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SOME SILICON-CONTAINING POLYMERS.

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STATISTICAL AND ELASTOMERIC PROPERTIES OF SOME
SILICON-CONTAINING POLYMERS

by
John Hsien-shyh Ko

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
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in The University of Michigan
1975

Doctoral Committee:

Professor James E. Mark, Chairman
Associate Professor Arthur J. Ashe
Professor Charles G. Overberger
Associate Professor Robert R. Sharp
Professor Gregory S. Y. Yeh

To

Mei-You, my Wife

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I. RANDOM-COIL DIMENSIONS AND DIPOLE MOMENTS OF POLY-
(DIMETHYLSILMETHYLENE)

A. Introduction

Studies of the configurational characteristics of macromolecules are essential for the rational interpretations of their properties both in solution and in the bulk amorphous state.¹⁻⁴ The spatial arrangements or configurations of a typical chain molecule in the randomly-coiled state are determined by (1) bond lengths, (2) bond angles, and (3) rotational (torsional) angles about its skeletal bonds. In general, the first two features, bond lengths and bond angles, are fixed within narrow limits at the temperature of interest. On the other hand, an almost unlimited number of spatial configurations may be generated through rotations about skeletal bonds, with the probability of occurrence of any particular configuration being determined by the associated conformational energy. Accordingly, the properties of polymeric materials are determined by the fixed parameters (bond lengths, bond angles) and by the statistical averages of the variable parameters (torsional angles). It is obviously of fundamental importance to study the configuration-dependent properties of chain molecules. Most desirable of course is a joint experimental-theoretical approach: measurements of a variety of such statistical properties followed by the interpretation of such results in terms of current statistical mechanical models of linear chain molecules.

One of the most important quantities used to characterize the spatial configuration of a randomly-coiled polymer molecule is the mean-square end-to-end distance $\langle r^2 \rangle$ of the chain.⁵⁻¹¹ In general, however, this quantity depends on interactions between the chain molecule and the solvent medium in which it is studied, and this circumstance of course complicates establishment of the desired relationships between chain structure and statistical properties. It is possible, fortunately, to correct for such interactions, thereby obtaining the dimensions of the polymer coil in the absence of such "long-range interactions" or "excluded volume effects."^{1,12-15} These so-called "unperturbed dimensions" $\langle r^2 \rangle_0$ ^{1,16-18} are fundamental to any quantitative study of chain configurations. They may be obtained experimentally in either of two ways. In the first, the unique temperature is found, for the particular polymer-solvent system, in which the attractive forces between polymer segments exactly nullify the polymer-solvent interactions and excluded volume effects. This temperature, quite analogous to the Boyle temperature at which a real gas obeys $PV = nRT$, is called the Flory temperature or (H) -temperature.^{12,13} Alternatively, one may carry out measurements in any solvent whatever and subsequently use current solution theories to convert values of $\langle r^2 \rangle$ thus obtained to the unperturbed values $\langle r^2 \rangle_0$.¹⁹⁻²²

The mean-square dipole moments²³⁻²⁶ $\langle \mu^2 \rangle_0$ are also

sensitive to chain configuration, and values of this quantity provide a great deal of information supplementary to that obtained from studies of the unperturbed dimensions $\langle r^2 \rangle_0$. Since different configurations of a chain molecule generally correspond to different energies, configuration-dependent properties are in general temperature dependent. For this reason, the coefficients²⁷⁻³² $d\ln\langle r^2 \rangle_0/dT$ and $d\ln\langle \mu^2 \rangle_0/dT$ are also widely used in the characterization of chain configurations.

This first part of the thesis consists of a thorough investigation of the configurational characteristics of poly(dimethylsilmethylene) (PDMSM) $[\text{Si}(\text{CH}_3)_2\text{-CH}_2\text{-}]_x$ in the randomly-coiled state. Of particular interest will be the comparison of the properties of this chain molecule with the properties of others with related structure. For example, PDMSM is obviously closely related to the extensively studied polymer poly(dimethylsiloxane) (PDMSO) $[\text{Si}(\text{CH}_3)_2\text{-O-}]_x$.³²⁻³⁴ There are also obvious structural similarities between PDMSM and polyisobutylene (PIB) $[\text{C}(\text{CH}_3)_2\text{-CH}_2\text{-}]_x$;^{26,35-38} in the case of this comparison, the most important difference might be the relief of steric interactions occasioned by the fact that Si-C skeletal bonds are considerably longer than C-C bonds. Comparison between the properties of PDMSM, PDMSMO, and PIB should therefore shed considerable light on the effect of structure on chain configuration and thus also on the properties of polymeric materials in general.

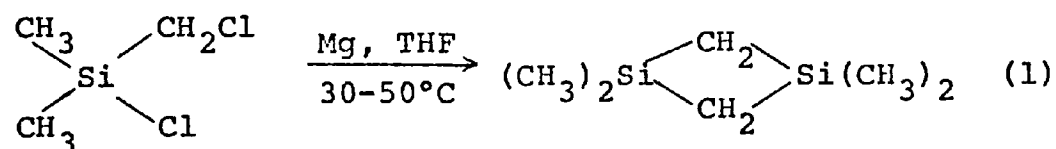
The experimental part of the investigation involves considerable synthetic work since neither the polymer PDMSM nor the monomer from which it is prepared is available commercially. Since most of the properties sought depend on molecular weight distribution as well as on the molecular weight itself, fractionation of the polymer into portions relatively narrow in molecular weight distribution is an essential part of the preparative scheme. Experimental values of $\langle r^2 \rangle_0$ and $d\ln\langle r^2 \rangle_0/dT$ may then be obtained by viscometric and osmometric measurements at a series of temperatures. Independent values of the coefficient $d\ln\langle r^2 \rangle_0/dT$ will be obtained by force-temperature measurements on networks of PDMSM chains.^{26,28} The related quantities $\langle \mu^2 \rangle_0$ and $d\ln\langle \mu^2 \rangle_0/dT$ will be obtained from dielectric constant and index of refraction measurements over a range of temperatures. The application of rotational isomeric state theory to PDMSM is to be explored using the limited structural and thermodynamic information available on inorganic materials of this type.

B. Experimental Details

1. Preparation of Materials

a. Synthesis of the Monomer, 1,1,3,3-Tetramethyl-1,3-disilacyclobutane. The solvent to be used in the synthesis was tetrahydrofuran (THF); it was obtained from the Fisher Scientific Co. as a reagent-grade material, but was dried in lithium aluminum hydride and collected at 65°C just

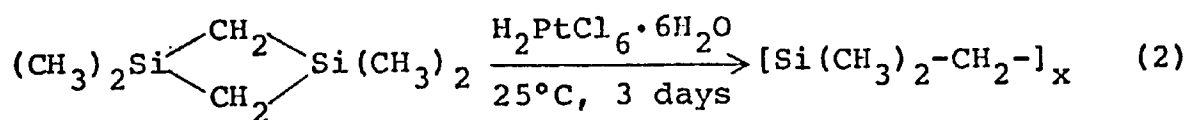
prior to use. The THF solvent was also purged with predried nitrogen to remove any dissolved oxygen. Chloromethyldimethylchlorosilane $\text{Si}(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{Cl}$ was obtained from Peninsular ChemResearch, Inc. and was distilled at ca. 115°C , before use. Methyl iodide was used as initiator to start the Grignard reaction; magnesium turnings for the reaction were obtained from J. T. Baker Chemical Co. The reaction as shown in the following equation was carried out by the procedure of Kriner:³⁹



The whole assembly of glassware was baked at approximately 80°C under vacuum for at least two hours. A stream of predried nitrogen was passed very slowly through the reaction flask to keep out moisture and oxygen during the period of the Grignard reaction. A few drops of methyl iodide were added to a small amount of magnesium turnings covered by THF solvent. Upon adding a portion of the total weight of $\text{Si}(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{Cl}$ to be used, the reaction started as was evidenced by a light yellowish bubbling from the magnesium turnings. More of the silane was then added to the THF to make its final concentration 33% by volume. The rest of the magnesium turnings was added slowly over a period of approximately two hours. The reaction system was kept at 30 to 50°C , with occasional cooling when necessary. Because a viscous white slurry of

magnesium chloride was produced during the reaction, additional portions of THF solvent were added from time to time to reduce the viscosity and thus permit the required rapid mechanical stirring. After approximately four hours, the reaction was cooled and about one liter of cold water was slowly added to the mixture. The organic layer was separated and the largest portion of THF in it was first removed by fractional distillation. The monomer itself was collected at 60°C under 100 mm pressure, giving a yield of 35%. Its H^1 nmr spectrum is given in Figure 1; it shows two singlets at chemical shift $\tau = 9.8$ and 10.0 with the relative intensities of the peaks in the ratio 3 to 1 in agreement with the literature values.^{40,41}

b. Polymerization of the Monomer. The method of polymerization was that of Weyenberg and Nelson⁴² shown in the equation



The monomer was purified by low-pressure distillation just prior to use. A mixture of monomer and approximately 1 mg $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ catalyst was placed in a 100-ml three-neck flask and kept at 25°C. A glass rod with an attached propeller was fitted through the center port and used to stir the mixture over the three-day reaction period. The resulting polymer, which was very viscous and clear, was

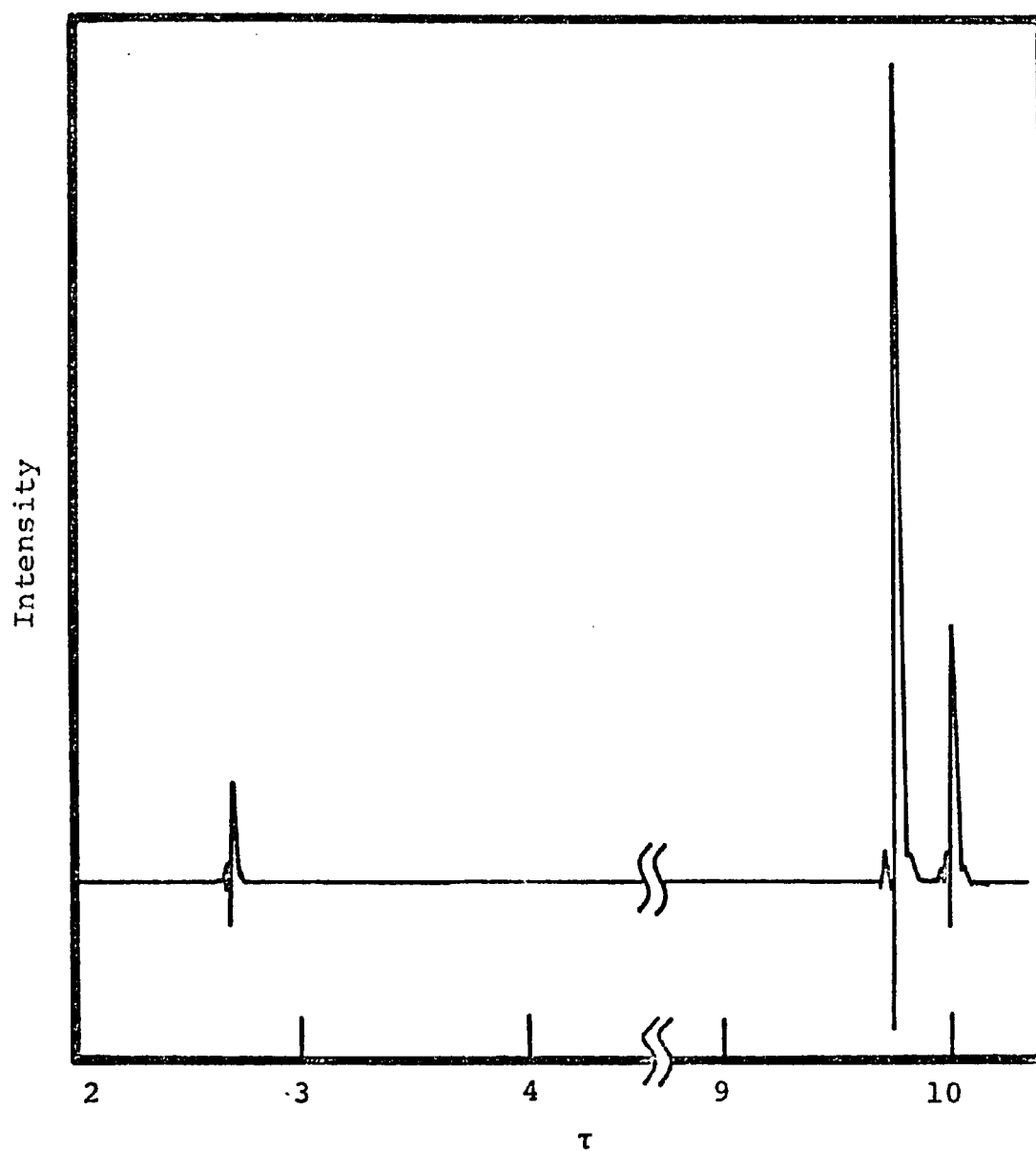


Figure 1. NMR spectrum of 1,1,3,3-tetramethyl-1,3-disilacyclobutane in carbon tetrachloride. The chemical shift at $\tau = 2.63$ for benzene was used as reference.

dissolved in benzene and the catalyst was filtered out by a fritted-disc Buchner funnel. The polymer solution was precipitated in methanol and dried in a vacuum oven at approximately 50°C to constant weight. The weight of the polymer PDMSM obtained in this way corresponded to a yield of 80% of the monomer. The nmr spectrum of the polymer in carbon tetrachloride is shown in Figure 2. It had the expected absorptions at chemical shifts $\tau = 9.9$ and 10.2, with the expected intensity ratio 3 to 1.⁴² The infrared spectra of the PDMSM in Nujol and in CCl_4 showed strong absorption bands, at 1050 and 1350 cm^{-1} ,⁴³ which are characteristic of SiCH_2Si groups; typical results are shown in Figure 3.

c. Fractionation of the Polymer, Poly(dimethylsil-methylene). There are many techniques for fractionating polymers,^{44,45} the main one and the one used here being based on the qualitative observation that the solubility of a polymer decreases as the molecular weight of the polymer increases. Thus, by adding a poor solvent (where attractions between polymer segments and solvent molecules are less important than those between polymer segments themselves) to a polymer solution, one can collect fractions of the polymer, each with a relatively narrow molecular weight distribution. In pursuit of such a separation of PDMSM into suitable fractions, the bulk sample was dissolved in reagent-grade benzene at a concentration of

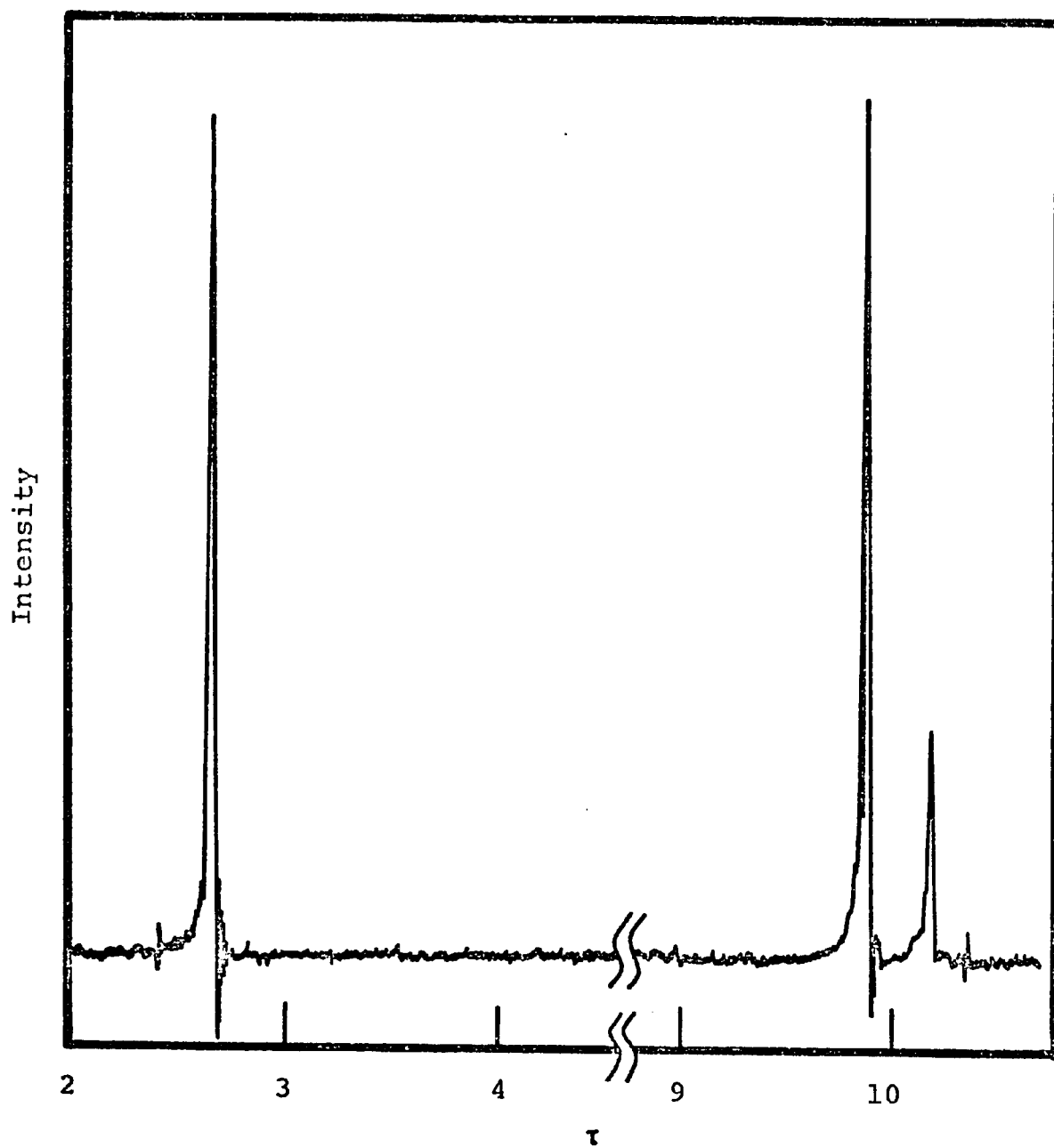


Figure 2. NMR spectrum of poly(dimethylsilmethylene) in carbon tetrachloride. The chemical shift at $\tau = 2.63$ for benzene was used as reference.

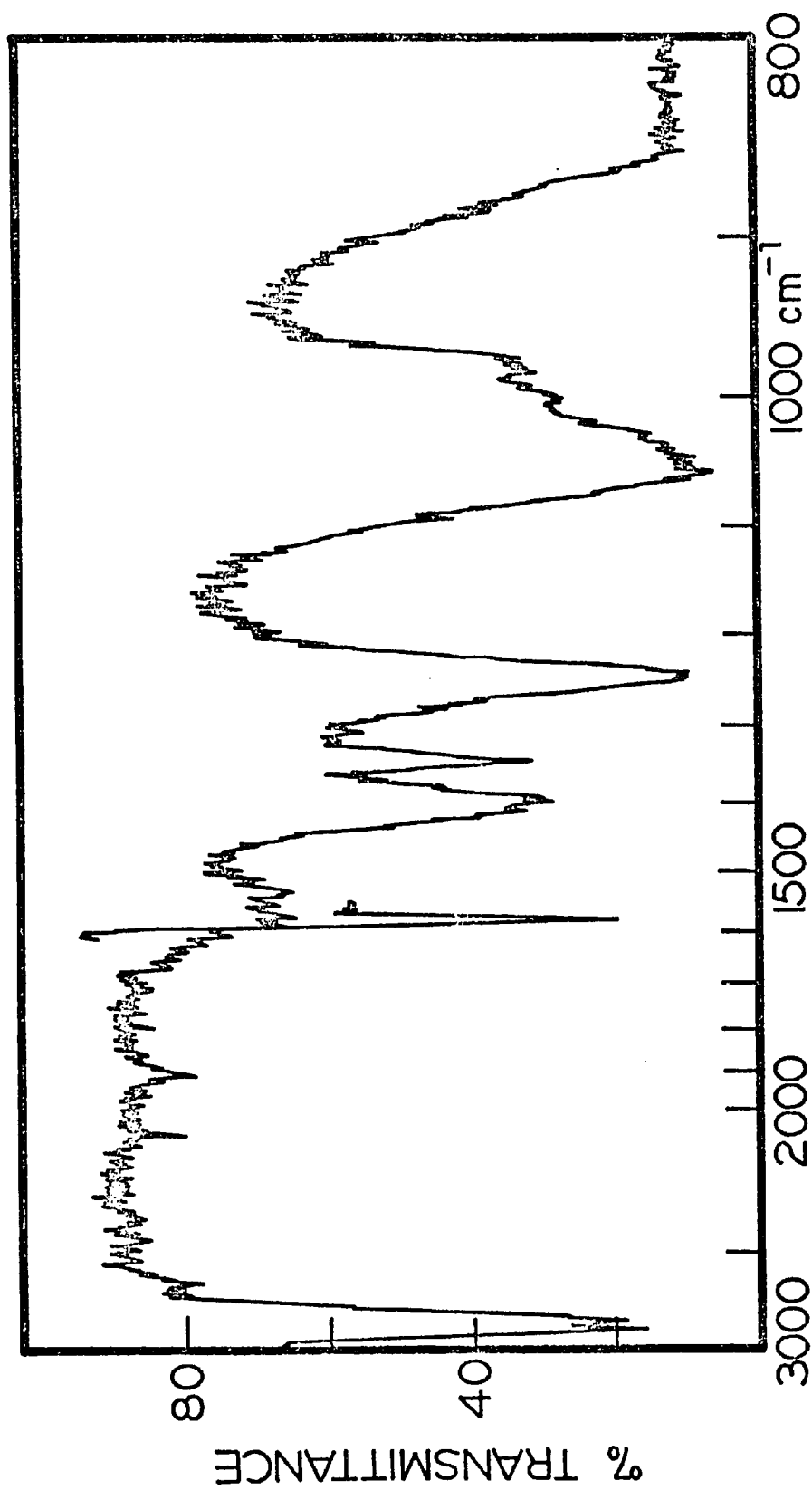


Figure 3. Infrared spectrum of poly(dimethylsilimethylene). The polystyrene absorption at 1650 cm^{-1} is given as reference.

approximately 1%. The poor solvent, methanol, was added slowly until a slight cloudiness developed at 25°C. The mixture was then warmed until the turbidity disappeared and then cooled slowly back to the original temperature. The precipitate (P_1) was allowed to settle for at least five hours and the supernatant (S_1) was then carefully poured off. Precipitate P_1 and liquid layer S_1 were fractionally precipitated again; four fractions were collected (P_1P , P_1S , S_1P , S_1S), and two of them (P_1S , S_1P) were combined. In this way, two successive fractionations yielded three fractions and N successive fractionations yielded $N + 1$ fractions. This technique is outlined in Figure 4. Four final fractions were thus collected; they were dried in vacuum at 50°C to constant weight.

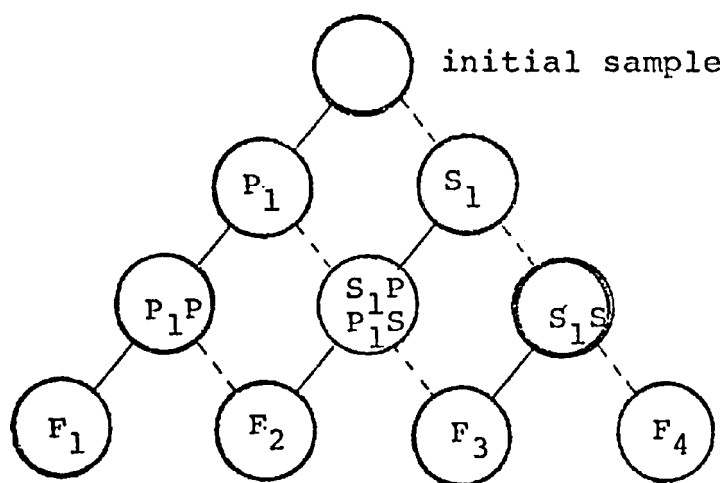


Figure 4. Schematic diagram of the precipitation fractionation.

2. Solution Properties

a. Viscosities. Two fractions (F_2 , F_4) of PDMSM prepared as described in the previous section were used for the viscosity measurements.* The polymers were purified several times by dissolving them in benzene, filtering the resulting polymer solution through a medium fritted-disc Buchner funnel and precipitating the polymer into methanol. Each polymer fraction thus purified was dried under vacuum at approximately 50°C to constant weight.

The solvent employed for the viscosity measurements was Matheson, Coleman and Bell Co. reagent-grade cyclohexane which was distilled at ca. 81°C, at atmospheric pressure, just prior to use. The density (D) at 20°C and the temperature coefficient of the density (dD/dt) for this solvent are 0.7782 g ml⁻¹ and -0.001 g ml⁻¹ °C⁻¹, respectively.⁴⁶ The density of PDMSM was determined using a pycnometer having a capacity of 2 ml; these measurements gave the value of 0.9185 g ml⁻¹ at 35°C. The temperature coefficient $d\ln V/dT$, obtained as described in a later section, was found to be 0.60×10^{-3} °K⁻¹.

Five solutions of each of the two fractions in cyclohexane were prepared by weighing the polymer in a 100 ml volumetric flask and diluting to the desired concentration

* Because of the variety of measurements being made and the small amounts of material available, it was not possible to obtain all the required data on the same fractions.

of one of the temperatures to be investigated. Values of the concentration at other temperatures were calculated from the specific volumes of polymer and solvent at the appropriate temperature, on the assumption of simple additivity of volumes. All concentrations c in these viscosity studies were expressed in grams per 100 ml (g dl^{-1}).

A Cannon-Ubbelohde Viscometer (no. 50 D626) having a capillary large enough to give an efflux time of the cyclohexane solvent greater than 200 seconds was chosen; this permitted the neglect of kinetic energy corrections to the observed efflux times. Efflux times of the solvent and polymer solutions were measured at 25, 30, 40, and 50°C, with the temperature being controlled to $\pm 0.02^\circ\text{C}$. Efflux times were measured three times and were found to be reproducible to ± 0.15 second. The relative viscosity

$$\eta_{\text{rel}} = \frac{\text{efflux time of polymer solution}}{\text{efflux time of solvent}}$$

was in the range 1.1 to 1.5.⁴⁴ Intrinsic viscosities $[\eta]$, which by definition^{44,47} are the values of either $(\eta_{\text{rel}} - 1)/c$ or $(\ln \eta_{\text{rel}})/c$ extrapolated to infinite dilution, were obtained by least-squares analysis of these data.

b. Osmotic Pressures. The osmotic pressures of dilute solutions of the polymer in cyclohexane were measured by a recording osmometer (Wescan Instrument Inc.).⁴⁸ The device consists of an osmometer cell, a strain-gage

transducer, an adjustable precision temperature controller, and associated power supplies. The osmometer cell itself consists of two compartments (solution chamber and solvent chamber) separated by a semi-permeable membrane. The solvent side is sealed by a flexible diaphragm with one side attached to a force transducer. Any volume change in the solvent chamber due to transfer of solvent to the solution compartment is sensed by the strain-gage detector and monitored by a recorder (0-1 mv full scale). The membranes chosen for this experiment were type 07 cellulose derivatives obtained from Schleicher and Schuell, Inc. Solutions of the PDMSM fractions F_2 and F_4 were prepared by the usual quantitative techniques at each desired concentration; reagent-grade cyclohexane, which has been redistilled, was used as the solvent. The osmotic pressure of each polymer solution was measured at least twice, at each of the temperatures, viz., 32.2, 42.4, and 50.5°C. The temperature was controlled to within $\pm 0.01^\circ\text{C}$ by means of the adjustable precision temperature controller. The pressure exhibited by each solution was monitored continuously and only after the readings showed no discernable change for at least 20 minutes were the pressure considered equilibrium values and recorded as values of π for final analysis.

The relationship among the osmotic pressure of a dilute polymer solution, its molecular weight, and its second virial coefficient have been derived and discussed

in great detail elsewhere.¹²⁻¹⁴ The most general form of this relationship is given by

$$\pi/c = RT (1/M + A_2c + A_3c^2 + \dots) \quad (3)$$

where $\pi = GD\Delta h$ is the osmotic pressure in dynes cm^{-2} , G is the gravitational constant, D is the density of the solution,* Δh is the observed equilibrium hydrostatic head, c is the concentration of the polymer solution in g cm^{-3} , R is the gas constant, and M is the number-average molecular weight of the polymer. The quantities A_2 and A_3 are the second and third virial coefficients, respectively, and are measures of the interactions between polymer segments and solvent molecules. For a dilute polymer solution, the effect of the third virial coefficient A_3 is negligibly small and equation 3 may be condensed to only the first two terms. It may therefore be given in the simpler form

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

Accordingly, plots of π/cT against c give R/M as the intercept and RA_2 as the slope.

c. Dielectric Constants and Refractive Indices. The apparatus used for the dielectric constant measurements on the PDMSM solutions was a DM01 Dipolemeter operating at a

* Solution densities are essentially those of the solvent in the case of dilute solutions.

fixed frequency of 2.0 MHz, and a cylindrical, gold-plated, thermostatted cell having a capacity of approximately 20 ml. The apparatus was calibrated at each temperature of measurement using n-hexane, benzene, cyclohexane, and carbon tetrachloride.⁴⁹ The solvents were reagent-grade and distilled just prior to their use.

The refractive indices of the polymer solutions were determined using a Bausch and Lomb Precision Refractometer of the Abbe design. The temperature was controlled to 0.01°C by a Lauda/Brinkmann Circulator. The four PDMSM fractions, designated F_1 - F_4 , were studied in cyclohexane and each solution used was separately prepared. The range of weight fractions w_2 for the solutions of each fraction was 0.003-0.025. Fraction F_3 was measured at two wavelengths 589 and 436 mμ; it was also studied over the range 20 to 50°C in order to estimate the temperature coefficient of its mean-square dipole moment. The other fractions were measured only at 589 mμ and 30°C.

3. Elastic Properties of Networks of the Polymer

a. Preparation of Cross-linked Samples. The poly-(dimethylsilmethylene) employed in this aspect of the study was an unfractionated portion, prepared separately for this experiment. The undiluted polymer sample was forced into an aluminum-foil-lined, aluminum mold having a well approximately 0.1 x 3 x 7 cm. The mold and its contents were degassed in vacuum at room temperature in

order to remove any absorbed gas which might interfere with the cross-linking procedure. After the degassing, the mold was quickly sealed by means of an aluminum-foil-lined aluminum cover which was tightly held in place by a series of screws. The sample in the sealed container was then cross-linked at room temperature by means of gamma radiation from a Co^{60} source. The dose rate was approximately 0.08 Mrad/hr and the total dose was 10 Mrad (corrected for attenuation of radiation intensity due to the aluminum mold itself). The mold was not opened for at least 6 hours after irradiation in order to permit decay of the free radicals generated within the sample. The two aluminum-foil liners with the cross-linked sample between it were peeled from the mold and placed in benzene to facilitate removal of the network from the aluminum-foil liners. The swollen network was then dried to constant weight at room temperature. A strip approximately 0.1 x 1.0 x 7.0 cm was cut from it; the network had been cooled on Dry Ice prior to the cutting to minimize distortion of the sample.⁵⁰ The strip was then immersed in a gently stirred benzene to remove any uncross-linked PDMSM from it. The soluble portions of the sample thus extracted amounted to approximately 20% of the total weight of the sample. Reference marks were placed on the extracted strip by putting two small dots of paint on its surface (while it was in the stretched state, in order to prevent their blurring in the subsequent stress-strain measurements).

b. Elasticity and Thermoelasticity (Force-temperature Measurements). The apparatus^{50,51} used to study the stress-strain behavior of the PDMSM network consisted of a pyrex cell (approximately 4 cm in diameter), a force transducer (Statham Model G1-16-350 having a capacity of ± 460 grams) run by a constant D.C. power supply (Hewlett-Packard Model 6217A) and calibrated by constant weights just prior to the measurements. A stream of predried nitrogen was slowly passed through the tube to eliminate any possibility of oxidative degradation during the experimental measurements. The sample was mounted in the cell by two clamps, the upper one of which was connected to the force transducer. The output (force) exhibited by network was displaying continuously on a recorder (Leeds and Northrup, Model Speedomax W Azar). The length of the sample unstretched and stretched, was measured to ± 0.001 cm using a Micro-meter Slide Cathetometer (Gaertner Model M940-303P).

Two types of experiments were carried out on the networks thus prepared: the isothermal measurement of the stress or force f as a function of strain at a number of constant temperatures, and the measurement of stress as a function of temperature at constant length. In both cases, the elongation α was defined as L/L_1 , where L is the length of the stretched sample at the chosen temperature of measurement, and L_1 is the length of the undeformed sample at a convenient constant temperature. Values of the elastic force were recorded only after they became

constant for a period of at least 15 minutes; up to 7 hours were required to attain this degree of constancy. In the constant temperature experiment, reversibility was checked by doing measurements on the same sample using both successively increasing strains and successively decreasing strains. In the experiments at constant length, measurements of a series of decreasing temperatures were followed by measurements at a series of increasing temperatures. Results thus obtained showed a high degree of reproducibility over the temperature range employed, 30-90 (± 0.05)°C.

The value of the thermal expansion coefficient $\beta = (\partial \ln V / \partial T)_p$ required for analysis of the above data was obtained by measurement of the undistorted length L_i of the sample as a function of temperature, and use of the relationship^{26,52} $\beta = 3(\partial \ln L_i / \partial T)_p$. These data are shown in Figure 5. Finally, the cross-sectional area A^* of the undistorted sample was measured by means of a micrometer.

