Configuration-Dependent Properties of Poly(dimethylsilmethylene) Chains. I. Experimental Results

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Received June 13, 1975

ABSTRACT: Poly(dimethylsilmethylene) $[Si(CH_3)_2–CH_2–]_x$ was prepared by the Grignard synthesis of the monomer 1,1,3,3-tetramethyl-1,3-disilacyclobutane followed by its ring-opening polymerization using a suitable platinum catalyst. Fractions of the polymer, obtained by fractional precipitations from the material thus prepared, were characterized by means of viscosity, osmotic pressure, and dielectric constant measurements carried out at a number of temperatures. In addition, portions of the unfractionated polymer cross-linked into network structures were studied with regard to their stress–strain isotherms and their thermoelastic (force–temperature) properties. These experimental results were used to calculate values for several important properties used to characterize the spatial configurations of randomly coiled chain molecules: the mean-square unperturbed dimensions, the mean-square dipole moments, and the temperature coefficients of both of these quantities. The most striking features of this chain molecule are its relative compactness, as indicated by the magnitude of its unperturbed dimensions, and the relative insensitivity of both its unperturbed dimensions and dipole moments to changes in temperature.

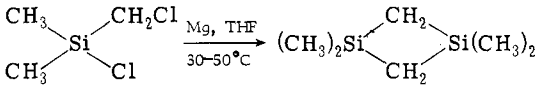
There have now been numerous experimental studies of the spatial configurations of random-coil chain molecules of both biopolymeric and nonbiopolymeric character.[1] In the nonbiopolymeric category, the studies have focused primarily on organic polymers such as polyethylene,[1,3] polytetrafluoroethylene,[1,4] monosubstituted and disubstituted vinyl polymers,[1,5] polyoxides,[1,6] polyesters,[1] polyamides,[1] and diene polymers.[1,7] With the notable exception of poly(dimethylsiloxane) (PDMSO), $[Si(CH_3)_2–O–]_x$,[1,8,9] relatively little work has been done on the configuration-dependent properties of polymers of a more inorganic nature. The inorganic polymer which is the subject of the present study is poly(dimethylsilmethylene) (PDMSM), which has the chemical structure $[Si(CH_3)_2–CH_2–]_x$. In addition to being a polymer of significant inorganic character, it is an exceedingly attractive candidate for analysis with regard to the general problem of the effect of structure on the statistical properties of a chain molecule. Like PDMSO, it is an amorphous, nonglassy material at room temperature, has excellent thermal stability, and is soluble in a variety of convenient solvents;[10–12] these circumstances obviously facilitate its characterization using a variety of appropriate experimental techniques. It is similarly attractive from the point of view of the subsequent interpretation of experimental results by means of the rotational isomeric state theory of chain configurations.[1] It is in this sense a considerably simpler molecule than PDMSO, in that it consists of only silicon atoms and two groups, methylene and methyl, which are very nearly identical[1] in the way in which they affect the configuration of a chain molecule through the intramolecular interactions in which they participate.

In the present paper, we report the preparation of PDMSM, its fractionation, and the characterization of the resulting fractions using viscosity, osmotic pressure, and dielectric constant measurements over a range of temperatures. These studies of PDMSM in solution are supplemented by stress–strain and stress–temperature measurements carried out on cross-linked PDMSM. The resulting data yield values of the mean-square unperturbed dimensions $\langle r^2 \rangle_0$ and dipole moments $\langle \mu^2 \rangle_0$, and the temperature coefficients $d \ln \langle r^2 \rangle_0/dT$ and $d \ln \langle \mu^2 \rangle_0/dT$. These four quantities are very widely used[1] to characterize the configurations of chain molecules in the random-coil state. Their determination for PDMSM chains thus provides much-needed additional information on the configuration-dependent properties of inorganic polymers.

