

On the Critical Molecular Chain Length of Polydimethylsiloxane

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SYNOPSIS

Because a study of the results reported for the chain dimensions of polydimethylsiloxane (PDMS), critical for the onset of this polymer's non-Newtonian flow behavior, obtained from the viscosity–molecular weight relationships available from the literature, clearly revealed that considerable differences exist between the reported data, a detailed analysis of these data was performed together with an additional examination of 10 new PDMS samples that were selected so as to have molecular weights that would fill the gaps observed in the polymer viscosity–chain length relationship constructed from the accepted literature data. The results obtained were analyzed by using several different procedures integrated into a recently described comparative method that could allow for determination of what is called the most realistic critical value, Z_{wc} . The latter was determined as 930 PDMS main-chain atoms, which corresponds to this polymer's degree of polymerization of 464.5 and the weight-average molecular weight of 34,500. It is not only shown that after elimination of some clearly erroneous data points from the previously reported relationships the obtained critical chain-length values could very well fit the earlier relationships, but also that appropriate “master” relationships were constructed including 48 pairs of the old and 10 pairs of the new data points. It is suggested that this relationship be accepted as the best-fit viscosity–polymer chain-length dependence for PDMS, and it is pointed out that the obtained PDMS critical chain-length value ranks this polymer's macromolecules as the most flexible of the corresponding long-chain molecules presently known. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

One of the most important fundamental properties of all members of the polysiloxane family is the highly pronounced inherent conformational flexibility of their completely inorganic main-chain backbones, $—[Si—O]_n—$, which enables unusually high mobility of their segments and entire molecules, not common to any other class of presently known polymers.^{1,2} Together with the very weak *inter-* and *intramolecular* interactions between neighboring segments and molecules, which result in relatively large free volumes, also typical for most members of this polymer group, this property is held

mainly responsible for some unique and very useful combinations of macroscopic properties of polysiloxanes, including (1) exceptionally pronounced elasticity, particularly at unusually low temperatures; (2) very low glass transition temperatures, which are among the lowest presently known; (3) relative ease to undergo viscous flow at rather low shear stresses, with almost Newtonian character of that flow; (4) high solubilities in nonpolar solvents; (5) high gas permeability; and (6) relatively high rates of crystallization on stretching, which is particularly pronounced for the symmetrically substituted members of the family.^{1,2}

Because such combinations of properties make polysiloxanes quite exceptional among other polymers, and since their backbone chains of alternating silicon and oxygen atoms are often considered as the most flexible long chains of atoms presently

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known, it is not surprising that many different theoretical and experimental methods have been used to study their molecular flexibility and that among these rheological studies have played an important role. These resulted in many reports on rheological properties of various polysiloxanes, including a considerable body of data on the polydimethylsiloxane (PDMS), which can be considered as the parent polymer of the entire polysiloxane family. Of the reported investigations on PDMS, several studies were devoted to determining the relationship between this polymer's viscosity and molecular weight,³⁻¹² which can further enable evaluation of an important molecular parameter, the so-called critical polymer chain length that can be defined as the chain length above which a polymer exposed to a steady-state shear stress changes its flow behavior from almost regular Newtonian to what is known as the non-Newtonian-type flow.

This critical polymer chain length can further be associated with the onset of what is often called entanglement formation,^{13,14} and since it is believed that the ability of long-chain polymers to entangle is related to the inherent flexibility of their main-chain backbones, it can be accepted that more flexible macromolecules should entangle at progressively longer chain lengths, so that the value of the critical chain-length parameter can be taken as a measure of polymer's inherent chain flexibility.

Therefore, if this view should hold, it would follow that if the polysiloxane $-\text{[Si-O]}_n-$ chains were indeed as exceptionally flexible as is presently believed, their critical chain lengths at the onset of the non-Newtonian flow behavior should be among the longest of the polymers known, with the values for different members of the polysiloxane family being, of course, dependent on the intensity of interactions that are established between the particular side groups. Concretely, from the available literature data for various polymers examined, which range from the critical chain-length values of only 20-30 main-chain atoms for very rigid polymers, such as various cellulose derivatives or poly(*p*-benzamide),^{13,14} to as high as 400-600 atoms for very flexible polymers, such as various polybutadienes or polyisoprenes,^{13,14} PDMS would be expected to attain its critical chain length at the values that are at least close to, or perhaps higher than, those found for the latter group.

Indeed, even a superficial overview of the data obtained from previous investigations³⁻¹² clearly confirms this expectation, but, surprisingly, it also reveals that rather significant differences exist between the different reports, so that they spread over

an unusually large range of values from about 660 (Ref. 9) to almost 1400 (Ref. 10) main-chain atoms. Puzzled by these large differences between the reported critical chain-length values for PDMS, which are not common to most other polymers examined, it was decided to reexamine the rheological behavior of this polymer in order to clarify the reasons for the observed differences and to determine the most probable value of the critical chain length of PDMS, because this important molecular parameter may help shed some more light on the real extent of inherent flexibility of the polysiloxane main-chain backbones and perhaps verify if, indeed, this structure represents the most flexible long chain of atoms presently known.

EXPERIMENTAL

Polymer Samples

PDMS samples used in this work were linear, completely soluble, trimethylsilyl-terminated polydimethylsiloxanes, which can be classified into two different groups.

The first of these groups included four commercially available viscosity standards that were purchased from Brookfield Engineering Laboratories, Inc., Prva Iskra Chemical Works, and Petrarch Systems Silanes and Silicones. Their declared viscosities ranged from 50 to over 2000 P and our own measurements confirmed a rather good agreement between declared and experimentally verified values.