C. Experimental Results and Discussion

1. The Mean-Square Unperturbed Dimensions $\langle r^2 \rangle_0$

Figures 6 and 7 show the extrapolations used to obtain values of the intrinsic viscosity $[\eta]$ for PDMSM fractions F_2 and F_4 , respectively. The results thus obtained, at temperatures of 25, 30, 40 and 50°C, are shown in the third column of Table I. The osmotic pressure data were treated by plotting π/cT against c , where π is in dynes

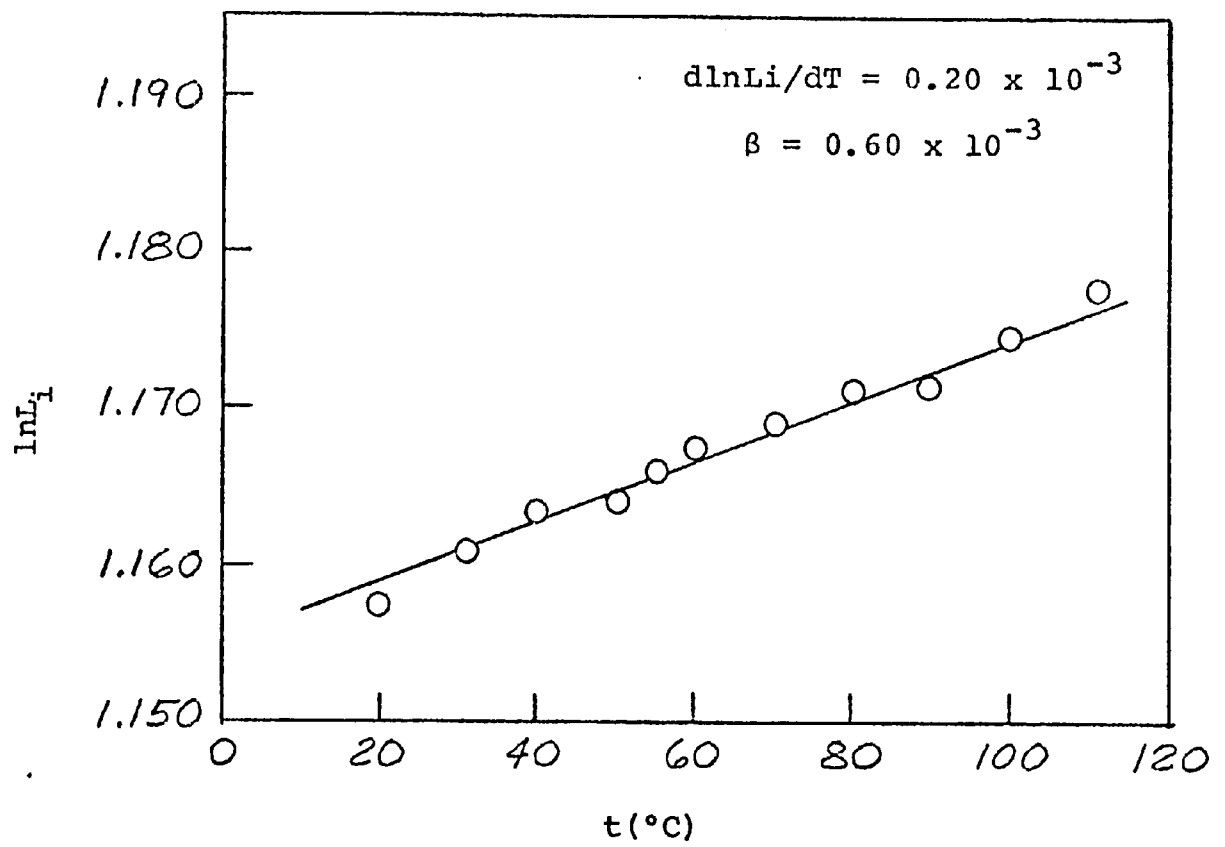


Figure 5. Measurement of the undistorted length L_i of a PDMSM network as a function of temperature.

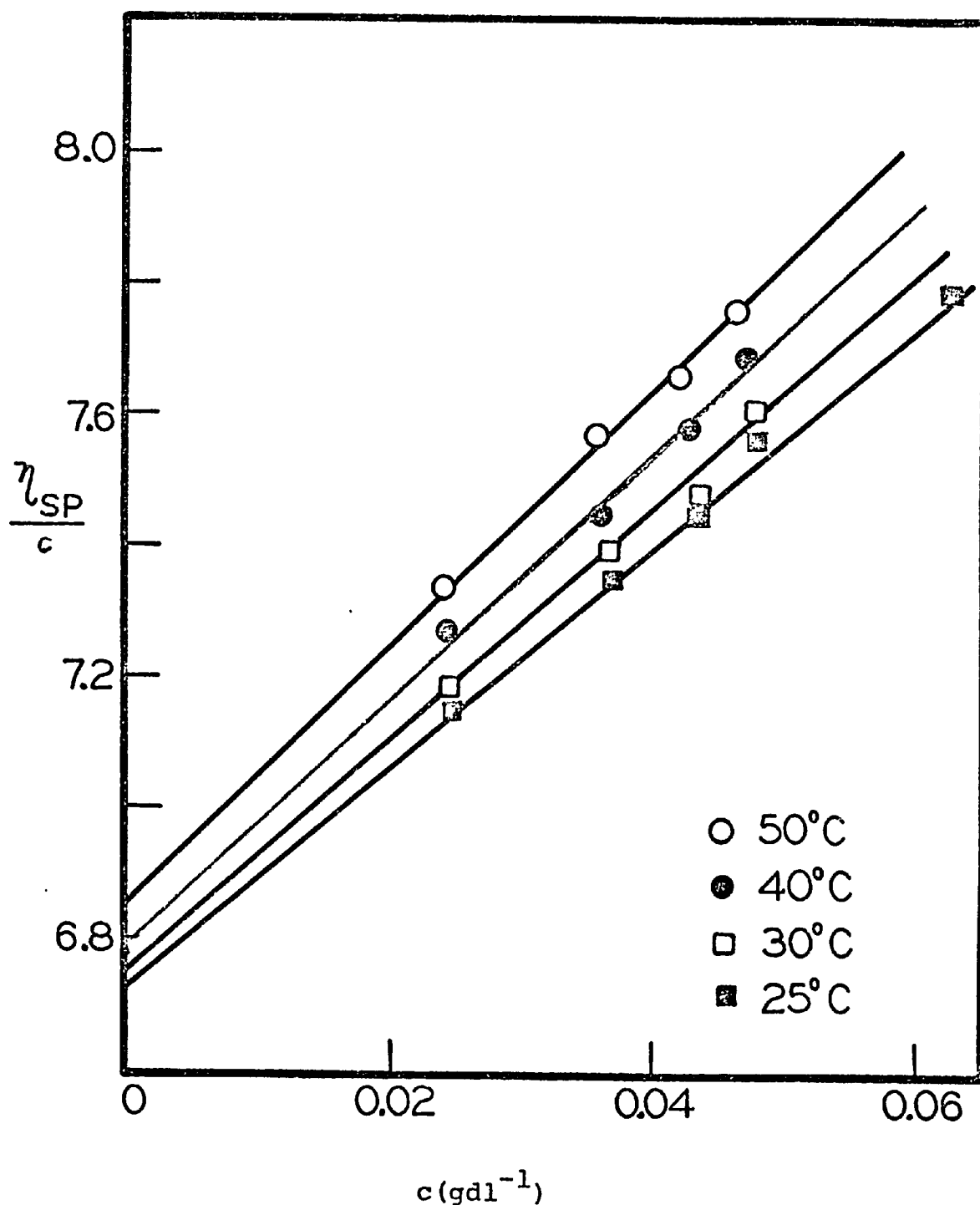


Figure 6. The reduced viscosity (η_{sp}/c) plotted against concentration for PDMSM fraction F_2 in cyclohexane at temperatures 25, 30, 40, and 50°C. The intrinsic viscosity, $[\eta]$ was obtained by extrapolating each line to infinite dilution by means of least-squares analysis.

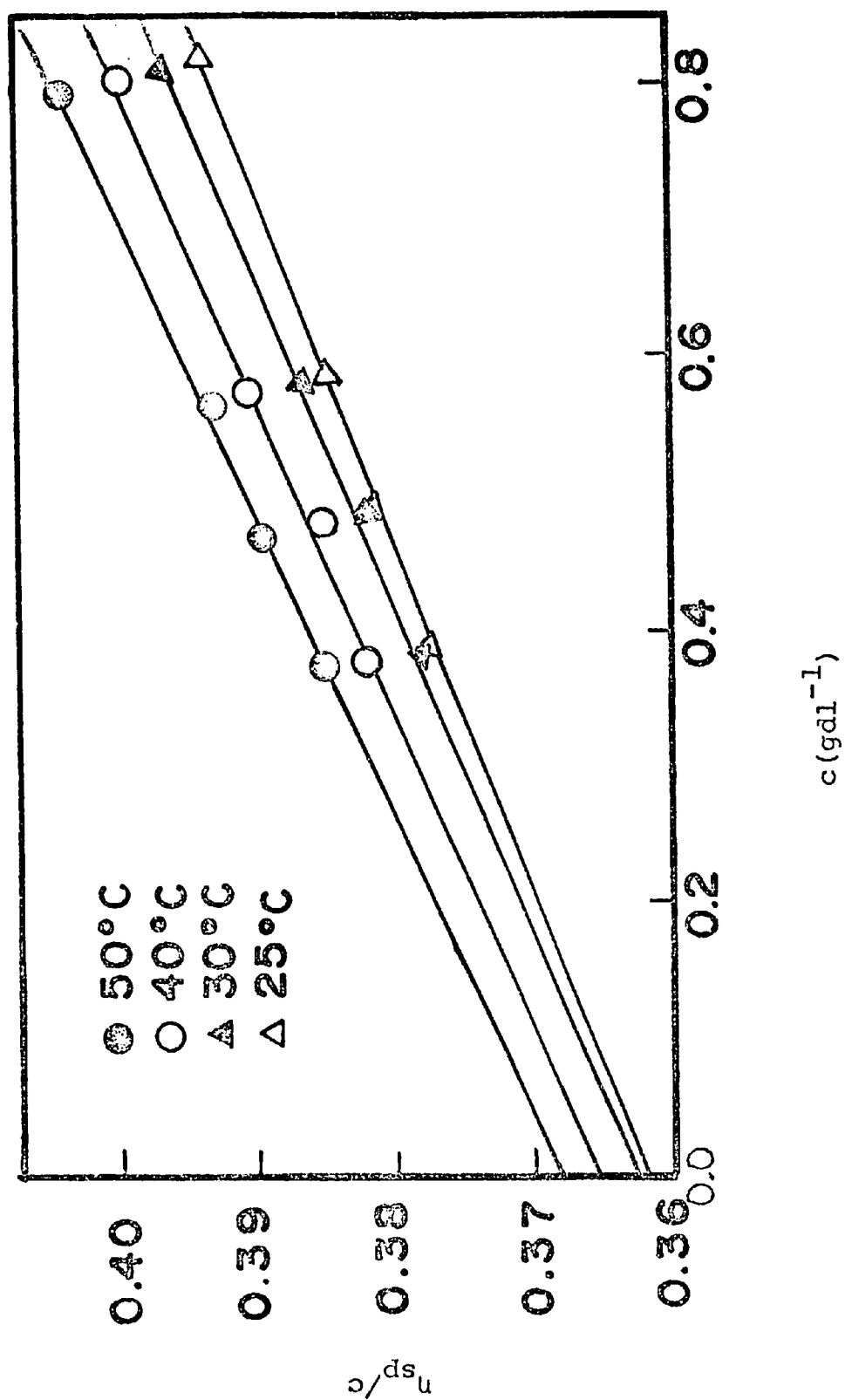


Figure 7. Values of η_{sp}/c plotted against concentration for PDMSM fraction F₄ in cyclohexane at the specified temperatures. See legend to preceding figure.

Table I. Viscosity and Osmometry Results for PDMSM Fractions

F_2 ($M = 2.10 \times 10^6$) and F_4 ($M = 2.74 \times 10^4$)						
Fraction	T, °C	$[\eta]$ dl g ⁻¹	$10^4 A_2'$ cm ³ mole g ⁻²	α	$\langle r^2 \rangle_0 / nl^2$	$10^3 \text{ dln} \langle r^2 \rangle_0 / dT$
F_2	25	6.728	6.52	1.786	5.32	
	30	6.741	6.55	1.788	5.32	-0.1
	40	6.798	6.63	1.792	5.32	
	50	6.861	6.76	1.802	5.30	
				Av. (F_2)	5.32 ± (0.01)	
F_4	25	0.362	15.04	1.391	5.31	
	30	0.363	15.13	1.392	5.31	0.1
	40	0.365	15.31	1.395	5.31	
	50	0.368	15.54	1.398	5.32	
				Av. (F_4)	5.31 (±0.01)	
				Av. (F_2, F_4)	5.32 ± (0.01)	0.0 ± (0.1)

cm^{-2} and c in g cm^{-3} ; in this way, each curve should extrapolate to R/M with a slope of RA_2 , as shown in equation 4. Results for fractions F_2 and F_4 are shown in Figures 8 and 9, respectively. Data on the same fraction at different temperatures give essentially the same intercept, as expected; values of the number-average molecular weight M for F_2 and F_4 calculated from these two intercepts are $2.10 (\pm 0.06) \times 10^6$ and $2.74 (\pm 0.03) \times 10^4$, respectively. The variation in slopes with change in temperature reflects of course the temperature dependence of the second virial coefficient A_2 . Values of A_2 , in $\text{cm}^3 \text{ mole g}^{-2}$, were calculated from the slopes of the lines in Figures 8 and 9, by means of equation 4. They were then plotted against temperature and the values for 25, 30, 40 and 50°C obtained from these curves are given in column four of the table.

The values of $[\eta]$, M , and A_2 thus obtained were then used to calculate values of the chain expansion factor $\alpha = [\langle r^2 \rangle / \langle r^2 \rangle_0]^{1/2}$ which characterizes the perturbations due to long-range interactions.^{1,12-15} The relationship employed for this purpose was the standard equation of Flory and Orofino²¹

$$\ln[1 + (\pi^{1/2}/2)(\alpha^2 - 1)] = (27\phi/2^{5/2}\pi N_{\text{avo}})(A_2 M / [\eta]) \quad (5)$$

where ϕ is a hydrodynamic constant equal to $2.1 \times 10^{21} \text{ dl cm}^{-3} \text{ mole}^{-1}$ in good solvents,^{12,13,36} N_{avo} is Avogadro's number, and π here is 3.1416. These results are listed in column five of the table. Values of $\langle r^2 \rangle_0$ were

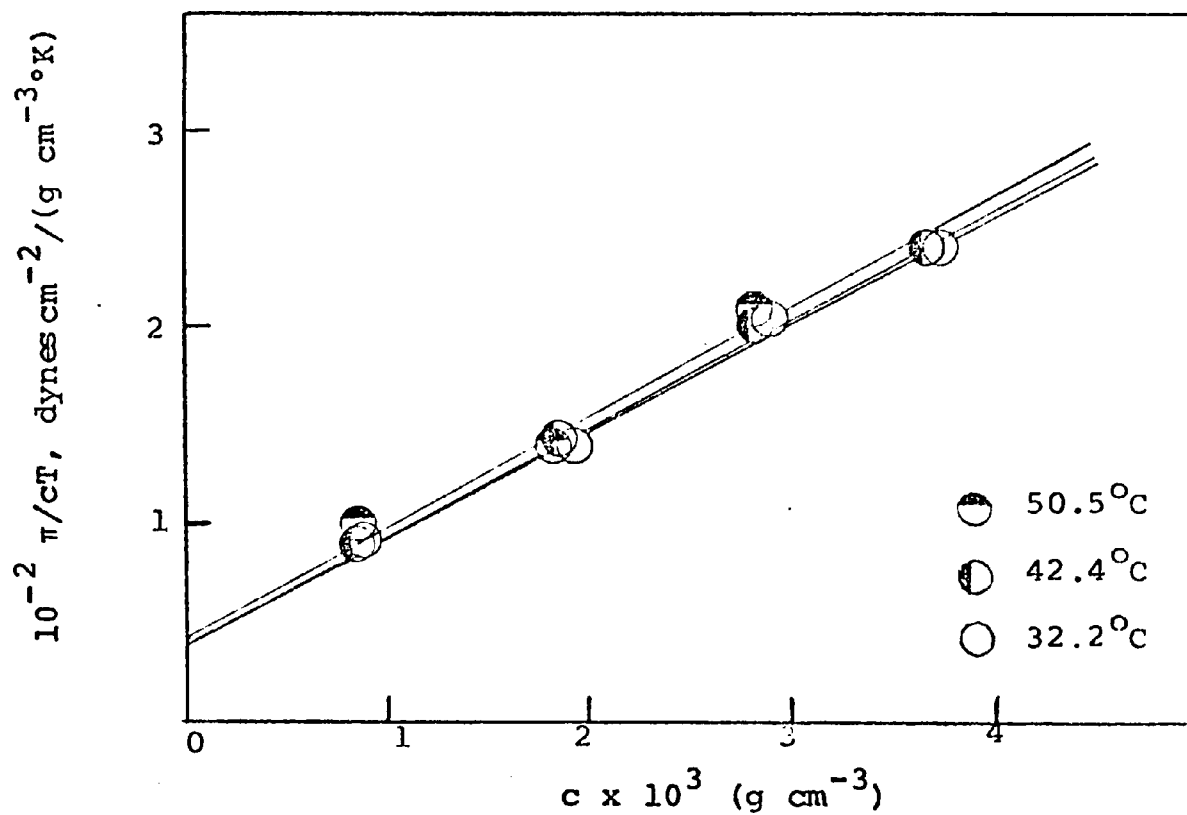


Figure 8. π/cT Plotted against concentration c in g cm^{-3} for PDMSM fraction F_2 in cyclohexane at temperatures 32.2, 42.4, and 50.5°C.

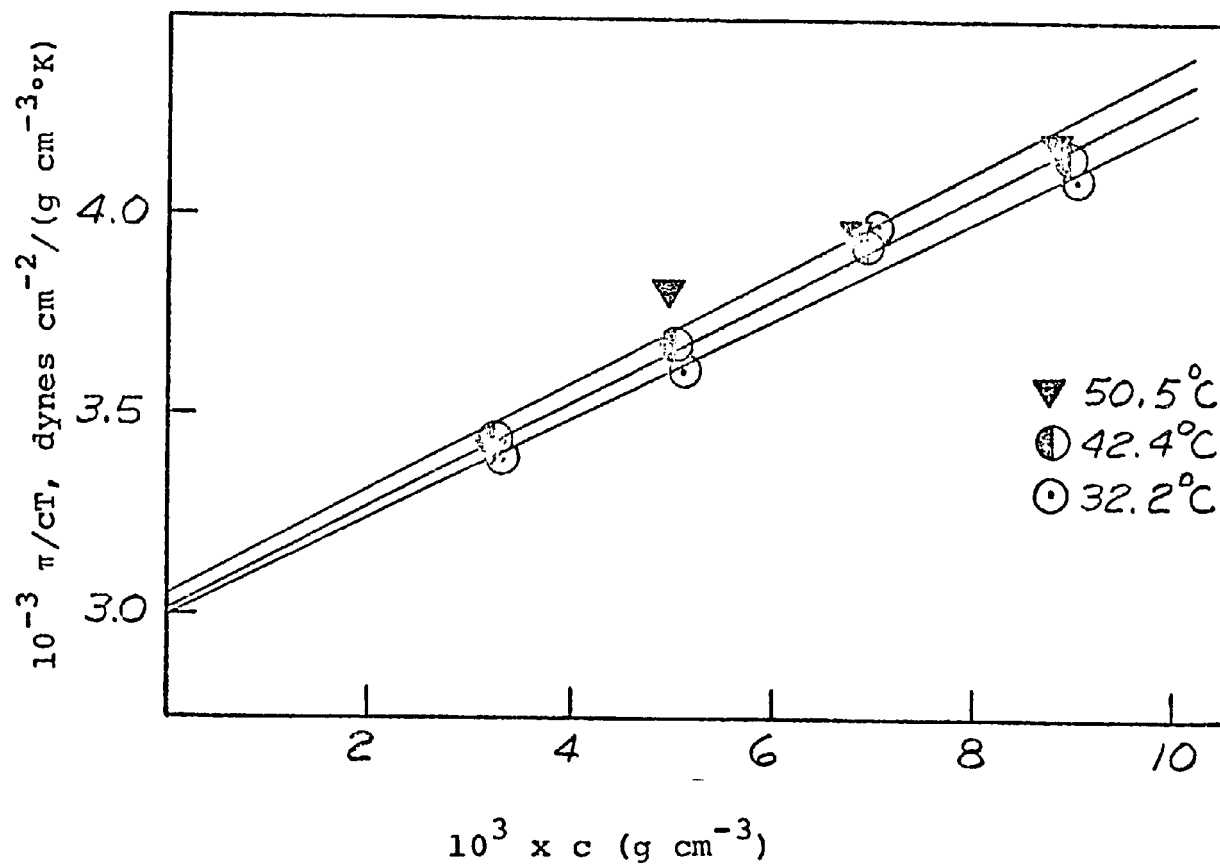


Figure 9. π/cT Plotted against concentration c in g cm^{-3} for PDMSM fraction F_4 in cyclohexane at temperatures 32.2 , 42.4 and 50.5°C .

then calculated from³⁶

$$[\eta] = \phi [\langle r^2 \rangle_0 / M]^{3/2} M^{1/2} \alpha^3 \quad (6)$$

Since $\langle r^2 \rangle_0$ itself depends on chain length, the dimensions were expressed as the "characteristic ratio" $\langle r^2 \rangle_0 / nl^2$, where n is the number of skeletal bonds, each of length $l = 1.90 \text{ \AA}$. This was done by noting that $M = nM_0/2$ where $M_0 = 72.2$ is the molecular weight per repeat unit of the PDMSM chain. The ratio $\langle r^2 \rangle_0 / nl^2$ thus defined is independent of chain length once n has exceeded 200 bonds. These results, shown in the following column are independent of molecular weight as expected, and give the average result $\langle r^2 \rangle_0 / nl^2 = 5.32 (\pm 0.01)$ for the PDMSM chain.

2. The Temperature Coefficient of $\langle r^2 \rangle_0$

It is difficult to extract values of $d \ln \langle r^2 \rangle_0 / dT$ directly from the above data because of difficulties in determining values of A_2 (and thus α) to the required degree of precision. Nonetheless an approximate value of this temperature coefficient was obtained by plotting $\ln[\langle r^2 \rangle_0 / nl^2]$ against the absolute temperature. These plots gave $d \ln \langle r^2 \rangle_0 / dT = -0.1 \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$ for F_2 and $0.1 \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$ for F_4 . The average result $0.0 (\pm 0.1) \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$ thus obtained from these viscometry and osmometry results at least has the qualitative significance that $d \ln \langle r^2 \rangle_0 / dT$ for the PDMSM chain is small and quite close to zero.

More reliable estimates of $d\ln\langle r^2 \rangle_0/dT$ were obtained from the elasticity behavior of the cross-linked PDMSM networks.^{26,28,52-54} In the treatment of these data, the reduced force $[f^*] = f/[\Lambda^*(\alpha - \alpha^{-2})]$ was first plotted against the reciprocal of $\alpha = L/L_i(35^\circ\text{C})^*$ in order to characterize the dependence of stress on strain for PDMSM networks. The sample employed for this purpose had a cross-sectional area $A^* = 0.0406 \text{ cm}^2$ in the undistorted state at 35°C . The results which pertain to 35, 45 and 70°C are shown in Figure 10. Values of the Mooney-Rivlin constant $2C_2$ defined in equation 7, where $2C_1, 2C_2$ are constants,⁵⁵

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \quad (7)$$

are simply the values of the slopes of the straight lines shown. They are 0.06, 0.08, and 0.05 kg cm^{-2} at 35, 45 and 70°C , respectively. These values are significantly smaller than is generally observed for polymer networks in elongation;²⁸ the small values of this $2C_2$ conversion terms indicate that PDMSM networks have stress-strain isotherms closely approaching the form predicted in the molecular theories of rubberlike elasticity. Although these results are quite limited, they can be used to provide an estimate of $d\ln\langle r^2 \rangle_0/dT$. To this end, values of $[f^*]$ at each temperature and at $\alpha = 1.2, 1.4$ and 1.6 were obtained from

* This α is of course to be distinguished from the expansion factor α used in the context of polymer solution methods in the previous sections.

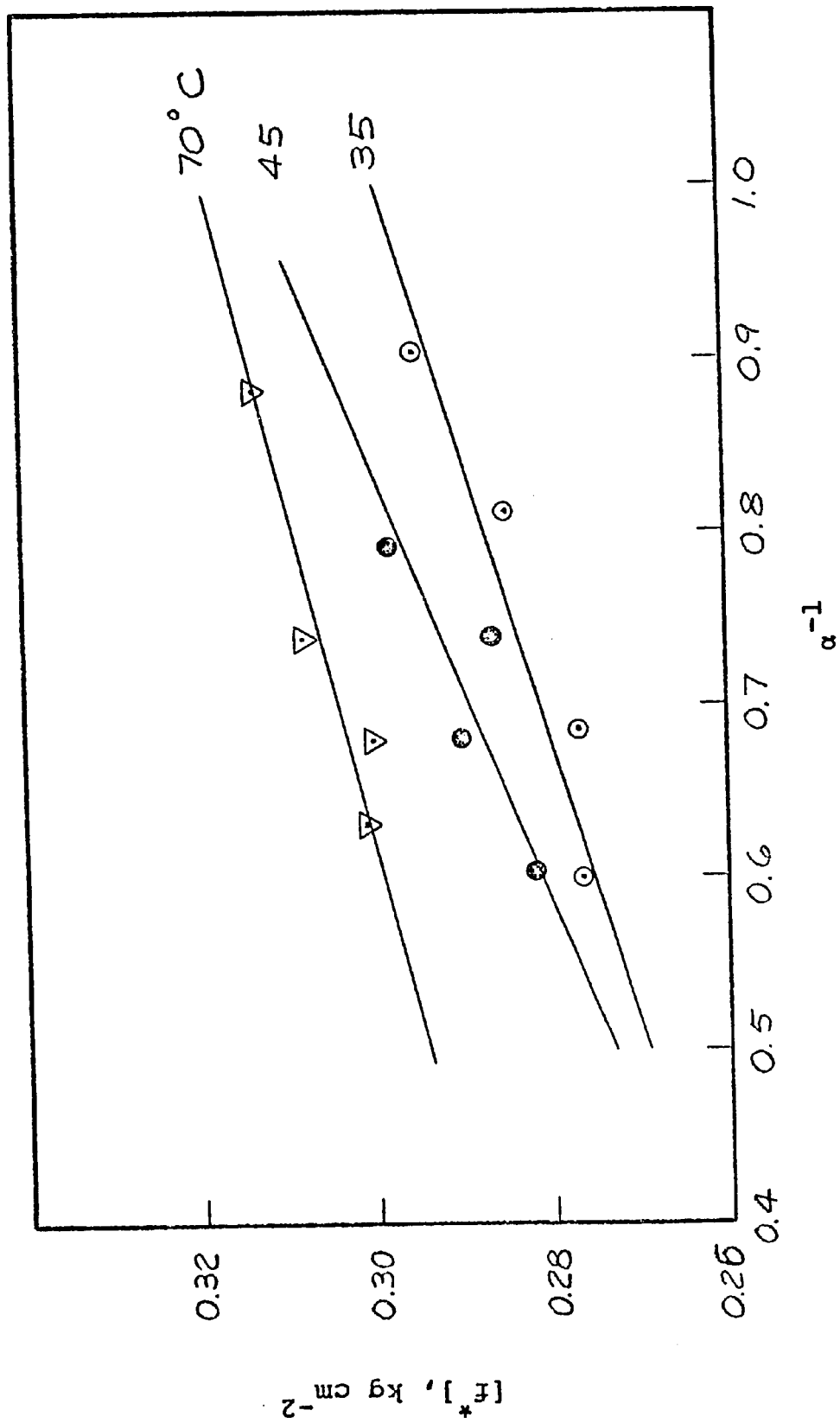


Figure 10. Stress-strain isotherms for a PDMSM network, at the three specified temperatures. The elongation α was defined as L/L_i (35°C).

Figure 10 by simple interpolation.^{28,56} The reduced forces are shown as a function of temperature in Figure 11, and correspond to measurements carried out at constant length. Their analysis proceeds through the use of theoretical elastic equation of state for networks of Gaussian chains^{28,56,57}

$$[f^*] = \nu kT [\langle r^2 \rangle_i / \langle r^2 \rangle_o] \quad (8)$$

where ν is the number of chains per unit volume, k is the Boltzmann constant, $\langle r^2 \rangle_i$ is the mean-square end-to-end distance of a network chain in the undistorted state but at the same volume as the distorted network, and $\langle r^2 \rangle_o$ is the already defined unperturbed dimensions. On this basis^{28,52-54}

$$d \ln \langle r^2 \rangle_o / dT = -[\partial \ln(f/T) / \partial T]_{p,L} \beta / (\alpha^3 - 1) \quad (9)$$

The value of the thermal expansion coefficient β was found to be $0.60 \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$ by the method described in a previous section.^{26,56} The three stress-strain isotherms, thus analyzed, yield $d \ln \langle r^2 \rangle_o / dT = 0.27, 0.52$ and $0.51 \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$ for $\alpha = 1.2, 1.4$ and 1.6 , respectively. The resulting average value is $d \ln \langle r^2 \rangle_o / dT = 0.43 (\pm 0.11) \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$.

The most reliable values of $d \ln \langle r^2 \rangle_o / dT$ are obtained by direct measurements of the reduced force $[f^*]$ as a function of temperature at constant length. The results of such measurements on a PDMSM network having a cross-sectional area A^* of 0.145 cm^2 at 25°C is shown at several

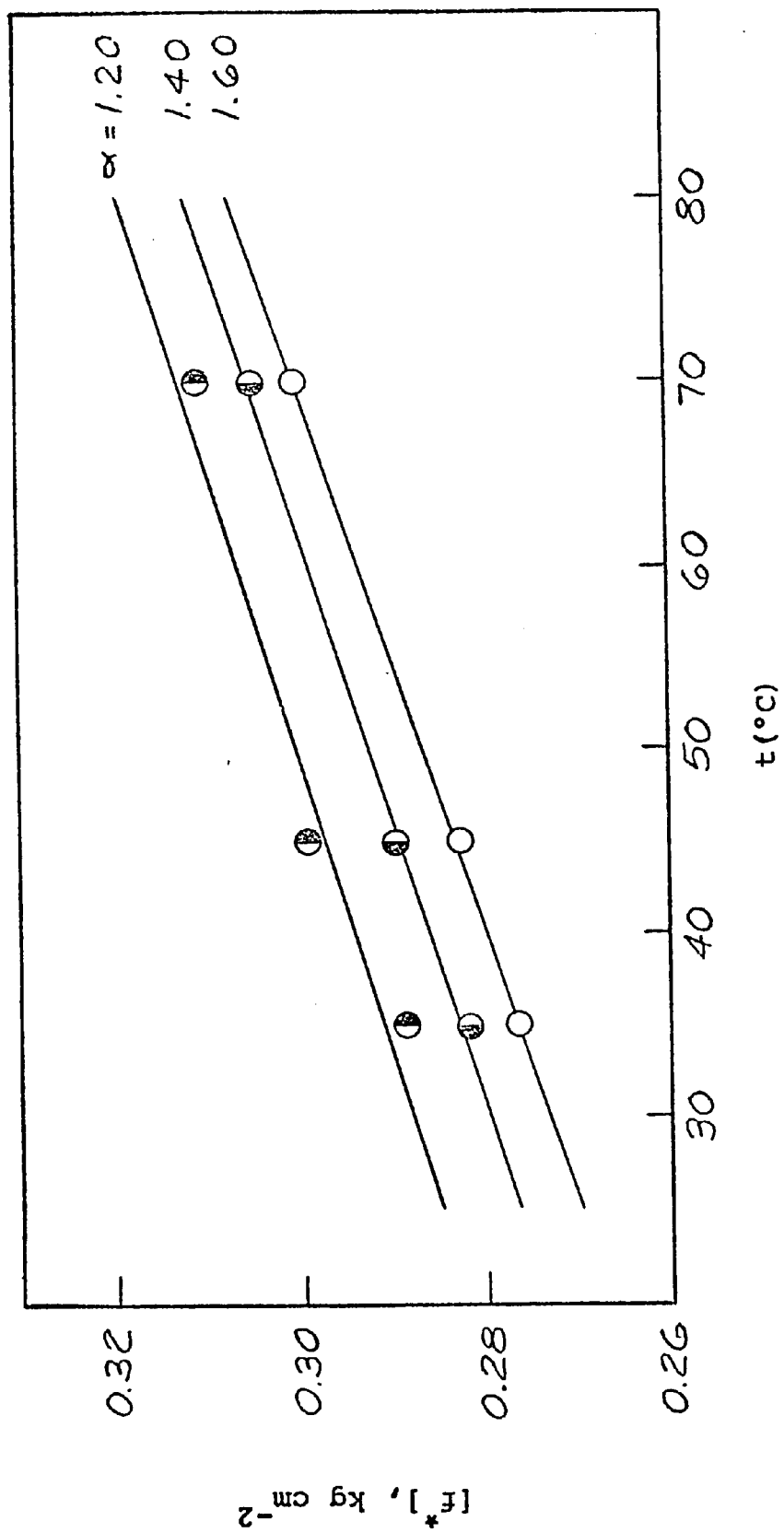


Figure 11. Values of the reduced force shown as a function of temperature for the illustrative values specified for the elongation α .

values of the elongation α in Figure 12. Pertinent quantities calculated therefrom are given in Table II.

