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# Kirkwood–Riseman Interpretation of the Diffusion Behavior of Short Polymer Chains in Dilute Solution

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ABSTRACT: Diffusion data for short polymethylene (PM), poly(oxyethylene) (POE), and poly(dimethylsiloxane) (PDMS) chains, which are sensibly unperturbed by excluded volume effects, are analyzed in terms of Kirkwood–Riseman theory. A graphical method of representing diffusion data is proposed and used to demonstrate the magnitude of the free-draining contributions in the systems studied. The systems show different types of behavior, characterized by different amounts of free-draining, which for PM and PDMS cannot be explained by constant friction coefficients per segment. For PDMS it is shown that the friction centers are best considered as $-(SiMe_2O)-$ segments. A function $\psi(x)$ which relates impermeable hydrodynamic radii and equilibrium radii of gyration is shown to have approximately the same values for the three flexible polymers considered.

## Introduction

The diffusion coefficient ($D$) of a polymer molecule of $x$ segments in dilute solution can be described by the now-classical equation due to Kirkwood,[1] which can also be derived[2] from Kirkwood–Riseman theory,[3] namely

$$D = \frac{kT}{x\zeta} + \frac{kT}{6\pi\eta_0}\frac{[R^{-1}]}{x^2} \qquad (1)$$

where the friction coefficient per segment $\zeta = 6\pi\eta_0 a$ and $a$ is the radius of a segment. $\eta_0$ is the solvent viscosity and

$$[R^{-1}] = \sum_{\substack{i,j=1\\(i\neq j)}}^{x} \langle r_{ij}^{-1}\rangle \qquad (2)$$

where $\langle r_{ij}^{-1}\rangle$ is the mean reciprocal separation of segments $i$ and $j$.

Equation 1 is based on several important assumptions. The polymer chain is treated as a collection of point centers of friction diffusing in a solvent continuum. Hydrodynamic interactions are calculated by using the Oseen tensor[4,5] preaveraged over orientations and configurations of the molecule, thus separating translational motion from the internal motions of the chain.[2,6,7] Equation 1 also assumes weak hydrodynamic interactions between segments.[2,6,7]

A recent paper by Burchard and Schmidt[8] suggests that eq 1 overestimates $D$ for high molar mass polystyrene in a variety of Θ solvents by about 15%. Zimm[7] and Fixman[9] have attempted to improve the calculation of $D$, using numerical techniques, but as yet no completely satisfactory treatment has been proposed. However, approximations in the theory notwithstanding, it has been possible[10-16] to correlate the values of $D$ for short polymer chains in terms of eq 1, allowing, for polymethylene chains, a semiempirical interpretation of the free-draining contribution to $D$ in terms of solvent properties.[15]

Equation 1 can be written in a form which is independent of solvent viscosity,[15] namely

$$1/r_D = 1/xa + [R^{-1}]/x^2 \qquad (3)$$

The first term in eq 1 and 3 is the so-called free-draining term, which results from solvent flow through the molecule, neglecting hydrodynamic interactions between segments. The second term is the impermeable term resulting from perturbations in the solvent flow introduced by hydrodynamic interactions between segments. Equation 3 shows that the total diffusion radius, $r_D$, is given by the sum-in-parallel of the free-draining radius ($r_F$) and the equivalent impermeable radius ($r_E$); that is

$$1/r_D = 1/r_F + 1/r_E \qquad (4)$$

The impermeable term is dominant at large chain lengths while the free-draining contribution increases in importance as the chain length decreases.

In our previous papers, translational diffusion coefficients for short polymethylene (PM),[13,15] poly(oxyethylene) (POE),[15,17] poly(hexamethylene oxide) (PHMO),[15] and poly(dimethylsiloxane) (PDMS)[16] chains in a variety of solvents were analyzed in terms of Kirkwood–Riseman theory. A complete analysis was only possible for PM as detailed calculations of the impermeable contribution ($r_E$) to the total diffusion radius were not available for POE and PHMO. However, it was shown that short PM chains deviated strongly from Kirkwood–Riseman behavior. The large apparent free-draining contribution to the total diffusion radius could only be explained in terms of a friction coefficient per segment ($\zeta$) which increased with chain length. This increase was found to be in proportion to the effective bond length, $b$, where $b = (\langle r^2\rangle/n)^{1/2}$ and $\langle r^2\rangle$ is the root-mean-square end-to-end distance of a chain of $n$ bonds. The freely jointed segments defined in this way are considered to be a better approximation to the disconnected segments assumed in Kirkwood–Riseman theory. In general,

$$\zeta = c_b 6\pi\eta_0 b \qquad (5)$$

where, given the assumptions implicit in the derivation of eq 1, $c_b$ can be thought of as characterizing the friction occurring at the segment–solvent interface.

