

Random coil dimensions of poly(diethyl siloxane)*

J. E. Mark†, D. S. Chiu, and T. -K. Su‡

Department of Chemistry and the Macromolecular Research Center, University of Michigan, Ann Arbor, Michigan 48109, USA

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A sample of high molecular weight poly(diethyl siloxane), $[\text{Si}(\text{C}_2\text{H}_5)_2\text{O}]_x$, (PDES) was separated into a series of fractions by means of liquid-liquid precipitations. Four of the fractions were studied by osmometry and viscometry in toluene at 25°C. The resulting values of the number-average molecular weight, second virial coefficient, and intrinsic viscosity indicate that the unperturbed dimensions of PDES are essentially the same as those of poly(dimethyl siloxane) (PDMS) of the same chain length. Thus, differences in intramolecular interactions between these two chains have little effect on their unperturbed dimensions. Most pertinent in this regard are interactions between the side chains, which are favourable in *trans* conformations in both PDES and PDMS. These favourable interactions in *trans* conformations would be enhanced in the case of the ethyl groups in PDES, but this effect is apparently offset by a comparable increase in favourable interactions between ethyl groups and oxygen atoms in the competing *gauche* conformations.

INTRODUCTION

The characterization of intramolecular interactions is of paramount importance in the interpretation and understanding of the configuration-dependent properties of a chain molecule¹. Such interactions are particularly numerous, of course, in the case of a polymer in which the skeletal atoms carry relatively bulky substituents, or 'side chains'. Their importance has been well documented for a variety of statistical properties¹⁻⁴ including the unperturbed dimensions $\langle r^2 \rangle_0$ ⁵. For example, polyoxides such as poly(ethylene oxide) $[(\text{CH}_2)_2\text{O}]_x$ ^{1,6} and poly(trimethylene oxide) $[(\text{CH}_2)_3\text{O}]_x$ ^{6,7} are relatively compact molecules in the random coil state because the unsubstituted O atom has very modest spatial requirements. Vinyl chains $[\text{CHR}-\text{CH}_2]_x$ tend to be much less compact^{1,8-10} however, particularly when R is for example the relatively large phenyl group, as it is in polystyrene.

Vinyl chains in which R is an unbranched or branched alkyl group have received the most attention^{1,8,9}. Increase in the size of R from $-\text{CH}_3$ to the articulated side chain $-\text{CH}_2-\text{CH}_3$, for example, increases $\langle r^2 \rangle_0$, primarily through a somewhat indirect effect. 'Pentane-type' interferences^{1,2} involve groups separated by four bonds, and in these chains the participants are either two R groups or one R group and a skeletal $-\text{CH}_2-$ group^{1,8}. These groups are at a very small distance of separation, $\sim 2.6 \text{ \AA}$ ^{1,8}, in conformations giving rise to these interactions. They are therefore already strongly suppressed for the simplest case, where R is CH_3 . Furthermore, the $-\text{CH}_2-\text{CH}_3$ groups should not have a significantly larger cross-section, particularly since some rotational

motion can occur about the first bond in this side chain. These interactions are therefore essentially the same for the $-\text{CH}_3$ and $-\text{CH}_2-\text{CH}_3$ side chains. The CH_3 group in $-\text{CH}_2-\text{CH}_3$ also interacts, however, with the skeletal $-\text{CH}_2-$ groups separated from it by three bonds. The resulting destabilization of *trans*, *trans* conformations about the $\text{CH}_2-\text{CHR}-\text{CH}_2$ bonds can greatly increase $\langle r^2 \rangle_0$, at least for some of the stereochemical forms of the polymer^{1,8}. Branched side chains having a substituent such as CH_3 attached to either their first or second C atom [for example $-\text{CH}(\text{CH}_3)_2$] are particularly effective in suppressing otherwise permitted conformations, with a correspondingly larger change in the unperturbed dimensions^{2,9}.

The situation should be rather different in the case of the polysiloxanes $[\text{SiR}_2\text{O}]_x$, an example of which is the poly(diethyl siloxane) chain shown in Figure 1. Because of the unusually large values of the Si-O bond length (1.64 Å) and the Si-O-Si bond angle (143°), pentane-type interac-