Table II. Thermoelastic Results from Direct Force-Temperature Measurements on a PDMSM Network over the Temperature Range 30-90°C

α^*	$10^3 [\partial \ln(f/T) / \partial T]_{p,L}$	$10^3 \beta / (\alpha^3 - 1)$	$10^3 d \ln \langle r^2 \rangle_o / dT$
1.391	-0.31	0.35	-0.04
1.493	-0.58	0.26	0.32
1.602	-0.54	0.19	0.35
1.691	-0.35	0.16	0.19
			Av. 0.21 (± 0.15)

* $\alpha = L(90^\circ\text{C}) / L_i(90^\circ\text{C})$.

Careful evaluation of these results, along with the less reliable results cited above, suggests the value $0.20 (\pm 0.15) \times 10^{-3} \text{ }^\circ\text{K}^{-1}$ as the best value for $d \ln \langle r^2 \rangle_o / dT$ for the PDMSM chain.

3. The Mean-Square Dipole Moments $\langle \mu^2 \rangle_o$ and Their Temperature Coefficient

The dielectric constant data on the four PDMSM fractions F_1 - F_4 were interpreted by means of the equation of Guggenheim and Smith⁵⁸⁻⁶⁰

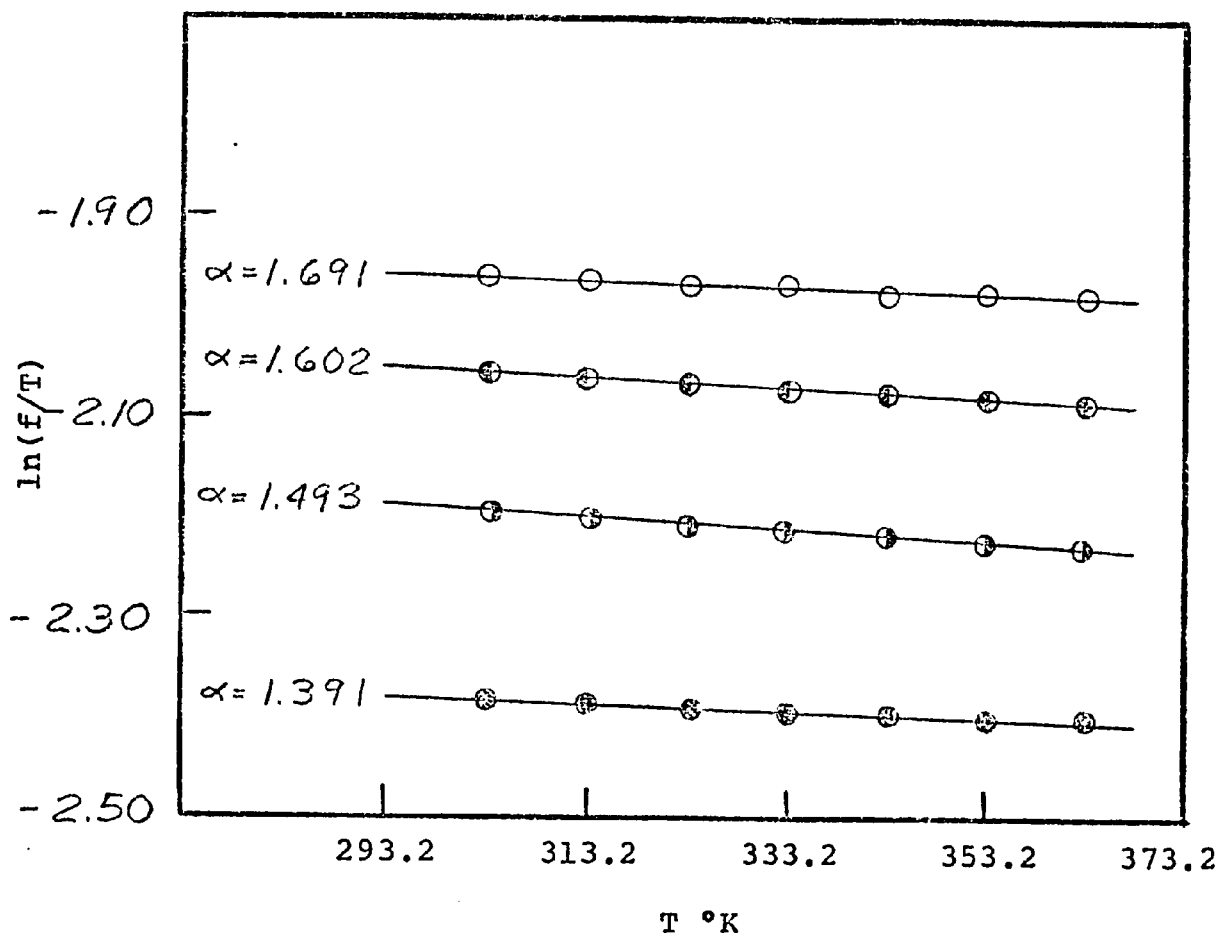


Figure 12. Values of $\ln(f/T)$ plotted against the absolute temperature for a PDMSM network at the specified values of the length $\alpha = L(90^\circ\text{C})/L_i(90^\circ\text{C})$.

$$\langle \mu^2 \rangle / nm^2 = \{ 27kT / [4\pi N_{\text{avo}} D_1 (e_1 + 2)^2] \} [de_{12}/dw_2 - dn_{12}^2/dw_2] [M_0 / 2m^2] \quad (10)$$

where k: Boltzmann constant

T: absolute temperature

N_{avo} : Avogadro's number

D_1 : density of cyclohexane (0.7682 g cm^{-3} at 30°C)

e_1 : dielectric constant of cyclohexane (2.0068 at 30°C)

e_{12} : dielectric constant of polymer solution

w_2 : weight fraction of polymer in the solution

n_{12} : refractive index of polymer solution

M_0 : molecular weight of the repeat unit (for PDMSM chain, $M_0 = 72.2$)

m : the effective dipole moment along Si-C and C-Si bonds in the PDMSM chain

The derivatives de_{12}/dw_2 and dn_{12}^2/dw_2 required in this equation were obtained from plots of e_{12} and n_{12}^2 vs. w_2 ; typical results are shown in Figures 13 and 14, respectively. Values of these two quantities for all four fractions are given in columns two and three of Table III. The effective bond moment $m = |\vec{m}|$ for Si-C and C-Si bonds was calculated from the dipole moment 0.60 D of the dimer $\text{Si}(\text{CH}_3)_3\text{-CH}_2\text{-Si}(\text{CH}_3)_3$ ^{61,62} using simple vector addition. As will be discussed in a later section, the most likely value for the Si-C-Si bond angle is 115° ;^{62,63} use of this value in the interpretation of the dipole moment of the

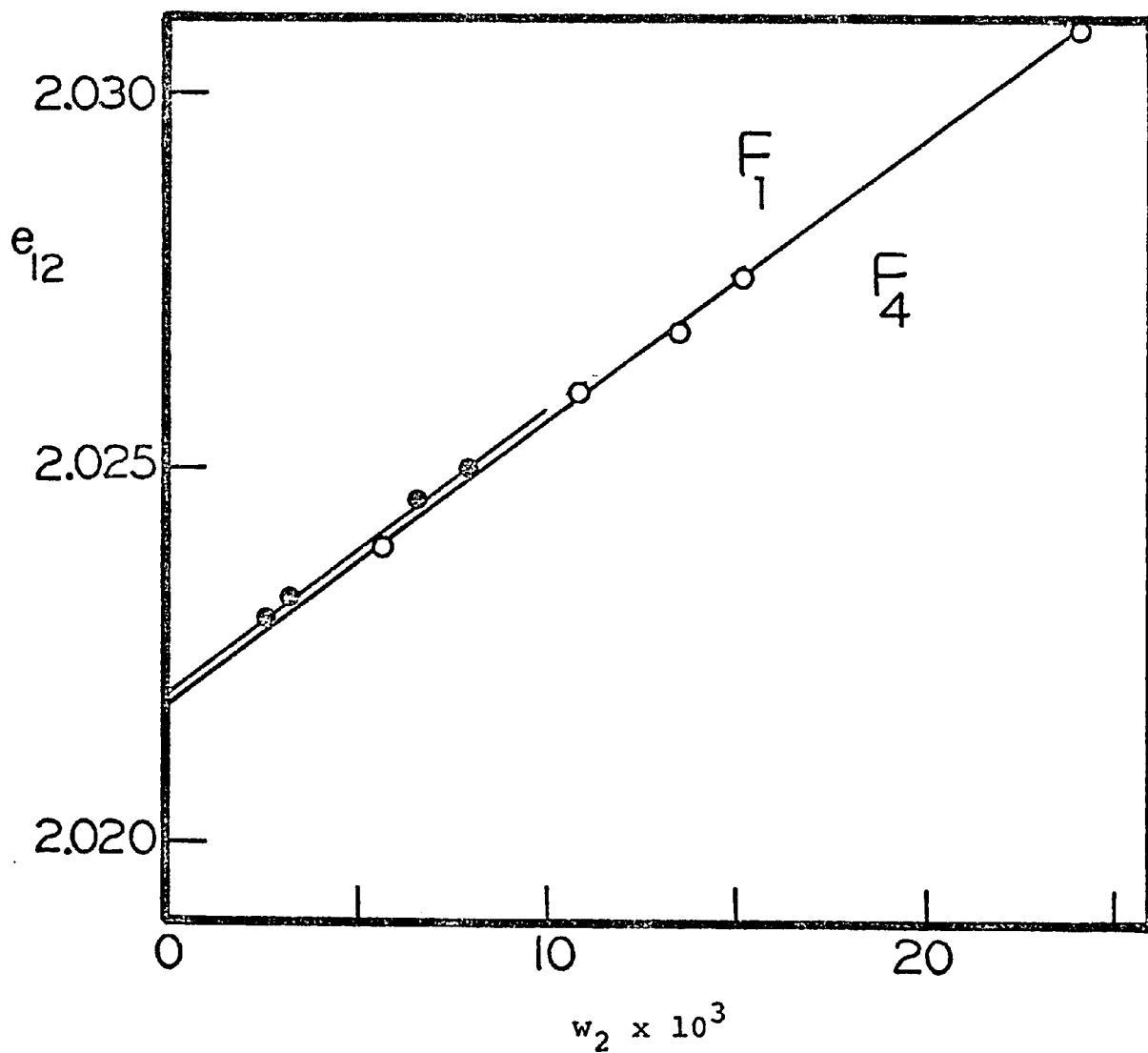


Figure 13. Dielectric constants e_{12} of PDMSM fractions F_1 and F_4 in cyclohexane solution plotted against the weight fraction w_2 at 30°C. The slope de_{12}/dw_2 was obtained by the least-squares method. For clarity, plots for the other two polymer fractions are omitted.

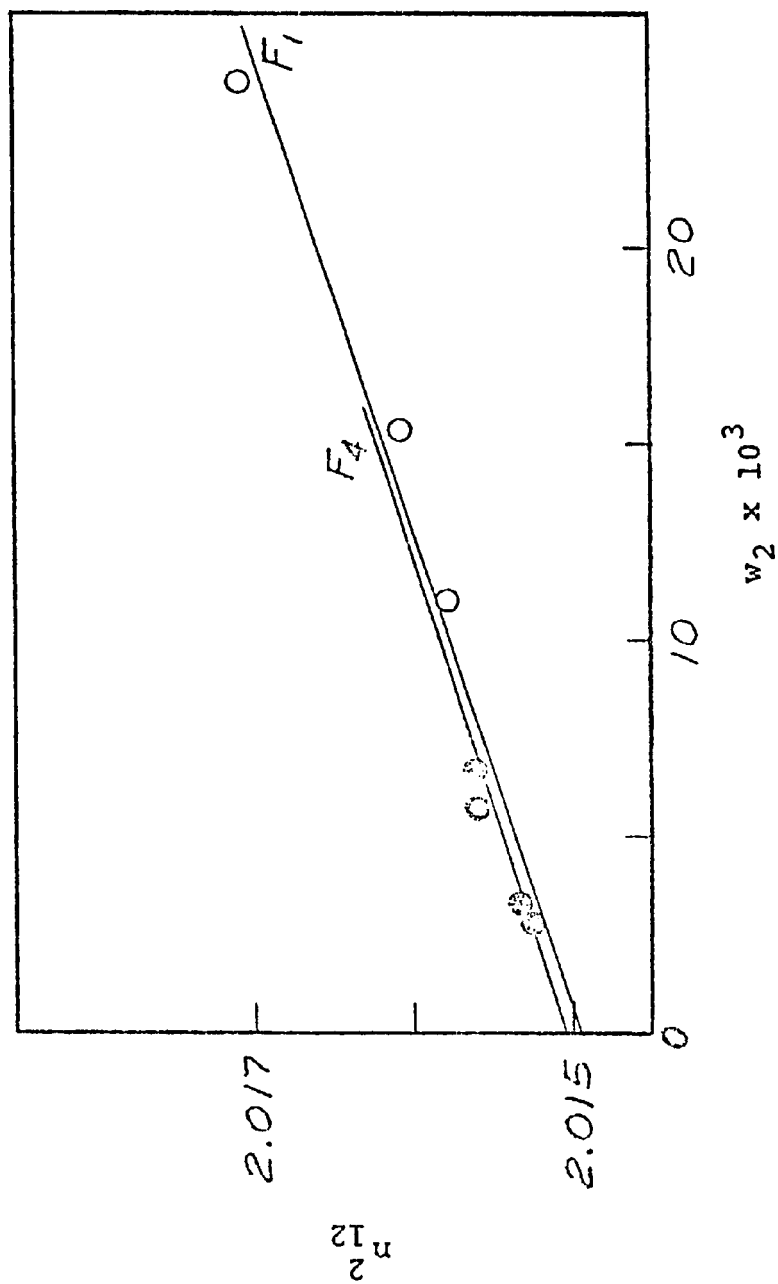


Figure 14. Indices of refraction n_{12}^2 of PDMSM fractions F_1 and F_4 in cyclohexane solution shown as a function of w_2 at 30°C. See legend to preceding figure.

Table III. Dielectric Results on PDMSM Fractions in Cyclohexane at 30°C

Fraction	de_{12}/dw_2	dn_{12}^2/dw_2	$\langle \mu^2 \rangle_O / nm^2$ $\theta_A = 70.5^\circ$	$\langle \mu^2 \rangle_O / nm^2$ $\theta_A = 65^\circ$	$\langle \mu^2 \rangle_O / nm^2$ $\theta_A = 60^\circ$
F ₁	0.385	0.085	0.484	0.417	0.364
F ₂	0.389	0.097	0.472	0.407	0.355
F ₃	0.390	0.134	0.391	0.337	0.294
F ₄	0.370	0.082	0.465	0.401	0.349
<hr/>					
Av.			0.453±0.036	0.391±0.031	0.341±0.027

dimer gives $m = 0.56$ D. The values of $\langle \mu^2 \rangle / \text{nm}^2$ calculated on this basis are given in the last column of the table; they yield the average result $0.391 (\pm 0.031)$ for $\theta_A = 65^\circ$. Revision of the Si-C-Si bond angle downward to 109.5° ($\theta_A = 70.5^\circ$) or upward to 120° ($\theta_A = 60^\circ$) would give $m = 0.52$ and 0.60 D, respectively and average experimental values of $\langle \mu^2 \rangle / \text{nm}^2$ of 0.453 ± 0.036 and 0.341 ± 0.027 , respectively.

In contrast to the case of the mean-square dimensions $\langle r^2 \rangle$, excluded volume interactions have a negligible effect on the mean-square dipole moments $\langle \mu^2 \rangle$ for a polymer chain in which the resultant dipole moment vector $\vec{m}$ has any one or more of the following symmetry elements:⁶⁴⁻⁶⁶ a plane of symmetry σ_v , an axis of two-fold symmetry C_2 , or a center of symmetry i in its all-trans planar conformation. The PDMSM chain has symmetry elements of σ_v and C_2 ; therefore the observed mean-square dipole moment $\langle \mu^2 \rangle$ must always have the unperturbed value $\langle \mu^2 \rangle_0$ and experimental results in any solvents are suitable for comparison with theoretical results. The ratio $\langle \mu^2 \rangle / \text{nm}^2$ will therefore henceforth be written $\langle \mu^2 \rangle_0 / \text{nm}^2$ and termed the dipole moment ratio, the dielectric analogue of the characteristic ratio $\langle r^2 \rangle_0 / nl^2$. As can be seen from the table, $\langle \mu^2 \rangle_0 / \text{nm}^2$ is independent of molecular weight with the most likely average value $0.391 (\pm 0.031)$ at 30°C .

In the case of one fraction, F_3 , dielectric measurements were carried out at 10° intervals over the tempera-

ture range 20-50°C. These results are presented in Table IV. They indicate that, within the experimental error of the dielectric measurements, the temperature coefficient $d\ln\langle\mu^2\rangle_0/dT$ for PDMSM chains is zero.

Table IV. The Temperature Dependence of the Mean-Square Dipole Moment of PDMSM Fraction F_3 in Cyclohexane

Temperature, °C	$\langle\mu^2\rangle_0/\text{nm}^2$
20	0.337
30	0.336
40	0.337
50	0.337

4. Discussion

The preceding experimental results characterizing the random-coil configurations of poly(dimethylsilmethylene) chains are summarized in the first column of Table V. Included for purposes of comparison in the other columns are the corresponding quantities for the two structurally related polymers, poly(dimethylsiloxane)^{1,32-34} and polyisobutylene;^{1,26,35-38} also included is polyethylene,^{1,27,67} since structurally it is the simplest polymer studied in regard to chain configuration.

The most striking feature of the PDMSM chain is its unusually small characteristic ratio $\langle r^2 \rangle_0/nl^2$; its value

Table V. Summary of Statistical Properties of Poly(dimethylsilmethylenes)
and Some Structurally Related Polymers

Repeat Unit	PDMSM	PDMSO	PIB	PE
$\langle r^2 \rangle_0 / nl^2$	Si(CH ₃) ₂ -CH ₂ - 5.3	Si(CH ₃) ₂ -O- 7.6 ^a	C(CH ₃) ₂ -CH ₂ - 6.6 ^a	CH ₂ -CH ₂ - 7.6 ^{a,b}
$10^3 d \ln \langle r^2 \rangle_0 / dT$	0.20	0.75 ^a	-0.20 ^a	-1.10 ^a
$\langle \mu^2 \rangle_0 / nm^2$	0.39	0.30 ^c	...	...
$10^3 d \ln \langle \mu^2 \rangle_0 / dT$	0.0	0.60 ^d	...	...

^a Taken from Reference 1.

^b Corrected from the temperature of measurement (140°C) to the vicinity of room temperature by means of $d \ln \langle r^2 \rangle_0 / dT$.

^c Taken from Reference 24.

^d Primarily a theoretical result; see References 22 and 24.

is one of the smallest cited in an extensive review¹ of the statistical properties of chain molecules. It is 20-30% smaller than the values of the characteristic ratio reported for PDMSO, PIB, and PE. Equally notable is the fact that $\langle r^2 \rangle_0$ and $\langle \mu^2 \rangle_0$ are relatively insensitive to temperature in the case of PDMSM. In this regard, it is quite similar to PIB, which also has values of $\langle r^2 \rangle_0$ almost insensitive to temperature.^{26,35} In contrast, an increase in temperature has the effect of significantly increasing $\langle r^2 \rangle_0$ in the case of PDMSO and significantly decreasing $\langle r^2 \rangle_0$ in the case of PE.^{1,68}

For the elucidation of these experimental results on PDMSM we now explore the application of the rotational isomeric state theory¹⁻⁴ of chain configuration to this chain molecule.

D. Theoretical Calculations of $\langle r^2 \rangle_0$ and $\langle \mu^2 \rangle_0$

1. Rotational Isomeric State (RIS) Theory

a. General Features of the Model. The rotational isomeric state (RIS) approximation¹⁻⁴ has been developed for the interpretation of configuration-dependent statistical properties of the random-coil polymer chain. In this scheme, each rotatable skeletal bond in the chain is assigned to one of a small number of discrete rotational states, generally chosen to occur at the minimum of the torsional potential or conformational energy for the parti-

cular bonds.¹ Such "conformers," which are confined to the bottom of potential wells, may be detected by spectroscopic methods at low temperatures.⁶⁹⁻⁷² The minima of rotational energies, in most cases, are situated at torsional angles ϕ of approximately 0° , 120° , and -120° ; these states are designated as trans(t), gauche⁺(g⁺) and gauche⁻(g⁻), respectively. The conformational energies of rotational isomeric states are calculated from the sum of the potential barrier contribution^{68,73-75} and nonbonded intramolecular interaction energies.¹ The relative probability or statistical weight of a rotational state is then represented by a Boltzmann factor, $\exp(-E_{\zeta\eta;i}/RT)$, where $E_{\zeta\eta;i}$ is the conformational energy characterizing the intramolecular interactions occurring in the associated conformation for a pair of consecutive rotational states with state ζ at bond $i-1$ and state η at bond i . Since these statistical weights are relative quantities, $E_{\zeta\eta;i}$ may be taken as the energy difference relative to some arbitrarily designated conformation of zero energy.

The RIS approximation has been remarkably successful for the interpretation of a number of configuration-dependent properties of chain molecules such as (1) the characteristic ratio,^{5-9,29} (2) the dipole moment ratio,^{10,11,22,23,29} (3) the energetics of deformation of rubber-like polymer networks,^{28,52-54} (4) light scattering and X-ray scattering at small angles,⁷⁶ and (5) nmr chemical shifts.^{77,78}

b. Statistical Weight Matrices and the Configurational Partition Function. The entire set of statistical weights required to describe all possible conformations of a pair of consecutive skeletal bonds is conveniently expressed in the form of a statistical weight matrix¹

$$\underline{U}_i = [u_{\zeta\eta}]_i = \begin{bmatrix} u_{tt} & u_{tg+} & u_{tg-} \\ u_{g+t} & u_{g+g+} & u_{g+g-} \\ u_{g-t} & u_{g-g+} & u_{g-g-} \end{bmatrix} \quad (11)$$

with state ζ for bond $i-1$ indexing the rows and rotational state η for bond i indexing the columns. The configuration partition function Z , which represents the summation of statistical weights of all conformations in a linear polymer chain having n identical bonds, is given by^{1,68}

$$Z = \sum_{i=2}^{n-1} \prod_{\zeta\eta} u_{\zeta\eta;i} = \underline{J}^* \left(\prod_{i=2}^{n-1} \underline{U}_i \right) \underline{J} \quad (12)$$

where $\prod_{i=2}^{n-1} u_{\zeta\eta;i}$ is the statistical weight for one specific conformation of the chain; the quantities $\underline{J}$ and $\underline{J}^*$ are the row and column vectors

$$\underline{J}^* = [1 \ 0 \ 0]; \quad \underline{J} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \quad (13)$$

Although an almost unlimited number of conformations can be generated by rotations of torsional angles, this partition

function can be evaluated by the above matrix multiplication scheme with only moderate computer calculation.

c. RIS Equations for $\langle r^2 \rangle_0$ and $\langle u^2 \rangle_0$. The configuration of the skeletal atoms of a hypothetical simple chain consisting of n bonds is shown in Figures 15 and 16.

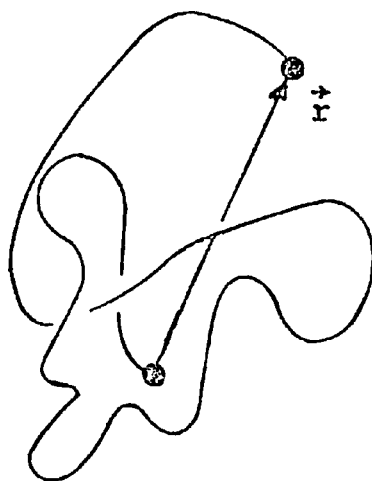


Figure 15. A spatial configuration of a polymer chain.

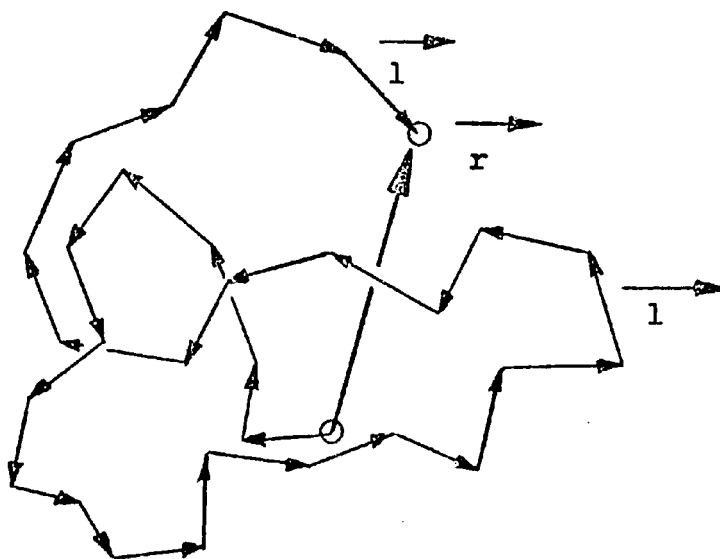


Figure 16. The end-to-end vector of a two dimensional polymer chain.

If each bond is represented by a bond vector $\vec{l}_i^*$ numbered from $i = 1$ to n , then the end-to-end vector $\vec{r}$ which connects the ends of the chain can be expressed as

$$\vec{r} = \sum_{i=1}^n \vec{l}_i \quad (14)$$

Our only interest will be the scalar magnitude of this chain dimension. The scalar magnitude of the vector $\vec{r}$ is obtained as follows:

$$\vec{r} \cdot \vec{r} = r^2 = \sum_{i=1}^n \vec{l}_i \cdot \sum_{i=1}^n \vec{l}_i \quad (15)$$

which may be written alternatively as

$$r^2 = \sum_{i=1}^n l_i^2 + 2 \sum_{\substack{i=1 \\ 0 < i < j \leq n}}^n (\vec{l}_i \cdot \vec{l}_j) \quad (16)$$

For a random-coil polymer chain, this quantity must be the average over all possible conformations in the molecular configuration space. We may write this required average as

$$\langle r^2 \rangle_0 = \sum_i l_i^2 + 2 \sum_{i < j} \langle \vec{l}_i \cdot \vec{l}_j \rangle \quad (17)$$

The average $\langle \vec{l}_i \cdot \vec{l}_j \rangle$ is a measure of the correlation of the direction of the pair of bonds i and j ; it is obviously

* A bond vector is denoted as $\vec{l}_i$, and its scalar magnitude as $l_i = |\vec{l}_i|$.

essential for obtaining a statistical average of the unperturbed mean-square dimension $\langle r^2 \rangle_0$. In order to construct a scheme for formulating the required scalar product $\vec{l}_i \cdot \vec{l}_j$, we have to define a Cartesian coordinate system for each bond of the chain. To this end, let coordinate x_i of the coordinate system be taken in the direction of bond i as shown in Figure 17. The y_i axis is taken in the plane $i-1$ and i , with the positive direction chosen to render its projection on x_{i-1} positive, and z_i axis is taken in the direction perpendicular to both x_i and y_i ; the positive z_i direction is located so as to obtain a "right-handed" Cartesian coordinate system. The torsional angle ϕ_i is the rotational angle of a single bond relative to the trans conformation which is assigned as $\phi_i^t = 0^\circ$; the sign of ϕ_i is taken as positive for a right-handed rotation. The angles θ are specified here as the supplements of the conventional skeletal bond angles as shown in Figure 17. Accordingly, the scalar product of $\vec{l}_i \cdot \vec{l}_{i+1}$, in which $\vec{l}_i$ is in coordinate system i and $\vec{l}_{i+1}$ in coordinate system $i+1$, is simply equal to $\vec{l}_i \cdot (\underline{T}_i \vec{l}_{i+1})$, where $\underline{T}_i$ is the transformation matrix which transforms vector $\vec{l}_{i+1}$ of the $i+1$ coordinate system into the coordinate system of vector $\vec{l}_i$. This transformation matrix has the form

$$\underline{T}_i = \begin{bmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i \cos\phi_i & -\cos\theta_i \cos\phi_i & \sin\phi_i \\ \sin\theta_i \sin\phi_i & -\cos\theta_i \sin\phi_i & -\cos\phi_i \end{bmatrix}_i \quad (18)$$

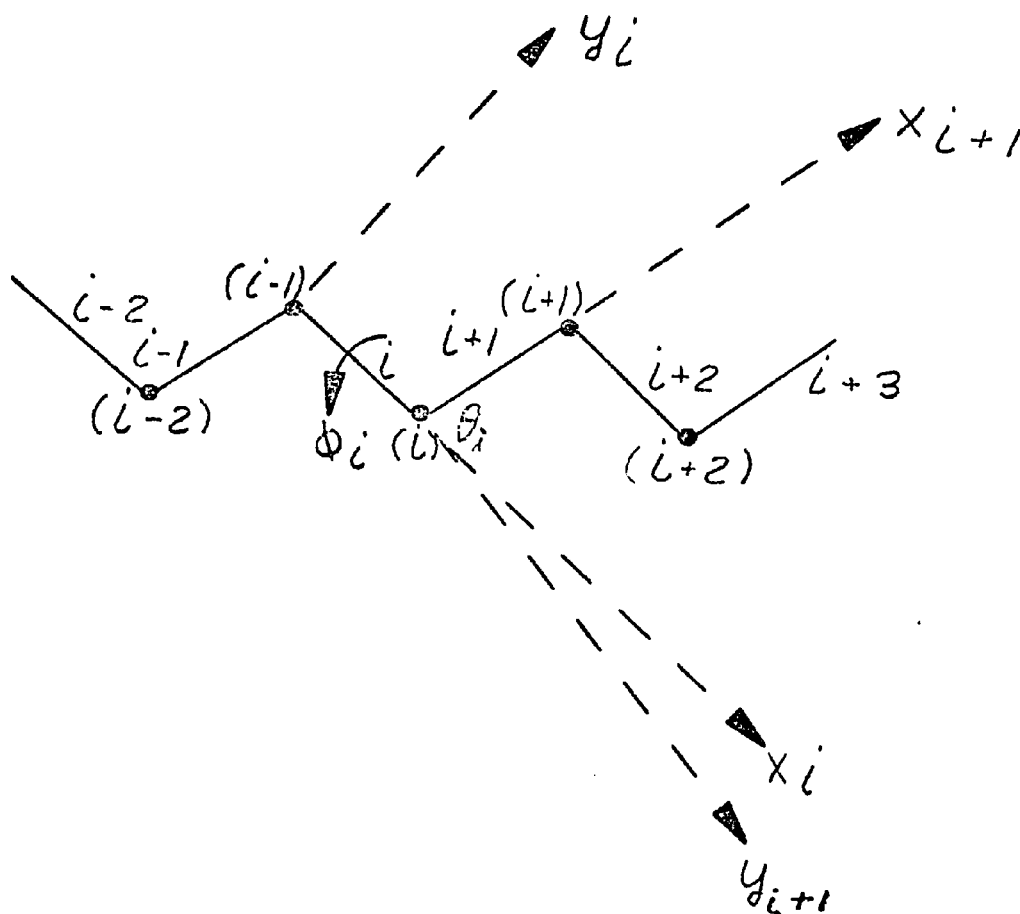


Figure 17. The Cartesian coordinate system defined about skeletal bond i .

The scalar product of bond vectors $\vec{l}_i$ and $\vec{l}_j$ is thus

$$\vec{l}_i \cdot \vec{l}_j = \vec{l}_i \cdot (\underline{T}_i \cdots \cdots \underline{T}_{j-i} \vec{l}_j) \quad (19)$$

and the average projection on bond i of a unit vector along bond j is given by

$$\langle \vec{l}_i \cdot \vec{l}_j \rangle = \vec{l}_i \langle T_i \dots T_{j-i} \rangle \vec{l}_j \quad (20)$$

As shown by Flory,¹ this statistical mechanical average can be derived mathematically by the summation of contributions from each individual conformation, and averaging over all conformations in the chain molecule. The result for the characteristic ratio $\langle r^2 \rangle_0 / nl^2$ of a chain of n skeletal bonds is given by^{1,68}

$$\langle r^2 \rangle_0 / nl^2 = 2 (Znl^2)^{-1} \underline{I}^* \prod_{i=1}^n \underline{G}_i \underline{I} \quad (21)$$

where $n = 2x + 2$ is the number of bonds in the chain, $\underline{I}^*$ is the row vector consisting of a single unit followed by 14 zeros, and $\underline{I}$ is the column vector consisting of 12 zeros followed by three unities. The matrices $\underline{G}_i$ have the form

$$\underline{G}_i = \begin{bmatrix} \underline{U} & (\underline{U} \otimes \vec{1}^T) \parallel \underline{T} \parallel & (1/2) l^2 \underline{U} \\ \underline{O} & (\underline{U} \otimes \underline{E}) \parallel \underline{T} \parallel & \underline{U} \otimes \vec{1} \\ \underline{O} & \underline{O} & \underline{U} \end{bmatrix}_i \quad (22)$$

with $\underline{U}$ being set equal to the unit matrix $\underline{E}$ in the case of the first ($i=1$) and last ($i=n$) bonds of the chain. The zeros $\underline{O}$ represent null submatrices of the required order; $\underline{U} \otimes \underline{E}$ is the direct product of matrices $\underline{U}$ and $\underline{E}$ and is defined as¹

$$\underline{U} \otimes \underline{E} = \begin{bmatrix} u_{tt}^{\underline{E}} & u_{tg}^{\underline{E}} & u_{tg}^{-\underline{E}} \\ u_{g+t}^{\underline{E}} & u_{g+g}^{\underline{E}} & u_{g+g}^{-\underline{E}} \\ u_{g-t}^{\underline{E}} & u_{g-g}^{\underline{E}} & u_{g-g}^{-\underline{E}} \end{bmatrix} \quad (23)$$

and $\vec{l}$ is the bond vector with $\vec{l}^T$ its transpose,

$$\vec{l} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}; \quad \vec{l}^T = [1 \ 0 \ 0] \quad (24)$$

The matrix $\|\underline{T}_i\|$ has the order of 9×9 and is given by the equation

$$\|\underline{T}_i\| = \begin{bmatrix} \underline{T}_i(\phi_i = 0^\circ) & \underline{0} & \underline{0} \\ \underline{0} & \underline{T}_i(\phi_i = 120^\circ) & \underline{0} \\ \underline{0} & \underline{0} & \underline{T}_i(\phi_i = -120^\circ) \end{bmatrix} \quad (25)$$

where zeros in the matrix $\|\underline{T}_i\|$ are null matrices of the order 3×3 , and the $\underline{T}_i$ are obtained from equation 18 for the three torsional angles $0, \pm 120^\circ$.