The magnitude of $c_b$ was shown to depend on both the molar volume of the solvent and the solvent viscosity, and a more detailed discussion of the physical significance of $c_b$ has been given elsewhere.[15] The variation of $\zeta$ with chain lengths had been noted previously by Freire and Horta.[14] However, no atttempt was made to account for the observed variation of $\zeta$ with solvent.

Here we present new experimental data for poly(dimethylsiloxane) (PDMS) in bromocyclohexane at 15 °C and reinterpret some recently published data for PDMS chains in toluene.[16] In addition, values of $r_E$ have been calculated for both POE and PDMS, enabling a unified interpretation of the diffusion behavior of PM, POE, and

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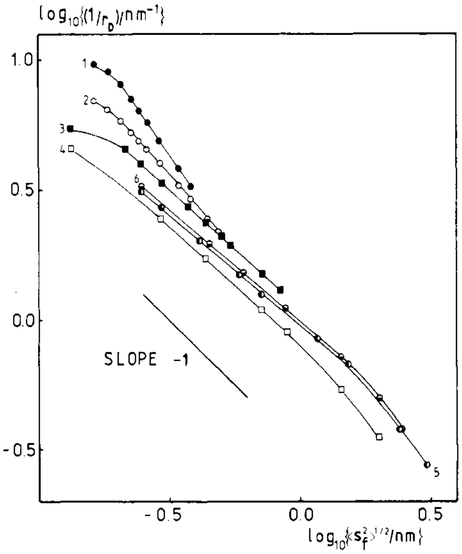

**Figure** 1. log $(1/r_D)$ vs. log $(\langle s_f^2\rangle^{1/2})$. Systems: (1) (●) PM/quinoline/25 °C; (2) (○) PM/benzene/25 °C; (3) (■) POE/quinoline/25 °C; (4) (□) POE/water/25 °C; (5) (◐) PDMS/toluene/25 °C; (6) (⊖) PDMS/bromocyclohexane/15 °C.

PDMS to be presented. The calculations have used the rotational isomeric state (RIS) models and molecular parameters due to Flory et al.[18-20] For the shorter chains ($x \leq 15$), $[R^{-1}]$ and hence $r_E$ were calculated by exact enumeration and for the longer chains a Monte Carlo technique,[21,22] employing Metropolis sampling, was used.

In addition, the calculated values of $r_E$ for POE and PDMS have been used to calculate $\psi(x)$ in the relationship[15,16]

$$\langle s^2\rangle^{1/2} = \psi(x) r_E \tag{6}$$

The function $\psi(x)$ enables $r_E$, which is equivalent to $r_D$ in the impermeable limit, to be calculated from values of $\langle s^2\rangle^{1/2}$ without resort to Monte Carlo calculations. Values of $\psi(x)$ have been calculated previously for PM[15] and have been used to calculate approximate values of $\langle s^2\rangle^{1/2}$ for PDMS from experimental diffusion radii.[16] The values of $\psi(x)$ for POE and PDMS are presented here and compared with those of PM.