The second group of samples was prepared in our laboratories using the so-called siloxane equilibration reactions that involved octamethylcyclotetrasiloxane, or dimethyldichlorosilane hydrolizate (Dow Corning Fluid 2.0176), and hexamethyldisiloxane, purchased from Petrarch. A sulfonated polystyrene cation-exchange resin, Duolite C 26, was used as the catalyst and synthetic procedures were performed according to a recently described method.¹⁵ Using the relationship that was earlier established between the composition of such equilibration reaction mixtures and the viscosity of the resulting polymer products,¹⁵ experimental conditions for the preparations performed in this work were selected so as to obtain linear PDMS products with predetermined viscosity values, which, together with the selected commercial samples of the first group, filled the gaps that were observed in the PDMS viscosity-molecular chain length relationship based on the data reported by the previous workers.³⁻¹²

Table I Rheological Properties and Average Chain Dimension of PDMS

| Sample | \bar{M}_v^a | \bar{M}_w^b | $[\eta]^c$ (dL/g) | $(\langle s^2 \rangle_0 / \bar{M}_w) \cdot 10^{17d}$ | Z_w^e | ν_2^f (cm ³ /g) | $\chi_w \cdot 10^{17g}$ | η_0^h (P) | Ref. |
|--------|---------------|---------------|----------------------|--|----------|-----------------------------------|-------------------------|-----------------|-------|
| 1 | 162 | 162 | | | 3.0 | 1.314 | | 0.0055 | 8, 9 |
| 2 | 236 | 236 | | | 5.0 | 1.222 | | 0.0085 | 8, 9 |
| 3 | 310 | 310 | | | 7.0 | 1.179 | | 0.0130 | 8, 9 |
| 4 | 384 | 384 | | | 9.0 | 1.160 | | 0.0180 | 5, 11 |
| 5 | 458 | 458 | | | 11.0 | 1.135 | | 0.0230 | 11 |
| 7 | 532 | 532 | | | 13.0 | 1.116 | | 0.0290 | 11 |
| 9 | 606 | 606 | | | 15.0 | 1.109 | | 0.0350 | 11 |
| 10 | 680 | 680 | | | 17.0 | 1.099 | | 0.0410 | 11 |
| 12 | 837 | 837 | | | 21.2 | 1.086 | | 0.0580 | 11 |
| 15 | 1,005 | 1,093 | | | 28.2 | 1.074 | | 0.0720 | 11 |
| 18 | 1,180 | 1,284 | | | 33.3 | 1.070 | | 0.0935 | 11 |
| 22 | 1,470 | 1,599 | | | 41.8 | 1.062 | | 0.1270 | 11 |
| 24 | 2,170 | 2,361 | 0.0317 | 0.965 | 62.4 | 1.053 | 57.2 | 0.2060 | 11 |
| 26 | 2,535 | 2,758 | 0.0351 | 0.981 | 73.2 | 1.049 | 68.4 | 0.2300 | 11 |
| 28 | 2,700 | 2,938 | 0.0365 | 0.986 | 78.0 | 1.047 | 73.4 | 0.2700 | 8, 9 |
| 29 | 2,840 | 3,090 | 0.0378 | 0.992 | 82.1 | 1.047 | 77.8 | 0.3580 | 11 |
| 32 | 3,700 | 4,026 | 0.0449 | 1.018 | 107.4 | 1.042 | 105.0 | 0.4760 | 4 |
| 35 | 3,900 | 4,243 | 0.0464 | 1.023 | 113.3 | 1.042 | 111.0 | 0.4800 | 3 |
| 38 | 5,170 | 5,625 | 0.0577 | 1.051 | 150.7 | 1.038 | 153.0 | 0.7410 | 11 |
| 39 | 5,700 | 6,202 | 0.0594 | 1.062 | 166.2 | 1.036 | 170.0 | 0.7910 | 11 |
| 40 | 6,700 | 7,290 | 0.0660 | 1.080 | 195.6 | 1.035 | 204.0 | 0.9650 | 4 |
| 41 | 7,140 | 7,768 | 0.0688 | 1.087 | 208.6 | 1.034 | 219.0 | 0.9860 | 11 |
| 43 | 8,250 | 8,976 | 0.0756 | 1.102 | 241.2 | 1.034 | 257.0 | 1.5100 | 11 |
| 47 | 11,300 | 12,294 | 0.0927 | 1.137 | 330.9 | 1.032 | 365.0 | 1.9400 | 4 |
| 49 | 14,100 | 15,341 | 0.1070 | 1.162 | 413.2 | 1.031 | 466.0 | 2.8250 | 11 |
| 50 | 15,800 | 17,190 | 0.1150 | 1.175 | 463.2 | 1.031 | 528.0 | 3.3900 | 4 |
| 51 | 19,000 | 20,672 | 0.1300 | 1.197 | 557.3 | 1.030 | 648.0 | 4.8500 | 4 |
| 52 | 22,000 | 23,936 | 0.1430 | 1.214 | 645.5 | 1.030 | 761.0 | 8.3000 | 8, 9 |
| 53 | 25,300 | 27,526 | 0.1570 | 1.231 | 742.6 | 1.030 | 888.0 | 9.0300 | 11 |
| 55 | 26,400 | 28,723 | 0.1610 | 1.236 | 775.0 | 1.030 | 930.0 | 9.7000 | 3, 4 |
| 57 | 36,800 | 40,038 | 0.2000 | 1.277 | 1,081.0 | 1.029 | 1,342.0 | 16.5200 | 11 |
| 61 | 50,800 | 55,270 | 0.2460 | 1.319 | 1,492.0 | 1.028 | 1,916.0 | 29.8000 | 11 |
| 62 | 57,000 | 62,016 | 0.2650 | 1.334 | 1,675.0 | 1.028 | 2,174.0 | 90.0000 | 8, 9 |
| 63 | 62,000 | 67,456 | 0.2800 | 1.345 | 1,822.0 | 1.027 | 2,387.0 | 121.7500 | 3 |
| 66 | 69,900 | 76,051 | 0.3030 | 1.361 | 2,054.0 | 1.027 | 2,723.0 | 227.5000 | 11 |
| 68 | 80,000 | 87,040 | 0.3310 | 1.380 | 2,351.0 | 1.026 | 3,163.0 | 292.5000 | 3 |
| 71 | 85,400 | 92,915 | 0.3450 | 1.389 | 2,509.0 | 1.026 | 3,398.0 | 390.0000 | 11 |
| 72 | 105,000 | 114,240 | 0.3950 | 1.417 | 3,086.0 | 1.025 | 4,270.0 | 770.0000 | 8, 9 |
| 73 | 140,000 | 152,320 | 0.4760 | 1.458 | 4,115.0 | 1.024 | 5,863.0 | 2,400.0000 | 8, 9 |
| 76 | 179,000 | 194,752 | 0.5580 | 1.494 | 5,262.0 | 1.024 | 7,682.0 | 4,600.0000 | 8, 9 |
| 77 | 205,000 | 223,000 | 0.6100 | 1.514 | 6,027.0 | 1.024 | 8,917.0 | 6,000.0000 | 3 |
| 80 | 214,000 | 232,832 | 0.6270 | 1.521 | 6,291.0 | 1.024 | 9,348.0 | 6,450.0000 | 8, 9 |
| 81 | 220,000 | 239,360 | 0.6340 | 1.525 | 6,468.0 | 1.024 | 9,637.0 | 8,000.0000 | 3 |
| 83 | 410,000 | 446,080 | 0.9570 | 1.622 | 12,055.0 | 1.023 | 19,122.0 | 110,000.0000 | 8, 9 |
| 84 | 450,000 | 489,600 | 1.0160 | 1.637 | 13,231.0 | 1.023 | 21,182.0 | 140,000.0000 | 8, 9 |
| 87 | 482,000 | 524,416 | 1.0630 | 1.648 | 14,172.0 | 1.023 | 22,843.0 | 190,000.0000 | 8, 9 |
| 89 | 851,000 | 925,888 | 1.5380 | 1.744 | 25,023.0 | 1.022 | 42,712.0 | 2,230,000.0000 | 7 |
| 91 | 1,260,000 | 1,370,880 | 1.9850 | 1.813 | 37,049.0 | 1.019 | 65,880.0 | 16,100,000.0000 | 7 |