The comparison of these experimental results with corresponding results obtained on other polymers of related structure, and the detailed interpretation of the present results in terms of rotational isomeric state theory, are the subjects of the following paper.[13]

Experimental Section

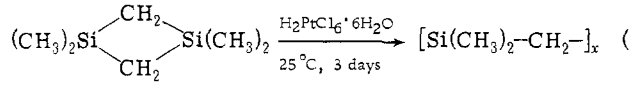
Preparation of Materials. A. Synthesis of the Monomer. The solvent to be used in the synthesis was tetrahydrofuran (THF); it was obtained from the Fisher Scientific Co. as a reagent grade material, but was dried in lithium aluminum hydride and distilled at 65°C just prior to use. The THF solvent was also purged with predried nitrogen to remove any dissolved oxygen. Chloromethyldimethylchlorosilane $Si(CH_2Cl)(CH_3)_2Cl$ was obtained from PCR, Inc., and was distilled at ~115°C, before use; magnesium turnings for the reaction were obtained from J. T. Baker Chemical Co. The whole assembly of glassware was baked at approximately 80°C under vacuum for at least 2 hr. The reaction as shown in the following equation was carried out by the procedure of Kriner:[14]



(1)

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.[14,15] A few drops of the initiator methyl iodide were added to a small amount of magnesium turnings covered by the solvent. Upon adding a portion of the total weight of $Si(CH_2Cl)(CH_3)_2Cl$ to be used, the reaction started, as was evidenced by a light yellowish bubbling from the magnesium turnings. Sufficient 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 2 hr. 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 the THF solvent were added from time to time to reduce the viscosity and thus permit the required rapid mechanical stirring. After approximately 4 hr, the reaction was cooled and about 1 l. 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, 1,1,3,3-tetramethyl-1,3-disilacyclobutane, was collected at 60°C under 100 mm of pressure, giving a yield of 35%. Its proton NMR spectrum[12] showed two singlets at chemical shifts τ 9.8 and 10.0 with the relative intensities of the peaks in the ratio 3 to 1, in agreement with the literature values.[16,17]

B. Polymerization of the Monomer. The method of polymerization[10,11,17] is shown in the equation



$$(CH_3)_2Si\langle{}^{CH_2}_{CH_2}\rangle Si(CH_3)_2 \xrightarrow[25\,^{\circ}C,\ 3\ days]{H_2PtCl_6\cdot 6H_2O} [Si(CH_3)_2{-}CH_2{-}]_x \quad (2)$$

The monomer was purified by low-pressure distillation just prior to use. A mixture of monomer and approximately 1 mg of $H_2PtCl_6{\cdot}6H_2O$ catalyst was placed in a 100-ml three-neck flask thermostatted at 25°C. A glass rod with an attached propeller was fitted through the center port and used to stir the mixture over the 3-day reaction period. The resulting polymer, which was very viscous and clear, was dissolved in benzene and the catalyst was filtered out by a fritted-disk Büchner funnel. The polymer was precipitated using methanol and was then dried in a vacuum oven at approximately 50°C to constant weight. The weight of the poly(dimethylsilmethylene) obtained in this way corresponded to a yield of 80% of the monomer. The NMR spectrum[12] of the polymer in carbon tetrachloride had the expected absorptions at chemical shifts τ 9.9 and 10.2, with the expected intensity ratio 3 to 1.[17] The infrared spectra[12] of the PDMSM in Nujol and in CCl_4 showed the expected strong absorption bands at 1050 and 1350 cm^{-1},[18] which are characteristic of linear $SiCH_2Si$ groups.

Characterization of the Polymer. The polymers resulting from several polymerizations were combined into a bulk sample of PDMSM which was dissolved in reagent grade benzene at a concentration of approximately 1%. A nonsolvent, methanol, was added slowly until a slight cloudiness developed at 25°C. The mixture was warmed until the turbidity disappeared and then cooled slowly back to the original temperature. The precipitate was allowed to settle for at least 5 hr and the supernatant was then carefully poured off. Both parts were refractionated several times, with some fractions being recombined[12] in such a way as to yield four final fractions, F1–F4, accounting for essentially the entire charge of polymer. The fractions were purified several times by dissolving them in benzene, filtering the resulting polymer solution through a medium fritted-disk Büchner funnel, and precipitating the polymer into methanol. Each polymer fraction thus purified was dried under vacuum at approximately 50°C to constant weight.