## Correlation of Diffusion Data for Short-Chain Molecules

**Experimental Data.** The diffusion data to be considered are shown in Figure 1 plotted as log $(1/r_D)$ vs. log $\langle s^2{}_f\rangle^{1/2})$. The ordinate, log $(1/r_D)$, was chosen rather than log $D$ to remove the gross effects of solvent viscosity. The abscissa, log $(\langle s^2{}_f\rangle^{1/2})$, is the logarithm of the calculated root-mean-square free-rotation radius of gyration and is taken as representing the core dimension of an impermeable chain.[15,17]

The data for PM (curves 1 and 2) have been published and interpreted previously.[13,15] The data for POE (curves 3 and 4) have also been published previously,[15,17] with the exception of the two points at the longest chain length.[23] They refer to POE samples of $M_w = 4050$ $M_w = 8000$, corresponding to 275 and 543 bonds, respectively. Curve 5 shows published data[16] for PDMS in toluene and curve 6 presents new data for PDMS in bromocyclohexane. These data have been obtained by using the boundary-spreading technique, which has been described elsewhere.[16,24]

The data for PM give slopes markedly less than $-1$, indicating a considerable free-draining contribution to the total diffusion radius, which also varies with solvent. In contrast, most of the data for POE and PDMS gives slopes approximately equal to $-1$, apparently indicating impermeable behavior over the wide range of chain lengths studied. For POE larger values of $r_D$ are observed in water than in quilonine, reflecting the hydrogen bonding of water molecules onto the skeletal oxygen atoms. For the same systems the curvature at short chain lengths ($4 \leq x \leq 7$) can be attributed to end effects resulting from hydrogen bonding with solvent molecules. The effect is greater in quinoline than in water.

Both POE and PDMS show the effects of chain expansion at long chain lengths as illustrated by curves 4, 5, and 6. The new data for PDMS in bromocyclohexane are consistent with the data in toluene and confirm that excluded volume becomes noticeable for approximately $x > 100$. For POE in water the curvature also becomes noticeable at ca. 100 segments. Classical polymer solution theory indicates that the "threshold" value of $x$ for chain expansion must depend on chain structure, solvent, and temperature, and the onset of downward curvature in curves 4, 5, and 6 defines the upper bound of what may be considered as "short chains" for present purposes. It may be noted that the $\Theta$ point for high molar mass PDMS and bromocyclohexane has been reported to be 28 °C.[25] However, the diffusion data in Figure 1 indicate that chain expansion still occurs at 15 °C for these relatively low molar mass chains. This apparent difference in behavior is currently being investigated.

**Proposed Kirkwood–Riseman Interpretation.** In a previous paper,[15] Kirkwood–Riseman behavior was illustrated by using a plot of $x^{1/2}/r_D$ vs. $x$. This type of plot has the advantage that calculated impermeable radii (plotted as $x^{1/2}/r_E$) and free-draining radii (calculated by using an assumed value of $a$ and plotted as $x^{1/2}/r_F$) can also be displayed and the relative magnitudes of these contributions to $x^{1/2}/r_D$ can be clearly seen. In addition, for unperturbed chains $x^{1/2}/r_D$ and $x^{1/2}/r_E$ tend to limiting values as $x$ increases and $x^{1/2}/r_F$ tends to zero. In this paper further use is made of this type of plot and experimental data are included for the first time (see Figures 2–5).

**PM/Benzene and PM/Quinoline.** The diffusion behavior of short PM chains in a variety of solvents has been discussed previously.[15] The relationship between experimental diffusion radii and the diffusion radii predicted by Kirkwood–Riseman theory is shown in Figure 2 for two solvents and the experimental data are included in the plot of calculated diffusion radii as just described. In both solvents the experimental values of $x^{1/2}/r_D$ are considerably larger than the calculated values (curve 3). Thus there are large apparent free-draining contributions to the total diffusion radii, with the contributions decreasing with increasing chain length and both sets of data approaching the calculated curve as free-draining disappears. However, this free draining cannot be accounted for by assuming a unique value of the segment radius $a$. As discussed previously (eq 5), the segment radius has been assumed to vary in proportion to the effective bond length $b$ and curves 4 and 5 have been drawn by using the mean values[15] for the constant of proportionality, $c_b$, namely, 0.216 for benzene and 0.121 for quinoline. Agreement with experiment is good except at the shortest chain lengths, where end effects apparently cause downturns in the experimental data. Thus for PM it is possible to calculate the diffusion coefficient, using Kirkwood–Riseman theory and a realistic chain model, given only the independent parameter $\langle c_b\rangle$, which is a function of solvent and temperature.