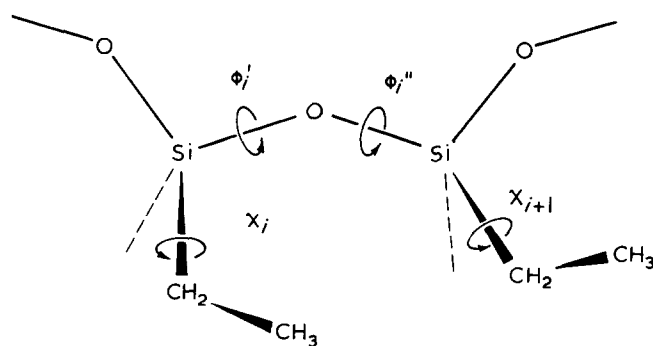


Figure 1 Schematic sketch of a portion of the poly(diethyl siloxane) chain in the all-*trans* conformation. Side chains which would appear behind the plane of the paper have been omitted for reasons of clarity. Rotations about the two skeletal bonds of repeat unit i are characterized by ϕ_i' and ϕ_i'' ; rotations within the side chain shown for this unit are characterized by χ_i

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† Present address: Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, USA.

‡ Present address: Deering Milliken Inc., Spartanburg, South Carolina 29301, USA.

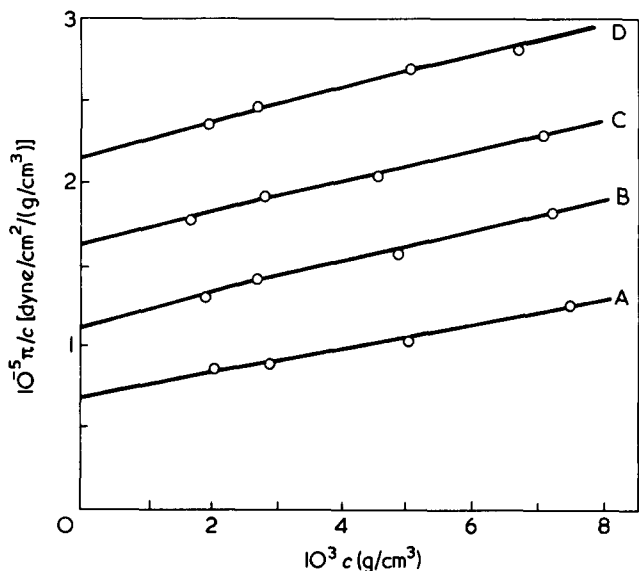


Figure 2 Osmotic pressure data, obtained in toluene at 25°C, for the four PDES fractions: A, F1; B, 2; C, 3; D, 4

tions between R groups and between an R group and a skeletal —O— atom are attractive rather than repulsive^{1,11,12}. Similarly, interactions between the CH₃ group in the articulated —CH₂—CH₃ side chain and the relatively small —O— atom removed from it by three bonds would not be expected to destabilize *trans*, *trans* conformations about O—Si—O bonds. Therefore, siloxane chains should probably be very different from vinyl chains in the way in which their configuration-dependent properties depend on the size and shape of the hydrocarbon side chain R. The simplest investigation relevant to this issue would involve comparison of values of $\langle r^2 \rangle_0$ for the two siloxane chains have side chains of —CH₃ and —CH₂—CH₃, i.e. poly(dimethyl siloxane), [Si(CH₃)₂—O]_x, (PDMS) and poly(diethyl siloxane), [Si(C₂H₅)₂—O]_x, (PDES). The former polymer has already been intensively studied, both experimentally and theoretically, with regard to its unperturbed dimensions^{1,11}. The latter, PDES, although much studied with regard to its solid-state properties^{13,14} has not been studied at all with regard to its spatial configurations. It is thus the subject of the present investigation, which focuses on its unperturbed dimensions as determined from osmometric and viscometric measurements carried out in a thermodynamically good solvent.

EXPERIMENTAL

A high molecular weight sample of PDES, generously provided by Dr C. L. Lee of the Dow Corning Corporation, was separated into a total of fourteen fractions by means of consecutive liquid—liquid precipitations. The solvent was toluene and the polymer was present to the extent of 1% by wt. Methanol was used as the non-solvent and the separations were carried out in the usual manner⁵, at 30°C. The four fractions used in the present study constituted 7.7, 9.2, 10.0 and 6.8% of the original sample; they were labelled F1—4.

Osmometry measurements were carried out in toluene at 25°C, using a high speed osmometer (Melabs CSM-2) containing a gel cellophane membrane conditioned for this solvent. Concentrations *c* were expressed in g/cm³, and

ranged from 1.6 to 7.4 × 10⁻³ in these units. Osmotic pressures π were expressed in dyne/cm², and second virial coefficients A_2 in cm³ mol/g².

Viscosities of the PDES fractions in toluene at 25°C were determined using a Cannon—Ubbelohde viscometer. Intrinsic viscosities $[\eta]$ were obtained by extrapolation of the viscosity data in the usual manner⁵.