Solution Properties. A. Viscosities. Two fractions, F2 and F4, of PDMSM prepared as described in the previous section were used for the viscosity measurements.[12,19] The solvent employed was reagent grade cyclohexane (Matheson Coleman and Bell) which was distilled at ~81°C, at atmospheric pressure, just prior to use. The density ρ at 20°C and the temperature coefficient $d\rho/dT$ of the density for this solvent are 0.7782 g ml^{-1} and -0.00096 g ml^{-1} K^{-1}, respectively.[20] 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 thermal expansion coefficient $\beta = (\partial \ln V/\partial T)_p$, obtained using a PDMSM network 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 at one of the temperatures to be investigated. Values of the concentration at other temperatures were calculated from the densities of polymer and solvent at the appropriate temperature, on the assumption of simple additivity of volumes. All concentrations c in the viscosity studies were expressed in grams per 100 ml (g dl^{-1}).

A Cannon-Ubbelohde Viscometer (No. 50 D626) having a capillary with radius small enough to give an efflux time of the cyclohexane solvent greater than 200 sec was chosen; this permitted the neglect of kinetic energy corrections to the observed efflux times. Efflux times of the solvent and polymer solutions were measrued at 25, 30, 40, and 50°C, with the temperature being controlled to ±0.02°C. Efflux times were measured three times and were found to be reproducible to ±0.15 sec. Values of the specific viscosity[21] η_{sp} were in the range 0.1 to 0.5. Intrinsic viscosities $[\eta]$ were obtained by extrapolation of the reduced viscosity η_{sp}/c to $c = 0$,[21] using least-squares analysis, as illustrated in Figure 1.

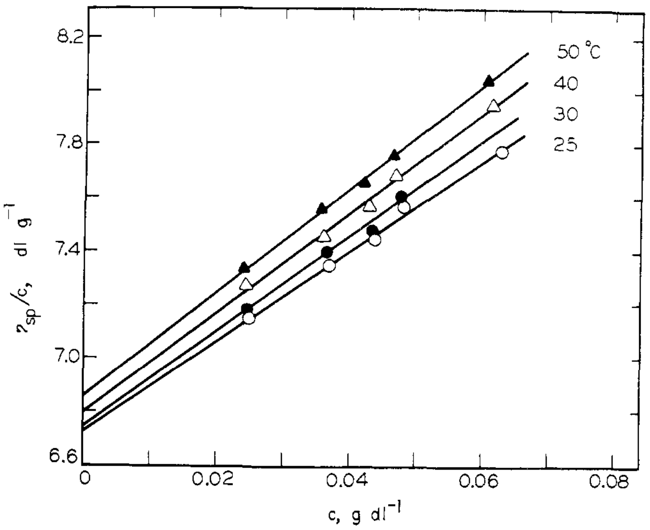


Figure 1. The reduced viscosity shown as a function of concentration for PDMSM fraction F2 in cyclohexane at the specified temperatures. Values of the intrinsic viscosity are given by the intercepts at $c = 0$.

B. Osmotic Pressures. The osmotic pressure, of dilute solutions of the polymer in cyclohexane were measured using a recording membrane osmometer (Wescan Instrument Co.).[22] The membranes employed were type 07 cellulose derivatives obtained from Schleicher and Schuell, Inc. Solutions of the PDMSM fractions F2 and F4 were prepared by the usual quantitative techniques at each desired concentration; reagent grade cyclohexane, which had been redistilled, was used as the solvent. The osmotic pressure π of each polymer solution was measured at least twice, at 32.2, 42.4, and 50.5°C. The temperature was controlled to within ±0.01°C by means of the adjustable precision temperature controller. The pressure exhibited by each solution was monitored continuously and only after a reading showed no discernible change for at least 20 min was it considered the equilibrium value. The osmotic pressure of each solution in dyn cm^{-2} was calculated from $\pi = \rho g \Delta h$, where ρ is (to good approximation)[12] the density of the solvent, g is the gravitational constant, and Δh is the equilibrium pressure in cm of the solvent head.

C. Dielectric Constants and Refractive Indices. The apparatus used for the dielectric constant measurements on the PDMSM solutions was a standard "DM 01 Dipolmeter" operating at a 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.[23] The solvents were reagent grade and distilled just prior to their use. The refractive indices of the polymer solutions at 589 mμ 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.

All four PDMSM fractions were thus studied in cyclohexane at 30°C.[12] Values of the weight fraction w_2 of polymer in the solutions ranged from 0.003 to 0.025. Fraction F3 was studied at 20, 40, and 50°C as well as at 30°C, in order to estimate the temperature coefficient of its mean-square dipole moment.