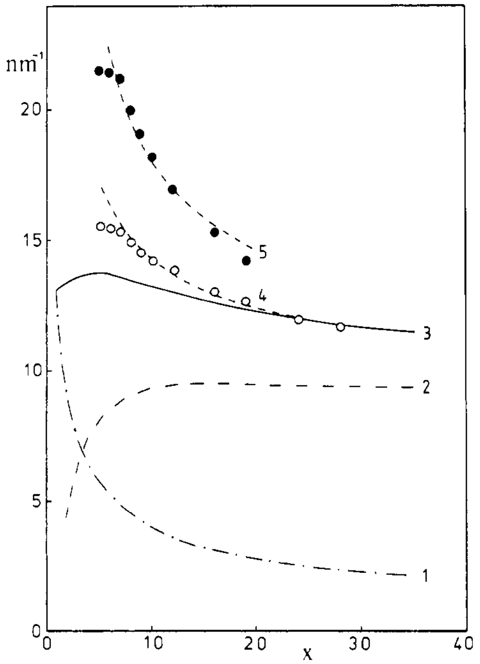

**Figure 2.** Reciprocal diffusion radii vs. chain length ($x$) for (●) PM/quinoline/25 °C and (○) PM/benzene/25 °C. Curves: (1) free-draining radius, $x^{1/2}/r_F$, with $r_F = xa$ and $a = 0.08$ nm; (2) impermeable radius, $x^{1/2}/r_E$, with $r_E = x^2/[R^{-1}]$; (3) Kirkwood–Riseman diffusion radius, $x^{1/2}/r_D = x^{1/2}/r_F + x^{1/2}/r_E$; (4) and (5) calculated diffusion radius with $a = \langle c_b \rangle b$, using (4) $\langle c_b \rangle = 0.216$ and (5) $\langle c_b \rangle = 0.121$.

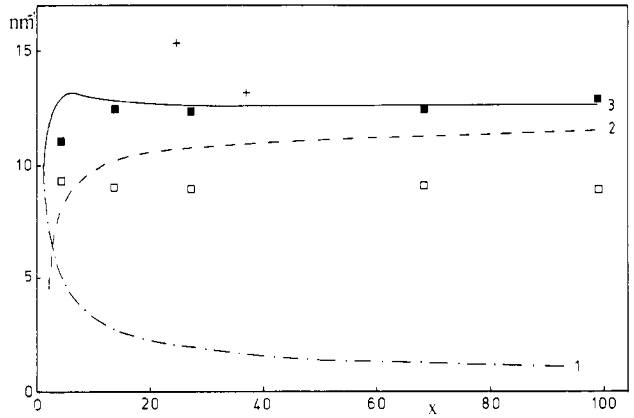

**Figure 3.** Reciprocal diffusion radii vs. chain length ($x$) for (■) POE/quinoline/25 °C and (□) POE/water/25 °C. The points marked with a plus refer to POE terminated by one OH and one OMe group in quinoline at 25 °C. Curves: (1) free-draining radius, $x^{1/2}/r_F$, $a = 0.1$ nm; (2) impermeable radius, $x^{1/2}/r_E$; (3) Kirkwood–Riseman diffusion radius, $x^{1/2}/r_D$.

**POE/Quinoline and POE/Water.** Figure 3 shows the experimental data for the systems POE/quinoline and POE/water for $x < 100$, together with the appropriate calculated curves for $r_F$, $r_E$, and $r_D$. It is immediately apparent that in both solvents, POE is behaving differently from the systems PM/benzene and PM/quinoline. The experimental values of $x^{1/2}/r_D$ for the system POE/quinoline are in excellent agreement with the calculated values (curve 3), which assumes a constant value of the segment radius $a$ (0.1 nm). The slippage observed previously for PM does not seem to occur in this case. However, it has been shown previously that quinoline molecules are hydrogen bonded to the ends of the chain.[15] This has the effect of increasing the diffusion radius, an effect which increases in importance as the chain length decreases and accounts for the apparent agreement between experiment and theory at short chain lengths. By way of illustration, two experimental points are shown in Figure 3 for POE chains with one end of each chain blocked by a methoxy group to prevent terminal hydrogen bonding at that point by solvent molecules. It is apparent that if POE were completely end blocked, its diffusion behavior in quinoline would probably resemble that of PM and that a constant value of the segment radius would not explain the experimental data.