RESULTS AND DISCUSSION

Values of the reduced osmotic pressure π/c were found to be well represented by the simple linear relationship⁵:

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

where *R* is the gas constant, *T* = 298.2K is the absolute temperature, and M_n is the number-average molecular weight. The results thus represented are shown in Figure 2. Values of M_n and A_2 obtained from the intercepts and slopes, respectively, of these curves are given in columns two and three of Table I. The following column lists the values obtained for the intrinsic viscosity, in dl/g.

The relationship between $[\eta]$ and M_n is shown logarithmically in Figure 3. The curve shown was located by least-squares analysis and corresponds to the equation:

$$[\eta] = 2.71 \times 10^{-4} M_n^{0.636} \quad (2)$$

Since the range of the data is relatively small, additional measurements would be required to establish the two numerical constants with a higher degree of accuracy. Nonetheless, the fact that the exponent on M_n is somewhat larger than 0.50 indicates that toluene at 25°C is a moderately good solvent for PDES in the thermodynamic sense⁵.

The values of $[\eta]$, M_n and A_2 obtained as described above were used to calculate values of the chain expansion factor $\alpha = \langle r^2 \rangle / \langle r^2 \rangle_0$ ^{1/2} which characterizes chain perturbations due to long range interactions⁵. The relationship employed for this purpose was the standard equation of Orfino and Flory¹⁵:

$$\ln[1 + (\pi^{1/2}/2)(\alpha^2 - 1)] = (27\Phi/2^{5/2}N_{avo})(A_2M/[\eta]) \quad (3)$$

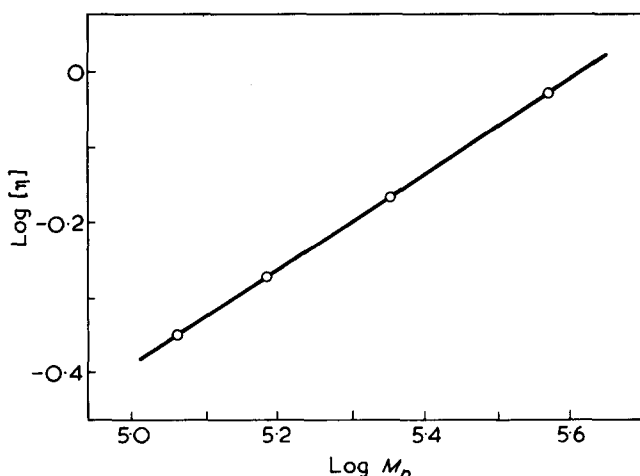


Figure 3 The intrinsic viscosity—molecular weight relationship for PDES in toluene at 25°C

Table 1 Osmometric and viscometric results^a

Fraction	$10^{-5}M_n$ (g/mol)	10^4A_2 (cm ³ mol/g ²)	[η] (dl/g)	α	$\langle r^2 \rangle_0/nl^2$
F1	3.70	2.96	0.945	1.40	7.9
2	2.23	3.83	0.683	1.44	7.2
3	1.53	3.73	0.539	1.36	7.8
4	1.15	3.93	0.448	1.34	7.8
				Average	7.7(± 0.2)

^aObtained in toluene at 25°C

where Φ is a hydrodynamic constant equal to 2.1×10^{21} dl/cm³ mol in thermodynamically good solvents^{5,16}, N_{avo} is Avogadro's number, and π here is the numerical constant 3.1416. These results are listed in column five of Table 1. Values of $\langle r^2 \rangle_0$ were then calculated from⁵:

$$[\eta] = \Phi \langle r^2 \rangle_0 / M^{3/2} M^{1/2} \alpha^3 \quad (4)$$

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 . The values thus obtained are given in the last column of the Table, and yield the average result $\langle r^2 \rangle_0/nl^2 = 7.7 (\pm 0.2)$ with a total uncertainty estimated to be approximately ± 0.8 .

The dimethyl polymer, PDMS, has been studied by means of light scattering and viscometric measurements in several Θ -solvents^{1,17} (in which long range interactions are known to be nullified⁵). The values thus obtained for $\langle r^2 \rangle_0/nl^2$ are 6.2 (± 0.1) in methyl ethyl ketone at 20°C, and 7.6 (± 0.2) in a fluorocarbon mixture at 22.5°C. The fact that the characteristic ratio is significantly high in the medium of lower dielectric constant and cohesive energy density is not well understood. It is generally termed a 'specific solvent effect', and has also been observed in swollen PDMS networks¹⁸. In any case, the value 7.6 obtained for PDMS in the fluorocarbon mixture is clearly the appropriate one for comparison with the present results obtained for PDES in toluene, which has a comparably small dielectric constant. The two polymers are seen to have values of $\langle r^2 \rangle_0/nl^2$ that are identical within experimental error. Also, some preliminary measurements¹⁹ indicate that PDES and PDMS have very similar values of another configuration-dependent property, the mean-square dipole moment.