Elastic Properties of Networks of PDMSM. A. Preparation of Cross-Linked Samples. The polymer 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 × 3 × 7 cm. The mold and its contents were degassed under 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 γ radiation from a ^{60}Co 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 hr 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 them were peeled from the mold and placed in benzene to facilitate removal of the network from the liners. The swollen network was then dried to constant weight at room temperature. A strip approximately 0.1 × 1.0 × 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. The strip was then immersed in gently stirred benzene to remove any uncross-linked polymer. The soluble portion 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

Table I
Viscometry and Osmometry Results for PDMSM Fractions F2 (M = 2.10 × 10^6) and F4 (M = 2.74 × 10^4)

Fraction	T, °C	$[\eta]$, dl g^{-1}	10^4A_2, cm^3 mol g^{-2}	α	$\langle r^2\rangle_0/nl^2$	10^3 d ln $\langle r^2\rangle_0/dT$
F_2	25	6.728	6.52	1.786	5.32	−0.1
	30	6.741	6.55	1.788	5.32	
	40	6.798	6.63	1.792	5.32	
	50	6.861	6.76	1.802	5.30	
					Av (F2) 5.32 ± 0.01	
F_4	25	0.362	15.0	1.391	5.31	0.1
	30	0.363	15.1	1.392	5.31	
	40	0.365	15.3	1.395	5.31	
	50	0.368	15.5	1.398	5.32	
					Av (F4) 5.31 ± 0.01	
					Av (F2,F4) 5.32 ± 0.01	0.0 ± 0.1

putting two small dots of paint on its surface (while it was in the stretched state, in order to prevent the blurring of these marks in the subsequent stress–strain measurements).

B. Elasticity and Thermoelasticity (Force–Temperature) Measurements. The apparatus[24] used to study the elastic behavior of the PDMSM network consisted of a Pyrex cell (approximately 4 cm in diameter) and a stress or force transducer (Statham Model G1-16-350 having a capacity of ±450 g) run by a constant voltage dc power supply (Hewlett-Packard Model 6217A) and calibrated by standard balance weights just prior to the measurements. A stream of predried nitrogen was slowly passed through the cell to eliminate any possibility of oxidative degradation during the experiments. The sample was mounted in the cell between two clamps, the upper one of which was connected to the force transducer. The force exhibited by the network was displayed 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 Micrometer Slide Cathetometer (Gaertner Model M940-303P).

Two types of experiments were carried out on the PDMSM networks: 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 the former experiments, the elongation α[25] was defined as $L(T)/L_i(35°)$, where $L(T)$ is the length of the stretched sample at the chosen temperatures of measurement (35, 45, 70°C), and L_i (35°) is the length of the undeformed sample at 35°C. In the latter type of experiment, α was defined as $L(90°)/L_i(90°)$. Values of the elastic force were recorded only after they became constant for a period of at least 15 min; up to 7 hr were required to attain this degree of constancy. In the constant-temperature experiments, 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 at 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 β 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] $\beta = 3(\partial \ln L_i/\partial T)_p$. The data are shown elsewhere[12] and the result is cited in an earlier section. Finally, the cross-sectional area A^* of each sample in the undistorted state was measured by means of a micrometer.

Results and Discussion

The Mean-Square Unperturbed Dimensions $\langle r^2\rangle_0$. Values of the intrinsic viscosity $[\eta]$, determined as described in an earlier section, are given for fractions F2 and F4 in the third column of Table I. The osmotic pressure data were all obtained on relatively dilute solutions and were therefore interpreted using the simple equation[21]

$$\pi/c = RT(1/M + A_2c) \qquad (3)$$

where R = 8.314 × 10^7 ergs K^{-1} mol^{-1} is the gas constant, and A_2 is the second virial coefficient. Accordingly, plots of π/cT against c give R/M as the intercept and RA_2 as the slope. Typical results, those pertaining to a temperature of 32.2°C, are shown in Figure 2; the additional results,[12] which pertain to 42.4 and 50.5°C, were omitted for purposes of clarity. Data on the same fraction at different temperatures gave essentially the same intercept, as expected; values of the number-average molecular weight M for F2 and F4 calculated from these intercepts are 2.10 ± 0.06 × 10^6 and 2.74 ± 0.03 × 10^4, respectively. Values of 10^4A_2 for F_2 at 32.2, 42.4, and 50.5°C were 6.56, 6.67, and 6.77 cm^3 mol g^{-2}, respectively; for F4, the values were 15.2, 15.4, and 15.6 cm^3 mol g^{-2}, respectively. As expected,[21] A_2 increases with increasing temperature and with decreasing molecular weight. These values of A_2 were 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.