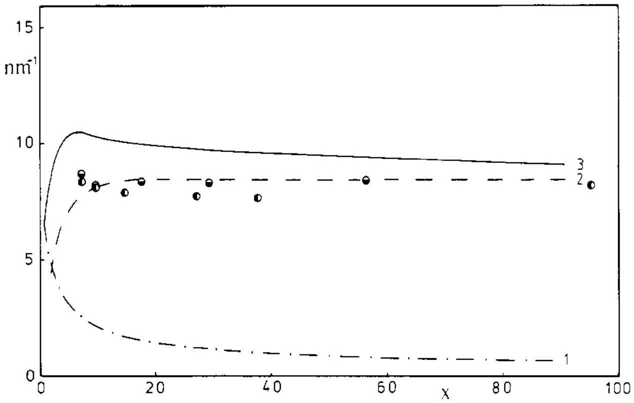

**Figure 4.** Reciprocal diffusion radii vs. chain length ($x$) for (◐) PDMS/toluene/25 °C and (⊖) PDMS/bromocyclohexane/15 °C. Curves: (1) free-draining radius, $x^{1/2}/r_F$, $a = 0.15$ nm; (2) impermeable radius, $x^{1/2}/r_E$; (3) Kirkwood–Riseman diffusion radius, $x^{1/2}/r_D$.

The system POE/water gives experimental values of $x^{1/2}/r_D$ which are consistently lower than even the calculated reciprocal impermeable radii. Again this can be attributed to hydrogen bonding of solvent molecules onto the polymer chain. However, in this case solvent also hydrogen bonds to the oxygens in the chain backbone, causing a large increase in $r_D$, so the ratio of experimental diffusion radii in water to those in quinoline is 1.39 and is approximately independent of chain length.

**PDMS/Toluene and PDMS/Bromocyclohexane.** Figure 4 shows experimental data for the systems PDMS/toluene at 25 °C and PDMS/bromocyclohexane at 15 °C. As before, curves 1–3 represent $x^{1/2}/r_F$, $x^{1/2}/r_E$, and $x^{1/2}/r_D$, respectively, with $x^{1/2}/r_E$ calculated for the PDMS chain at 25 °C (negligible changes in $r_E$ result if the calculation is repeated with statistical weights appropriate to 15 °C).

It can be seen from Figure 4 that the experimental values of $x^{1/2}/r_D$ generally lie just below the calculated values of $x^{1/2}/r_E$. Such behavior cannot be explained in terms of Kirkwood–Riseman theory, according to which $x^{1/2}/r_D$ must be greater than $x^{1/2}/r_E$. Curve 3, showing calculated values of $x^{1/2}/r_D$ with $a = 0.15$ nm, illustrates this apparent breakdown of the Kirkwood–Riseman theory. The segment radius of 0.15 nm was chosen to represent the mean radius of –(SiMe$_2$)– and –(O)– segments, but it is apparent from Figure 4 that no choice of segment radius will improve the agreement between experiment and theory.

The Kirkwood–Riseman theory assumes that the chain is comprised of identical friction centers, whereas in Figure 4 the chain has been assumed to consist of –(SiMe$_2$)– and –(O)– segments, which differ greatly in size. For this reason better agreement with Kirkwood–Riseman theory may be expected if the PDMS chain is considered to be made up from a smaller number of –(SiMe$_2$O)– friction centers. To this end, values of $r_E$ have been recalculated by summing only over the separation of silicon atoms, and the resulting reciprocal diffusion radii are shown in Figure 5 as a function of the number of silicon atoms in the chain