In the case of the dipole moment ratio $\langle \mu^2 \rangle_o / nm^2$, the same equations apply except the bond vector $\vec{l}$ is replaced by the bond dipole moment vector $\vec{m}$. The equation for the calculation of the dipole moment ratio is thus given by¹

$$\langle \mu^2 \rangle_o / nm^2 = 2(Znm^2)^{-1} \underline{I}^* \prod_{i=1} \underline{G}_i \underline{I} \quad (26)$$

where the prime notation on $\underline{G}_i'$ specifies that $\vec{l}_i$ has been replaced by $\vec{m}_i$, and l_i by m_i .

2. Application to Poly(dimethylsilmethylene)

a. Structural Features of the Polymer Repeat Unit.

A portion of the PDMSM chain is shown in Figure 18; for convenience in representation, the chain is shown in its

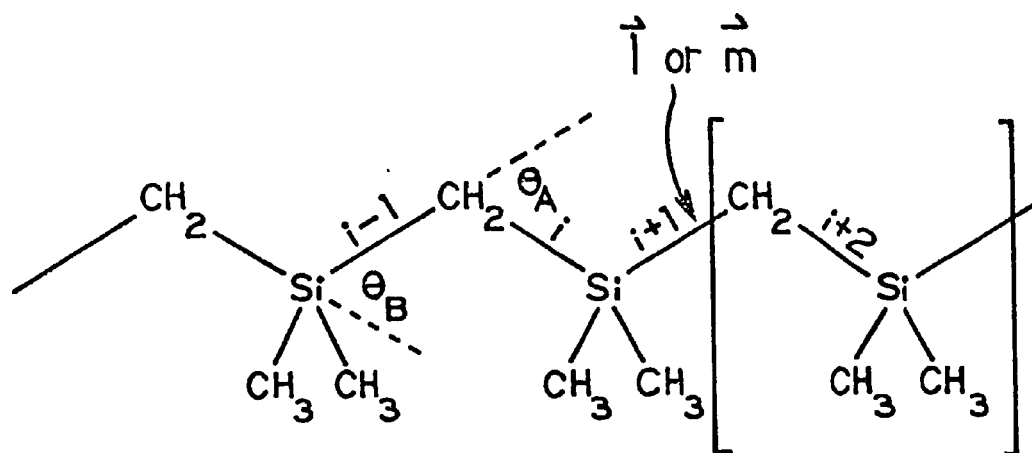


Figure 18. Schematic representation of the poly(dimethylsilmethylene) chain in the all-trans conformation (all torsional angles $\phi_i = 0^\circ$).

planar, all-trans form. The C-Si-C bond angle is very nearly tetrahedral according to the tabulated structural data of Bowen and Sutton.⁷⁹ Thus the bond angle supplement θ_B may be assigned the value $(180-109.5^\circ) = 70.5^\circ$. For the other type of skeletal bond angle, that occurring about the CH_2 groups, there is relatively little information at the

present time. A recent electron diffraction study of disilapropane $\text{H}_3\text{Si}-\text{CH}_2-\text{SiH}_3$ suggests a Si-C-Si bond angle of 114.4° .^{62,63} Replacement of two H atoms by CH_3 groups in forming the $\text{Si}(\text{CH}_3)_2-\text{CH}_2-$ repeat unit may increase this bond angle further beyond the tetrahedral value of 109.5° . Such an increase is very marked in the PIB, illustrated schematically in Figure 19; here the bond angle α is very much greater than 109.5° . Structural information obtained

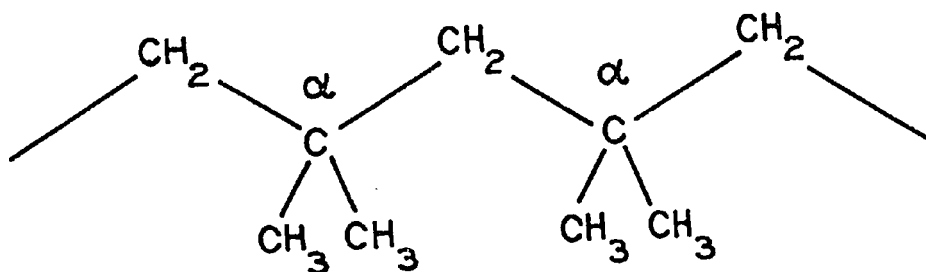


Figure 19. Conformation of the polyisobutylene chain in its planar all-trans conformation.

from the X-ray crystallographic analysis of 2,2,4,4-tetramethyladipic acid $\text{HOOC}(\text{CH}_3)_2-\text{CH}_2-\text{C}(\text{CH}_3)_2\text{CH}_2\text{COOH}$ suggests $\alpha = 122.6^\circ$,⁸⁰ and X-ray analysis of crystalline PIB itself suggests $\alpha = 126^\circ$.^{81,82} Since the Si-C bond is very much longer than the C-C bond (1.90 vs. 1.53 Å), CH_3 groups are further separated in PDMSM than in PIB (3.3 vs. 2.5 Å in the all-trans conformation). For this reason, increase in the Si-C-Si bond angle due to steric repulsions should be relatively minor in PDMSM and we therefore adopt the value

$(180-115^\circ) = 65^\circ$ for θ_A . For purposes of illustration, other values of θ_A (70.5 and 60°) will also be considered in the subsequent calculations of $\langle r^2 \rangle_o / nl^2$ and $\langle \mu^2 \rangle_o / nm^2$.

As already mentioned, $l_i = 1.90 \text{ \AA}$ for the PDMSM chain. The bond moment m_i is harder to fix precisely since it requires analysis of the dipole moment of PDMSM dimer (see Section I.C.3). For $\theta_A = 65^\circ$, $m_{\text{Si-C}} = -m_{\text{Si-C}} = 0.56 \text{ D}$; for the other illustrative values of θ_A , 70.5 and 60° , the values are 0.52 and 0.60 D, respectively. The fact that C is more electronegative than Si (2.50 vs. 1.74),⁸³ suggests that the negative end of the skeletal bond dipole is on the skeletal carbon atoms. Whether or not this is the case in the PDMSM chain is irrelevant in calculations of quantities such as $\langle \mu^2 \rangle_o / nm^2$; all that needs be specified in this regard is the fact that the Si-C bond moment $m_{\text{Si-C}}$ is opposite in sign to the C-Si bond moment $m_{\text{C-Si}}$.

b. Construction of Statistical Weight Matrices.

Since rotations about Si-C bonds give rise to intramolecular interactions different from those experienced upon rotating about C-Si bonds, the PDMSM chain requires two statistical weight matrices for its characterization. For pairs of consecutive skeletal bonds (Si-CH₂-Si) meeting at a CH₂ group, the statistical weight matrix is designated $\underline{U}_a$; for pairs (CH₂-Si-CH₂) meeting at a Si atom, the designation is $\underline{U}_b$.

The nine rotational isomeric states which are possible about Si-CH₂-Si bonds are shown in Figure 20. In configurational analysis of other chain molecules it has been concluded that CH₃ and CH₂ groups are sterically very nearly equivalent.¹ There is a possibility that the Coulombic energies of these conformations differ somewhat due to possibly different charges on skeletal CH₂ groups and pendant CH₃ groups. If this complication is temporarily neglected in a first-order approximation, then the assumed steric equivalence of the CH₂ and CH₃ groups leads to the conclusion that all of the conformational pairs shown in Figure 20 are of the same energy. On this basis, the statistical weight for each rotational state can be assigned a value of unity. The corresponding matrix for bond pairs meeting at a methylene group, such as bonds i-1 and i of Figure 18, is therefore

$$\underline{U}_a = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \quad (27)$$

For pairs of skeletal bonds meeting at a silicon atom, the conformational energies for these isomeric rotational states are the same as previously discussed except for $g_i^+ g_{i+1}^-$ and $g_i^- g_{i+1}^+$ states, where the conflict between Si(CH₃)₂ groups are so severe that the probabilities for these two states are effectively zero. These interactions

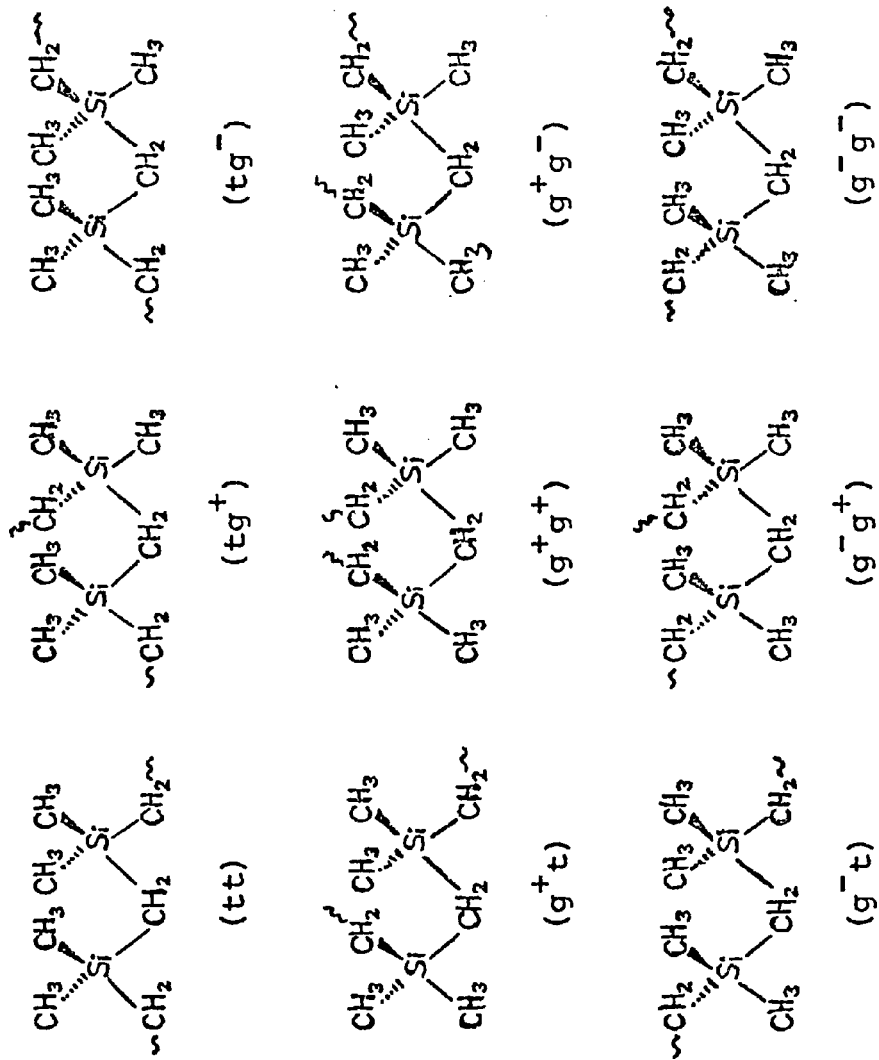


Figure 20. The nine rotational isomeric states for pairs of bonds meeting at a methylene group in the poly(dimethylsilomethylene) chain.

are frequently called "pentane-type interferences" because n-pentane is the simplest hydrocarbon in which they occur. In summary, then, the statistical weight matrix for these pairs of bonds is expressed by

$$\underline{U}_b = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \quad (28)$$

3. Calculated Results and Discussion

Calculations were carried out on a PDMSM chain having x internal repeat units, with two additional bonds, one at the beginning and one at the end. This chain molecule would have a degree of polymerization DP of $x + 1$ and contain $n = 2x + 2$ skeletal bonds. For a chain molecule such as PDMSM which has a two-bond repeat unit, equation 12 for the configurational partition function takes the more specific form^{22,84}

$$Z = \underline{J}^* \underline{E}_3 (\underline{U}_a \underline{U}_b)^x \underline{E}_3 \underline{J} \quad (29)$$

where $\underline{E}_3$ is the unit matrix of order 3 (since rotations about bonds 1 and n are irrelevant in the present calculations). Similarly, the characteristic ratio and dipole moment ratio equations become^{22,84}

$$\langle r^2 \rangle_o / nl^2 = 2(Znl^2)^{-1} \underline{I}^* \underline{G}_{B1} (\underline{G}_A \underline{G}_B)^x \underline{G}_{An} \underline{I} \quad (30)$$

$$\langle \mu^2 \rangle_o / nm^2 = 2 (Znm^2)^{-1} \underline{I}^* \underline{G}'_{B1} (\underline{G}'_A \underline{G}'_B)^x \underline{G}'_{An} \underline{I} \quad (31)$$

where the atypical matrices $\underline{G}_{B1}$, $\underline{G}_{An}$, $\underline{G}'_{B1}$, and $\underline{G}'_{An}$, have been factored out since the statistical weight matrix appearing in them is simply the unit matrix $\underline{E}_3$. To save computer time, matrix multiplications such as those required in the two preceding equations are carried out by successive squarings of products; for example, $(\underline{G}_a \underline{G}_b)^x$ is calculated by the successive squares $\{[(\underline{G}_a \underline{G}_b)^2]^2\}^2 \dots$ etc. The computer program for the calculation of $\langle r^2 \rangle_o / nl^2$ and $\langle \mu^2 \rangle_o / nm^2$ is reproduced in Appendix A and illustrates this method of matrix squaring.

In the above manner, values of both $\langle r^2 \rangle_o / nl^2$ and $\langle \mu^2 \rangle_o / nm^2$ were calculated as a function of x , using 65° for the Si-C-Si bond angle supplement (and the corresponding value 0.56 D for the skeletal bond moment). These results are shown in Figures 21 and 22. As is readily obvious from the curves obtained, both the characteristic ratio and dipole moment ratio essentially reach their limiting values for long chain length for $n \geq 200$ bonds. These calculated results may thus be directly compared with experimental results obtained on any PDMSM polymer having a molecular weight in excess of approximately 20000, which is approximately 600 times the molecular weight per skeletal bond in PDMSM. Since little additional computation is required to raise x from 100 to 512, all additional cal-

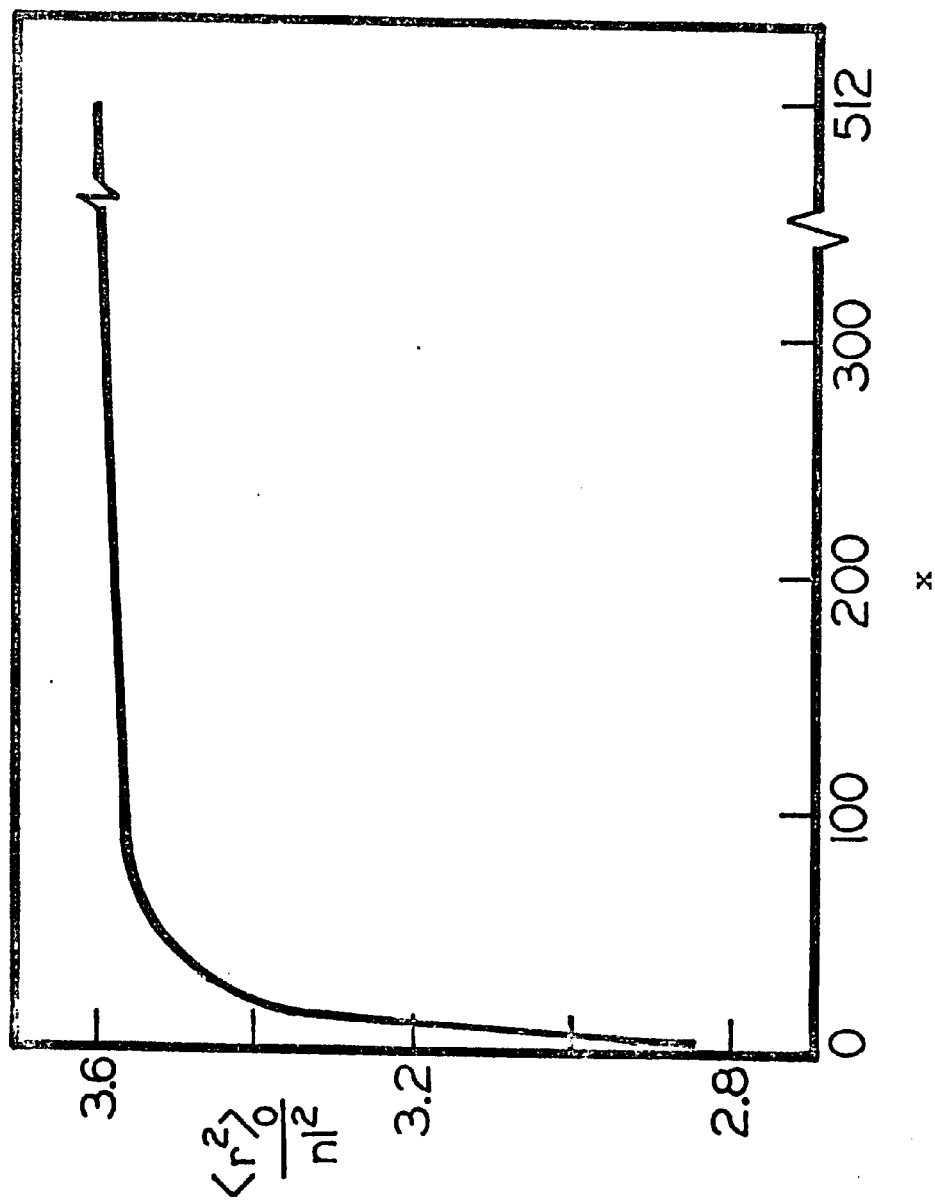


Figure 21. The characteristic ratio plotted as a function of x for the PDMSM chain; the skeletal bond angle $\angle \text{SiCSi}$ was taken to be 115° .

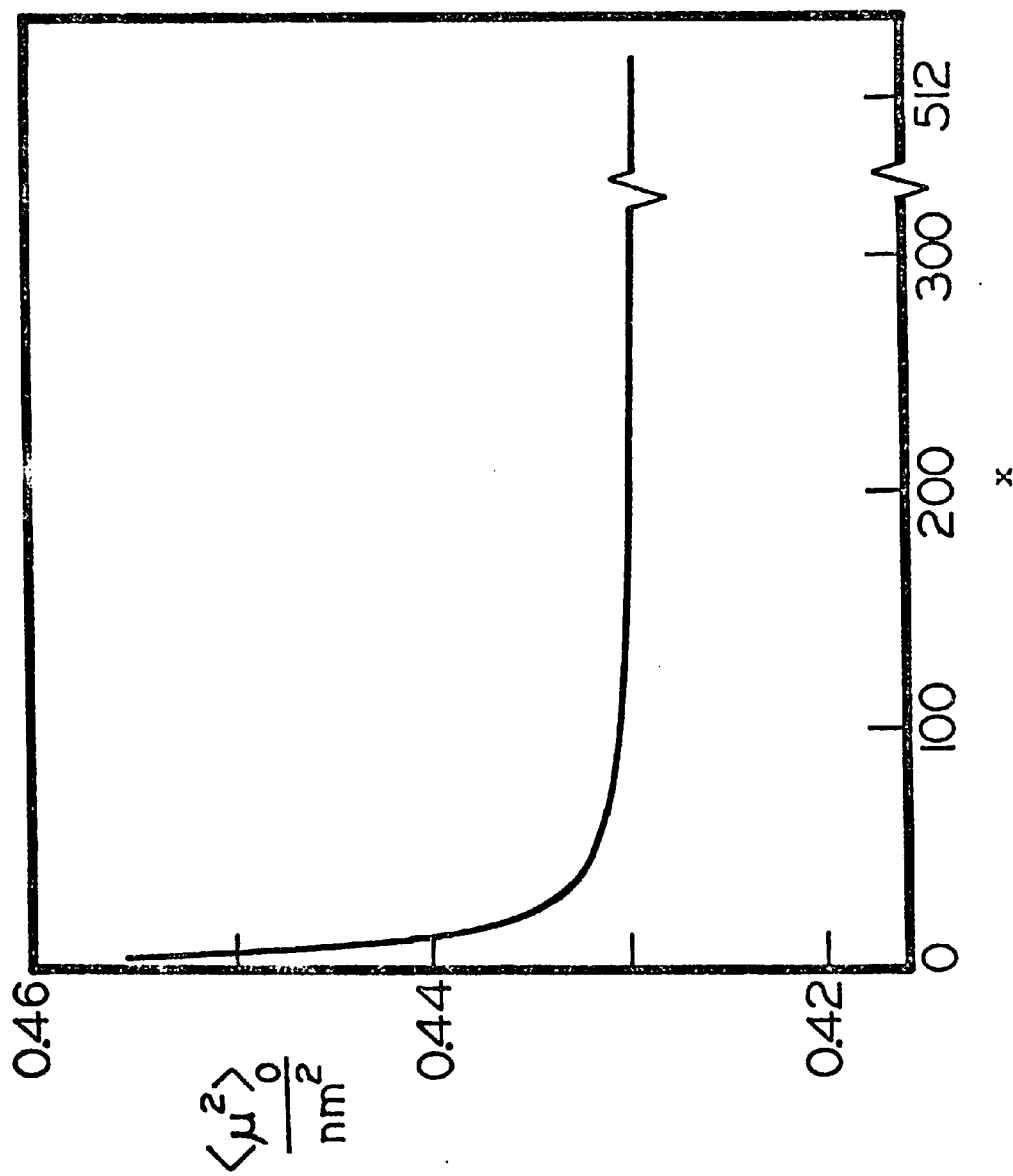


Figure 22. The dipole moment ratio plotted as a function of x for the PDMSM chain; the skeletal bond angle $\angle \text{SiCSi}$ was taken to be 115° .

culations were carried out at the constant value $x = 512$.

The limiting values of $\langle r^2 \rangle_0 / nl^2$ and $\langle \mu^2 \rangle_0 / nm^2$ thus obtained in these simplest calculations are 3.60 and 0.43, respectively. The value calculated for the dipole moment ratio, 0.43, is in quite satisfactory agreement with the experimental result, 0.39 (± 0.03). The calculated value for the characteristic ratio, 3.60, is however in only approximate agreement with the experimental result 5.32 (± 0.01). Since all of the statistical weights are either unity or zero, both $\langle r^2 \rangle_0$ and $\langle \mu^2 \rangle_0$ are predicted to be independent of temperature, in excellent agreement with experiments. Even this simplest model for the PDMSM chain is thus seen to give a good qualitative interpretation of the most striking features of this chain molecule. The characteristic ratio for PDMSM is unusually low because of the large number of conformational states of almost exactly the same energy and therefore of essentially the same probability of occurrence. This lack of preference in PDMSM means of course that there are no strong conformational regularities in this chain molecule, and such conformational regularities are required for high spatial extension as reflected in large values of $\langle r^2 \rangle_0 / nl^2$.^{1,68,85} Relatively simple examples of this effect are polyethylene,^{1,68} where the strong preference for extended trans states causes $\langle r^2 \rangle_0 / nl^2$ to be relatively large and isotactic vinyl polymers where the restriction of the chain into helical segments accounts for the relatively large values of $\langle r^2 \rangle_0 / nl^2$ in this case.^{85,86}

In summary, it is simply the lack of conformational regularity in PDMSM that is the origin of the relatively low experimental values obtained for $\langle r^2 \rangle_0 / nl^2$. This circumstance also explains the fact that both $\langle r^2 \rangle_0$ and $\langle \mu^2 \rangle_0$ were experimentally found to be relatively insensitive to temperature. In this simplest model of PDMSM chain, none of the statistical weights are temperature-dependent; two states with very severe steric repulsions are suppressed entirely, with statistical weights constant at zero, and all other states are equally likely, with statistical weights uniformly assigned the reference value of unity. In more physical terms, $\langle r^2 \rangle_0$ and $\langle \mu^2 \rangle_0$ do not change with changes in temperature because all of the accessible conformational states are of essentially the same energy. The polyisobutylene chain $C(CH_3)_2-CH_2-C(CH_3)_2-$ etc. can also be thought of as having some free rotational characteristics, which would of course explain the small value $-0.20^\circ K^{-1}$ found for $10^3 d \ln \langle r^2 \rangle_0 / dT$ for this chain molecule.^{1,26,35} The configurational analysis of PIB is greatly complicated by the fact, however, that the relatively short C-C skeletal bonds make the intramolecular interactions much more severe in PIB than they are in PDMSM. This causes displacement of rotational states from their normal positions of $\phi = 0, \pm 120^\circ$ and possibly also causes long-range correlations between rotational states in the PIB chain.⁸⁷

The above simplest model of the PDMSM chain is very similar to one of the classic earliest models of a chain molecule, the "freely-rotating" chain.^{1,88} In such an idealized chain, all rotational angles are equally likely; its characteristic ratio can be calculated from the simple algebraic equation¹

$$\langle r^2 \rangle_0 / nl^2 = (1 + \cos \theta_A)(1 + \cos \theta_B) / (1 - \cos \theta_A \cos \theta_B) \quad (32)$$

In rotational isomeric state theory, the same simple equation results if the rotational states are at $\phi_i = 0, 120$ and -120° and correspond to the same energy; it is in this sense that the PDMSM chain exhibits some characteristics of the idealized freely rotating chain. It differs of course from the freely-rotating chain in that $g^\pm g^\mp$ states about C-Si-C bonds are excluded because of pentane-type interferences. For purposes of comparison, values of the characteristic ratio and dipole moment ratio for freely-rotating chains are given in Table VI.

Table VI. Values of the Characteristic Ratio and Dipole Moment Ratio for PDMSM Chains in the Idealization of Free Rotation

θ_A^*	$\langle r^2 \rangle_0 / nl^2$	$\langle \mu^2 \rangle_0 / nm^2$
65.0	2.21	0.448
70.5	2.00	0.500
60.0	2.40	0.400

* $\theta_B = 70.5^\circ$, as usual.

Since the discrepancy between theoretical and experimental values of the characteristic ratio (3.6 vs. 5.3) could be due to uncertainty in θ_A , both $\langle r^2 \rangle_0/nl^2$ and $\langle \mu^2 \rangle_0/nm^2$ were calculated as a function of the Si-C-Si bond angle. These results are shown in Figure 23. Increase in this bond angle increases $\langle r^2 \rangle_0/nl^2$ but decreases $\langle \mu^2 \rangle_0/nm^2$. At a Si-C-Si bond angle of 120° ($\theta_A = 60^\circ$), the calculated value of $\langle r^2 \rangle_0/nl^2$ is 3.80, in somewhat better agreement with the experimental value of 5.3. The value of $\langle \mu^2 \rangle_0/nm^2$ becomes 0.35 which is also in better agreement with the experimental value 0.34 (calculated using the value $m = 0.60$ D, appropriate for $\theta_A = 60^\circ$). Although agreement between theory and experiment is improved by this adjustment, additional structural information on small Si-C compounds would be required to accept objectively a Si-C-Si bond angle in excess of 115° . We therefore restore the Si-C-Si bond angle to 115° and explore the possibility that not all permitted conformational states in PDMSM chains are of exactly the same energy.

A more detailed consideration of the structural characteristics of the PDMSM chain suggests that skeletal CH_2 groups may have different partial charges than pendant CH_3 groups. Carbon atoms are more electronegative than silicon atoms and in the PDMSM sequence $-\text{Si}(\text{CH}_3)_2-\text{CH}_2-\text{Si}(\text{CH}_3)_2-$ etc., skeletal carbon atoms can withdraw negative charge from two silicon atoms, but pendant carbon atoms can withdraw negative charge only from the single silicon atom to

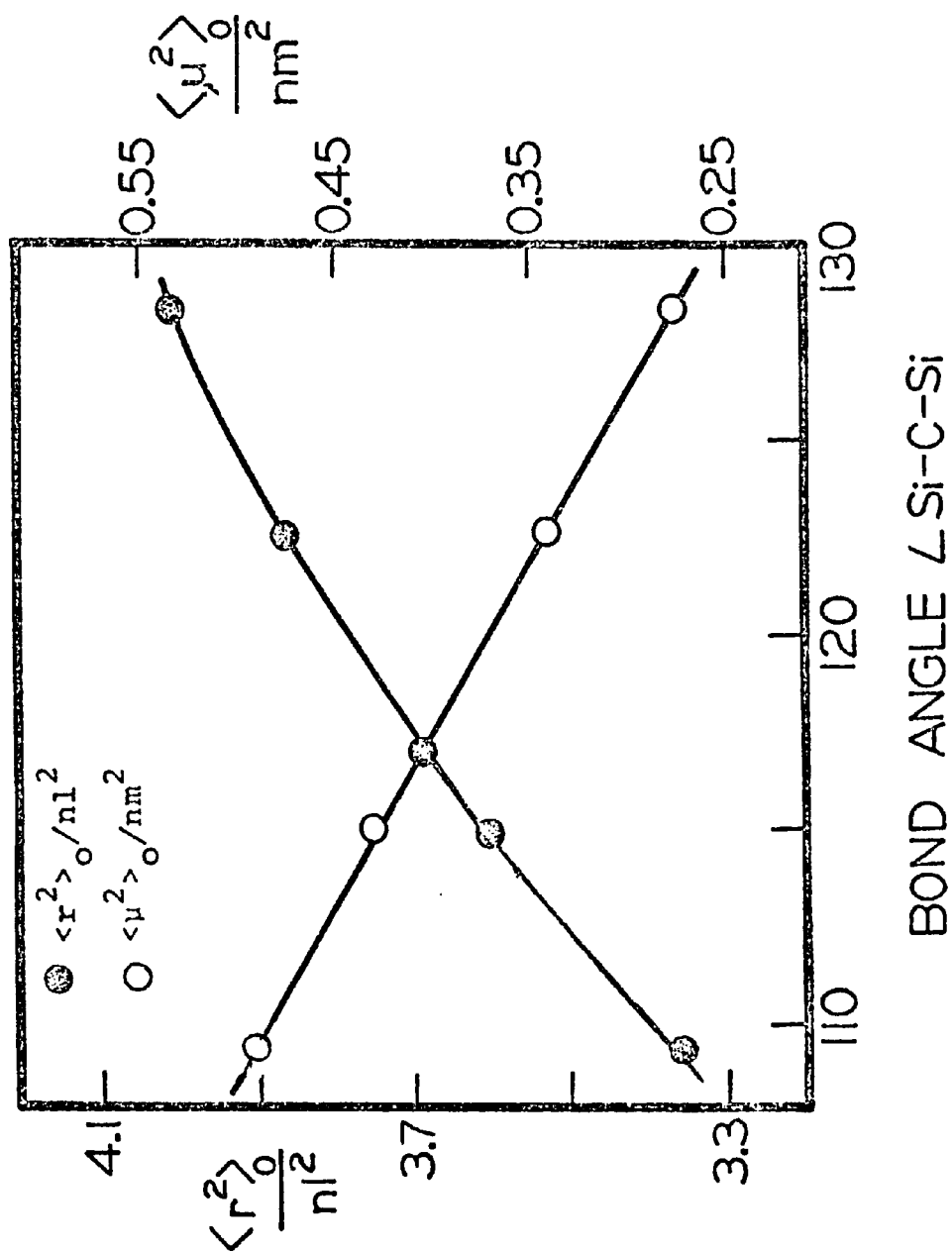


Figure 23. The characteristic ratio and dipole moment ratio for poly(dimethylsilmethylene) plotted against the bond angle $\angle \text{SiCSi}$.

which they are appended. If this effect strongly predominates over charge distribution effects involving the single-electron hydrogen atoms, then the skeletal CH_2 groups should have a larger negative partial charge than the pendant CH_3 groups. This difference in partial charges can probably be ignored except for interactions involving groups at very small distances of separation, and this suggests reconsideration of the statistical weights assigned to conformations giving rise to pentane-type interferences. We retain the statistical weight of unity for the trans-trans state about Si-C-Si bond pairs; this conformation involves pentane-type interferences between pendant CH_3 groups. The $g^{\pm}g^{\mp}$ states, however, involve pentane-type interferences between skeletal CH_2 groups, of higher negative charge and the Coulombic repulsions between these more highly charged- CH_2^- may be sufficient to suppress the statistical weights significantly below the reference statistical weight of unity. Unfortunately, the Coulombic energy of repulsion is almost impossible to calculate since, even if the partial charges were known, it is extremely difficult to obtain an effective dielectric constant for the medium through which the electrostatic lines of force act and the Coulombic energy is inversely proportional to this quantity. We therefore treat this statistical weight for $g^{\pm}g^{\mp}$ states about Si-C-Si bonds as an adjustable parameter ω and investigate the effect of assigning values less than unity to ω for the reasons cited above. In this refine-

ment of the original, simplest scheme, the statistical weight matrix for Si-C-Si bonds becomes

$$\underline{U}_a = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & \omega \\ 1 & \omega & 1 \end{bmatrix} \quad (33)$$

Since, as is shown in Figure 24, g^+g^- states are very compact, their suppression by assignment of $\omega < 1$ would be expected to significantly increase $\langle r^2 \rangle_o / nl^2$. The values thus obtained for $\langle r^2 \rangle_o / nl^2$ and $\langle \mu^2 \rangle_o / nm^2$ for illustrative values of ω are given in columns two and three of Table VII. Temperature coefficients of these quantities similarly calculated for an average temperature of 60°C, are given in the last two columns of the table. Careful comparisons between these calculated results and the corresponding experimental results indicate that for this model, possibly still greatly oversimplified, $\omega = 0.75$ gives the best presently attainable agreement between theory and experiment. Further refinements of the chain model for PDMSM must await more definitive information on the bond angles in Si-C-Si compounds and charge distributions in such molecules; also of great utility would be reliable interatomic potential functions for interactions involving Si atoms since this would permit direct semi-empirical calculations of conformational energies of the PDMSM chain.