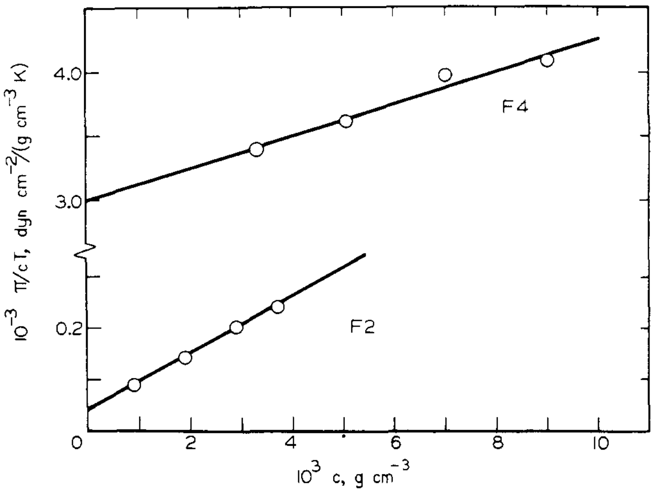


Figure 2. Osmotic pressure data for PDMSM fractions F2 and F4 in cyclohexane at 32.2°C.

The values of $[\eta]$, M, and A_2 thus obtained were 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.[21] The relationship employed for this purpose was the standard equation of Orofino and Flory[27]

$$\ln [1 + (\pi^{1/2}/2)(\alpha^2 - 1)] = (27\Phi/2^{5/2}\pi N)(A_2M/[\eta]) \qquad (4)$$

where Φ is a hydrodynamic constant equal to 2.1 × 10^{21} dl cm^{-3} mol^{-1} in thermodynamically good solvents,[21,28] N is Avogadro's number, and π here is the numerical constant 3.1416. These results are listed in column five of the table. Values of $\langle r^2\rangle_0$ were then calculated from[21]

$$[\eta] = \Phi[\langle r^2\rangle_0/M]^{3/2}M^{1/2}\alpha^3 \qquad (5)$$

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 $l = 1.90$ Å.[29] 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 ($M \simeq 7000$).[13] These results, shown in the following column, are independent of molecular weight as expected; if the small temperature dependence of $\langle r^2\rangle_0/nl^2$ is temporarily ignored, the average value of $\langle r^2\rangle_0/nl^2$ for the PDMSM chain is found to be 5.32 ± 0.01.

The Temperature Coefficient of $\langle r^2\rangle_0$. It is difficult to extract reliable values of d ln $\langle r^2\rangle_0/dT$ 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 $\langle r^2\rangle_0/dT = -0.1 \times 10^{-3}$ K^{-1} for F2, and 0.1×10^{-3} K^{-1} for F4, as shown in the last column of Table I. The average result $0.0 \pm 0.1 \times 10^{-3}$ K^{-1} thus obtained from these viscometry and osmometry results has at least the qualitative significance that d ln $\langle r^2\rangle_0/dT$ for the PDMSM chain is small and possibly 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. In the treatment of the stress–strain data obtained at the constant temperatures of 35, 45, and 70°C, the reduced force $[f^*]$ defined by

$$[f^*] = f/[A^*(\alpha - \alpha^{-2})] \tag{6}$$

was first plotted[12] against the reciprocal of $\alpha = L(T)/L_i(35°)$ in order to characterize the dependence of stress on strain for PDMSM networks. (The sample employed for this purpose had a cross-sectional area $A^* = 0.0406$ cm^2 in the undistorted state at 35°C.) Linear relationships were obtained;[12] their representation in terms of the Mooney–Rivlin equation[30]