^a Viscosity-average molecular weights calculated from intrinsic viscosities determined in toluene at 25 or 30°C. Mark-Houwink constants used: $K = 2.15 \cdot 10^{-4}$ and $\alpha = 0.65$.

^b Weight-average molecular weights calculated from $\bar{M}_w/\bar{M}_n = 1.088$ for PDMS of most probable molecular weight distribution. \bar{M}_w values for samples 1–10 are assumed to be equal to \bar{M}_v .

^c Calculated from reported \bar{M}_v values using $[\eta] = K \cdot \bar{M}_v^\alpha$, where $K = 2.5 \cdot 10^{-4}$ and $\alpha = 0.65$. This equation is valid for \bar{M}_v values above 2000.

^d Calculated from eq. (7).

^e Weight-average number of main-chain atoms calculated from $Z_w = 1 + 2(\bar{M}_w - 88)/74$ [see eq. (8)].

^f Determined from calibration curve based on data from Ref. 6.

^g Calculated from eq. (3).

^h Zero-shear viscosities of bulk PDMS at 25°C.

Polymer Molecular Weights

Molecular weights, \bar{M}_v , of all synthesized PDMS samples were calculated from the intrinsic viscosity values that were determined from polymer solutions in toluene at 30°C. Mark-Houwink-type constants used for these calculations were $K = 2.15 \cdot 10^{-4}$ and $a = 0.65$.¹⁶ From the obtained \bar{M}_v values, weight-average molecular weights, \bar{M}_w , were calculated by multiplying the former by 1.088, because it was verified by HPLC that, as expected, all samples had the most probable molecular weight distribution.¹⁷

Rheological Measurements

Steady-state shear viscosities were determined as a function of shear rate for bulk PDMS samples at 25°C. A Ferranti-Shirley cone-and-plate viscometer that had a plate diameter of 8.3 cm, a cone diameter of 3.5 cm, and a cone angle of 0.0057 Rad was used. The shear rates applied were from 1.84 to $1.84 \cdot 10^3$ s⁻¹. Zero-shear viscosities, η_0 , were determined by a standard extrapolation procedure of the linear low-shear parts of the obtained viscosity vs. shear rate double logarithmic plots.

RESULTS AND DISCUSSION

Preliminary Analysis of Available Literature Data

Literature data on PDMS bulk viscosity-molecular weight relationships were available from 10 different reference sources.³⁻¹² These references offered 119 pairs of η_0 and \bar{M}_w values for different members of the PDMS family. Of these, 72 pairs were original experimentally obtained results,^{3-8,11,12} whereas the remaining 47 pairs were repeated values of the former groups reused by other authors.^{9,10} The 72 pairs of the original values spanned the molecular weight range from 162 (degree of polymerization: $n = 1$) to \bar{M}_w over 1,370,000 ($n > 18,500$), with the corresponding viscosities ranging from 0.5 cP to over 16,000,000 P.

An interesting set of values, consisting of 25 pairs that covered the molecular weight range from 162 to 423,000 ($n > 5700$), was found in the Petrarch Systems commercial catalog.⁶ However, for seven of 10 polymers with molecular weights above about 30,000 reported therein, the viscosity values were considerably lower than those reported for very similar molecular weights by other sources. Therefore, having no way to further verify these data, these seven pairs of values were regrettably neglected from consideration.

The Contact Parameter Analysis

The 65 pairs of viscosity-molecular weight values selected by the preliminary analysis of available literature data, as described in the previous section, were used for the evaluation of the PDMS critical chain length by a method that was previously described by one of us.¹⁸ In its essence, this method consisted of a combination of procedures developed earlier by other workers (Bueche,^{19,20} Ferry and co-workers,²¹⁻²³ Fox and co-workers^{9,10}), which results in a comparison of the results obtained by these

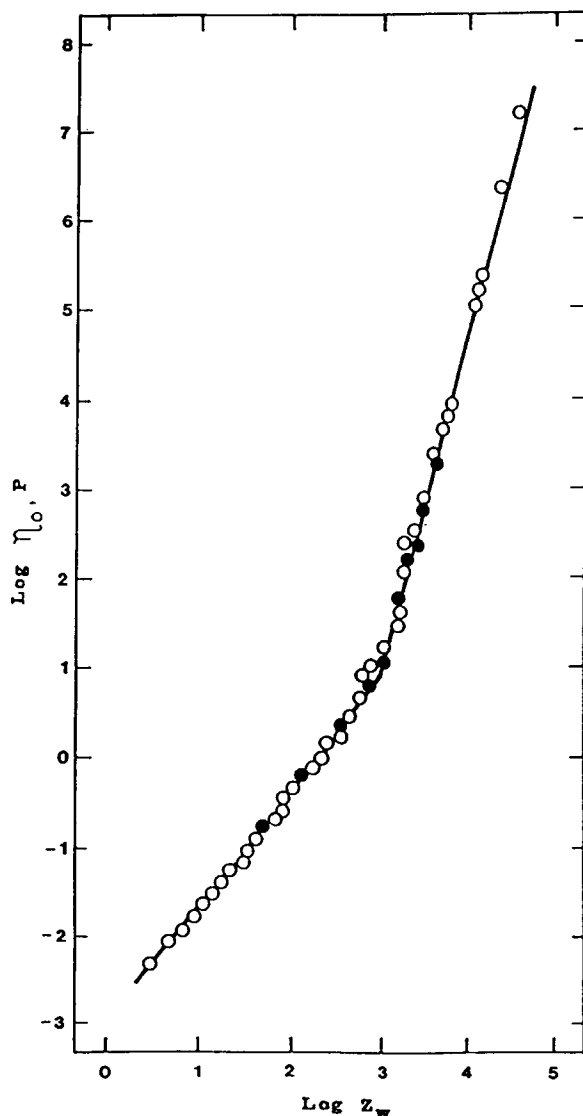


Figure 1 Zero-shear viscosity η_0 vs. weight-average number of chain atoms, Z_w , for bulk PDMS at 25°C. Note that for this case the Z_w is equal to the segment contact parameter cZ_w : (O) from the analysis of literature values; (●) experimental data.