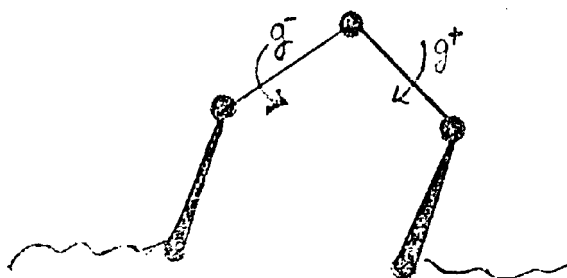


Figure 24. Example of a pair of gauche states of opposite sign, shown to illustrate how occurrence of g^+g^- states makes a chain more compact.

Table VII. Values^a of $\langle r^2 \rangle_0/nl^2$ and $\langle \mu^2 \rangle_0/nm^2$, and their Temperature Coefficients as a Function of the Parameter ω for the PDMSM Chain

ω	$\langle r^2 \rangle_0/nl^2$	$\langle \mu^2 \rangle_0/nm^2$	$10^3 d\ln \langle r^2 \rangle_0/dT$	$10^3 d\ln \langle \mu^2 \rangle_0/dT$
1.00	3.60	0.43	0.00	0.00
0.86	3.83	0.44	-0.17	-0.08
0.71	4.09	0.46	-0.34	-0.14
0.57	4.40	0.47	-0.48	-0.19
0.29	5.14	0.50	-0.56	-0.20
0.00	6.21	0.53	0.00	0.0

^a $\theta_A = 65^\circ$ throughout.

E. Conclusions

In summary, the best model for the PDMSM chain at the present time is one in which most conformational sequences are of identical energy. The only conformational states not of this type are g^+g^- states about C-Si-C bond pairs which are totally suppressed because of interferences between very bulky $\text{Si}(\text{CH}_3)_2$ groups, and g^+g^- states about Si-C-Si bond pairs which are partially suppressed because of Coulombic repulsions between relatively highly charged CH_2 groups. This model, although highly simplified, is at least semi-quantitatively successful in that it explains the most striking configurational characteristics of the PDMSM chain.

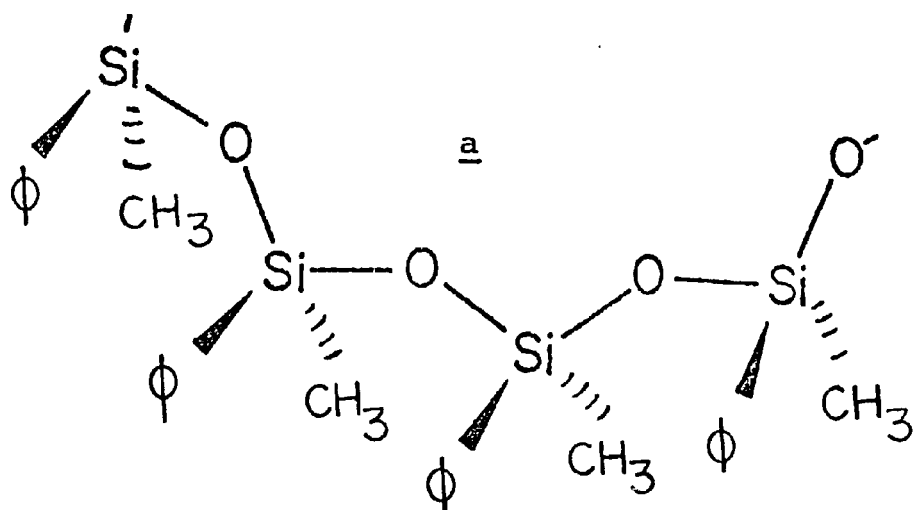
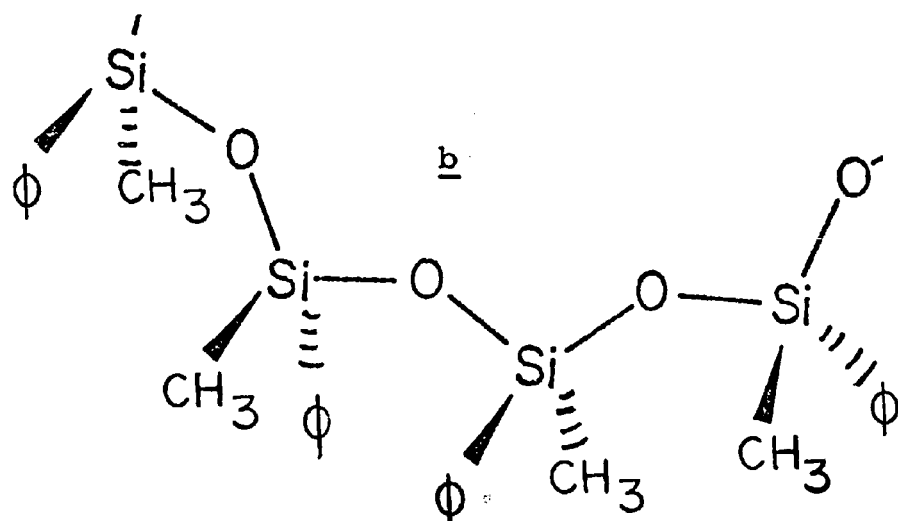
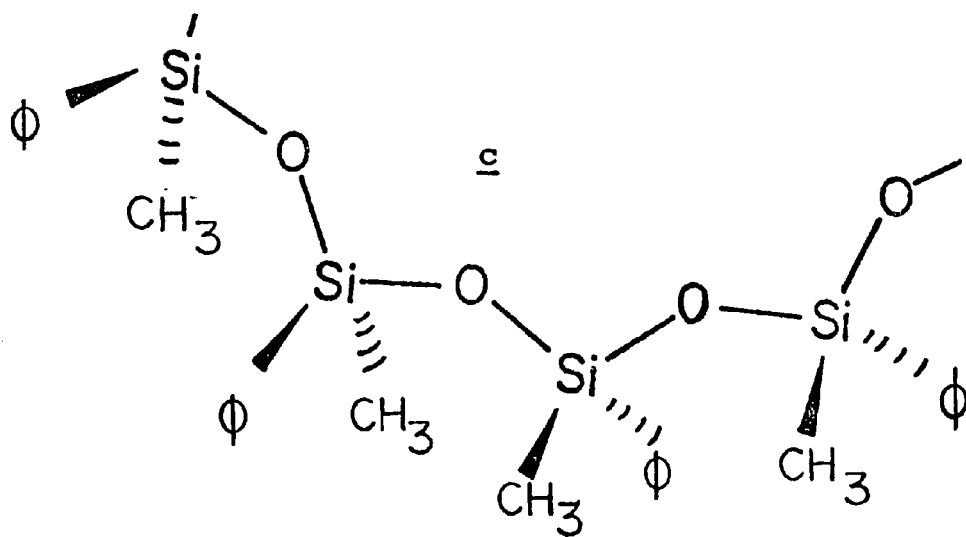
II. RANDOM-COIL DIMENSIONS OF POLY(METHYLPHENYLSILOXANE) AND THEIR DEPENDENCE ON STEREOCHEMICAL STRUCTURE

A. Introduction

The inorganic polymer poly(methylphenylsiloxane) (PMPSO) $[\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{-O-}]_x$ is an important member of the class of disubstituted siloxanes of general structure $[\text{SiRR}'\text{-O-}]_x$. Since, in PMPSO, $\text{R} \neq \text{R}'$ this polymer has a stereochemical variability in that Si atoms are pseudo-asymmetric.⁸⁹ This variability makes PMPSO a much more complicated chain molecule than the polymers described in the preceding part, namely PDMSM $[\text{Si}(\text{CH}_3)_2\text{-CH}_2\text{-}]_x$, PDMSO $[\text{Si}(\text{CH}_3)_2\text{-O-}]_x$ ^{32,34,84} and PIB $[\text{C}(\text{CH}_3)_2\text{-CH}_2\text{-}]_x$.^{26,35-38}

The stereochemical forms of PMPSO are illustrated in Figure 25, where the chain is shown in the planar all-trans conformation to facilitate definition of the required stereochemical characteristics.^{1,25,44} When all of the phenyl (C_6H_5 or ϕ) groups are above the plane in this conformation, the Si atoms are said to be of d configuration; when they are all below the Si atoms, are all designated l. In either case (dddddd..... or llllll.....) the polymer has a regular, replicating stereochemical structure which is said to be "isotactic." The two isotactic forms of the polymer are virtually identical in properties since they differ, at most, only in the end groups on the chain. On the other hand, if the phenyl groups regularly alternate above and below the plane in such a representation, the Si atoms are

Figure 25. Portions of the poly(methylphenylsiloxane) chain shown to illustrate the concept of variable stereochemistry. The chain is shown in the all-trans conformation, in which it is planar; it is, however, non-linear in this conformation because of the inequality of the skeletal bond angles. Parts a, b, and c illustrate isotactic, syndiotactic, and atactic sequences, respectively.



designated dldl.... and the polymer is said to be "syndiotactic." Finally, absence of either type of regularity leads to irregular sequences such as ddld..., and the polymer is said to be "atactic."

The stereochemical nature of the PMPSO chain, as described above, closely parallels that of the extensively studied vinyl type polymers.^{1,25,89-97} The isotactic, syndiotactic, and atactic classifications apply to both monosubstituted vinyl chains $[\text{CHR}-\text{CH}_2-]_x$ ^{1,25,94} and disubstituted vinyl chains $[\text{CRR}'-\text{CH}_2-]_x$.^{89,92} Because of the wealth of information obtained on vinyl-type polymers, the effect of stereochemical composition on their statistical properties is now quite well understood. In contrast, relatively little is known about the stereochemical structure and statistical properties of chains of the type $[\text{SiRR}'-\text{O}]_x$. Comparison between structure-property relationships for the two types of stereochemically variable polymers would obviously be of very great interest. In this regard, PMPSO has pendant groups $\text{R} = \text{C}_6\text{H}_5$ and $\text{R}' = \text{CH}_3$, both of which are relatively large groups. The vinyl-type polymers chosen for purposes of such comparisons should therefore also have $\text{R} \geq \text{CH}_3$. An appropriate monosubstituted chain would therefore be polystyrene (PS) $[\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2-]_x$;^{1,25,85,90,97} correspondingly, a suitable disubstituted chain would be poly(methyl methacrylate) (PMMA) $[\text{C}(\text{CH}_3)(\text{COOCH}_3)-\text{CH}_2-]_x$.⁸⁹

The purpose of this part of the general investigation of silicon-containing polymers is, therefore, to study the characteristic ratio $\langle r^2 \rangle_0 / nl^2$ and the temperature coefficient $d\ln\langle r^2 \rangle_0 / dT$ for PMPSO chains. In pursuit of this goal, rotational isomeric state calculations will be employed, with the required conformational energies being obtained either from published semi-empirical interatomic potential functions⁹⁸ or from known interaction energies in the related polymer, PDMSO.⁸⁴ Calculations carried out as a function of stereochemical composition will therefore elucidate the relationship between the statistical properties of the PMPSO chain and its stereochemical structure.^{25,89-96} Some of these results may then be directly compared with corresponding results obtained for PS and PMMA chains. Such a comparison is of particularly great interest since, in PMPSO the relatively long Si-O bonds (1.64 Å) and the rather large Si-O-Si bond angles (143°)^{79,84} should greatly reduce crowding between R,R' pendant groups. It is now well-known that it is such repulsions between R,R' groups in vinyl chains which are of paramount importance with regard to their spatial configurations;^{25,89-96} in this case, the C-C skeletal bonds are relatively short (1.53 Å) and the C-C-C skeletal bond angles are relatively small (112°).⁸⁹

In addition, the values of $\langle r^2 \rangle_0 / nl^2$ and $d\ln\langle r^2 \rangle_0 / dT$ calculated for PMPSO should be useful for interpreting several experimental studies on this polymer which have

been reported in the literature.⁹⁹⁻¹⁰¹ These experimental studies have been carried out on PMPSO samples of entirely unspecified, and presumably unknown, stereochemical structure. Comparison of theoretical and experimental values of $\langle r^2 \rangle_0 / nl^2$ and its temperature coefficient could therefore indicate the stereochemical composition of the typical PMPSO polymers which have been thus studied previously. Under favorable conditions, such information on the stereochemical structure of a polymer could even elucidate aspects of the polymerization mechanism by which the polymer was formed.

B. Application of Rotational Isomeric State Theory to Poly(methylphenylsiloxane)

1. Structural Features of the Polymer Repeat Unit

The structural parameters used to characterize the PMPSO repeat unit were adopted on the basis of structural information reported in the literature^{79,84} for related small molecules. The bond lengths thus assigned were $l_{\text{Si-O}} = 1.64 \text{ \AA}$, $l_{\text{Si-C}} = 1.90 \text{ \AA}$, $l_{\text{C-H}} = 1.09 \text{ \AA}$, and $l_{\text{C}\cdots\text{C}} = 1.39 \text{ \AA}$ (partial double bond character in the phenyl group). Skeletal bond angles were taken to be 109.5° about Si atoms and 143° about O atoms; these are the values employed in the extensive configurational analysis which have been carried out for PDMSO chains,⁸⁴ and preliminary energy calculations on PMPSO did not disclose any intramolecular

repulsions which could cause distortions of these bond angles. The bond angles within the planar hexagonal phenyl group were of course taken to be 120° . Rotational states were located at $\phi = 0, 120, \text{ and } -120^\circ$, as usual.¹

2. Calculation of Conformational Energies

As is almost invariably done in the configurational analysis of chain molecules, only those nonbonded intramolecular interactions between nearest neighbors are taken into account. This is almost always a perfectly acceptable assumption since for longer-range intramolecular interactions to be important,¹ one or more pentane-type states g^+g^- must occur in the conformational sequence, and steric repulsions in such states cause them to be of very low frequency. Of the interactions requiring characterization, the interactions between pendant groups ($C_6H_5 \dots C_6H_5$, $C_6H_5 \dots CH_3$, and $CH_3 \dots CH_3$) will be obtained by the conformational energy calculations described in this section. These groups are separated by four bonds and their interactions are therefore called "four-bond interactions." Other intramolecular interactions of importance will be obtained from the known conformational energies of the closely related chain molecule PDMSO.

The energy of interaction ϵ_{ij} between two atoms i, j at a distance of separation r_{ij} can be calculated from the Lennard-Jones equation^{1,68,75}

$$\epsilon_{ij} = A_{ij}r_{ij}^{-12} - B_{ij}r_{ij}^{-6} \quad (34)$$

where A_{ij} and B_{ij} are constants depending only on the nature of the atoms i and j . The constant B_{ij} , associated with interparticle attractions, is usually calculated from atomic polarizabilities (such as those compiled by Ketelaar)¹⁰² by means of the Slater-Kirkwood equation.^{73,103,104} The constant A_{ij} , associated with interparticle repulsions is then fixed by either requiring ϵ_{ij} to be a minimum at the sum of van der Waals radii of the two atoms, or by requiring that ϵ_{ij} reproduce the known energy difference between trans and gauche rotational states in an appropriate small molecule.^{68,94} Since energies are to be calculated only at the rotational states t, g^+ , and g^- ($\phi = 0, 120, -120^\circ$), there is no contribution to ϵ_{ij} from the intrinsic torsional potential $(E_0/2)(1-\cos 3\phi)$ about any of the skeletal bonds (where E_0 is the torsional barrier height).^{74,75} Similarly, the relatively non-polar nature of the C_6H_5 and CH_3 groups under consideration permits neglect of Coulombic contributions to the energies of pendant group interactions.

Flory and Sundararajan have recently derived potential energy functions⁹⁸ suitable for the present calculations. They distinguish between alkyl carbon atoms C_{alk} and aromatic carbon atoms C_{ar} by introducing the experimentally observed fact that the carbon van der Waals radius is $1.80 \text{ \AA}$ in n-alkane crystals⁶⁸ but $1.95 \text{ \AA}$ in benzene and other aromatic crystals.⁹⁸ The polarizabilities of C_{alk}

and C_{ar} would be expected to differ as well.¹⁰² In terms of the Lennard-Jones equation already cited, the values of the constants A_{ij} and B_{ij} they suggest for the various interactions of interest are given in Table VIII. (The units are such as to give ϵ_{ij} in kcal mole⁻¹ when r_{ij} is in Å.)

Table VIII. Values of the Lennard-Jones Constants for Calculations of Intramolecular Interaction Energies in PMPSO

Atom Pair	A_{ij}	B_{ij}
$C_{ar} \cdots C_{ar}$	9.794×10^5	556.7
$C_{ar} \cdots C_{alk}$	6.261×10^5	450.3
$C_{alk} \cdots C_{alk}$	3.983×10^5	366.0
$C_{alk} \cdots H$	5.677×10^4	127.9
$C_{ar} \cdots H$	9.422×10^4	159.9
$H \cdots H$	7.278×10^3	47.1

To obtain the total conformational energy $E_{\zeta\eta}$ for the rotational pair, it is necessary to sum the interaction energies ϵ_{ij} for each pair of atoms interacting in that conformational sequence:

$$E_{\zeta\eta} = \sum_{i < j} \epsilon_{ij} \quad (35)$$

The sum is so defined, of course, that each pairwise interaction is counted only once. For example, in the case of $C_6H_5...C_6H_5$ there are 121 (11×11) separate pairwise interactions, in the case of $C_6H_5...CH_3$, there are 44 (11×4), and in the case of $CH_3...CH_3$ there are 16 (4×4). In carrying out the calculations, the C_6H_5 groups and CH_3 groups were placed in minimum energy orientations relative to the chain backbone. In the case of the C_6H_5 groups, the ring is located perpendicular to the chain backbone, in the plane splitting the O-Si-O skeletal bond angle.¹⁰⁷ Similarly the CH_3 group was placed to give a trans sequence for H-C-Si- C_6H_5 , within this same plane.¹ The distances r_{ij} required in the calculation were obtained in the usual manner, using geometric transformation matrices. For the purpose of illustration, the computer program written to calculate distances of separation r_{ij} and interaction energies ϵ_{ij} for a pair of atoms separated by 12 bonds is given in Appendix B.

In the summing of the separate contributions ϵ_{ij} to the total conformational energy E it was found to be convenient to group the ϵ_{ij} on the basis of the number of bonds N_{ij} separating the two atoms. Although there are nine possible rotational isomeric states to be considered ($\zeta = t, g^+, g^-$ and $\eta = t, g^+, g^-$) there are only three different interactions possible; $C_6H_5...C_6H_5$, $C_6H_5...CH_3$,¹ and $CH_3...CH_3$, in the pentane-type interferences



The results obtained for these interactions, when the specified groups are in such pentane-type dispositions, are given in Table IX. The most striking feature of these results is the fact that interactions between the pendant groups are favorable ($E < 0$), with a particularly strong energy preference ($-2.50 \text{ kcal mole}^{-1}$) for $\text{C}_6\text{H}_5 \dots \text{C}_6\text{H}_5$ interactions. The favorable nature of these interactions results from the fact that the pendant groups are at a distance of separation of $3.78 \text{ \AA}$ which is very close to the sum of the van der Waals radii for the interacting species. (The van der Waals radius for CH_3 is approximately $2.0 \text{ \AA}$,⁸⁹ and the already cited value $1.95 \text{ \AA}$ for the van der Waals radius of an aromatic carbon atom suggests that the thickness of the phenyl ring is also approximately $2.0 \text{ \AA}$).^{98,105,106} As is of course well known, the energy of interaction of two atoms or groups is near the minimum value of the sum of the van der Waals radii of the interacting species. The same $\text{CH}_3 \dots \text{CH}_3$ interactions occur in PDMSO and the value of the energy of this interaction calculated here, $-0.5 \text{ kcal mole}^{-1}$, is in the range -0.5 to $-1.0 \text{ kcal mole}^{-1}$ qualitatively estimated for this interaction in PDMSO.⁸⁴

3. Statistical Weight Factors

The statistical weight factors for those pentane-type interactions were designated ω' , ω'' , and ω''' for the pairs

Table IX. Nonbonded Interaction Energies, in Kcal Mole⁻¹, for the PMPSO Chain

Number of Bonds N_{ij} Separating Atoms i and j	$\epsilon_{ij}(\text{C}_6\text{H}_5 \cdots \text{C}_6\text{H}_5)$	$\epsilon_{ij}(\text{C}_6\text{H}_5 \cdots \text{CH}_3)$	$\epsilon_{ij}(\text{CH}_3 \cdots \text{CH}_3)$
4	-0.076	-0.081	-0.079
5	-0.778	-0.260	-0.254
6	-0.379	-0.300	-0.162
7	-0.638	-0.227	----
8	-0.592	-0.064	----
9	-0.356	-0.006	----
10	-0.145	----	----
11	-0.028	----	----
12	-0.003	----	----
E =	-2.495	-0.938	-0.495

$\text{C}_6\text{H}_5\cdots\text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\cdots\text{CH}_3$, and $\text{CH}_3\cdots\text{CH}_3$, respectively ($E_{\omega'} \approx -2,500 \text{ cal mole}^{-1}$, $E_{\omega''} \approx -900 \text{ cal mole}^{-1}$, and $E_{\omega'''} \approx -500 \text{ cal mole}^{-1}$). For purposes of illustration, a dd segment of the PMPSO chain is shown in Figure 26. In this trans-trans conformation, the statistical weight factor $\omega' = \exp[-2,500/RT]$ would characterize the $\phi\cdots\phi$ ($\text{C}_6\text{H}_5\cdots\text{C}_6\text{H}_5$) pentane-type interaction, and the factor $\omega''' = \exp[-500/RT]$ would characterize the pentane-type interaction between the CH_3 groups. If one of the Si atoms had been l instead of the d, there would have been two $\text{C}_6\text{H}_5\cdots\text{CH}_3$ pentane-type interactions, each characterized by the statistical weight factor $\omega'' = \exp[-900/RT]$.

Rotations about the skeletal bonds in PMPSO from trans to gauche[±] states give rise to the new pentane-type interactions $\text{CH}_3\cdots\text{O}$, $\text{O}\cdots\text{O}$, and $\text{C}_6\text{H}_5\cdots\text{O}$. Before consideration of these four-bond interactions, it is essential to consider first the statistical weight factors which must be introduced to take into account interactions between groups separated by three bonds ("three-bond interactions"). These assignments require reference to the scheme used to characterize PDMSO chains.^{1,84} Extraction of the required information is somewhat complicated by the fact that both pendant groups in PDMSO are methyl groups and therefore in the analysis of this chain molecule it was possible to use statistical weight factors that simultaneously accounted for some of the four-bond interactions as well as the three-bond interactions.^{1,84} The variable stereochemical struc-

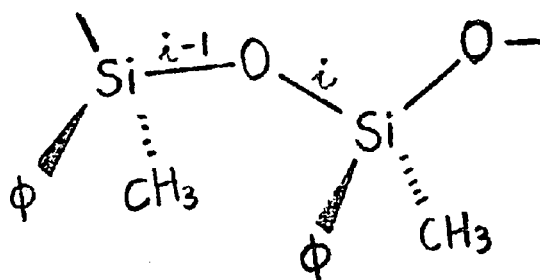


Figure 26. A dd segment of the PMPSO chain showing the two pentane-type interferences $\phi \cdots \phi$ (or $C_6H_5 \cdots C_6H_5$) and $CH_3 \cdots CH_3$.

ture of PMPSO, however, makes this simplification impossible and it is thus necessary first to resolve the interactions in PDMSO into separate three-bond and four-bond contributions. The desired quantity is the statistical weight factor for a gauche⁺ state about a Si-O or O-Si bond relative to a statistical weight of unity for a trans state. In the PDMSO chain, such a rotation from t→g⁺ involves two effects. The first is rupture of one of the favorable CH₃...CH₃ interactions and its replacement by a CH₃...O interaction which was presumed negligible at the distance of separation 3.71 Å because of the relatively small domain of the O atom and relatively small number of separate interactions (1 x 4 = 4). (The van der Waals radius of the O atom is 1.60 Å and thus the sum of the van der Waals radii for the O and CH₃ group is 3.6 Å).⁸⁹ On the basis of the results reported in the preceding section, this effect would give rise to an increase in energy of approximately 500 cal mole⁻¹. The second effect is the relocation of a Si atom closer to the O atom removed from it by three bonds along the PDMSO chain; the distance decreases from 4.32 Å to 3.75 Å. The change is illustrated in Figure 27. Comparison of theoretical and experimental values of $\langle r^2 \rangle_0 / nl^2$ and its temperature coefficient for PDMSO indicated that the total energy change amounted to 850 cal mole⁻¹.⁸⁴ This means that the latter effect, namely the interactions which are exclusively between groups separated by three bonds, must contribute 850-500 =

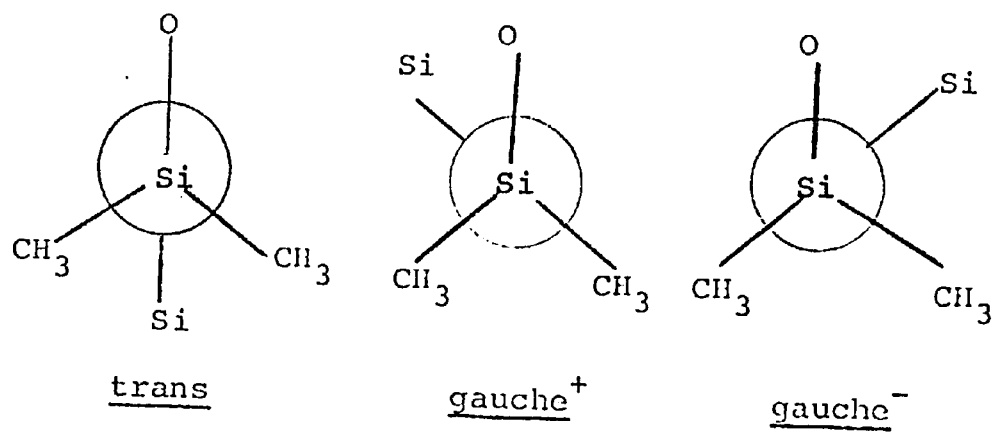


Figure 27. Rotational states about Si-O bonds in PDMSO.

350 cal mole⁻¹. The corresponding three-bond interactions in PMPSO are, to a good approximation, the same as those just characterized for PDMSO. The required change is the replacement of one of the CH₃ groups by a C₆H₅ group in the PDMSO chain segment in Figure 27. In the case of three-bond interactions, it is the part of the pendant group closest to the chain backbone which is of primary importance, and the C_{ar}H part of the phenyl group should not be very different in its interactions from those exhibited by C_{alk}H₃. We therefore accept 350 cal mole⁻¹ as the three-bond contribution to the energy of a gauche state relative to a trans state about Si-O and O-Si bonds in PMPSO. The corresponding statistical weight factor is designated σ and thus has the value $\exp[-350/RT]$. Additional contributions for four-bond interactions will of course be superposed on these three-bond interactions, as will be shown below.

Of the remaining interactions to be considered, the CH₃...O pentane-type four-bond interactions are assumed to be of negligible importance because of the relatively small size of the interacting species and the magnitude 3.71 Å of their distance of separation in this conformation; the same assumption was made in the configurational analysis of the PDMSO chain. The corresponding O...O pentane-type interactions in PMPSO occur at a distance of separation of 3.69 Å and Coulombic repulsions would be expected to make this an important interaction. The total four-bond interactions in these g⁺g⁻ conformation about Si-O-Si bonds

were found to amount to $1,100 \text{ cal mole}^{-1}$,⁸⁴ again by comparison of theoretical and experimental values of the chain dimensions of PDMSO. The three-bond interactions in this conformation would contribute another $2 \times 850 = 1,700 \text{ cal mole}^{-1}$ according to the PDMSO scheme. (One $\text{CH}_3 \dots \text{CH}_3$ interaction is not lost in the transition $\text{tt} \rightarrow \text{g}^+ \text{g}^-$ to this conformation, but the effect of this complication has been absorbed into the cited value of $1,100 \text{ cal mole}^{-1}$). The total interaction energy for this conformation is thus $2,800 \text{ cal mole}^{-1}$. In the modified accounting scheme required for the PMPSO chain, this total energy is ascribed to three contributions: (i) two three-bond interactions ($2 \times 350 = 700 \text{ cal mole}^{-1}$), (ii) the loss of one pair of four-bond $\text{CH}_3 \dots \text{CH}_3$ interactions ($500 \text{ cal mole}^{-1}$), and (iii) the addition of one $\text{O} \dots \text{O}$ four-bond interaction of unknown energy. The fact that a total energy of $2,800 \text{ cal mole}^{-1}$ must of course be given by either scheme indicates that the $\text{O} \dots \text{O}$ four-bond interaction must amount to $2,800 - 1,200 = 1,600 \text{ cal mole}^{-1}$. It is thus characterized by the statistical weight factor $\omega = \exp[-1,600/RT]$.

The final interaction requiring characterization is the pentane-type four-bond interaction between C_6H_5 groups and O atoms. Although the interacting species are rather widely separated (the carbon atom closest to the chain is $3.71 \text{ \AA}$ from the oxygen atom), the large number of separate interactions ($11 \times 1 = 11$) involved in this case make it essential to estimate the conformational energy. Inter-

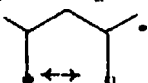
actions involving an O atom are difficult to characterize quantitatively because of the non-bonding electron pairs of oxygen atoms. Use of one of the $C_{alk}...O$ potential functions which have been reported in the literature suggests an interaction energy of approximately $-500 \text{ cal mole}^{-1}$.¹⁰³ The fact that the C atoms involved in the present case are aromatic rather than alkyl should greatly increase the cited value of E for the following two reasons. According to Ketelaar,¹⁰² the polarizability of a C_{ar} atom is very significantly larger than that of a C_{alk} atom, and the significantly larger van der Waals radius of a C_{ar} atom ($1.95 \text{ \AA}$ vs. $1.80 \text{ \AA}$ for C_{alk}) would make the actual distance of separation $3.71 \text{ \AA}$ in the $C_6H_5...O$ interaction closer to the sum $3.6 \text{ \AA}$ of the van der Waals radii of the O atom and the approximate thickness of the C_6H_5 group. Both effects would increase the magnitude of the favorable interactions and one might expect the conformational energy for this interaction to lie in the range -800 to $-1,200 \text{ cal mole}^{-1}$. The $C_6H_5...O$ interaction is thus characterized by a statistical weight factor of δ , again a Boltzmann factor in the associated energy E_δ as herein estimated.

The various interactions, their corresponding statistical weight factors, and the associated energies are summarized in Table X.

Table X. Summary of Interactions, Statistical Weight Factors, and Associated Conformational Energies for the PMPSO Chain

Interaction	Statistical Weight Factor	Associated Conformational Energy(kcal mole ⁻¹)
Si...O*	σ	0.35
C ₆ H ₅ ...C ₆ H ₅	ω'	-2.50
C ₆ H ₅ ...CH ₃	ω''	-0.90
CH ₃ ...CH ₃	ω'''	-0.50
O...O	ω	1.60
C ₆ H ₅ ...O	δ	-0.80- -1.20

* Si...O interactions occurring between these atoms separated by three bonds; all other interactions are between atoms or groups separated by four bonds, in pentane-type conformations



4. The Statistical Weight Matrices

The quantity fundamental to the calculation of the configuration-dependent properties of PMPSO chains is the statistical weight matrix $\underline{U}_i = [u_{\zeta\eta}]_i^{1-4}$ in which the element $u_{\zeta\eta}$ represents the statistical weight for a $\zeta\eta$ pair of rotational states about skeletal bonds $i-1$ and i . Each such statistical weight is the product of statistical weight factors, one for each significant interaction occurring in the conformation being characterized.