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

directly yielded values of the important constant $2C_2$. These values are 0.0059, 0.0079, and 0.0057 N mm^{-2} at 35, 45, and 70°C, respectively. These values are significantly smaller than is generally observed for polymer networks in elongation;[31] the small values obtained for $2C_2$ indicate that PDMSM networks have stress–strain isotherms closely approaching the form predicted in the molecular theories of rubber-like elasticity.[31] Although these results are obviously 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 α = 1.2, 1.4, and 1.6 were obtained[12] from each of these three stress–strain isotherms by simple interpolation. The resulting data, although obtained indirectly, should be equivalent to thermoelastic data directly obtained at constant length. Their analysis proceeds through the use of the theoretical elastic equation of state for networks of Gaussian chains[32,33]

$$[f^*] = \nu kT[\langle r^2\rangle_i/\langle r^2\rangle_0] \tag{8}$$

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 $\langle r^2\rangle_0$ is the already defined unperturbed dimensions. On this basis[3,26,33,34]

$$\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = -[\partial \ln (f/T)/\partial T]_{p,L} - \beta/(\alpha^3 - 1) \tag{9}$$

The stress–strain isotherms, thus analyzed, yield d ln $\langle r^2\rangle_0/dT$ = 0.27, 0.52, and 0.51×10^{-3} K^{-1} for α = 1.2, 1.4, and 1.6, respectively. The resulting average value is d ln $\langle r^2\rangle_0/dT = 0.43 \pm 0.11 \times 10^{-3}$ K^{-1}.

Table II
Values of d ln $\langle r^2\rangle_0/dT$ from Direct Thermoelastic Measurements on a PDMSM Network over the Temperature Range 30–90° C

α[a]	$10^3[\partial \ln (f/T)/\partial T]_{p,L}$	$10^3\beta/(\alpha^3 - 1)$	10^3d ln $\langle r^2\rangle_0/dT$
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

[a] $\alpha = L(90°)/L_i(90°)$.

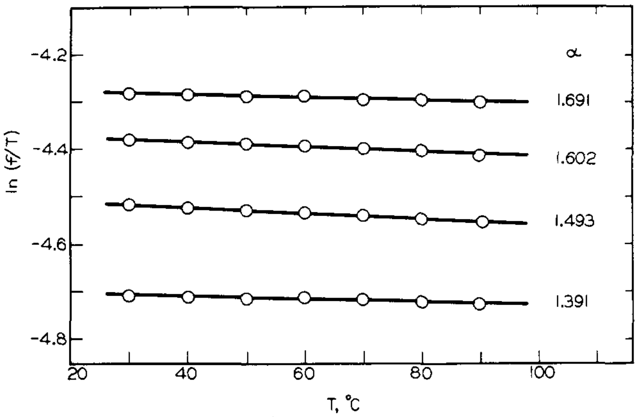


Figure 3. Thermoelastic results on a PDMSM network in elongation at constant length. The elongation α is expressed as $L(90°)/L_i(90°)$.

The most reliable values of d ln $\langle r^2\rangle_0/dT$, however, are obtained by *direct* measurements of the elastic force f as a function of temperature at constant length. Such measurements were carried out on a PDMSM network having a cross-sectional area A^* of 0.145 cm^2 at 25°C; measurements were made at 10° intervals over the range 30–90°C, with the elongation α varying from 1.391 to 1.691. The results are shown in Figure 3; pertinent quantities calculated therefrom are given in Table II. Careful evaluation of these results, along with the less reliable results cited above, suggests the value $0.20 \pm 0.20 \times 10^{-3}$ K^{-1} as the best value for d ln $\langle r^2\rangle_0/dT$ for the PDMSM chain.

The Mean-Square Dipole Moments $\langle\mu^2\rangle_0$ and Their Temperature Coefficient. The dielectric constant data on the four PDMSM fractions F1–F4 were interpreted by means of the equation of Guggenheim and Smith[35–37]

$$\langle\mu^2\rangle/nm^2 = \{27kT/[4\pi N\rho(\epsilon_1 + 2)^2]\} \times [\mathrm{d}\epsilon_{12}/\mathrm{d}w_2 - \mathrm{d}n_{12}^2/\mathrm{d}w_2][M_0/2m^2] \tag{10}$$

where ρ = the density of cyclohexane, ϵ_1 = the dielectric constant of cyclohexane, ϵ_{12} = the dielectric constant of the PDMSM solution, w_2 = the weight fraction of PDMSM in the solution, n_{12} = the refractive index of the PDMSM solution, and m = the effective dipole moment along Si–C and C–Si bonds in the PDMSM chain

