79
	1.892	1.44	2.89	0.90	.15	.26	.75
	2.101	1.59	3.32	0.83	.11	.25	.72
Si-3	1.487	1.05	1.85	1.15	.38	.26	.77
Si-4	1.341	0.916	1.27	1.50	.62	.30	.88
	1.492	1.13	1.93	1.21	.38	.28	.83
	1.691	1.41	2.77	0.94	.23	.24	.71
	1.897	1.60	3.29	0.85	.15	.24	.70

Av. 0.27 ± 0.02

0.78 ± 0.06

The coefficient $[\partial \ln(f/T)/\partial T]_{p,L}$ was calculated from $(\partial f/\partial T)_{p,L}$ as given in Table II, together with the value f of the tension at the mean temperature T . The value of $[\partial \ln(f/T)/\partial T]_{p,L}$ together with the small correction term in eq. 2, were used to calculate both f_e/f and $d \ln \langle r^2 \rangle_0/dT$.

The results of thirteen experiments treated in this manner are presented in Fig. 2 and Table II. Tensions observed over decreasing and increasing phases of the temperature cycle were identical within limits of observations in each of these experiments. Temperature coefficients of $\langle r^2 \rangle_0$ given in the last column of the table are independent of the method of cross-linking but appear to decrease somewhat with increasing α . No explanation is apparent for this trend if indeed it is significant. A parallel effect has not been observed for other systems investigated previously.¹

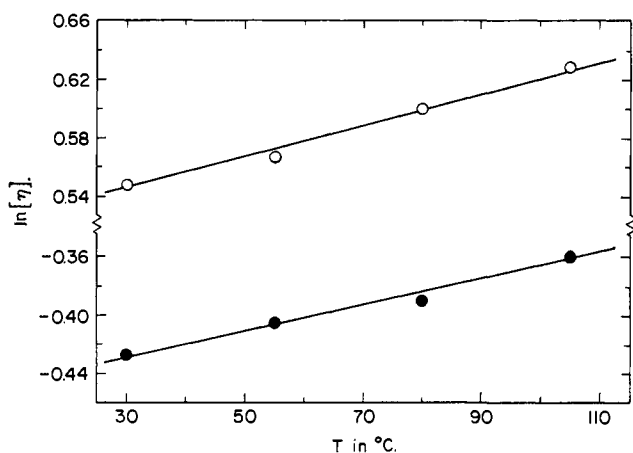


Fig. 3.—Intrinsic viscosity vs. temperature for PDMS in silicone fluid SF-96(10): O, $M = 2.5 \times 10^6$; ●, $M = 0.43 \times 10^6$.

In five additional experiments not included in Table II the tensions for the temperature-ascending sequence of measurements fall slightly below those for the initial temperature-descending sequence. In no case did the discrepancy exceed 4% of the total change with temperature. Whether it was attributable to the sample or to "drift" in the electronic system was not ascertained. Application of corrections assuming the drift to be linear with time gave $d \ln \langle r^2 \rangle_0/dT = 0.84 (\pm 0.10) \times 10^{-3} \text{ deg.}^{-1}$ as the average for these five experiments. This result corroborates the average for the thirteen reversible experiments summarized in Table II, namely, $0.78 (\pm 0.06) \times 10^{-3} \text{ deg.}^{-1}$ which we take as the best value based on our stress-temperature

studies. Our experiments consistently yielded higher values than found by Ciferri, namely $0.46 (\pm 0.14) \times 10^{-3} \text{ deg.}^{-1}$, by application of the same method.

Temperature Coefficient of the Intrinsic Viscosity.—Intrinsic viscosities of two PDMS fractions of high molecular weight were determined at a series of temperatures from 30 to 105° as described in the Experimental section, using as solvent a dimethylsiloxane fluid having a molecular weight of ca. 1200. The concentration was computed at each temperature of measurement from the thermal expansion coefficient of the solvent. Results are plotted against temperature in Fig. 3.

Evaluation of $d \ln \langle r^2 \rangle_0/dT$ from each of the slopes in Fig. 3 was carried out in the manner previously set forth,² using as basis the Flory-Fox relationship¹⁴ between $[\eta]$ and chain dimensions

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

and their theoretical expression¹⁴ for this expansion factor¹⁶ α , namely, where $\Phi = 2.5 \times 10^{21}$ for gaussian

$$\alpha^5 - \alpha^3 = 27(2\pi)^{-1/2} (v^2/N_A V_1) (\langle r^2 \rangle_0 / M)^{-1/2} M^{1/2} \psi_1 (1 - \Theta/T) \quad (4)$$

chains, M is the molecular weight of the polymer, v is the specific volume of the polymer, V_1 is the molar volume of the solvent, N_A is the Avogadro number, ψ_1 is the entropy of dilution parameter, and Θ is the "ideal" or theta temperature, at which the chain dimensions are unperturbed, *i.e.*, at which $\alpha = 1$. We require the temperature coefficient of α which, according to eq. 4, depends in general on both $d \langle r^2 \rangle_0/dT$ and on the solvent-polymer interactions as represented by the parameters, ψ_1 and Θ . Differentiation of eq. 3 and 4 yields

$$d \ln \langle r^2 \rangle_0/dT = (5/3 - \alpha^{-2}) d \ln [\eta]/dT - (1 - \alpha^{-2}) [d \ln (v^2/V_1)/dT + \Theta/T(T - \Theta)] \quad (5)$$

Values of $d \ln [\eta]/dT$ were obtained directly from the plots of $[\eta]$ against temperature (Fig. 3) and $d \ln (v^2/V_1)/dT$ was calculated from the specific volumes and expansion coefficients given in Table I. As would be expected from the close similarity of solvent and solute, the enthalpy of mixing for the solutions is virtually zero.¹⁶ Hence, we take $\Theta = 0$ in eq. 4 and 5. The values of α required in eq. 5 were calculated from eq. 4 taking $(\langle r^2 \rangle_0/M)^{1/2} = 680 \times 10^{-11} \text{ cm. (g./mole)}^{-1/2}$ in accordance with results of the following

(14) P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904, 1909, 1915 (1951); P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(15) This α is not to be confused with the α previously used to specify the strain of an elongated polymer network.

(16) G. Delmas, D. Patterson, and D. Böhme, *Trans. Faraday Soc.*, **58**, 2116 (1962).

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

	$M = 2.5 \times 10^6$	$M = 0.43 \times 10^6$
$[\eta]_{30^\circ}$	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 ² 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

(1) NATO Fellow on leave from Istituto Chimico-Fisica, Naples, academic year 1962-1963.

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.