We consider first rotations about the O-Si-O bond pair. If all of the four-bond interactions are reserved for inclu-

sions in the complementary matrices for Si-O-Si bond pairs then, in the approximations set forth in the preceding section, the elements in the matrix $\underline{U}$ characterizing rotations about O-Si-O bonds takes a particularly simple form. The states tg^+ and tg^- contain Si...O three-bond interactions and therefore receive a statistical weight of σ relative to the statistical weight of unity for the tt reference state. The g^+t and g^-t states also receive a statistical weight of unity since three-bond interactions occurring in these conformations will have been taken care of in the analysis of the preceding Si-O-Si bond pair in the chain. Since there are no new interactions of significance in g^+g^+ and g^-g^- states beyond those experienced in tg^+ and tg^- states, the statistical weight for each of these is simply σ . In the case of g^+g^- and g^-g^+ states, however, bulky $Si(CH_3)_2$ groups are located in close proximity in pentane-type interferences and these states must therefore be entirely suppressed by assignment of statistical weights of zero. The thus-completed statistical weight matrix for the pair of bonds O-Si-O bracketing a Si atom of either d or l atomic configuration is thus

$$\underline{U} = \underline{U}_d = \underline{U}_l = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{bmatrix} \quad (36)$$

As described in Part I, rows are associated with states about bond $i-1$, and columns with states about bond i ; both

are indexed in the order t , g^+ , g^- .

In the case of pairs of bonds Si-O-Si separating two Si atoms, the atomic configuration of each Si must be specified. For purposes of illustration, we consider a dd Si-O-Si sequence, as is illustrated in Figure 26. The tt state gives rise to a four-bond $C_6H_5...C_6H_5$ interaction and a four-bond $CH_3...CH_3$ interaction, and thus receives a statistical weight of $\omega'\omega''$. Rotation to tg^+ replaces the $C_6H_5...C_6H_5$ interaction by a $C_6H_5...O$ interaction, replaces the $CH_3...CH_3$ interaction by a $CH_3...C_6H_5$ interaction, and adds a new three-bond Si...O interaction; its statistical weight is therefore $\delta\omega''\sigma$. On the other hand, rotation to g^+t replaces $C_6H_5...C_6H_5$ by $CH_3...C_6H_5$, and replaces $CH_3...CH_3$ by a negligible $O...CH_3$ interaction; this conformation thus receives the simple statistical weight ω'' (the Si...O three-bond interaction having been taken into account in the assignment of statistical weights about the preceding O-Si-O bond). In this manner, all of the elements of the matrix associated with dd Si-O-Si bond pairs are established. The corresponding statistical weight matrix is

$$U_{dd} = \begin{bmatrix} \omega'\omega'' & \sigma\omega''\delta & \sigma\omega'' \\ \omega'' & \sigma\delta & \sigma\omega\omega'' \\ \omega''\delta & \sigma\omega\omega' & \sigma\delta \end{bmatrix} \quad (37)$$

In the case of two consecutive Si atoms of dl configuration, the statistical weight matrix is found by the same

analysis to be

$$\underline{U}_{dl} = \begin{bmatrix} (\omega'')^2 & \sigma\omega'''\delta & \sigma\omega' \\ \omega'''\delta & \sigma & \sigma\omega\omega'' \\ \omega' & \sigma\omega\omega'' & \sigma\delta^2 \end{bmatrix} \quad (38)$$

The matrices for the other possible combinations (11 and 1d) about the Si-O-Si bond pair may be obtained by simple symmetry arguments. The matrix $\underline{U}_{11}$ may be obtained from $\underline{U}_{dd}$ by interchange of rows two and three followed by interchange of columns two and three; the same two operations generate $\underline{U}_{1d}$ from $\underline{U}_{dl}$. The statistical weight matrices completing the characterization of the PMPSO chain are therefore

$$\underline{U}_{11} = \begin{bmatrix} \omega'\omega''' & \sigma\omega'' & \sigma\omega'''\delta \\ \omega''\delta & \sigma\delta & \sigma\omega\omega' \\ \omega'' & \sigma\omega\omega''' & \sigma\delta \end{bmatrix} \quad (39)$$

$$\underline{U}_{1d} = \begin{bmatrix} (\omega'')^2 & \sigma\omega' & \sigma\omega'''\delta \\ \omega' & \sigma\delta^2 & \sigma\omega\omega'' \\ \omega'''\delta & \sigma\omega\omega'' & \sigma \end{bmatrix} \quad (40)$$

5. The Configurational Partition Function and the Characteristic Ratio

The standard, rotational isomeric state theory equations for the configurational partition function Z and the characteristic ratio $\langle r^2 \rangle_0 / nl^2$ have already been given in Part I (equations 12 and 21). In the case of PMPSO, however, the matrix multiplication schemes are more complicated because

of the variable stereochemical structure of the chain. It is necessary first to generate chains representative of various stereochemical structures. For this purpose, we define the replication probability p_r ,^{86,89-96} which is the probability that a repeat unit being added to the growing chain will have the same atomic configuration (d or l) as its predecessor. On the average, for a long chain molecule, p_r will also represent the fraction of pairs of consecutive repeat units (or Si atoms) which are of identical stereochemistry. Thus, $p_r = 0.0$ corresponds to a perfectly syndiotactic chain, $p_r = 1.0$ corresponds to a perfectly isotactic chain, and $p_r \approx 0.5$ corresponds to an atactic chain. A typical PMPSO chain of degree of polymerization DP or x may be generated, by Monte Carlo methods, by specification of the desired value of p_r . A set of $x = DP = \frac{n-2}{2}$ random numbers, each in the range 0.0-1.0, is first computer-generated.¹⁰⁸ Each number, in sequence, is then compared with the specified value of p_r ; a number less than p_r is taken to mean an isotactic placement, and a number greater than p_r , a syndiotactic placement. In this way, the entire stereochemical structure of a PMPSO chain representative of the specified value of p_r is generated. This structure is then used to fix the nature of the $\underline{U}$'s and $\underline{G}$'s multiplied in sequence to give Z and $\langle r^2 \rangle_0 / nl^2$.

For example, if the specified value of p_r were 0.80, then the random number sequence0.61, 0.97, 0.13,

0.24, 0.75..... would yield the stereochemical sequence ...ddllll.. (or ... iso, syn, iso, iso, iso,...). The corresponding product of $\underline{U}$ matrices for this illustrative sequence would be $\dots \underline{U} \underline{U}_{dd} \underline{U}_{dl} \underline{U}_{ll} \underline{U}_{ll} \dots$, with the product of the $\underline{G}$ matrices following the same scheme.

The computer program developed for the calculation of Z and $\langle r^2 \rangle_0 / nl^2$ in this more complicated case of a stereochemically variable chain molecule is given in Appendix C.

C. Calculated Results

1. The Characteristic Ratio

Values of the characteristic ratio $\langle r^2 \rangle_0 / nl^2$ for PMPSO chains were calculated as described in the preceding section. The values of the statistical weight factors were calculated from the conformational energies for temperatures of 30, 60, and 90°C (303.2, 333.2, and 363.2°K), since these temperatures will best facilitate later comparisons between theory and experiment.⁹⁹⁻¹⁰¹ In the case of the structural characteristics, the values employed were those described in Section II.B.1. For the stereochemically regular chains, those of perfect syndiotacticity ($p_r = 0.0$) and those of perfect isotacticity ($p_r = 1.0$), only one chain had to be generated for each of these extreme cases. For the stereochemically irregular chains, values of p_r of 0.25, 0.50, and 0.75 were chosen; a number of chains were generated for each of these three values of

p_r . In these cases, a generated chain was discarded as unrepresentative if its actual fraction of isotacticity differed from the desired value of p_r by more than 0.05 unit. Five acceptedly representative chains, thus generated, were used for each of these intermediate values $p_r = 0.25, 0.50, \text{ and } 0.75$. The average of the five values calculated for $\langle r^2 \rangle_o / nl^2$ was then used as the characteristic ratio for that value of p_r .

The first series of calculations was carried out as a function of the degree of polymerization DP so that all subsequent calculations could be carried out at a value of DP sufficiently large that $\langle r^2 \rangle_o / nl^2$ would no longer depend on DP. Typical results, those obtained at $p_r = 0.0, 0.25, \text{ and } 1.00$, are shown in Figure 28. They were obtained for the illustration value $E_\delta = -1.0 \text{ kcal mole}^{-1}$ (from the range -0.8 to $-1.2 \text{ kcal mole}^{-1}$). The values of the characteristic ratio are seen to be independent of DP for $DP \gtrsim 60$. This having been established, all remaining calculations will be carried out using $DP = 100$. These calculated results may then be directly compared with pertinent, published experimental results,⁹⁹⁻¹⁰¹ all of which were obtained on PMPSO samples of very high molecular weight.

The most important calculated results, the dependence of the characteristic ratio on the stereochemical structure of PMPSO, are presented in Figure 29. There, $\langle r^2 \rangle_o / nl^2$ is shown as a function of the replication probability p_r for the illustrative values $E_\delta = -0.8, -1.0, \text{ and } -1.2 \text{ kcal}$

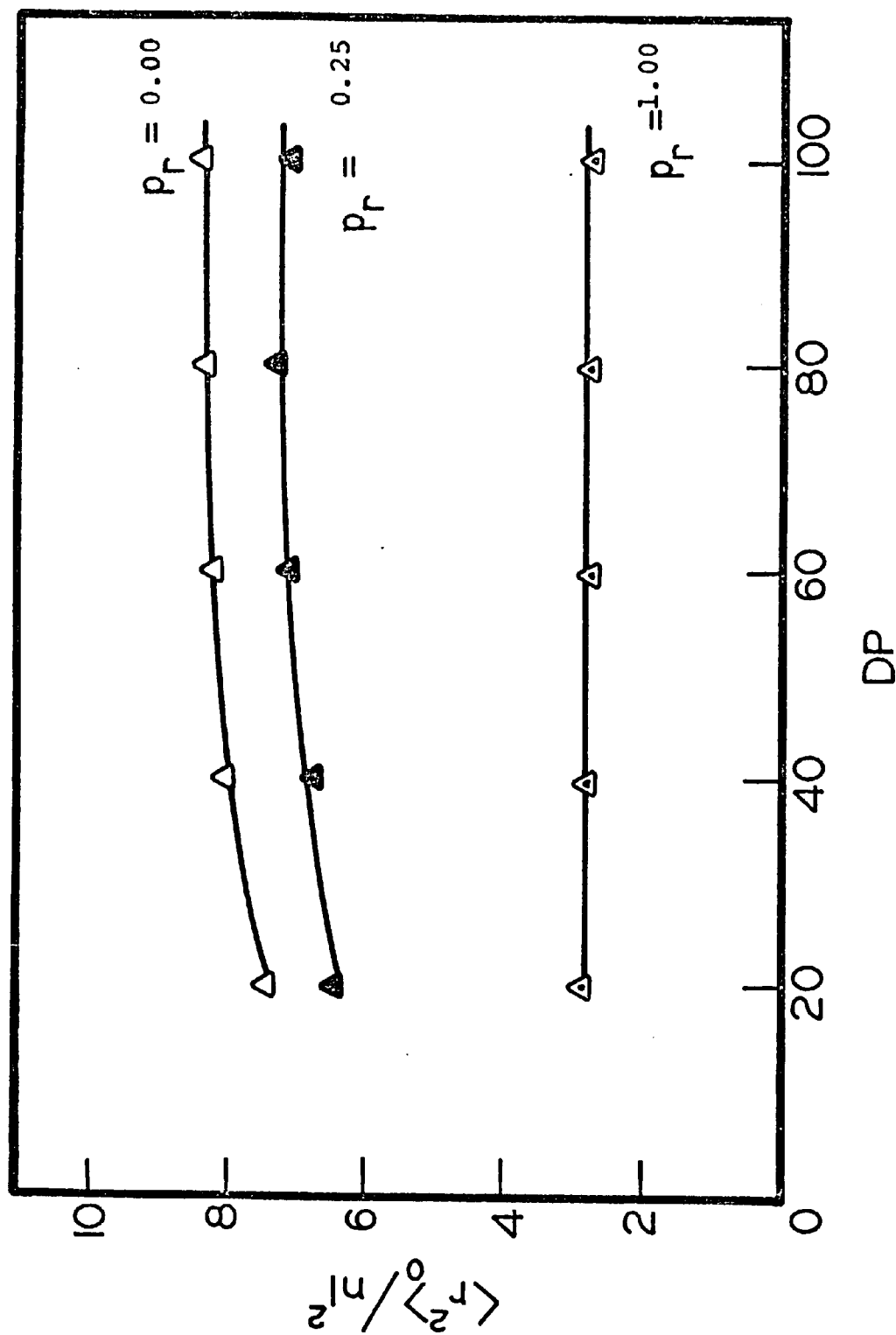


Figure 28. The characteristic ratio of poly(methylphenylsiloxane) at 60°C shown as a function of the degree of polymerization DP for selected values of p_r , for $E_\delta = -1.0 \text{ kcal mole}^{-1}$.

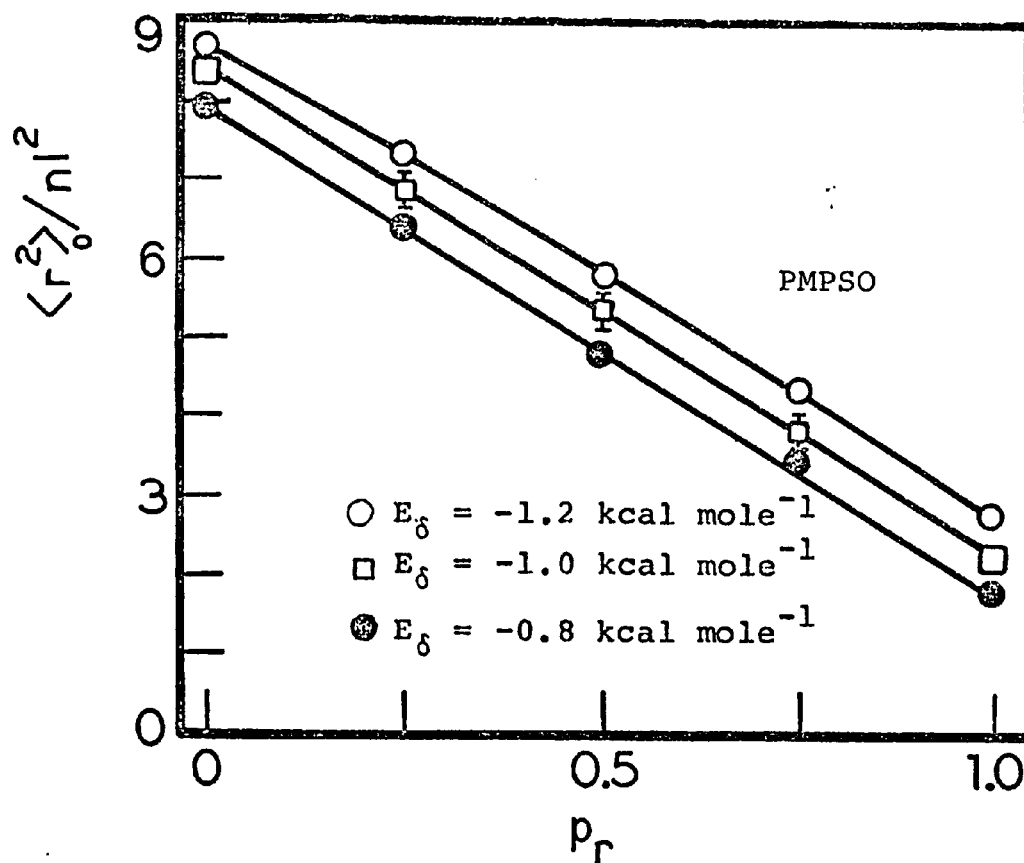


Figure 29. The characteristic ratio of poly(methylphenylsiloxane)(PMPSO) at 30°C plotted against the probability of replication for the illustrative values specified for E_δ .

mole^{-1} . The characteristic ratio is seen to decrease markedly, in an approximately linear manner, with increasing replication probability or degree of isotacticity. This dependence is a direct consequence of the fact that the unequal bond angles in Si-O chains cause the all-trans form to approximate a closed figure.²² Such a closed figure or polygon is illustrated in Figure 30, and obviously corresponds to a very small end-to-end distance. Although three-bond interactions in PMPSO cause a preference for this trans conformation, the very favorable $\text{C}_6\text{H}_5 \dots \text{C}_6\text{H}_5$ four-bond interactions play the dominant role with regard to $\langle r^2 \rangle_0$ for this chain molecule. In the case of highly syndiotacticity (low p_r), the C_6H_5 groups are on opposite sides of the chain in the all-trans form. The lowering of energy accompanying formation of favorable $\text{C}_6\text{H}_5 \dots \text{C}_6\text{H}_5$ interactions therefore causes transitions away from the trans states, of small $\langle r^2 \rangle_0$. This tends to make the characteristic ratio relatively large at small values of p_r , as is shown in Figure 29. On the other hand, at high isotacticity (high p_r), the C_6H_5 groups are already on the same side of the chain in the all-trans conformation and thus the favorable $\text{C}_6\text{H}_5 \dots \text{C}_6\text{H}_5$ interactions stabilize the compact trans conformations. This is the reason $\langle r^2 \rangle_0 / nl^2$ is so small at large values of p_r , again as illustrated in Figure 30.

For the stereochemically variable vinyl chains poly-

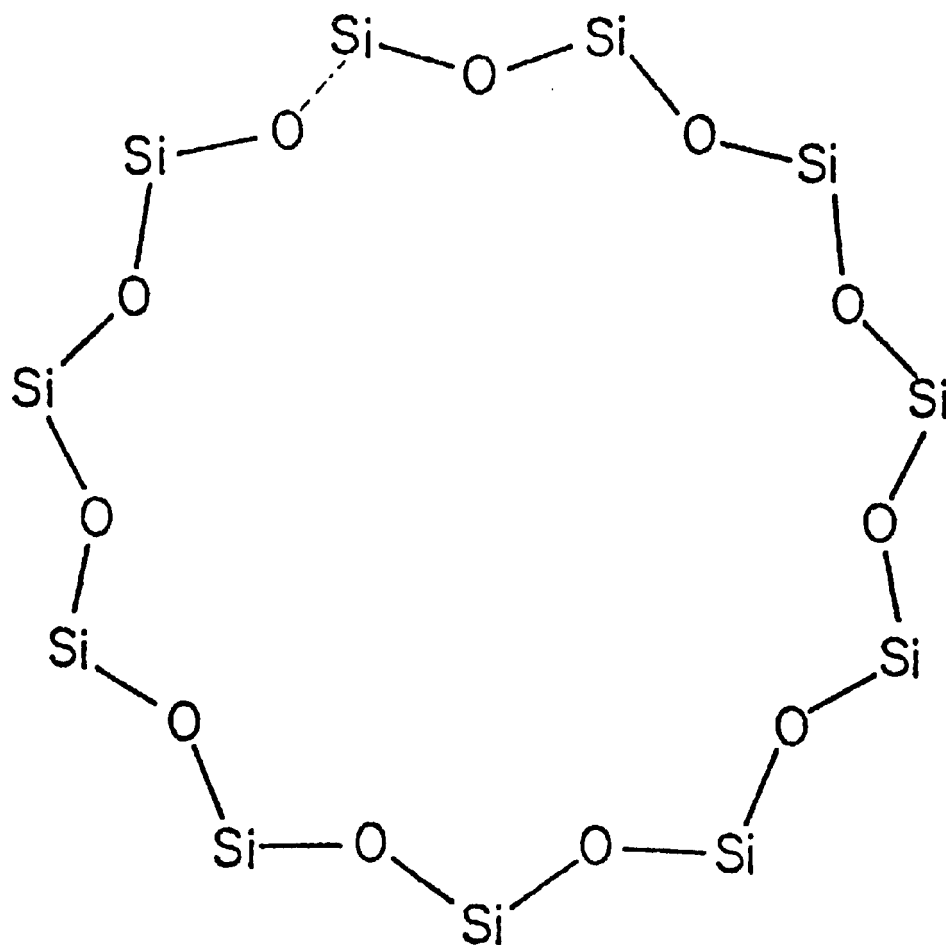


Figure 30. The Si-O backbone in the all-trans conformation, shown to illustrate the fact that trans states tend to decrease the chain dimensions.

styrene (PS) $[\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2-]_x$ ^{25,85,90} and poly(methyl methacrylate) (PMMA) $[\text{C}(\text{CH}_3)(\text{COOCH}_3)-\text{CH}_2-]_x$,⁸⁹ the characteristic ratio shows a very different dependence on stereochemical structure, according to published calculated results on these polymers.^{1,25,85,89,90} These results, taken from the literature, are shown in Figure 31. The most striking feature of the results on PS^{25,109} is the dramatic increase in $\langle r^2 \rangle_0/nl^2$ in the range $p_r = 0.8-1.0$. This occurs because the distance of separation of the C_6H_5 groups in pentane-type interactions in PS is only 2.54 Å. In the case of isotactic PS, these C_6H_5 groups are on the same side of the chain in the all-trans form and so severely interfere with one another sterically that alternating skeletal bonds must rotate to gauche states in a regular manner. The resulting conformations, ...tg⁺tg⁺tg⁺... or g⁻tg⁻tg⁻t..., are helical and thus correspond to very large end-to-end distance.^{25,107,109} This explains the very large value of $\langle r^2 \rangle_0/nl^2$ predicted for PS in the region of high isotacticity. In the case of the disubstituted vinyl chain, PMMA,⁸⁹ the two pendant groups CH_3 and COOCH_3 are not of very different effective size. Since changes in stereochemistry involve interchanges of these two groups around the substituted carbon atoms, the fact that their interactions are not very different accounts for the observed fact that the characteristic ratio of PMMA is not strongly dependent on the stereochemistry of the chain.

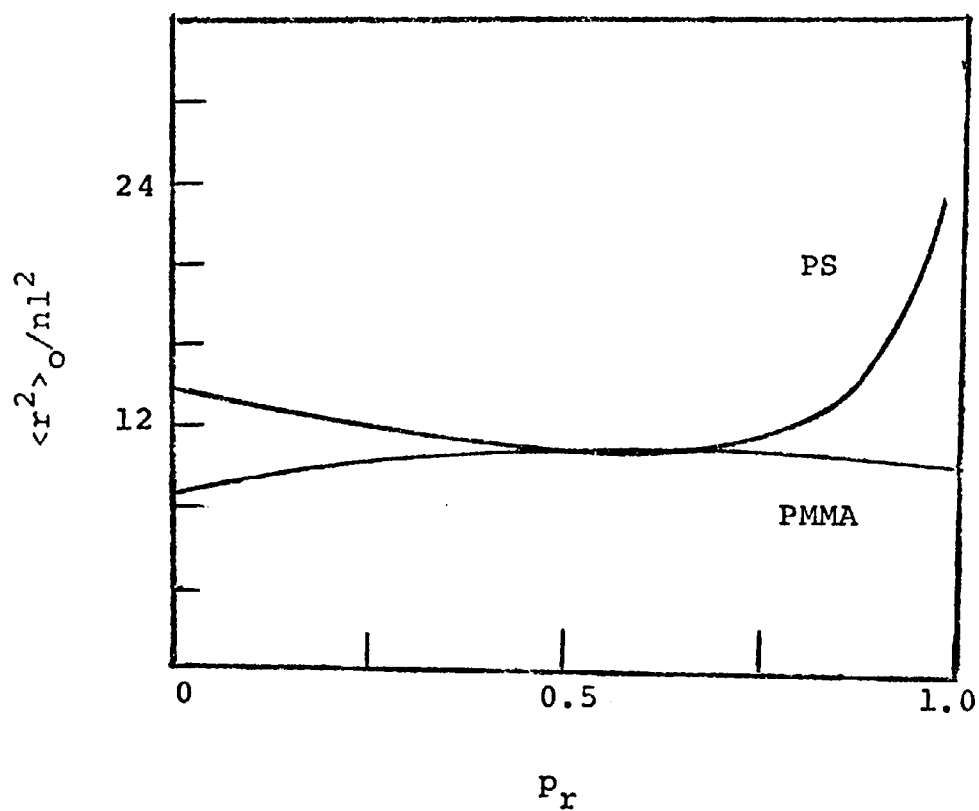


Figure 31. Published calculated values of the characteristic ratio of polystyrene^{25,109} and poly(methylmethacrylate),⁸⁹ shown as a function of the replication probability, at temperatures of 298.2°K and 300°K, respectively.

2. The Temperature Coefficient of $\langle r^2 \rangle_o$

Values of $\langle r^2 \rangle_o / nl^2$ were calculated as a function of temperature for $p_r = 0.00, 0.25, 0.50, 0.75$, and 1.00 and for $E_\delta = -0.8, -1.0$, and -1.2 kcal mole⁻¹. (Instead of using five chains for each value of $p_r = 0.25, 0.50$, and 0.75 , the single chain most representative in each group of five was chosen on the basis of the proximity of its characteristic ratio to the overall average for that collection of five chains. In the present calculations, therefore, one chain is used for each value of p_r , thereby considerably reducing computational costs.) One set of typical results, those pertaining to $E_\delta = -1.0$ kcal mole⁻¹, are shown in Figure 32. The slopes of these curves were used to calculate values of $d\ln\langle r^2 \rangle_o / dT$ at the average temperature of 60°C. The complete set of values of $d\ln\langle r^2 \rangle_o / dT$ thus obtained are presented in Figure 33. As can readily be seen, values of $10^3 d\ln\langle r^2 \rangle_o / dT$ are generally positive and range from 0.0 to 6.0°K⁻¹. The largest values correspond of course to highly isotactic PMPSO chains, for which an increase in temperature causes transitions from the low energy compact trans states to alternative states of higher energy and higher spatial extension.²²

D. Comparison of Theory and Experiment

Although some experimental values⁹⁹⁻¹⁰¹ of $\langle r^2 \rangle_o / nl^2$ and $d\ln\langle r^2 \rangle_o / dT$ have been reported for PMPSO, the polymers studied were totally uncharacterized with regard to stereo-

Figure 32. The characteristic ratio of poly(methylphenylsiloxane) shown as a function of temperature for $E_{\delta} = -1.0 \text{ kcal mole}^{-1}$ at selected values of p_r . The plots for $E_{\delta} = -1.2$ and $-0.8 \text{ kcal mole}^{-1}$ were omitted for purposes of clarity.

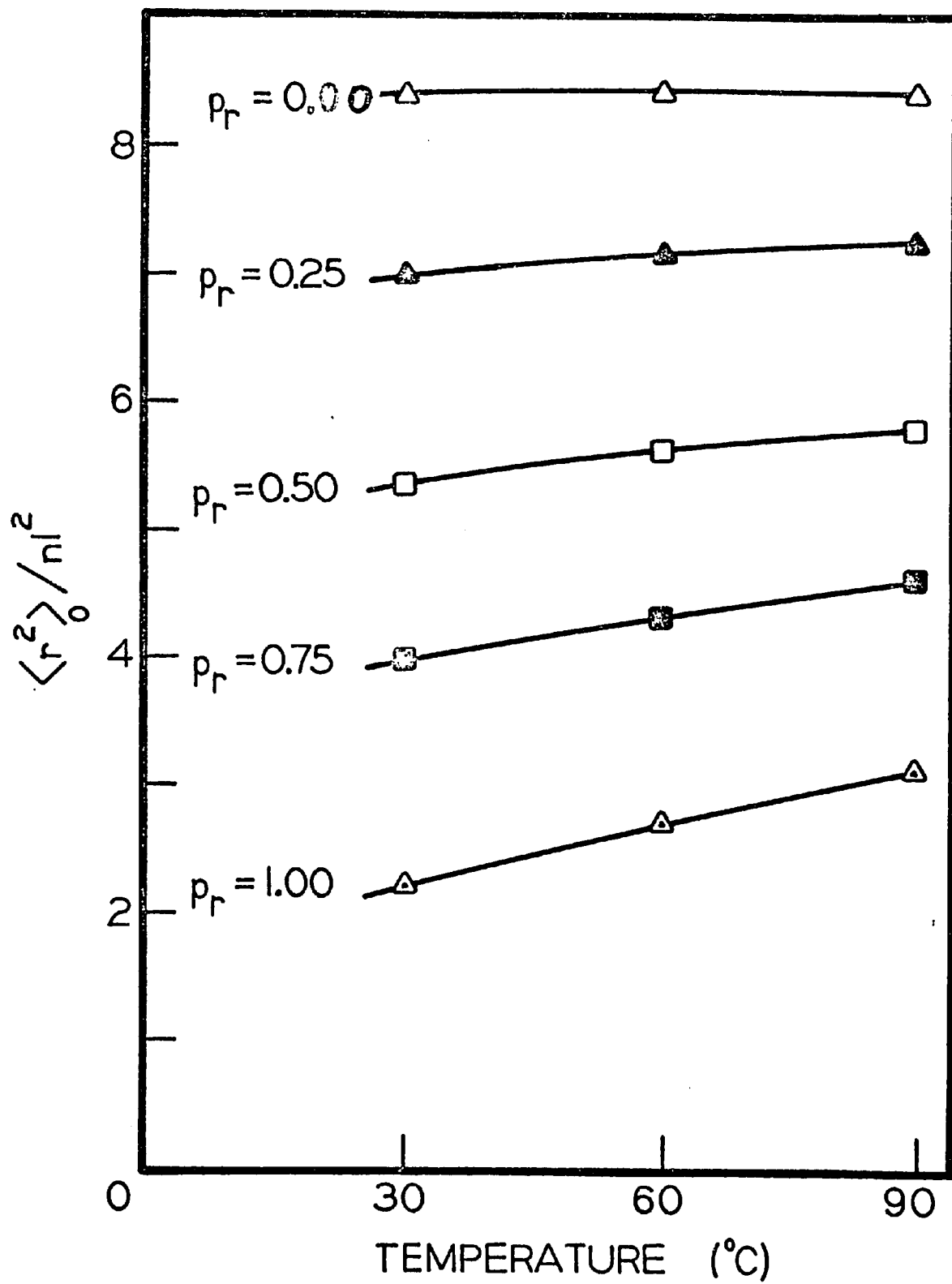
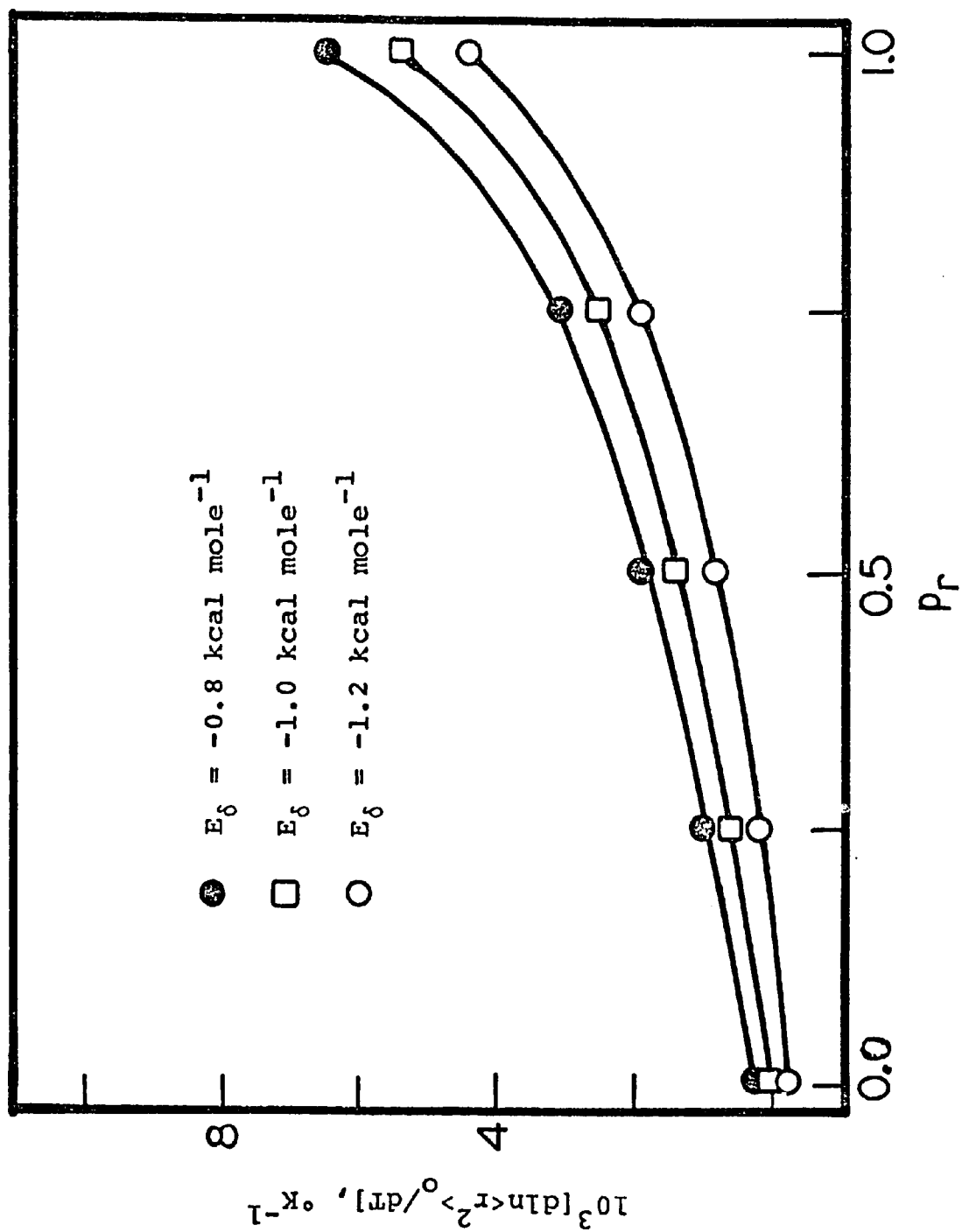


Figure 33. The temperature coefficient $d\ln\langle r^2 \rangle_0/dT$ for poly(methylphenylsiloxane) plotted against P_r at selected values of E_δ .



chemical structure. This circumstance obviously greatly complicates matters, and the comparison of theory and experiment attempted here must therefore be considered very tentative.