procedures and allows determination of the most realistic average of the obtained values.¹⁸

Thus, available literature data were first treated according to Ferry's reduction procedure,²¹⁻²³ which allows determination of the critical polymer chain dimensions using the so-called Bueche contact parameter, $c\bar{M}_w$, or cZ_w , which represents a measure of the intensity of polymer *inter-* and *intramolecular* contacts, where Z_w is the weight-average number of main-chain atoms while c is concentration, which is, of course, equal to unity for bulk polymer samples.

However, when calculations required by this procedure were performed, and when the results obtained were plotted as $\log \eta_0$ vs. $\log Z_w$, it was found that the desired value for the critical PDMS chain length could not be determined with a satisfactory degree of certainty, because 17 of 65 points involved deviated from the most probable trend of the relationship by more than the standard deviation allowed (6% of the respective logarithmic values). Because of this, these 17 points were also eliminated from further analysis, and further considerations were restricted to the remaining 48 pairs of the literature η_0 and \bar{M}_w values listed in Table I.

However, when the $\log \eta_0$ vs. $\log Z_w$ plot, shown in Figure 1, was constructed only with the values of Table I, it could be seen that several relatively large regions of the relationship were left uncomfortably empty of points, so that, in order to compensate for this, it was decided to fill these regions by producing our own experimental data for new PDMS samples of appropriate molecular weights. As described in the Experimental section, these samples, a total of 10 of them, were either purchased or prepared in our laboratories, and their molecular weights were determined and rheological behavior examined. The results obtained are listed in Table II and plotted

together with the 48 pairs of values from Table I in Figure 1.

It can be seen from this figure that our experimental points fitted very well with the main trend established by the previously reported literature data and that the resulting $\log \eta_0$ vs. $\log Z_w$ plot allowed for a rather straightforward determination of the intersection between the two differently sloped regions of this relationship ($s_{LMW} = 1.347$ and $s_{HMW} = 3.618$, respectively). Since that point of intersection represents the onset of non-Newtonian flow behavior with respect to the polymer's molecular chain length, its coordinates give critical PDMS values, which, from Figure 1, equaled $Z_{wc} = 925$ and $\eta_{0c} = 8.57$ P, respectively.

The Onset of Entangled Behavior Analysis

Implicit to Bueche's contact parameter used in the preceding analysis is the neglect of the real nature of interactions that establish between the neighboring polymer segments at the onset of non-Newtonian flow. Instead, disregarding their type and nature, this treatment restricts itself only to consideration of the intensity of these interactions, or contacts, resulting in the observed change in flow behavior.

Another approach to the same problem is the so-called entanglement view. According to this view, because of the inherent molecular chain flexibility, polymer chains can coil in the available space surrounding them, and in doing so, their segments can interpenetrate and "entangle" with each other, creating a situation in which resulting entanglements exert resistance to an unrestricted flow of polymer chain segments relative to each other. Although to this day the physical meaning of "entanglements"

Table II Rheological Properties and Average Chain Dimensions of Examined PDMS^a

| Sample | $[\eta]$ (dL/g) | \bar{M}_v | \bar{M}_w | $(\langle s^2 \rangle_0 / \bar{M}_w) \cdot 10^{17}$ | Z_w | ν_2 (cm ³ /g) | $\chi_w \cdot 10^{17}$ | η_0 (P) |
|--------|-----------------|-------------|-------------|---|--------|------------------------------|------------------------|--------------|
| PS 1 | | 1,790 | 1,948 | | 51.3 | 1.055 | | 0.178 |
| PS 2 | 0.0502 | 4,400 | 4,787 | 1.035 | 128.0 | 1.039 | 128 | 0.638 |
| PS 3 | 0.0921 | 11,200 | 12,186 | 1.135 | 328.0 | 1.032 | 361 | 2.290 |
| PS 4 | 0.1530 | 24,400 | 26,547 | 1.226 | 716.1 | 1.030 | 853 | 6.240 |
| PS 5 | 0.1940 | 35,200 | 38,298 | 1.272 | 1033.7 | 1.029 | 1278 | 11.750 |
| B 4 | 0.2510 | 52,300 | 56,902 | 1.323 | 1536.5 | 1.028 | 1978 | 53.200 |
| B 5 | 0.2920 | 65,900 | 71,699 | 1.354 | 1936.4 | 1.027 | 2553 | 141.800 |
| PS 101 | 0.3240 | 77,400 | 84,211 | 1.375 | 2274.6 | 1.026 | 3050 | 208.000 |
| PS 6 | 0.3820 | 99,000 | 108,691 | 1.410 | 2936.2 | 1.025 | 4042 | 602.000 |
| B 6 | 0.4850 | 144,000 | 156,672 | 1.462 | 4233.0 | 1.024 | 6048 | 2154.000 |

^a See footnotes to Table I.