The above results suggest that if intramolecular interactions are different in these two polymers, the differences must be largely compensating, at least with regard to the unperturbed dimensions. Such differences may be examined, at least qualitatively, by reference to Figure 1. In the all-*trans* conformation shown, the two $-\text{CH}_2-$ groups in PDES or the two $-\text{CH}_3$ groups in PDMS are at a distance of separation of approximately 3.8 Å^{1,11}, and attract one another with an energy of approximately 500 cal/mol^{1,11,12}. Replacement of the $-\text{CH}_3$ groups in PDMS by phenyl groups, which have a thickness approximately twice the van der Waals' radius of a CH_3 group, greatly increases the magnitude of these attractions, because of the larger number of interacting atoms¹². It is therefore quite reasonable to assume that attractions between the ethyl groups shown in Figure 1 are larger than those between the methyl groups in the corresponding conformation in PDMS. (The location of the $-\text{CH}_3$ groups in PDES varies of course with the side chain angles, such as χ_i and χ_{i+1} in Figure 1. These rotations would be geometrically dependent on skeletal bond rotations

such as ϕ_i' and ϕ_i'' , which determine the configuration of the chain backbone. The two types of rotations are also coupled in the statistical mechanical sense, in that side chain rotations which maximize favourable interactions lower the total energy of the molecule, thereby increasing the statistical weight or probability of occurrence of the associated conformation and configuration of the chain.) A lowering of the energy of *trans* states in a siloxane chain would decrease $\langle r^2 \rangle_0$, since the all-*trans* form of the molecule approximates a closed polygon and thus has a very small end-to-end distance^{1,11,20}. This effect, however, is apparently offset by favourable ethyl-oxygen four-bond interactions which occur in the alternative *gauche* states of higher spatial extension. These competing states are obtained by rotations, such as ϕ_i' and ϕ_i'' , about Si-O and O-Si skeletal bonds. (The comparable methyl-oxygen attractions occurring in PDMS were assumed to be relatively small and were, in effect, absorbed into the energy difference of 500 cal/mol cited above for the disruption of one of the methyl-methyl interactions¹¹.) Since the corresponding favourable interactions between a phenyl group and an oxygen atom are quite large¹², it is very reasonable to expect that in PDES the increase in the magnitude of the ethyl-oxygen attractions in *gauche* states could largely offset the increase in ethyl-ethyl attractions in the *trans* states. This compensating effect would mean that PDES and PDMS would have approximately the same populations of compact *trans* states and more extended *gauche* states, and therefore approximately the same value of the characteristic ratio.

One puzzling aspect of the problem of understanding spatial configurations of polysiloxanes concerns some experimental results reported for poly(dipropyl siloxane)²¹, in which the side chains are unbranched, i.e. $-\text{CH}_2-\text{CH}_2-\text{CH}_3$ groups²². Viscometric measurements on this polymer in two Θ -solvents give values of $\langle r^2 \rangle_0/nl^2$ of 12.0 (2-pentanone, 76°C) and 14.0 (toluene, 10°C)²¹. Although part of the difference between these two values may be due to the temperature dependence of $\langle r^2 \rangle_0$, this is unlikely since siloxane chains generally have positive values of $d\ln\langle r^2 \rangle_0/dT$ ^{1,11,12,23}. It therefore appears that this polymer exhibits a specific solvent effect very similar to that shown by PDMS^{17,18}. In any case, these values of $\langle r^2 \rangle_0/nl^2$ are much higher than would be expected on the basis of the arguments presented above for PDES. Perhaps also pertinent is the fact that an articulated side chain such as $-\text{CH}_2-\text{CH}_2-\text{CH}_3$ would apparently be able to adopt more conformations in *trans-gauche* states than in the spatially more restrictive *trans-trans* states shown in Figure 1²⁴. Although this entropic destabilization of *trans* states would of course increase $\langle r^2 \rangle_0$, one would not expect the characteristic ratio to increase to such large values (12.0, 14.0) from the relatively small values (6.2, 7.6) reported for PDMS. Therefore, these experimental results on poly(di-n-propyl siloxane), if confirmed, would seem to call for a careful, quantitative analysis of the configurational characteristics of both poly(diethyl siloxane) and poly(di-n-propyl siloxane) in terms of rotational isomeric state theory.

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