Intrinsic viscosity and light scattering measurements on stereochemically uncharacterized PMPSO fractions in a (H)-solvent (diisobutylamine, 30.4°C) interpreted with the appropriate value $2.5 \times 10^{21} \text{ dl cm}^{-3} \text{ mole}^{-1}$ for the hydrodynamic constant ϕ gives the result $\langle r^2 \rangle_0 / nl^2 = 8.8^{100}$. Some similar measurements in the thermodynamically good solvents benzene and toluene in the vicinity of 25°C can be used to estimate a value of $\langle r^2 \rangle_0 / nl^2$ by means of a very approximate extrapolation technique to correct for excluded volume effects. The approximate result thus obtained is 8.7^{99} . Comparison of these experimental results with the theoretical results shown in Figure 29 suggests that the polymer samples studied must have been highly syndiotactic in stereochemical structure.

A value of $d \ln \langle r^2 \rangle_0 / dT$ may also be calculated from some force-temperature measurements carried out on amorphous PMPSO networks,¹⁰¹ again unfortunately of totally unspecified stereochemical structure. Comparison of the experimental result $10^3 d \ln \langle r^2 \rangle_0 / dT = 0.61 (\pm 0.09) \text{ K}^{-1}$ with the calculated results shown in Figure 33 strongly supports the above conclusion that typical PMPSO samples studied thus far must be highly syndiotactic in stereochemical structure. Both comparisons suggest that the parameter E_δ

is of relatively large magnitude, amounting to at least $-1.0 \text{ kcal mole}^{-1}$.

The samples of PMPSO described in the literature^{99,100,110} have generally been prepared by anionic polymerization of the trimer cis-1,3,5-trimethyl-1,3,5-triphenylcyclotri-siloxane which has the structure shown in Figure 34. In the cis isomer, all of the phenyl groups are on one side of the ring and all the methyl groups on the other. If the ring could be opened without any inversions, the cis isomer would yield a sequence of Si atoms of the same atomic configuration. In the actual ring-opening polymerization, however, one of the Si atoms is almost certainly susceptible to inversion.^{111,112} Such stereochemical irregularities would of course constitute syndiotactic sequences. Additional syndiotactic placements could be introduced in the coupling of such $[\text{Si}(\text{C}_6\text{H}_5)(\text{CH}_3)\text{-O-}]_3$ triplets in the formation of the PMPSO chain. This tentative conclusion is supported by the fact that PMPSO formed from the trans isomer was found to be identical to that formed from the cis in unperturbed dimensions, ideal or (H) -temperature, and second virial coefficient in a thermodynamically good solvent.¹⁰⁰

E. Conclusions

Stereochemical structure is found to have a rather different effect on the unperturbed dimensions of PMPSO

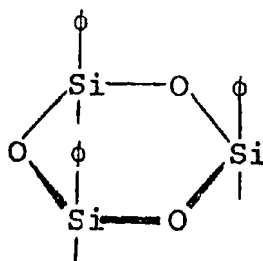


Figure 34. The trimer 1,3,5-trimethyl-1,3,5-triphenyl-cyclotrisiloxane, presented to show the above-the-ring locations of the phenyl (ϕ) groups in the cis isomer. For reasons of clarity, the methyl groups, all on the opposite side of the ring, have been deleted from this schematic diagram.

than in the case for the closely related mono- and disubstituted vinyl polymers. The primary reason for this difference is the fact that the relatively long Si-O skeletal bonds and relatively large Si-O-Si skeletal bond angles in PMPSO increase intramolecular distances between interacting groups so that the interactions are generally attractive, rather than repulsive as they are in the more congested vinyl chains.

Comparisons between theoretical and experimental values of $\langle r^2 \rangle_0 / nl^2$ and $d \ln \langle r^2 \rangle_0 / dT$, although tentative, suggest that PMPSO polymers studied to date are highly syndiotactic in stereochemical structure. Much more work, however, is needed to characterize the stereochemistry of this polymer and the mechanism by which it is formed. Particularly important in this regard would be high resolution nmr studies¹¹³⁻¹¹⁵ of samples of the polymer prepared from both the cis and trans forms of the trimer, under a variety of polymerization conditions.

III. STRESS-STRAIN BEHAVIOR OF POLY (DIMETHYLSILOXANE) NETWORKS AT HIGH ELONGATION

A. Introduction

As already mentioned in Part I, the analysis of stress-strain isotherms for an amorphous polymer network in elongation proceeds most directly through the reduced force $[f^*]$ defined by^{26,28,52-54}

$$[f^*] = f/[A^*(\alpha - \alpha^2)] \quad (41)$$

where, as before, f is the force or stress, A^* is the cross-sectional area of the undistorted network, and $\alpha = L/L_i$ is the elongation, where L and L_i are the length of the sample in the distorted and undistorted states, respectively. According to the statistical theories of rubberlike elasticity^{28,56,57}

$$[f^*] = (\nu kT/V) [\langle r^2 \rangle_i / \langle r^2 \rangle_o] \quad (42)$$

The various quantities appearing in this equation have been defined in Part I; the definitions are not repeated here since the only point of immediate interest is the obvious fact that the statistical theory indicates that $[f^*]$ should be independent of α . In actual practice, however, the reduced force measured over the range of moderate elongation ($\alpha = 1-3$) is generally observed to have

a significant dependence on α . The dependence is such that virtually all stress-strain isotherms in elongation obey the relatively simple or phenomenological equation⁵⁵

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \quad (43)$$

at least over the cited range $\alpha = 1-3$.

The main subject of interest in the present investigation is the fact that at least in the case of some polymer networks, deviations from this relatively simple phenomenological equation^{12,116-121} appear at very high elongation ($\alpha > 3$). Natural rubber networks show this anomalous behavior particularly clearly, and Figure 35 illustrates the type of deviation which has been observed.¹¹⁷ The simple linear relationship is seen to be obeyed over the approximate range $\alpha = 1-2$ ($\alpha^{-1} = 1.0-0.5$). Further increase in α (decrease in α^{-1}), however, causes a very marked upturn in the reduced force, as is shown in the left portion of the figure.¹¹⁷

In studies of such networks, the anomalous behavior has almost invariably been attributed to the limited extensibility of the network chains.¹¹⁶⁻¹¹⁸ The statistical theories of rubberlike elasticity are generally based on network models made up of chains, each of which obeys a Gaussian distribution function. This assumed Gaussian distribution function is known to be adequate at moderate deformations, but must become increasingly inaccurate for

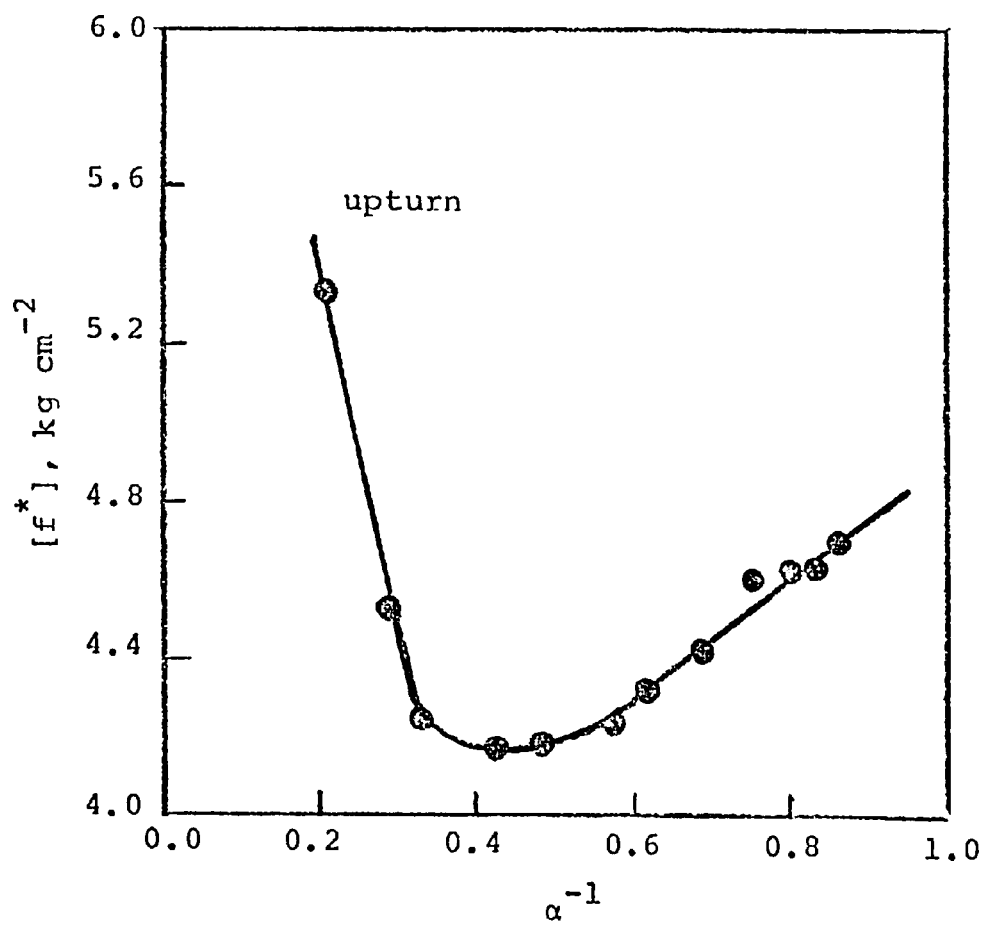


Figure 35. The stress-strain behavior for natural rubber at 25°C, over a wide range of elongation.¹¹⁷

a network chain close to its maximum extension.¹¹⁶⁻¹²⁰ In fact this distribution function does not assign zero probability for a given end-to-end distance until that distance is infinite! This explanation in terms of limited chain extensibility has become so widely accepted that the terms "upturn in the reduced force" and "non-Gaussian behavior" are used essentially interchangeably in the literature on rubberlike elasticity.^{116,117,122} This had led to the adoption of less approximate, non-Gaussian distribution functions for the network chains.^{116,117,123} Such more complicated distribution functions have one or more adjustable parameters, and most work has been carried out to determine the values of these non-Gaussian parameters which give the best fit of these anomalous stress-strain isotherms.¹¹⁷⁻¹²³

Flory, however, pointed out decades ago that the evidence on this point was extremely ambiguous in that the only networks studied at high elongations were those which are highly susceptible to strain-induced crystallization.^{12,121} Even very small amounts of crystallites would greatly increase the reduced force in the manner observed experimentally, for three reasons. Each crystallite would tie together a large number of chains, possibly the order of a hundred or more. Since each such crystallite would act as a physical cross-link of exceedingly high functionality, this would greatly increase the number ν of network chains

(by definition those parts of polymer molecules lying between cross-links). As shown in equation 42, $[f^*]$ is proportional to v and would therefore be greatly increased by this increase in v . Secondly, the crystallites would be essentially non-deformable at the stress levels involved so that significant amounts of crystallization would reduce the fraction of the polymeric network which could exhibit a rubber-elastic response.^{12,121} The non-crystallizable portion would therefore be at a higher elongation than the average macroscopic elongation experimentally measured for the entire semi-crystalline sample. This effect would also tend to increase $[f^*]$. Finally, the crystallites could act in the well-known, although admittedly poorly understood, manner of "filler" particles in rubberlike networks in general.¹² The addition of carbon-black particles to natural rubber, for example, increases its modulus or reduced force substantially. The above comments with regard to crystallites would pertain as well to the formation of hard, glassy regions such as polystyrene domains in an elastomeric copolymer such as a butadiene-styrene elastomer.^{116,124}

In spite of the fact that even small amounts of such strain-induced crystallinity could alone account for the upturn in $[f^*]$ at high α , this possibility has been essentially ignored over the years. Even to date, the only networks studied in the region of high elongation have been

(i) natural rubber, which is highly crystallizable,¹¹⁶⁻¹¹⁸
 (ii) styrene-butadiene elastomers,¹¹⁶ in which the butadiene regions, if stereoregular, could crystallize, or in which the styrene units could conceivably form glassy regions, and (iii) "Viton" fluoroelastomers,¹²⁴ in which the high crystallinity of the homopolymers is suppressed but probably not totally excluded by chemical copolymerization.

It is therefore the purpose of the present study to determine stress-strain isotherms at high elongation for a polymer network in which crystallization could be excluded beyond any reasonable doubt. Poly(dimethylsiloxane) (PDMSO) is ideal for this purpose since its normal melting point is $\sim 50^{\circ}\text{C}$;¹²⁵ when the PDMSO chains are part of a polymer network, the melting point increases with strain, but even at high elongations, its melting point is well below room temperature.¹²⁵ Stress-strain measurements at a temperature of 50°C would therefore unquestionably pertain to a totally amorphous network. The possibility of forming glassy regions in the network can likewise be excluded in view of the very low glass transition temperature, -122°C ,¹²⁶ of PDMSO.

If limited chain extensibility is indeed the origin of the marked upturn in $[f^*]$ at high α , this behavior should be readily observed in these experiments on PDMSO networks. If, however, the origin is primarily strain-induced crystallization, the upturn should be absent, or

at least very much diminished. The proposed experiments on PDMSO networks should therefore clearly distinguish between the two explanations given for this anomalous type of elastic behavior in the very important region of high elongation.

B. Experimental Details

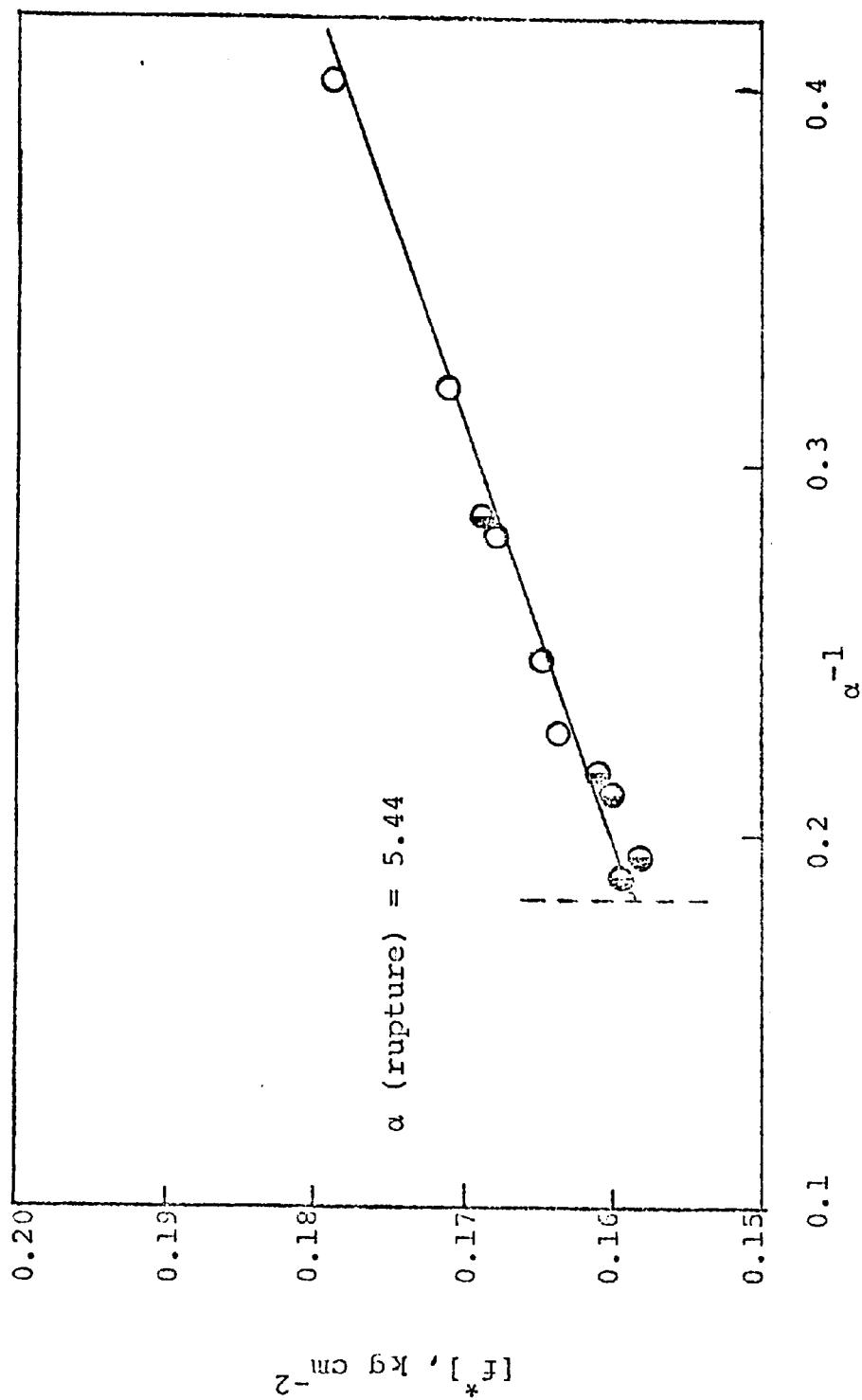
The sample of PDMSO¹²⁷ used in this study had a molecular weight of approximately 0.5×10^6 and, to facilitate cross-linking, contained 0.5 mole% $\text{CH}_3(\text{CH}_2=\text{CH})\text{SiO}$ units.¹²³ The preparation of networks from this sample followed the techniques described in Part I for the cross-linking of poly(dimethylsilmethylene). The dose rates in the γ -irradiations was 0.09 Mrad/hr. Three networks, labelled B1, B2, and B3, were prepared using total doses ranging from 1.0-1.4 Mrads. A sample having the dimensions 0.1 x 0.3 x 3.0 cm was cut from each of the extracted, dried networks by means of a suitable die. The central portion of each sample was marked up by two thin lines of paint applied while the sample was in the stretched state.

The stress-strain measurements were obtained as described in Part I, at a temperature of 50 (± 0.5)°C, under an inert atmosphere of dried nitrogen. Thin rubber sheets were placed at the surfaces of the clamps to prevent premature rupture at these points. Measurements at values of α in decreasing order were first carried out to provide a

reversibility check for the later points carried out at increasing values of α up to the point of sample rupture. Stress-strain isotherms thus established showed, in general, a high degree of reproducibility.

C. Experimental Results

The stress-strain isotherms thus obtained for the three PDMSO samples are shown in Figures 36-38. The results obtained by consecutively decreasing values of α (open circles) are in good agreement with those obtained in increasing α (filled circles) thus demonstrating good reproducibility. The lines shown were located by least-squares analysis, and the rupture point is shown by the vertical dotted line in each figure. Except for a very small increase in $[f^*]$ just prior to rupture, there is no evidence whatever for the pronounced, extensive upturn in $[f^*]$ of the type shown for natural rubber in Figure 35. These results strongly suggest, therefore, that such upturns in $[f^*]$ at high α are due to partial crystallization of the network rather than to inherent shortcomings in the Gaussian theory of rubberlike elasticity. This must mean, in turn, that although some chains may be stretched to near their limits, such chains must remain a relatively small fraction of the total number of elastically effective chains in the network, at least until just prior to final rupture.



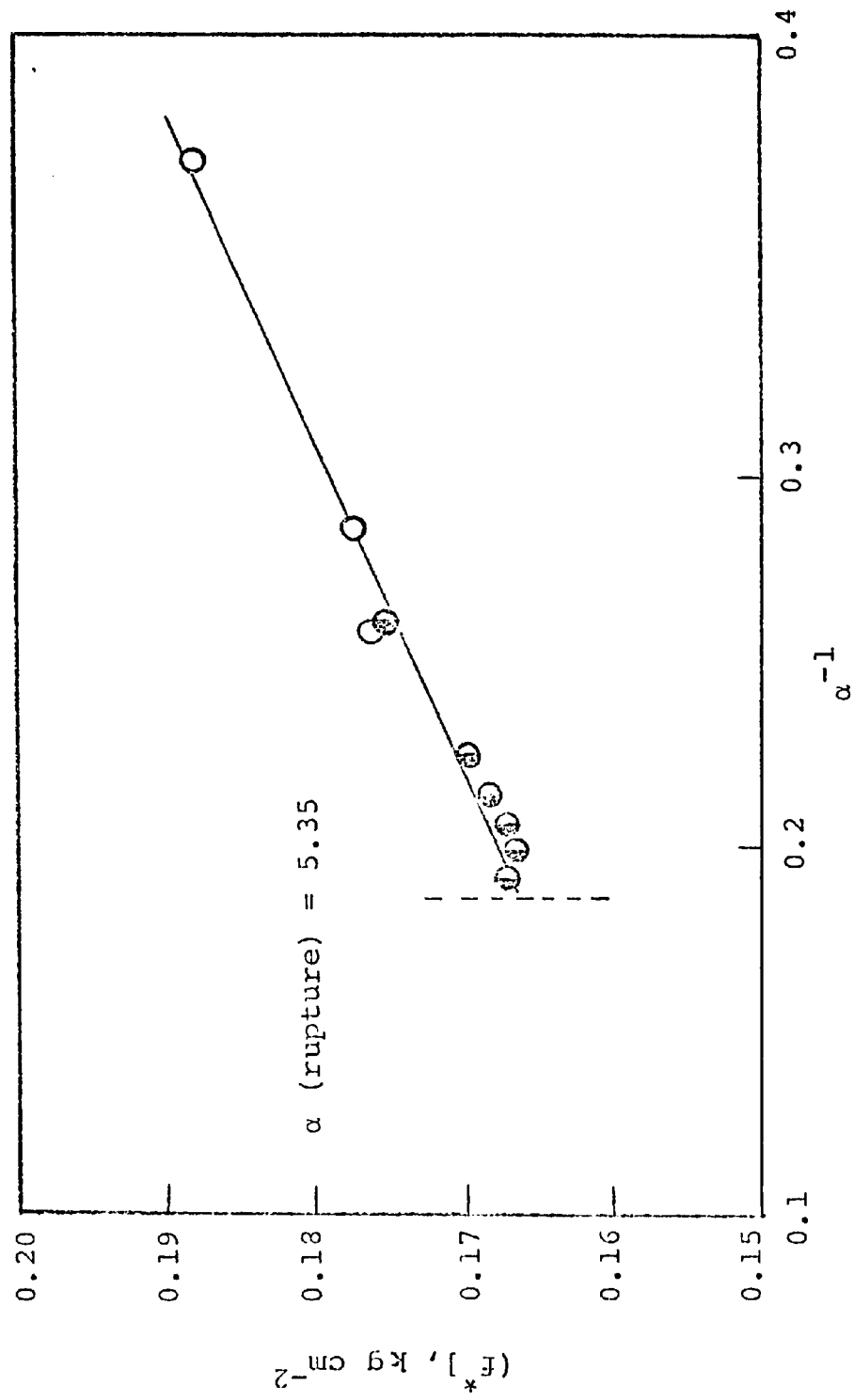


Figure 37. The stress-strain isotherm for PDMSO sample B2. See legend to Figure 36.

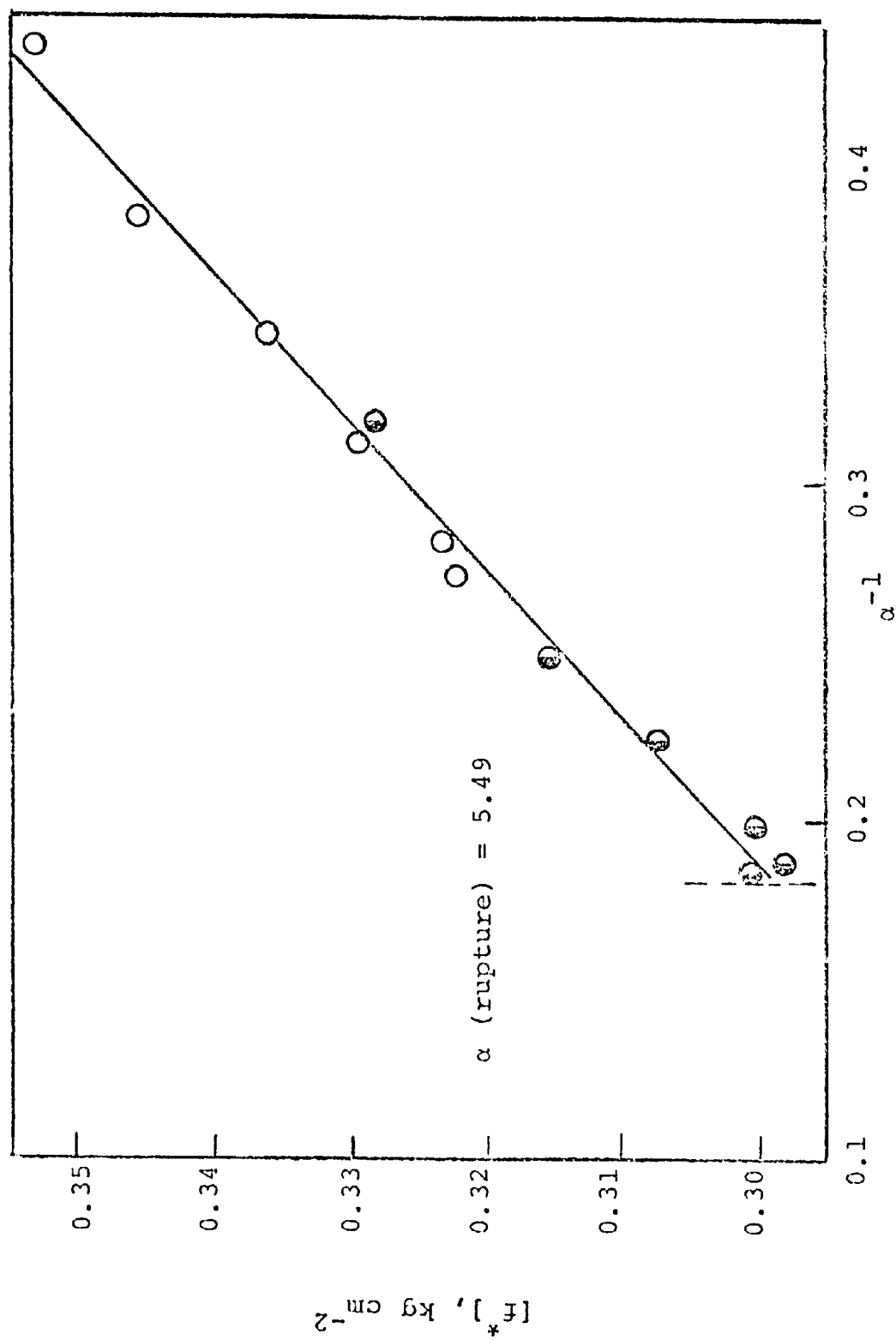


Figure 38. The stress-strain isotherm for PDMSO sample B3. See legend to Figure 36.

D. Conclusions

The results presented here seem to discredit the notation that limited chain extensibility is important in the use of polymeric network at high elongation.¹¹⁶⁻¹¹⁸ Implied instead is strain-induced network crystallization.^{12,121} Even more definite results, of course, could be obtained on some elastomeric, stereochemically irregular polymer such as atactic poly(ethyl acrylate). Because of irregularities inherent in the stereochemical structure of the atactic form, such polymers are totally incapable of crystallization, irrespective of the temperature or range of elongation employed in their investigation.

Appendix A. Calculation of Dipole Moment Ratio for PDMSM

```

C      CALCULATION OF DIPOLE MOMENT RATIO FOR :
C      POLY (DIMETHYLSILMETHYLENE)
C
      DIMENSION G1(15,15),TG(3,9),GAE(15,15)
      DIMENSION T(9,9),IT(3,3,3),FI(3),TH(3)
      DIMENSION GA(15,15),GB(15,15),
C GU(15,15),GW(15,15),GV(15,15)
      DIMENSION TB(9,9),TTB(3,3,3),FIB(3),THB(3)
      DIMENSION UA(3,3),UB(3,3),S(3,3),
C W(3,3),V(3,3),X(3,3),UF(3,3)
100    READ(5,3,END=99)IX
3      FORMAT(I10)
      READ(5,1)((UE(I,J),J=1,3),I=1,3)
      READ(5,10)(FI(I),I=1,3),(TH(I),I=1,3)
10     FORMAT(3F10.5)
      READ(5,44)(FIB(I),I=1,3),(THB(I),I=1,3)
44     FORMAT(3F10.5)
501    READ(5,500)A
500    FORMAT(F10.5)
1001   READ(5,13)TEMP
13     FORMAT(F10.5)
      READ(5,1)((UA(I,J),J=1,3),I=1,3),
C ((UB(I,J),J=1,3),I=1,3)
1      FORMAT(3F15.5)
      WRITE(6,15)((UA(I,J),J=1,3),I=1,3),
C ((UB(I,J),J=1,3),I=1,3)
      WRITE(6,15)((UE(I,J),J=1,3),I=1,3)
15     FORMAT(3F15.5)
C      MULTIPLY UA BY UB
      DO 2 I=1,3
      DO 2 J=1,3
      SUM=0.
      DO 2 K=1,3
      SUM=SUM+UA(I,K)*UB(K,J)
2      W(I,J)=SUM
C      CONSTRUCT (UA*UB)**X=S USE IX INSTEAD OF X
      WRITE(6,1000)IX,TEMP
1000   FORMAT('POLYMERCHAIN IX=',I10,3X,'TEMP= ',F10.2)
      DO 4 I=1,3
      DO 4 J=1,3
4      S(I,J)=W(I,J)
      DO 7 L=2,IX
      DO 5 I=1,3
      DO 5 J=1,3
      SUM=0.
      DO 5 K=1,3
      SUM=SUM+S(I,K)*S(K,J)
C      TO CALCULATE SPECIFIC DP, SET:
C      SUM=SUM+S(I,K)*W(K,J)
5      V(I,J)=SUM
      DO 9 I=1,3
      DO 9 J=1,3
9      S(I,J)=V(I,J)

```

```

7      CONTINUE
C      CONSTRUCTION OF (UA*UB)**X*UE
      DO 6 I=1,3
      DO 6 J=1,3
      SUM=0.0
      DO 6 K=1,3
      SUM=SUM+S(I,K)*UE(K,J)
6      X(I,J)=SUM
      Z=X(1,1)+X(1,2)+X(1,3)
      WRITE (6,8) Z
8      FORMAT (//,1H,5X,'PARTITION FUNCTION Z=',F30.15)
C      CONSTRUCT MATRIX T
C      CONSTRUCT MATRIX T1, THE SUPER ONE
C      T(9,9) IS SUPERMATRIX
      DO 11 I=1,3
      TT(I,1,1)=COS(TH(I))
      TT(I,1,2)=SIN(TH(I))
      TT(I,1,3)=0.
      TT(I,2,1)=SIN(TH(I))*COS(FI(I))
      TT(I,2,2)=-COS(TH(I))*COS(FI(I))
      TT(I,2,3)=SIN(FI(I))
      TT(I,3,1)=SIN(TH(I))*SIN(FI(I))
      TT(I,3,2)=-COS(TH(I))*SIN(FI(I))
11     TT(I,3,3)=-COS(FI(I))
      DATA 1/81*0.0D0/
      DO 12 I=1,3
      DO 12 J=1,3
      T(I,J)=TT(1,I,J)
      II=I+3
      JJ=J+3
      T(II,JJ)=TT(2,I,J)
      III=I+6
      JJJ=J+6
12     T(III,JJJ)=TT(3,I,J)
      DO 41 I=1,3
      ITB(I,1,1)=COS(THB(I))
      ITB(I,1,2)=SIN(THB(I))
      ITB(I,1,3)=0.
      ITB(I,2,1)=SIN(THB(I))*COS(FIB(I))
      ITB(I,2,2)=-COS(THB(I))*COS(FIB(I))
      ITB(I,2,3)=SIN(FIB(I))
      ITB(I,3,1)=SIN(THB(I))*SIN(FIB(I))
      ITB(I,3,2)=-COS(THB(I))*SIN(FIB(I))
41     ITB(I,3,3)=-COS(FIB(I))
      DATA TB/81*0.0D0/
      DO 42 I=1,3
      DO 42 J=1,3

```

```

      TB (I,J) =TTB (1,I,J)
      II=I+3
      JJ=J+3
      TB (II,JJ) =TTB (2,I,J)
      III=I+6
      JJJ=J+6
42    TB (III,JJJ) =TTB (3,I,J)
C     CONSTRUCT G1
      DATA G1/225*C.0DC/
C     A IS THE BOND MOMENT
C     TG=U (F) DIRECT PRODUCT MOMENT TRANSPOSE
      DO 21 J=1,9
21    TG (1,J) =A*TB (1,J)
      DO 25 J=1,9
25    TG (2,J) =A*TB (4,J)
      DO 26 J=1,9
26    TG (3,J) =A*TB (7,J)
      DO 22 I=1,3
      DO 22 J=1,9
      JJ=J+3
22    G1(I,JJ) =TG (I,J)
      DO 23 I=1,9
      DO 23 J=1,9
      II=I+3
      JJ=J+3
23    G1(II,JJ) =TB (I,J)
      G1(1,1) =1.
      G1(2,2) =1.
      G1(3,3) =1.
      G1(4,13) =A
      G1(7,14) =A
      G1(10,15) =A
      B=A**2./2.
      G1(1,13) =B
      G1(2,14) =B
      G1(3,15) =B
      G1(13,13) =1.
      G1(14,14) =1.
      G1(15,15) =1.
C     CONSTRUCT GAE, THE END BCND OF GA
      DATA GAE/225*C.0DC/
      Y=-A
C     TO CALCULATE CHARACTERISTIC RATIO SET Y=A