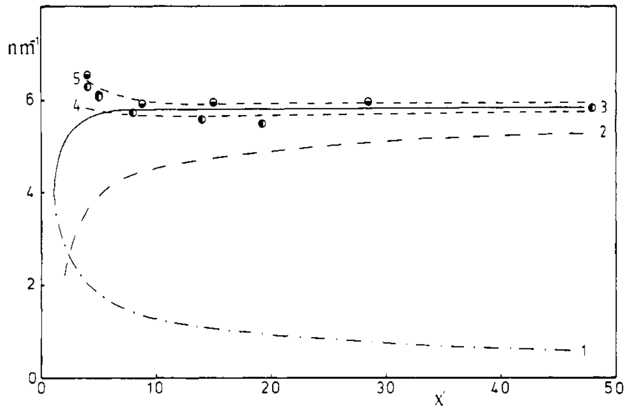

**Figure 5.** Reciprocal diffusion radii vs. chain length ($x'$) for (◐) PDMS/toluene/25 °C and (◒) PDMS/bromocyclohexane/15 °C. Curves: (1) free-draining radius, $x'^{1/2}/r_F$, $a = 0.25$ nm; (2) impermeable radius, $x'^{1/2}/r_E$; (3) Kirkwood–Riseman diffusion radius, $x'^{1/2}/r_D$; (4) and (5) calculated diffusion radius with $a = \langle c_b \rangle b$, using (4) $\langle c_b \rangle = 0.509$ and (5) $\langle c_b \rangle = 0.405$.

Table I
**Calculated Values of $c_b$ on the Basis of -(SiMe$_2$O)- Segments for PDMS in Toluene and Bromocyclohexane** [a]

| toluene | | | | bromocyclohexane | | | |
|---|---|---|---|---|---|---|---|
| $n_n$ | $x'$ | $b$/nm | $c_b$ | $n_n$ | $x'$ | $b$/nm | $c_b$ |
| 6 | 4 | 0.447 | 0.419 | 6 | 4 | 0.477 | 0.379 |
| 8 | 5 | 0.478 | 0.433 | 8 | 5 | 0.478 | 0.425 |
| 14 | 8 | 0.520 | 0.511 | 16.5 | 9.25 | 0.528 | 0.429 |
| 26 | 14 | 0.543 | 0.560 | 28 | 15 | 0.544 | 0.396 |
| 36.5 | 19.25 | 0.546 | 0.663 | 55 | 28.5 | 0.555 | 0.397 |
| 94 | 48 | 0.560 | 0.468 | | | | |

[a] $n_n$ = number-average number of bonds in chain; $x'$, $b$, $\langle c_b \rangle$, $\eta_0$, $V_0$ as defined in text. Toluene: $\langle c_b \rangle = 0.509$, $\eta_0$/cP = 0.522, $V_0$/cm³ mol⁻¹ = 106.4; bromocyclohexane: $c_b = 0.405$, $\eta_0$/cP = 2.44, $V_0$/cm³ mol⁻¹ = 122.5.

$x'$. Figure 5 shows that the values of $x'^{1/2}/r_E$ (curve 2) calculated in this way are smaller than those calculated previously and that good agreement between experimental data and the calculated values of $x'^{1/2}/r_D$ (curve 3) can be obtained for $a = 0.25$ nm. Molecular models indicate that this value of $a$ is a reasonable estimate of the -(SiMe$_2$O)- segment radius. For values of $x' > 10$ the range of experimental values of $x'^{1/2}/r_D$ for the two systems can be covered by allowing $a$ to vary between 0.21 and 0.33 nm.

The shortest PDMS chains ($x' \leq 10$) give experimental values of $x'^{1/2}/r_D$ which are higher than the values predicted by theory. As for PM, a single value of the segment radius will not describe the diffusion behavior at short chain lengths. This variation of the effective segment radius can be analyzed in the same way as for PM using eq 5 with the effective bond length $b = [\langle r^2 \rangle (2/n)]^{1/2}$, where $n/2$ is the number of chain bonds for $x'$ segments. The values of $c_b$ calculated in this way are given in Table I together with the mean value of $c_b$ in each solvent, $\langle c_b \rangle$. The values of $c_b$ are again found to be approximately independent of chain length and the greater variation in $c_b$ for PDMS in toluene reflects the shallow minimum in the corresponding values of $x'^{1/2}/r_D$ in Figure 5. The values of $\langle c_b \rangle$ found for PDMS are greater than those found previously for PM by a factor of between 2 and 4, indicating that, subject to the assumptions in the present analysis, less slippage is occurring for PDMS in toluene and bromocyclohexane than for PM in a variety of solvents. Also $\langle c_b \rangle$ decreases with increasing solvent viscosity, $\eta_0$, and solvent molar volume, $V_0$. Similar trends in $\langle c_b \rangle$ were observed for PM and a rationale of this behavior has been given previously.[15] As for PM, the mean values of $c_b$ have been used to recalculate the diffusion radii using eq 4. Curves 4 and 5 in Figure 5 show the reciprocal diffusion radii calculated in this way for PDMS in the two solvents, using $\langle c_b \rangle = 0.509$ and $\langle c_b \rangle = 0.405$, respectively. Again the calculated curves reproduce the main features of the experimental data, although the agreement is worse than that shown in Figure 2 for PM over a narrower range of chain lengths.