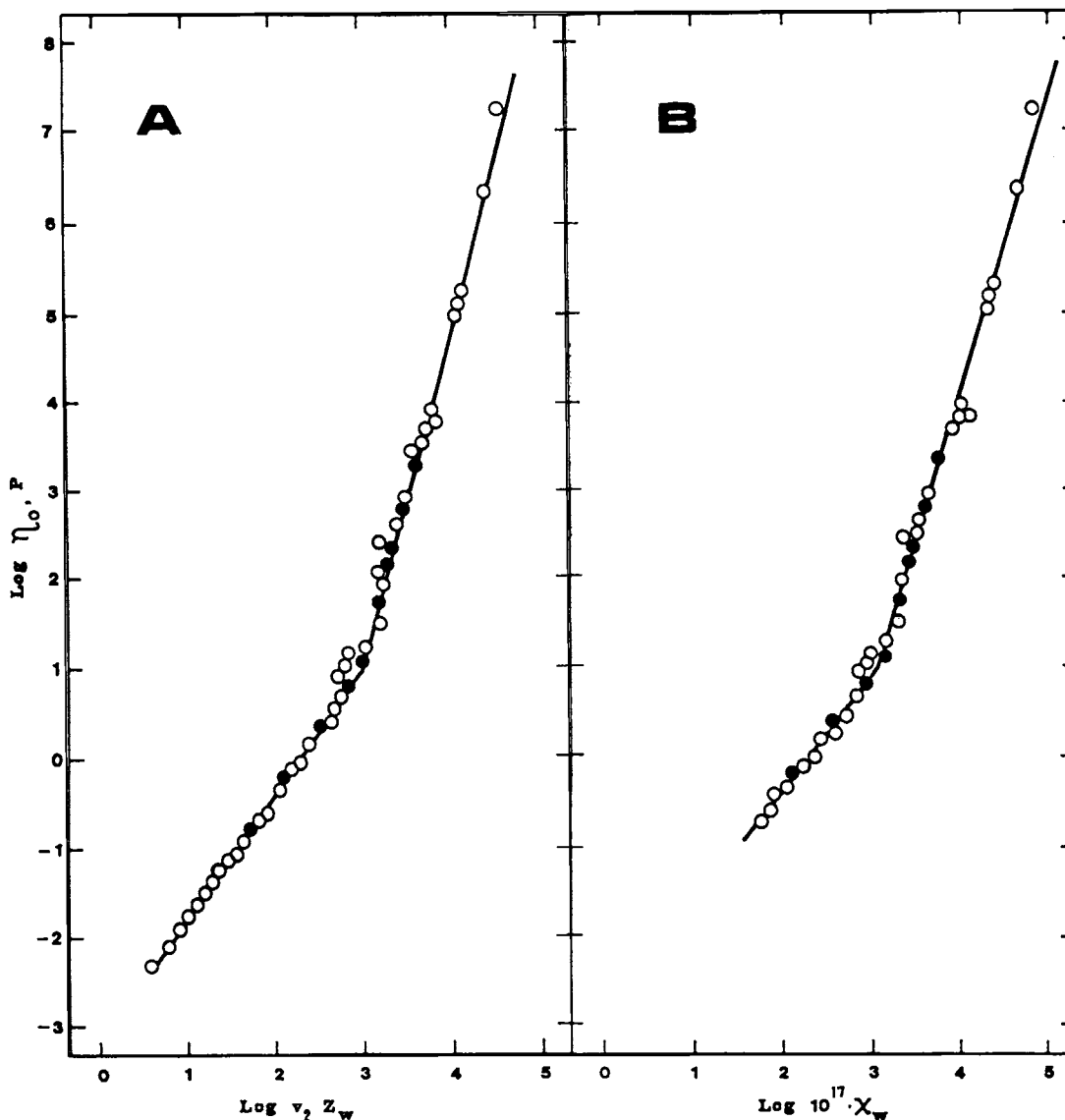


Figure 2 (A) $\text{Log } \eta_0$ vs. $\text{log } v_2 Z_w$ and (B) $\text{log } \eta_0$ vs. $\text{log } 10^{17} \chi_w$ plots for PDMS at 25°C: (○) calculated from the literature values; (●) calculated from the experimental data.

remains obscure, it is believed, according to this view, that a polymer segment must attain a certain minimum length before it can coil into entangled interaction with its neighbor, or with itself, and that it is this minimum chain length that represents a critical limit above which the polymer starts to show typical polymeric properties, one of which is the non-Newtonian flow behavior.

According to Fox and co-workers,^{9,10} a polymer chain length critical for the onset of entangled behavior can be evaluated from the viscosity-molecular weight data by taking into account that polymer viscosity can be considered as a product of two fac-

tors: (1) a structure-sensitive factor $F(\chi)$, dependent primarily on the number of atoms or atomic groups present in the polymer chain backbone, Z , and (2) a temperature-, or density-, dependent friction factor per polymer chain atom, $\zeta(\rho)$, as follows:

$$\eta = F(\chi) \cdot \zeta(\rho) \quad (1)$$

Of these, the structural factor $F(\chi)$ can be defined as

$$F(\chi) = (N_0/6) \cdot \chi_c (\chi/\chi_c)^\alpha \quad (2)$$

where, N_0 is Avogadro's number; and if appropriate weight averages are used, the chain length parameter, χ_w , can be defined, for undiluted, bulk polymer melt as follows:

$$\chi_w = Z_w (\langle s^2 \rangle_0 / \bar{M}_w) / \nu_2 \quad (3)$$

In this equation, Z_w is the weight-average number of polymer chain atoms; ν_2 , the polymer specific volume; $\langle s^2 \rangle_0$, the square of the unperturbed radius of gyration; and \bar{M}_w , the polymer weight-average molecular weight.

Based on numerous experimental evidence, exponent α in eq. (2) could be defined as follows:

$$\alpha = 3.4 \quad \text{for } \chi > \chi_c \quad (4)$$

$$\alpha = 1.0 \quad \text{for } \chi \leq \chi_c \quad (5)$$

so that the critical value of the chain dimension pa-

rameter, above which non-Newtonian behavior is observed, χ_{wc} , can be obtained as

$$\chi_{wc} = Z_{wc} (\langle s^2 \rangle_0 / \bar{M}_w) / \nu_2 \quad (6)$$

where $\langle s^2 \rangle_0 / \bar{M}_w$, which represents a measure of polymer chain expansion, or rigidity per unit molecular weight, can be calculated from the intrinsic viscosity using the following equation:

$$[\langle s^2 \rangle_0 / \bar{M}_w]^{3/2} = [\eta] / \bar{M}_w^{1/2} \Phi \quad (7)$$

in which Φ is a constant equal to $39.4 \cdot 10^{21}$ (Refs. 24 and 25) and $[\eta]$ is in dL/g.