```

```

GAE(1,1)=1.0
GAE(2,2)=1.0
GAE(3,3)=1.0
GAE(1,4)=+Y*COS(TH(1))
GAE(2,7)=+Y*COS(TH(2))
GAE(3,10)=+Y*COS(TH(3))
GAF(1,13)=0.5*A*A
GAE(2,14)=0.5*A*A
GAF(3,15)=0.5*A*A
GAE(4,13)=Y
GAE(7,14)=Y
GAE(10,15)=Y
GAE(13,13)=1.0
GAE(14,14)=1.0
GAE(15,15)=1.0
C  SHIFT SUPPMATRIX TT(I,J)  GA TO GAE
DO 1010 I=1,9
DO 1010 J=1,9
II=I+3
JJ=J+3
1010 GAF(II,JJ)=I(I,J)
DATA GA,GB/225*0.000,225*0.000/
CALL BUILD(UA,T,GA,Y)
CALL BUILD(UE,TB,GB,A)
DO 50 I=1,15
DO 50 J=1,15
SUM=0.
DO 50 K=1,15
SUM=SUM+GA(T,K)*GB(K,J)
50 GU(I,J)=SUM
DO 51 I=1,15
DO 51 J=1,15
51 GW(I,J)=GU(T,J)
DO 52 L=2,IX
DO 53 I=1,15
DO 53 J=1,15
SUM=0.
DO 53 K=1,15
SUM=SUM+GW(I,K)*GW(K,J)
C  FOR SPECIFIC DEGREE OF POLYMERIZATION SET AS:
C  SUM=SUM+GW(I,K)*GU(K,J)

```

```

53  GV(I,J)=SUM
    DO 54 I=1,15
    DO 54 J=1,15
54  GW(I,J)=GV(I,J)
52  CONTINUE
    DO 60 I=1,15
    DO 60 J=1,15
    SUM=0.
    DO 60 K=1,15
    SUM=SUM+G1(I,K)*GW(K,J)
60  GU(I,J)=SUM
    DO 61 I=1,15
    DO 61 J=1,15
    SUM=0.
    DO 61 K=1,15
    SUM=SUM+GU(I,K)*GAE(K,J)
61  GW(I,J)=SUM
    US1=2.*(1./Z)*(GW(1,13)+GW(1,14)+GW(1,15))
    XN=IX
    XN=2.*XN+2.
    US2=US1/(XN*A**2.)
    WRITE (6,62) US1
    WRITE (6,63) US2
62  FORMAT (//,1H ,5X,'MEAN SQUARE DIPOLE MOMENT=',F30.15)
63  FORMAT (//,1H ,5X,'DP RATIO=',F30.15)
    GO TO 501
99  STOP
    END
C   CONSTRUCT GA AND GB READ IN U, PUT RESULT IN G
    SUBROUTINE BUILD(U,T,G,Y)
    DIMENSION WW(3,9),U(3,3),G(15,15),WWA(3,9),T(9,9)
    DIMENSION WU(9,9),WUW(9,9)
    DATA WW/27*0.000/
    DO 32 I=1,3
    WW(I,1)=Y*U(1,1)
    WW(I,4)=Y*U(1,2)
    WW(I,7)=Y*U(1,3)
32  CCNTINUE
    DO 34 I=1,3
    DO 34 J=1,9
    SUM=0.
    DO 34 K=1,9
    SUM=SUM+WW(I,K)*T(K,J)
34  WWA(I,J)=SUM
    DO 35 I=1,3
    DO 35 J=1,9
    JJ=J+3
35  G(I,JJ)=WWA(I,J)
    DO 33 I=1,3

```

```

DO 33 J=1,3
JJ=J+12
33  G(I,JJ)=Y*Y/2.*U(I,J)
DATA WU/81*0.0D0/
DO 101 I=1,3
WU(I,I)=U(1,1)
II=I+3
WU(II,I)=U(2,1)
III=I+6
101 WU(III,I)=U(3,1)
DO 102 I=1,3
II=I+3
WU(I,II)=U(1,2)
WU(II,II)=U(2,2)
III=I+6
102 WU(III,II)=U(3,2)
DO 103 I=1,3
II=I+3
III=I+6
WU(I,III)=U(1,3)
WU(II,III)=U(2,3)
103 WU(III,III)=U(3,3)
DO 37 I=1,9
DO 37 J=1,9
SUM=0.
DO 37 K=1,9
SUM=SUM+WU(I,K)*T(K,J)
37  WUW(I,J)=SUM
DO 38 I=1,9
DO 38 J=1,9
II=I+3
JJ=J+3
38  G(II,JJ)=WUW(I,J)
DO 39 J=1,3
JJ=12+J
G(4,JJ)=Y*U(1,J)
G(7,JJ)=Y*U(2,J)
39  G(10,JJ)=Y*U(3,J)
DO 40 I=1,3
DO 40 J=1,3
G(I,J)=U(I,J)
II=I+12
JJ=J+12
40  G(II,JJ)=U(I,J)
RETURN
END
$ENDFILE
$RUN -LOAD+*SSP

```

Appendix B. Calculation of Nonbonded Interaction Energy of an Atom Pair Separated by 12 Bonds.

```

      DIMENSION V1(3), V2(3), V3(3), V4(3), V5(3), V6(3), T1(3,3),
C   T2(3,3), T3(3,3), T4(3,3), T5(3,3), A(3), R(3), C(3), D(3), E(3),
C   V7(3), T6(3,3), F(3), V8(3), T7(3,3), F(3), V9(3), T8(3,3), G(3),
C   T9(3,3), H(3), V10(3), R11(3), T10(3,3), P(3), R12(3), T11(3,3), O(3)
9   READ(5,10)V11,V21,V31,V41,V51,V61,V71,V81,V91,V101,R111,R121
10  FORMAT(8F10.2/4F10.2)
      READ(5,15)TH1,TH2,TH3,TH4,TH5,TH6,TH7,TH8,TH9,TH10,TH11
15  FORMAT(8F10.2/3F10.2)
      READ(5,1000)P1,P2,P3,P4,P5,P6,P7,P8,P9,P10,P11
1000 FORMAT(8F10.2/3F10.2)
      READ (5,75) AA, RR
75  FORMAT (2F10.2)
C   CLEAR ARRAYS
      DO 11 I=1,3
      V1(I)=0.0
      V2(I)=0.0
      V3(I)=0.0
      V4(I)=0.0
      V5(I)=0.0
      V6(I)=0.0
      V7(I)=0.0
      V8(I)=0.0
      V9(I)=0.0
      V10(I)=0.0
      R11(I)=0.0
      R12(I)=0.0
      A(I)=0.0
      R(I)=0.0
      C(I)=0.0
      D(I)=0.0
      E(I)=0.0
      F(I)=0.0
      G(I)=0.0
      H(I)=0.0
      P(I)=0.0
      O(I)=0.0
11  R(I)=0.0
C
      V1(1)=V11
      V2(1)=V21
      V3(1)=V31
      V4(1)=V41
      V5(1)=V51
      V6(1)=V61
      V7(1)=V71
      V8(1)=V81
      V9(1)=V91
      V10(1)=V101
      R11(1)=R111
      R12(1)=R121
C
      CALL FILIT (T1, TH1, P1)
      CALL FILIT (T2, TH2, P2)
      CALL FILIT (T3, TH3, P3)

```

```

CALL FILLT (T4, TH4, P4)
CALL FILLT (T5, TH5, P5)
CALL FILLT (T6, TH6, P6)
CALL FILLT (T7, TH7, P7)
CALL FILLT (T8, TH8, P8)
CALL FILLT (T9, TH9, P9)
CALL FILLT (T10, TH10, P10)
CALL FILLT (T11, TH11, P11)
C
DO 107 I=1,3
DO 107 J=1,3
107 O(I)=T11(I,J)*R12(J)+O(I)
DO 106 I=1,3
106 O(I)=O(I)+R11(I)
DO 105 I=1,3
DO 105 J=1,3
105 P(I)=T10(I,J)*O(J)+P(I)
DO 104 I=1,3
104 P(I)=P(I)+V10(I)
DO 103 I=1,3
DO 103 J=1,3
103 H(I)=T9(I,J)*P(J)+H(I)
DO 102 I=1,3
102 H(I)=H(I)+V9(I)
DO 101 I=1,3
DO 101 J=1,3
101 G(I)=T8(I,J)*H(J)+G(I)
DO 100 I=1,3
100 G(I)=G(I)+V8(I)
DO 99 I=1,3
DO 99 J=1,3
99 F(I)=T7(I,J)*G(J)+F(I)
DO 98 I=1,3
98 F(I)=F(I)+V7(I)
DO 97 I=1,3
DO 97 J=1,3
97 F(I)=T6(I,J)*F(J)+F(I)
DO 94 I=1,3
94 F(I)=F(I)+V6(I)
DO 93 I=1,3
DO 93 J=1,3
93 D(I)=T5(I,J)*F(J)+D(I)
DO 91 I=1,3
91 D(I)=D(I)+V5(I)
DO 19 I=1,3
DO 19 J=1,3
19 C(I)=T4(I,J)*D(J)+C(I)
DO 20 I=1,3
20 C(I)= C(I) + V4(I)
DO 21 I=1,3
DO 21 J=1,3
21 A(I)= T3(I,J)*C(J) + A(I)
DO 31 I=1,3
31 A(I)= A(I) + V3(I)
DO 41 I=1,3
DO 41 J=1,3
41 R(I)= T2(I,J)*A(J) + R(I)
DO 51 I=1,3
51 R(I)= R(I) + V2(I)
DO 61 I=1,3

```

```

      DO 61 J=1,3
61  R(I)= T1(I,J)*R(I) + P(I)
      DO 71 I=1,3
71  R(I)= P(I) + V1(I)
      ANS = SQRT(P(I)**2 + P(2)**2 + P(3)**2)
      EN = AA/ANS**3 - RR/ANS**6
      WRITE(6,12)V11,V21,V31,V41,V51,V61,V71,V81,V91,V101,R111,R121
12  FORMAT(///' V11= ',F10.2,3X,' V21= ',F10.2,3X,' V31= ',F10.2,3X,
C' V41= ',F10.2,3X,' V51= ',F10.2,3X,' V61= ',F10.2,3X,
C' V71= ',F10.2,3X,' V81= ',F10.2,3X,' V91= ',F10.2,3X,
C' V101= ',F10.2,3X,' V111= ',F10.2,3X,' V121= ',F10.2)
      WRITE(6,13)TH1,TH2,TH3,TH4,TH5,TH6,TH7,TH8,TH9,TH10,TH11
13  FORMAT(' TH1= ',F10.2,3X,' TH2= ',F10.2,3X,' TH3= ',F10.2,3X,
C' TH4= ',F10.2,3X,' TH5= ',F10.2,3X,' TH6= ',F10.2,3X,' TH7= ',
C' TH8= ',F10.2,3X,' TH9= ',F10.2,3X,' TH10= ',F10.2,3X,
C' TH11= ',F10.2)
      WRITE(6,14)P1,P2,P3,P4,P5,P6,P7,P8,P9,P10,P11
14  FORMAT(' P1= ',F10.2,3X,' P2= ',F10.2,3X,' P3= ',F10.2,3X,
C' P4= ',F10.2,3X,' P5= ',F10.2,3X,' P6= ',F10.2,3X,' P7= ',F10.2,
C' P8= ',F10.2,3X,' P9= ',F10.2,3X,' P10= ',F10.2,3X,' P11= ',
C' F10.2)
      WRITE(6,500)AA,RR
500  FORMAT(' AA= ',F10.2,3X,' RR= ',F10.2)
      WRITE(6,24) ANS, EN
24  FORMAT(' DISTANCE= ',F10.2,3X,' ENERGY= ',F10.3)
      GO TO 9
      END
      SUBROUTINE FILIT (T, TH, P)
      DIMENSION T(3,3)
      THR= TH/(180.0/3.141593)
      PR= P/(180.0/3.141593)
      CT= COS(THR)
      ST = SIN(THR)
      CP = COS(PR)
      SP = SIN(PR)
      T(1,1)= CT
      T(2,1)= ST*CP
      T(3,1)= ST*SP
      T(1,2)= ST
      T(2,2)= -CT*CP
      T(3,2)= -CT*SP
      T(1,3)= 0.0
      T(2,3)= SP
      T(3,3)= -CP
      RETURN
      END

```

Appendix C. Computation of the Characteristic Ratio of Poly(methylphenylsiloxane)

```

      DIMENSION IN(200), RN(200)
C *****IN HOLDS THE STEREOCHEM INTEGERS, RN, THE RANDOM NO
      DIMENSION DD(3), DL(3), DZ(3)
C *****DD IS THE BOND DIPOLE AT A D CARBON, DL AT AN L
C *****DZ IS THE BOND DIPOLE AT A CH2 GROUP
      DIMENSION UD(3,3), UL(3,3), UDD(3,3), UDL(3,3), ULL(3,3),
1      ULD(3,3), UE(3,3), UX(3,3), UY(3,3), AJ(3), AJS(3), AH(3)
      DIMENSION UZ(3,3)
C
      DIMENSION GD(15,15), GL(15,15), GDD(15,15), GDL(15,15), GLL(15,15)
1      , GLD(15,15), GX(15,15), GY(15,15), GS(15,15), GJ(15,15),
2      GJS(15,15), GH(15,15), GZ(15,15), GDF(15,15), GLF(15,15)
C
14 READ (5,15) THS,THU,DPH,TEMP
15 FORMAT (4F10.4)
      WRITE(6,700)TEMP
700  FORMAT(//,'TEMP= ',F10.4)
C      THU IS FOR BOND ANGLE AT UNSUBSTITUTE ATOM
C      DPH IS DELTA PHI
13 READ (5,10) DD(1),DD(2),DD(3),DL(1),DL(2),DL(3)
10 FORMAT (6F10.3)
      READ (5,25) DZ(1), DZ(2), DZ(3)
25 FORMAT (3F10.3)
16 READ(5,20)EC,DELTA,SIGMA,AMEGA1,AMEGA2,AMEGA3,AMEGA
20 FORMAT (7F10.3)
C *****EC IS THE EIGENVALUE CORRECTION REQUIRED
11 READ (5,5) IDP, IXS, TI
5 FORMAT (2I10, 1F10.0)
C *****IDP = JDP = DEGREE OF POLYMERIZATION
C *****IXS IS THE STARTING NO FOR SUBROUTINE RANDU
C *****TI IS THE DESIRED TACTICITY INDEX (PER CENT ISO PLACEMENTS)
      IF (IDP .LT. 10) GO TO 320
      DEV = 0.05
C *****DEV IS THE DEV PERMITTED IN THE TACTICITY INDEX TI
      GO TO 321
320 DEV = 0.101
321 CONTINUE
501 CONTINUE
6 FORMAT (1X, 130(1H*))
      WRITE (6,6)
      WRITE (6,12) IDP, IXS, TI, DEV
12 FORMAT(1X, 'DP IS ', 1I3, 5X, 'IXS IS ', 1I10, 5X,
1      'DESIRED TI IS ', 1F10.3, 5X, 'PERMITTED DEV IN TI IS ',
2      1F10.3/)
      IX = IXS
C
      M = 0
      DO 50 J = 1, IDP
      CALL RANDU (IX, IY, YN)
      RN(J) = YN
      IF (J .EQ. 1) GO TO 400
      GO TO 401
400 IF (0.5 - YN) 90, 90, 91
90 IN(J) = 1

```

```

      GO TO 402
91  IN(J) = C
      GO TO 402
C
401  JMI = J - 1
      IF (IN(JMI) .EQ. 1) GO TO 403
C
      IF (TI - YN) 404, 404, 405
404  IN(J) = IN(JMI) + 1
      GO TO 402
405  IN(J) = IN(JMI)
      M = M + 1
      GO TO 402
C
403  IF (TI - YN) 406, 406, 407
406  IN(J) = IN(JMI) - 1
      GO TO 402
407  IN(J) = IN(JMI)
      M = M + 1
C
402  CONTINUE
50  IX = IY
C
      DP = IDP
      DPM1 = IDP - 1
      AM = M
      ATI = AM/DPM1
      WRITE (6,30) ATI
30  FORMAT (1X, 'ACTUAL TI IS ', 1F10.5/)
C
      IF (ABS(TI - ATI) .GT. DEV) GO TO 500
      GO TO 800
500  WRITE (6,666) IXS
666  FORMAT (1X, 'IXS = ', I10, 3X, 'DOES NOT GIVE A SUITABLE TI'/)
      IXS = IXS + 10000
      GO TO 501
C
800  CONTINUE
      WRITE (6,6)
      WRITE (6,18)
18  FORMAT (1X, 'RANDOM NO ASSIGNMENTS ARE '/)
      WRITE (6,24) (IN(J), J=1,IDP)
24  FORMAT (1X, 8011)
C
      *****0 INDICATES A D UNIT, '1', AN L UNIT
      WRITE (6,6)
      WRITE (6,36) DD(1), DD(2), DD(3)
36  FORMAT (1X, 'X,Y,Z COMPONENTS OF DD ARE ', 3F10.5/)
      WRITE (6,42) DL(1), DL(2), DL(3)
42  FORMAT (1X, 'X,Y,Z COMPONENTS OF DL ARE ', 3F10.5/)
      WRITE (6,72) DZ(1), DZ(2), DZ(3)
72  FORMAT (1X, 'X,Y,Z COMPONENTS OF DZ ARE ', 3F10.5/)
      WRITE (6,48) THS, THU, DPH, EC
48  FORMAT (1X, 'THS IS ', 1F10.3, 5X, 'THU IS ', 1F10.3, 5X,
2    'DPH IS ', 1F10.3, 5X, 'EIGENVALUE CORRECTION IS ', 1F10.3/)
      WRITE (6,6)
C
C
      WRITE(6,60) EC, SIGMA, AMEGA1, AMEGA2, AMEGA3, AMEGA
60  FORMAT('EC= ', F10.4, 2X, 'SIGMA= ', F10.4,
2X, 'AMEGA1= ', F10.4, 2X, 'AMEGA2= ', F10.4, 2X, 'AMEGA3= ', F10.4,

```

```

      C2X,'AMEGA= ',F10.4)
C      ****FMAXD IS THE MAX EIGENVALUE, AND MSQRA IS THE MEAN-SQ RATIO
      WRITE (6,6)
      DO 81 I = 1,3
      DO 81 J = 1,3
      UX(I,J) = 0.0
      UY(I,J) = 0.0
      UZ(I,J) = 0.0
81    UE(I,J) = 0.0
      DO 71 I = 1,3
      AJ(I) = 1.0
      AJS(I) = 0.0
71    AH(I) = 0.0
      AJS(1) = 1.0
      DO 93 I = 1,3
93    UE(I,I) = 1.0
C
      UD(1,1) = 1.0
      UD(1,2) = SIGMA
      UD(1,3) = SIGMA
      UD(2,1) = 1.0
      UD(2,2) = SIGMA
      UD(2,3) = 0.0
      UD(3,1) = 1.0
      UD(3,2) = 0.0
      UD(3,3) = SIGMA
      WRITE(6,1050)
1050    FORMAT(/,'UD IS',/)
      WRITE(6,1010)((UD(I,J),J=1,3),I=1,3)
1010    FORMAT(3F15.5)
C
      UL(1,1) = 1.0
      UL(1,2) = SIGMA
      UL(1,3) = SIGMA
      UL(2,1) = 1.0
      UL(2,2) = SIGMA
      UL(2,3) = 0.0
      UL(3,1) = 1.0
      UL(3,2) = 0.
      UL(3,3) = SIGMA
      WRITE(6,1001)
1001    FORMAT(/,'UL IS',/)
      WRITE(6,1012)((UL(I,J),J=1,3),I=1,3)
1012    FORMAT(3F15.5)
C
      UDD(1,1) = AMEGA1*AMEGA3
      UDD(1,2) = SIGMA*AMEGA2*DELTA
      UDD(1,3) = SIGMA*AMEGA2
      UDD(2,1) = AMEGA2
      UDD(2,2) = SIGMA*DELTA
      UDD(2,3) = SIGMA*AMEGA*AMEGA3
      UDD(3,1) = AMEGA2*DELTA
      UDD(3,2) = SIGMA*AMEGA*AMEGA1
      UDD(3,3) = SIGMA*DELTA
C
      WRITE(6,1002)
1002    FORMAT(/,'UDD IS',/)
      WRITE(6,1011)((UDD(I,J),J=1,3),I=1,3)
1011    FORMAT(3F15.5)
      ULL(1,1) = AMEGA1*AMEGA3

```

```

      ULL(1,2) = SIGMA*AMEGA2
      ULL(1,3) = SIGMA*AMEGA2*DELTA
      ULL(2,1) = AMEGA2*DELTA
      ULL(2,2) = SIGMA*DELTA
      ULL(2,3) = AMEGA*SIGMA*AMEGA1
      ULL(3,1) = AMEGA2
      ULL(3,2) = SIGMA*AMEGA*AMEGA3
      ULL(3,3) = SIGMA*DELTA
      WRITE(6,1080)
1080   FORMAT(/, 'ULL IS',/)
      WRITE(6,1013)((ULL(I,J),J=1,3),I=1,3)
1013   FORMAT(3F15.5)
C
      UDL(1,1) = AMEGA2*AMEGA2
      UDL(1,2) = SIGMA*AMEGA3*DELTA
      UDL(1,3) = SIGMA*AMEGA1
      UDL(2,1) = AMEGA3*DELTA
      UDL(2,2) = SIGMA
      UDL(2,3) = AMEGA*SIGMA*AMEGA2
      UDL(3,1) = AMEGA1
      UDL(3,2) = SIGMA*AMEGA*AMEGA2
      UDL(3,3) = SIGMA*DELTA*DELTA
C
      WRITE(6,1004)
1004   FORMAT(/, 'UDL IS',/)
      WRITE(6,1014)((UDL(I,J),J=1,3),I=1,3)
1014   FORMAT(3F15.5)
      ULD(1,1) = AMEGA2*AMEGA2
      ULD(1,2) = SIGMA*AMEGA1
      ULD(1,3) = SIGMA*AMEGA3*DELTA
      ULD(2,1) = AMEGA1
      ULD(2,2) = SIGMA*DELTA*DELTA
      ULD(2,3) = SIGMA*AMEGA*AMEGA2
      ULD(3,1) = AMEGA3*DELTA
      ULD(3,2) = AMEGA*SIGMA*AMEGA2
      ULD(3,3) = SIGMA
      WRITE(6,1111)
1111   FORMAT(/, 'ULD IS',/)
      WRITE(6,1000)((ULD(I,J),J=1,3),I=1,3)
1000   FORMAT(3F15.5)
C   CALCULATION OF MAXIMUM EIGENVALUE OF UD
C
      DIMENSION XCOF(4), COF(4), ER(3), EI(3)
C
      XCOF(1) = -SIGMA*SIGMA
      XCOF(2) = -SIGMA*SIGMA
      XCOF(3) = (1+2.*SIGMA)
      XCOF(4) = -1.
C
      CALL POLRT (XCOF, COF, 3, ER, EI, IER)
      EMAXD = AMAX1 (ER(1), ER(2), ER(3) )
      EMAXD = EMAXD + EC
      DO 600 I = 1,3
      DO 600 J = 1,3
      UD(I,J) = UD(I,J)/EMAXD
      UL(I,J) = UL(I,J)/EMAXD
      UDD(I,J) = UDD(I,J)/EMAXD
      UDL(I,J) = UDL(I,J)/EMAXD
      ULD(I,J) = ULD(I,J)/EMAXD
      ULL(I,J) = ULL(I,J)/EMAXD

```

600 CONTINUE

C

```

      DO 51 I = 1,15
        GJ(I) = 0.0
        GJS(I) = 0.0
51    GH(I) = 0.0
      DO 61 I = 1,15
        DO 61 J = 1,15
          GX(I,J) = 0.0
          GY(I,J) = 0.0
61    GZ(I,J) = 0.0

```

C

```

      DO 101 I = 1,3
101   GJ(I+12) = 1.0
      GJS(1) = 1.0

```

C

```

      RP = DPH
      RM = -DPH
      RU = 0.0
      CALL GETG (GD,UD,DD,THU, RP,RM,RU)
      CALL GETG (GL,UL,DL,THU, RM,RU,RP)
      CALL GETG (GDD,UDD,DZ,THS,RM,RU,RP)
      CALL GETG (GDL,UDL,DZ,THS,RP,RM,RU)
      CALL GETG (GLL,ULL,DZ,THS,RP,RM,RU)
      CALL GETG (GLD,ULD,DZ,THS,RM,RU,RP)
      CALL GETG (GS,UE,DZ,THS, RU,RU,RU)
      CALL GETG (GDF,UE,DD,THU, RU,RU,RU)
      CALL GETG (GLF,UF,DL,THU, RU,RU,RU)

```

C

```

      IF (IN(1) .EQ. 1) GO TO 52
      DO 82 I = 1,3
      DO 82 J = 1,3
82    UY(I,J) = UD(I,J)
      DO 83 I = 1,15
      DO 83 J = 1,15
83    GY(I,J) = GD(I,J)
      GO TO 53

```

C

```

52   DO 84 I = 1,3
      DO 84 J = 1,3
84    UY(I,J) = UL(I,J)
      DO 85 I = 1,15
      DO 85 J = 1,15
85    GY(I,J) = GL(I,J)

```

C

```

53   IDPM1 = IDP - 1
      IF (IDPM1 .EQ. 1) GO TO 222
      DO 54 J = 2, IDPM1
        JM1 = J - 1
        IF (IN(JM1) .EQ. 1) GO TO 55
        IF (IN(J) .EQ. 1) GO TO 56
        CALL GMPRD (UY,UDD,UZ,3,3,3)
        CALL GMPRD (UZ,UD,UY,3,3,3)
        CALL GMPRD (GY,GDD,GZ,15,15,15)
        CALL GMPRD (GZ,GD,GY,15,15,15)
      GO TO 58

```

C

```

55   CALL GMPRD (UY,UDL,UZ,3,3,3)
      CALL GMPRD (UZ,UL,UY,3,3,3)
      CALL GMPRD (GY,GDL,GZ,15,15,15)

```

```

      CALL GMPRD (GZ, GL, GY, 15, 15, 15)
      GO TO 56
C
55 IF (IN(J) .EQ. 1) GO TO 57
   CALL GMPRD (UY, ULD, UZ, 3, 3, 3)
   CALL GMPRD (UZ, UD, UY, 3, 3, 3)
   CALL GMPRD (GY, GLD, GZ, 15, 15, 15)
   CALL GMPRD (GZ, GD, GY, 15, 15, 15)
   GO TO 58
C
57 CALL GMPRD (UY, ULL, UZ, 3, 3, 3)
   CALL GMPRD (UZ, UL, UY, 3, 3, 3)
   CALL GMPRD (GY, GLL, GZ, 15, 15, 15)
   CALL GMPRD (GZ, GL, GY, 15, 15, 15)
58 CONTINUE
54 CONTINUE
C
222 CONTINUE
C
      IF (IN(IDPM1) .EQ. 1) GO TO 62
      IF (IN(IDP) .EQ. 1) GO TO 63
      CALL GMPRD (UY, UDD, UZ, 3, 3, 3)
      CALL GMPRD (GY, GDD, GZ, 15, 15, 15)
      CALL GMPRD (GZ, GDF, GY, 15, 15, 15)
      GO TO 64
C
63 CALL GMPRD (UY, UDL, UZ, 3, 3, 3)
   CALL GMPRD (GY, GDL, GZ, 15, 15, 15)
   CALL GMPRD (GZ, GLF, GY, 15, 15, 15)
   GO TO 64
C
62 IF (IN(ICP) .EQ. 1) GO TO 65
   CALL GMPRD (UY, UCD, UZ, 3, 3, 3)
   CALL GMPRD (GY, GCD, GZ, 15, 15, 15)
   CALL GMPRD (GZ, GCF, GY, 15, 15, 15)
   GO TO 64
C
65 CALL GMPRD (UY, UCL, UZ, 3, 3, 3)
   CALL GMPRD (GY, GCL, GZ, 15, 15, 15)
   CALL GMPRD (GZ, GLF, GY, 15, 15, 15)
C
64 CONTINUE
C
      EXTRA G FACTOR
      CALL GMPRD (GS, GY, GZ, 15, 15, 15)
C
      ROW AND COLUMN MULTIPLICATIONS
      CALL GMPRD (UZ, AJ, AH, 3, 3, 1)
      CALL GMPRD (AJS, AH, Z, 1, 3, 1)
C
      CALL GMPRD (GZ, CJ, GH, 15, 15, 1)
      CALL GMPRD (GJS, GH, FGP, 1, 15, 1)
C
      FJND2=DP*(DD(1)**2+CD(2)**2+DC(3)**2+DZ(1)**2
C+DZ(2)**2+DZ(3)**2)
      AMSQRA= (2.0*FGP)/(Z*FJND2)
C
      WRITE(6,66)AMSQRA
66      FORMAT(1E15.7)
      WRITE (6,6)

```

```

GO TO 11
END
SUBROUTINE GETG(G,U,D,THETA,X1,X2,X3)
DIMENSION G(15,15), U(3,3), TT(9,9), EX1(3,9), EX2(9,3), EX3(9,9),
1 DUM1(3,9), DUM3(9,9), EX4(3,3), D(3)
DO 302 I = 1,15
DO 302 J = 1,15
G(I,J) = 0.0
302 CONTINUE
DO 52 I = 1,3
DO 52 J = 1,3
G(I,J) = U(I,J)
G(I+12,J+12) = U(I,J)
52 CONTINUE
DO 53 I = 1,3
DO 53 J = 1,3
DSQ = D(1)**2 + D(2)**2 + D(3)**2
EX4(I,J) = 0.5*DSQ*U(I,J)
G(I,J+12) = EX4(I,J)
53 CONTINUE
P1 = 0.0 + X1
P2 = 120.0 + X2
P3 = 240.0 + X3
CALL GETTT(TT,THETA,P1,P2,P3)
CALL EXPD1(EX1,U,D)
CALL GMPRD(EX1,TT,DUM1,3,9,9)
DO 54 I = 1,3
DO 54 J = 1,9
G(I,J+3) = DUM1(I,J)
54 CONTINUE
CALL EXPD2(EX2,U,D)
DO 55 I = 1,9
DO 55 J = 1,3
G(I+3,J+12) = EX2(I,J)
55 CONTINUE
CALL EXPD3(EX3,U)
CALL GMPRD(EX3,TT,DUM3,9,9,9)
DO 56 I = 1,9
DO 56 J = 1,3
G(I+3,J+3) = DUM3(I,J)
56 CONTINUE
RETURN
END
SUBROUTINE GETTT(TT,THETA,P1,P2,P3)
DIMENSION TT(9,9), T1(3,3), T2(3,3), T3(3,3)
DO 303 I = 1,9
DO 303 J = 1,9
TT(I,J) = 0.0
303 CONTINUE
CALL FILLT(T1,THETA,P1)
CALL FILLT(T2,THETA,P2)
CALL FILLT(T3,THETA,P3)
DO 62 I = 1,3
DO 62 J = 1,3
TT(I,J) = T1(I,J)
TT(I+3,J+3) = T2(I,J)
TT(I+6,J+6) = T3(I,J)
62 CONTINUE
RETURN
END

```

```

SUBROUTINE FILLT (T, TH, P)
  DIMENSION T(3,3)
  THR= TH/(180.0/3.141593)
  PR= P/(180.0/3.141593)
  CT= COS(THR)
  ST = SIN(THR)
  CP = COS(PR)
  SP = SIN(PR)
  T(1,1)= CT
  T(2,1)= ST*CP
  T(3,1)= ST*SP
  T(1,2)= ST
  T(2,2)= -CT*CP
  T(3,2)= -CT*SP
  T(1,3)= C.O
  T(2,3)= SP
  T(3,3)= -CP
  RETURN
END
SUBROUTINE EXPD1(EX1,U,D)
  DIMENSION EX1(3,9), U(3,3), D(3)
  DO 304 I = 1,3
  DO 304 J = 1,9
  EX1(I,J) = 0.0
304 CONTINUE
  DO 62 I = 1,3
  DO 62 J = 1,3
    K1=J+2*(J-1)
    K2 = K1 + 1
    K3 = K1 + 2
    EX1(I,K1) = D(1)*U(I,J)
    EX1(I,K2) = D(2)*U(I,J)
    EX1(I,K3) = D(3)*U(I,J)
  62 CONTINUE
  RETURN
END
SUBROUTINE EXPD2(EX2,U,D)
  DIMENSION EX2(9,3), U(3,3), D(3)
  DO 305 I = 1,9
  DO 305 J = 1,3
  EX2(I,J) = 0.0
305 CONTINUE
  DO 72 I = 1,3
  DO 72 J = 1,3
    K1= I + 2*(I-1)
    K2 = K1 + 1
    K3 = K1 + 2
    EX2(K1,J) = D(1)*U(I,J)
    EX2(K2,J) = D(2)*U(I,J)
    EX2(K3,J) = D(3)*U(I,J)
  72 CCNTINUE
  RETURN
END
SUBROUTINE EXPD3(EX3,U)
  DIMENSION EX3(9,9), U(3,3)
  DO 306 I = 1,9
  DO 306 J = 1,9
  EX3(I,J) = 0.0
306 CONTINUE
  DO 82 K = 1,3

```

```
DO 82 I = 1,3
  J = I + 3*(K-1)
  EX3(J,I) = U(K,1)
  EX3(J,I+3) = U(K,2)
  EX3(J,I+6) = U(K,3)
82 CONTINUE
  RETURN
END
```

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