The derivatives $\mathrm{d}\epsilon_{12}/\mathrm{d}w_2$ and $\mathrm{d}n_{12}^2/\mathrm{d}w_2$ required in this equation were obtained from plots of ϵ_{12} and n_{12}^2 against w_2; results for F4 are shown in Figure 4. Values of these two quantities for all four fractions are given in columns two and three of Table III. The effective bond moment $m = |\mathbf{m}|$ for Si–C and C–Si bonds was calculated from the dipole

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

			$\langle\mu^2\rangle_0/nm^2$		
Fraction	$d\epsilon_{12}/dw_2$	dn_{12}^2/dw_2	$\theta' = 70.5°$	$\theta' = 65°$	$\theta' = 60°$
F1	0.385	0.085	0.484	0.417	0.364
F2	0.389	0.097	0.472	0.407	0.355
F3	0.390	0.134	0.391	0.337	0.294
F4	0.370	0.082	0.465	0.401	0.349
			Av 0.453 ± 0.031	0.391 ± 0.027	0.341 ± 0.023

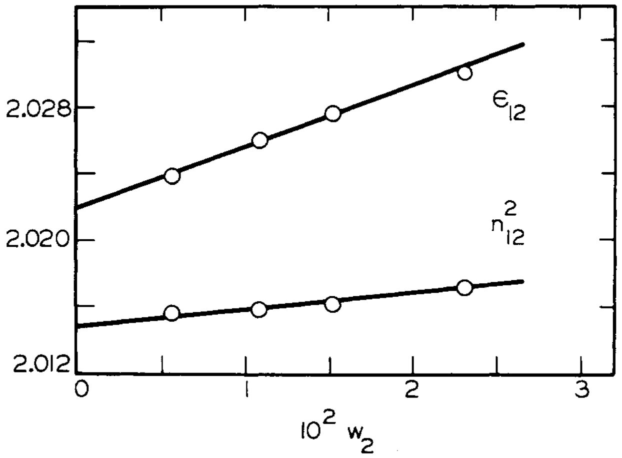


Figure 4. The concentration dependence of the dielectric constant ϵ_{12} and squared index of refraction n_{12}^2 for PDMSM fraction F4 in cyclohexane at 30°C.

moment 0.60 D of the dimer $Si(CH_3)_3$–CH_2–$Si(CH_3)_3$[38] using simple vector addition. As will be discussed in the following paper,[13] the most likely value for the Si–C–Si bond angle is 115°;[39,40] this corresponds to a value of 65° for the bond angle supplement[13] θ'. Use of this value in the interpretation of the dimer gives $m = 0.56$ D. The values of $\langle\mu^2\rangle/nm^2 = \langle\mu^2\rangle_0/nm^2$ (see below) which were calculated on this basis are given in the fifth column of the table. They yield the average result 0.391 ± 0.027. Revision of the Si–C–Si bond angle downward to 109.5° ($\theta' = 70.5°$) or upward to 120° ($\theta' = 60°$) would give $m = 0.52$ and 0.60 D, respectively, and average experimental values of $\langle\mu^2\rangle/nm^2$ of 0.453 ± 0.031 and 0.341 ± 0.023, respectively, as shown in columns four and six of the table.

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 $\langle\mu^2\rangle$ of a polymer chain having one or more of the following symmetry elements:[41,42] a plane of symmetry, an axis of twofold symmetry, or a center of symmetry, in its all-trans planar conformation. The PDMSM chain has such symmetry[13] and the observed mean-square dipole moment $\langle\mu^2\rangle$ must therefore always have the unperturbed value $\langle\mu^2\rangle_0$. Experimental results in any solvent are thus suitable for comparison with theoretical results.[13] The ratio $\langle\mu^2\rangle/nm^2$ will therefore henceforth be written $\langle\mu^2\rangle_0/nm^2$ 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, $\langle\mu^2\rangle_0/nm^2$ is independent of molecular weight as expected, with the most likely average value being 0.391 ± 0.027 at 30°C.

In the case of fraction F3, dielectric measurements were carried out at 10° intervals over the temperature 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 is zero.