Using this approach, Z_w values for PDMS samples examined in this work were calculated from the following equation:

$$Z_w = 1 + Z_0 (\bar{M}_w / M_0) \quad (8)$$

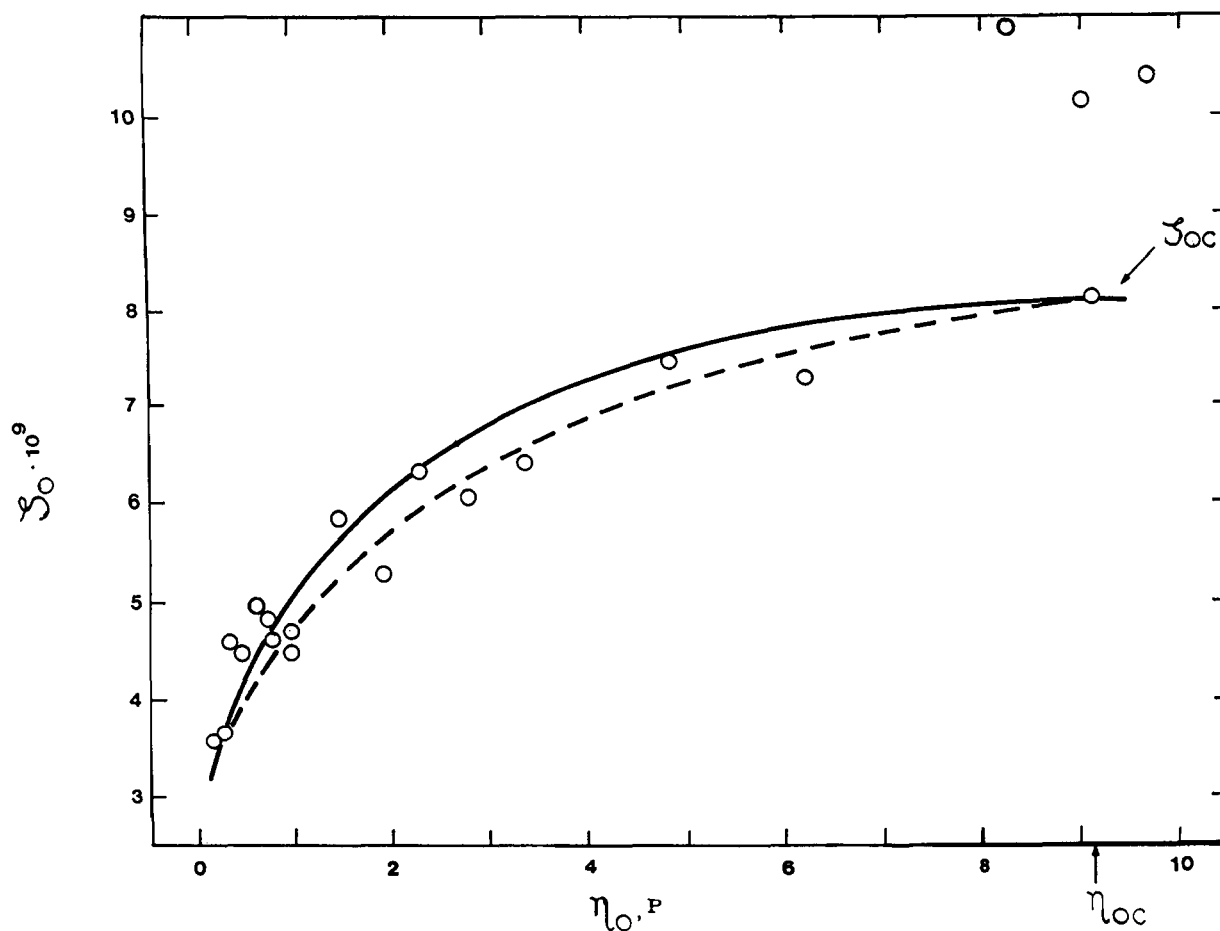
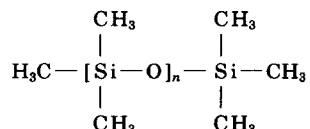


Figure 3 Dependence of the PDMS molecular friction coefficient, ζ_0 , on the polymer's zero-shear viscosity, η_0 at 25°C.

which yielded:

$$Z_w = 1 + 2(\bar{M}_w - 88)/74$$

where 74 is molecular weight of the PDMS repeating unit; 2, the number of main-chain atoms per repeating unit; 88, the sum of atomic weights of the $\text{Si}(\text{CH}_3)_3$ and CH_3 PDMS end groups; and digit 1, the main-chain Si atom that belongs to the $\text{Si}(\text{CH}_3)_3$ end group as required by the PDMS structural formula:



The results obtained by this calculation for PDMS samples of Tables I and II are plotted as $\log \eta_0$ vs. $\log \nu_2 Z_w$ and $\log \eta_0$ vs. $\log 10^{17} \chi_w$ in Figure 2 (A) and (B), respectively.

It can be seen from these figures that the inter-sects of the two differently sloped regions of these relationships had the following coordinates: $Z_{wc} = 931.5$ and $\eta_{0c} = 8.71$ P in Figure 2 (A) and $10^{17} \chi_{wc} = 1.122$ and $\eta_{0c} = 9.12$ P in Figure 2 (B). In addition, the slopes of the low and high molecular weight regions were $s_{LMW} = 1.368$ and $s_{HMW} = 3.68$ in Figure 2 (A) and $s_{LMW} = 1.267$ and $s_{HMW} = 3.342$ in Figure 2 (B), respectively.

The Friction Factor Analysis

Deviations of the slopes of the low molecular weight regions of the viscosity-polymer chain dimensions relationships from unity (which is the value predicted by the Rouse theory), as observed in Figures 1 and 2, are quite common^{9,18} for many different polymers, and they usually indicate that the polymer chain length exerts influence on the value of the inherent friction factor $\zeta(\rho)$, which, in turn, reflects the resistance of the polymer chain segments to flow through environment of other surrounding segments by some mechanism of coordinated segmental motions. Since this resistance depends on the magnitude of local *intersegmental* forces, the value of $\zeta(\rho)$ depends on the length of mobile segments so that it increases with this length, reaching some constant asymptotic value for the length of the longest mobile segment. To illustrate this point, dependence of the inherent friction factor, calculated from eq. (9), on the polydimethylsiloxane chain length in the low

molecular weight region, where polymer flow is Newtonian in character, is shown in Figure 3.

As a consequence, since under normal conditions the longest mobile segments are the segments that spread between two neighboring entanglement points (through which segmental mobility is either prevented or at least greatly restricted), this view implies that the analyses of viscosity data as a function of polymer chain length should be performed at constant $\zeta(\rho)$ rather than at constant temperature. This, in turn, requires determination of the segmental length at which $\zeta(\rho)$ becomes constant before that value can be used to correct the experimentally obtained viscosity data for shorter chain lengths at constant temperature to the respective viscosities at constant $\zeta(\rho)$.

Following this approach, the Z_{wc} values corrected for the constant friction factor could be determined from eq. (6) by using $10^{17} \chi_{wc} = 1.122$ from Figure 2 (B) and $\langle s^2 \rangle_0 / \bar{M}_w = 1.236$ and $\nu_2 = 1.03$ from Table I for sample 55 to obtain $Z_{wc} = 935$.

Critical PDMS chain parameters were also calculated from the general viscosity relationship originally proposed by Bueche.²⁰ Substitution of the χ_{wc} value obtained from Figure 2 (B) into eqs. (1) and (2) yielded the following relationship:

Table III Calculation of Viscosity Data Corrected to Constant Internal Friction Factor

| Sample | $\chi_w \cdot 10^{17}$ | η_0 (P) | Log η_0 |
|--------|------------------------|--------------|--------------|
| 24 | 57.2 | 0.466 | -0.332 |
| 26 | 68.4 | 0.557 | -0.254 |
| 28 | 73.4 | 0.597 | -0.224 |
| 29 | 77.8 | 0.633 | -0.198 |
| 32 | 105.0 | 0.855 | -0.068 |
| 35 | 111.0 | 0.904 | -0.044 |
| PS 2 | 128.0 | 1.042 | 0.018 |
| 38 | 153.0 | 1.245 | 0.095 |
| 39 | 170.0 | 1.384 | 0.141 |
| 40 | 204.0 | 1.661 | 0.220 |
| 41 | 219.0 | 1.783 | 0.251 |
| 43 | 257.0 | 2.092 | 0.321 |
| PS 3 | 361.0 | 2.939 | 0.468 |
| 47 | 365.0 | 2.971 | 0.473 |
| 49 | 466.0 | 3.793 | 0.579 |
| 50 | 528.0 | 4.298 | 0.633 |
| 51 | 648.0 | 5.275 | 0.722 |
| 52 | 761.0 | 6.195 | 0.792 |
| PS 4 | 853.0 | 6.943 | 0.842 |
| 53 | 888.0 | 7.228 | 0.859 |
| 55 | 930.0 | 7.570 | 0.879 |

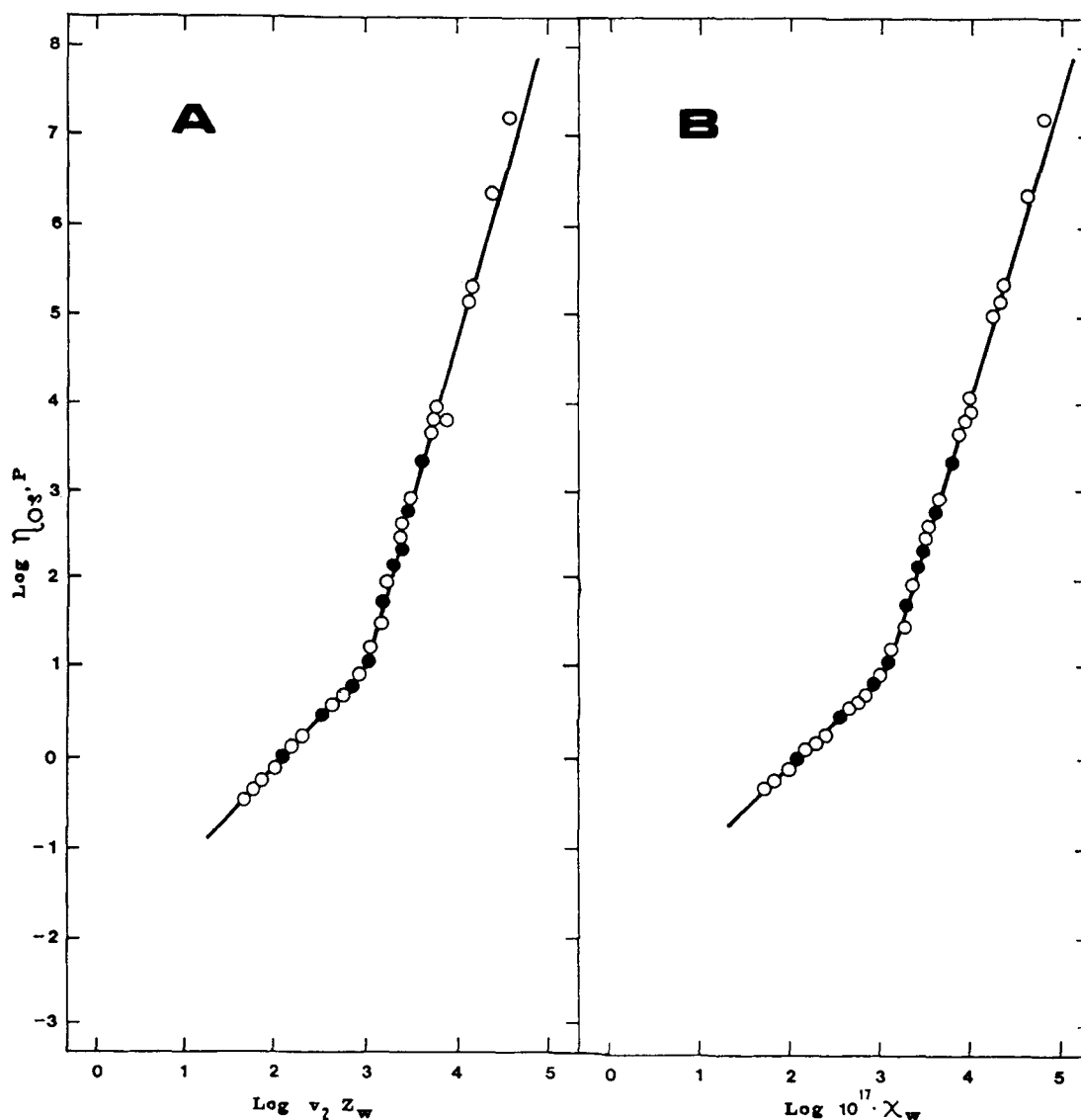


Figure 4 (A) $\log \eta_{0f}$ vs. $\log \nu_2 Z_w$ and (B) $\log \eta_{0f}$ vs. $\log 10^{17} \chi_w$ plots for PDMS at 25°C: (O) calculated from the literature values; (●) calculated from the experimental data.

$$\eta_0 = 1.12 \cdot 10^9 (\chi_w / 1.12 \cdot 10^{-14})^\alpha \zeta_0 \quad (9)$$

where $\alpha = 1.0$ for $\chi_w < 1.12 \cdot 10^{-14}$ and $\alpha = 3.4$ for $\chi_w > 1.12 \cdot 10^{-14}$.