Table IV
The Temperature Dependence of the Dipole Moment Ratio of PDMSM Fraction F3 in Cyclohexane

Temp, °C	$\langle\mu^2\rangle_0/nm^2$
20	0.337
30	0.336
40	0.337
50	0.337

Discussion

The most striking feature of the PDMSM chain uncovered in the present investigation is its unusually small characteristic ratio $\langle r^2\rangle_0/nl^2$. Its value, 5.3, is one of the smallest cited in an extensive review[1] of the statistical properties of chain molecules. Equally notable is the fact that $\langle r^2\rangle_0$ and $\langle\mu^2\rangle_0$ are found to be quite insensitive to temperature. For the interpretation of these experimental results we now explore, in the following paper,[13] the application of the rotational isomeric state theory[1] of chain configuration to the PDMSM chain.

Acknowledgment. It is a pleasure to acknowledge financial support of this work by the National Science Foundation. J. H. Ko also wishes to thank the Macromolecular Research Center of the University of Michigan for a predoctoral fellowship, and to acknowledge, with gratitude, some experimental assistance given by Drs. M. Kato and Y. Takahashi.

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Configuration-Dependent Properties of Poly(dimethylsilmethylene) Chains. II. Correlation of Theory and Experiment

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Received June 13, 1975

ABSTRACT: Rotational isomeric state theory was used to calculate values of the same configuration-dependent properties of poly(dimethylsilmethylene) (PDMSM) which were determined in the experimental study described in the preceding paper. The analysis of this chain molecule indicates that conformations bringing about pentane-type interferences between bulky $Si(CH_3)_2$ groups are completely suppressed. All other conformations are accessible and, within the approximation that methylene and methyl groups give rise to very similar intramolecular interactions, they are all of the same energy. This lack of any strong conformational preference is the origin of the relatively small value of the unperturbed dimensions of PDMSM, and the insensitivity of both its unperturbed dimensions and dipole moments to changes in temperature. This simplest model for the PDMSM chain gives fairly good quantitative agreement between theory and experiment. The agreement can be improved by taking into account more subtle features of the molecule, such as the fact that the skeletal methylene groups must have larger partial charges than the pendant methyl groups.

The experimental results obtained in the experimental study of poly(dimethylsilmethylene) (PDMSM) reported in the preceding paper[1] are summarized in the first column of Table I. Included for purposes of comparison in the other columns are the corresponding values of the same properties for the two structurally related polymers, poly(dimethylsiloxane) (PDMSO),[2-5] and polyisobutylene (PIB);[1] also included are results on polyethylene (PE),[1] since structurally it is the simplest polymer studied in any detail with regard to chain configuration. For convenience, the structural repeat unit of each of these polymers is given in the first row of the table. As already pointed out,[1] one of the most interesting aspects of the PDMSM chain is its relatively small characteristic ratio $\langle r^2\rangle_0/nl^2$. As shown in the table, it is 20–30% smaller than the values of the characteristic ratio reported for PDMSO, PIB, and PE. Equally notable[1] is the fact that both the mean-square unperturbed dimensions $\langle r^2\rangle_0$ and dipole moments $\langle\mu^2\rangle_0$ of PDMSM are essentially independent of temperature. In this regard, it is quite similar to PIB, which also has values of $\langle r^2\rangle_0$ almost insensitive to temperature.[2] In contrast, an increase in temperature has the effect of significantly increasing $\langle r^2\rangle_0$ and $\langle\mu^2\rangle_0$ in the case of PDMSO[2-5] and significantly decreasing $\langle r^2\rangle_0$ in the case of PE.[2]

The purpose of the present study is to use rotational isomeric state theory to interpret the properties of the PDMSM chain cited above, in an attempt to elucidate the marked differences in the configurational characteristics of PDMSM, PDMSO, PIB, and PE. Such analysis and comparisons should shed considerable light on the effect of structure on the configurations of chain molecules in general.

Rotational Isomeric State Theory

General Aspects. In the rotational isomeric state approximation, each rotatable skeletal bond in the chain molecule is assigned to one of a small number of discrete rotational states, generally chosen to occur at the minima in the torsional potential or conformational energy for the particular bonds.[2] These minima are, in most cases, situated at rotational angles ϕ of 0, 120, and $-120°$; such states are designated as trans (t), gauche$^+$ (g$^+$), and gauche$^-$ (g$^-$), respectively. The relative probability or statistical weight of each rotational state is generally represented by a simple 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 bond $i - 1$ in state ζ