For $\alpha = 1.0$ and for the critical viscosity, η_{0c} , of 9.12 P, this yielded $8.14 \cdot 10^{-9}$ [†] for the critical friction coefficient, ζ_0 , which was then used to correct the low molecular weight viscosity data and construct $\log \eta_0$ vs. $\log \nu_2 Z_w$ and $\log \eta_0$ vs. $\log 10^{17} \chi_w$ plots in which experimental η_0 values were corrected

[†] This value is in a very good agreement with the value of $7.4 \cdot 10^{-9}$ obtained for the same parameter for polydimethylsiloxane-decamethylcyclopentasiloxane blends in Ref. 26.

to constant ζ_0 as listed in Table III and shown in Figure 4 (A) and (B).

It can be seen from this figure that when these corrections were used a new set of PDMS chain dimensions critical for the onset of entangled behavior was obtained as follows: $Z_{wc} = 896$; $s_{LMW} = 1.038$ and $s_{HMW} = 3.569$ from Figure 4 (A) and $10^{17} \chi_{wc} = 1.199$; $s_{LMW} = 1.00$ and $s_{HMW} = 3.34$ from Figure 4 (B).

CONCLUSIONS

To summarize and compare the values obtained by the previous analyses, the results obtained are sum-

Table IV Summary of the Critical Chain Dimensions of PDMS

| Determination Method | Z_{wc} | $10^{17} \cdot \chi_{wc}$ | s_{LMW} | s_{HMW} |
|------------------------------------|----------|---------------------------|-----------|-----------|
| From Figure 1 | 925.0 | — | 1.347 | 3.618 |
| From Figure 2(A) | 931.5 | — | 1.368 | 3.680 |
| From Figure 2(B) | — | 1122.0 | 1.267 | 3.342 |
| From eq. (6) and Figure 2(B) | 935.0 | — | — | — |
| From Figure 4(A) | 896.0 | — | 1.038 | 3.569 |
| From Figure 4(B) | — | 1199.0 | 1.000 | 3.340 |
| From eq. (6) and Figure 4(B) | 970.0 | — | — | — |
| Average of the values listed above | 930.0 | 1160.5 | 1.204 | 3.510 |

marized in Table IV. It can be seen from this table that, as it had been also found in other similar investigations,^{9,18} different calculation methods led to different values of the critical rheological parameters characteristic for PDMS. Nevertheless, the maximum difference between the obtained critical chain-length values was less than 3% of the average, which in this case equaled 930, so that this can certainly be considered as an excellent agreement between the obtained data, considering the expected limits of experimental errors. Therefore, if the average Z_{wc} obtained is accepted for the most realistic critical number of chain atoms at which PDMS macromolecules undergo chain entanglement, a critical degree

of polymerization of this polymer for the onset of non-Newtonian behavior can be calculated from the following equation:

$$\overline{DP}_{wc} = (Z_{wc} - 1)/2 = 464.5 \quad (10)$$

and corresponding polymer molecular weight can be obtained from eq. (8) as follows:

$$\bar{M}_{wc} = 88 + [74(Z_{wc} - 1)/2] = 34,461 \quad (11)$$

This value can be now compared with other corresponding values that have been reported earlier in the literature as shown in Table V. It can be seen from this table that the average of all previously reported values for Z_c of PDMS equaled 868, or 839.5 if the lowest⁷ and the highest¹⁰ of the values listed in Table V were neglected. The corresponding limits of deviations of the reported data of Table V from these averages were 32.1 and 51.8% from 868 and 25 and 15.1% from 839.5, respectively. Both of these averages were lower than the most probable value obtained in this work, and their corresponding differences were 6.7% of the most probable value for the former and 9.7% for the latter average.

Most importantly, however, is that this analysis clearly shows that the critical chain length at which PDMS shows the first signs of the so-called entangled behavior is longer than was earlier believed and that if one accepts the view that a longer critical polymer chain length reflects a more pronounced flexibility of the polymer macromolecules, then the value obtained for this parameter in this work ranks PDMS among the most flexible macromolecules, second only to several polymethacrylates that contain very long side groups (such as *n*-butyl, $Z_c = 1080$; *n*-hexyl, $Z_c = 1150$; or *n*-octyl, $Z_c = 1,465$)¹³ and where other effects, such as unusually large free volumes created by these very long side

Table V Summary of the Characteristic Parameters Reported for the PDMS Zero-Shear Viscosity—Number of Polymer Chain Atoms Relationships*

| Reference | s_{LMW} | s_{HMW} | Z_c | η_{0c} (P) |
|-----------------|-----------|--------------------|------------------|--------------------|
| 3 | 1.468 | 3.557 | 908 | 13.80 |
| 4 | 1.263 | — | — | — |
| 5 | 1.148 | — | — | — |
| 6 | 1.149 | 2.886 | 794 | 10.47 |
| 7 | 1.129 | 3.394 | 589 ^b | 1.95 ^b |
| 8 | 1.475 | 3.545 | 955 | 17.78 |
| 9 | 1.418 | 3.500 | 660 | 18.62 |
| 10 ^c | 1.569 | 3.925 | 1318 | 17.76 |
| 11 | 1.720 | 4.190 | 861 | 7.94 |
| 12 | 1.990 | 3.390 | 889 | 7.10 |
| 26 | — | 3.500 ^d | 728 | 5.94 |
| 27 | 1.400 | 3.000 | 765 | — |

* Obtained by regression analysis of the reported data.

^b Highly "problematic" values obtained by extrapolation since no experimental points exist in near vicinity of the intercept.

^c The author claimed $s_{LMW} = 1.00$, $s_{HMW} = 3.4$, and $Z_c = 960$.

^d This value was assumed by the authors.

groups, are responsible for their apparently longer critical chain dimensions. This conclusion is in clear agreement with the well-known exceptional elasticity of the polysiloxanes in general and it seems to support the view that $-\text{[Si-O]}_n-$ chains may well be perhaps the most flexible chains of atoms presently known.

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Received September 9, 1992

Accepted December 21, 1992