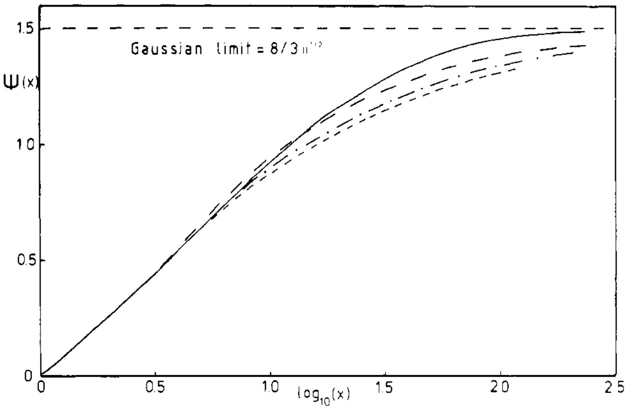

**Figure 6.** $\psi(x)$ vs. log $x$ for (——) PM, (·--) POE, and (– – –) PDMS counting –(SiMe$_2$)– and –(O)– segments, together with $\psi(x')$ vs. log $x'$ (- - -) for PDMS counting –(SiMe$_2$O)– segments.

### Relationship between $r_E$ and $\langle s^2 \rangle^{1/2}$

Figure 6 shows the function $\psi(x)$ for PM, POE, and PDMS, where $\psi(x)$ relates impermeable[15] hydrodynamic radii ($r_E$) and equilibrium radii of gyration ($\langle s^2 \rangle^{1/2}$) according to eq 6. Two curves are shown for PDMS, corresponding to $\psi(x)$ calculated on the basis of all skeletal atoms and $\psi(x')$ on the basis of silicon atoms only. It can be seen that the functions are similar for all three of these flexible polymers, although they tend to the Gaussian limit of $8/3\pi^{1/2}$ at different rates, thus reflecting differences in chain structure. The maximum difference between the four curves is approximately 10% at $x$ or $x'$ equal to about 30. This relative insensitivity of $\psi(x)$ to chain structure arises because $\psi(x)$ is essentially a *ratio* of moments of the distribution of segments about the center of mass.

Thus, assuming impermeable behavior and the absence of excluded volume, $\psi(x)$ can be used as an approximately universal function to relate values of $r_E$ and $\langle s^2 \rangle^{1/2}$ for flexible polymers. In practice, its usefulness is limited by the difficulty in calculating the free-draining contribution to the total diffusion radius. The present work has shown that $r_F$ for PM and PDMS cannot be neglected at short chain lengths and that the constant segment radius, $a$, can be replaced by $\langle c_b \rangle b$, where $\langle c_b \rangle$ is approximately constant for a given polymer/solvent system and cannot be predicted a priori.

It should be noted that the relative insensitivity of $\psi(x)$ to chain structure validates the previous[16] use of $\psi(x)_{PM}$ to calculate values of $\langle s^2 \rangle^{1/2}$ from experimental hydrodynamic radii for PDMS.

### Conclusions

The experimental diffusion data considered illustrate different types of behavior when interpreted in terms of Kirkwood–Riseman theory. Short PM chains show large free-draining contributions to the total diffusion radius, which cannot be explained by assuming a constant segment radius. A detailed interpretation of the behavior in terms of the friction factor $c_b$ has been given previously.[15]

A cursory inspection of Figure 1 suggests that both POE and PDMS are diffusing impermeably down to short chain lengths. However, the present paper shows that free draining is important for short PDMS chains and that the impermeable behavior of POE is confirmed as being due to strong polymer–solvent interactions.[15,17] The friction coefficient per segment, $\zeta$, for PDMS has also been shown to vary with chain length and solvent in a manner similar to that found previously[15] for PM.

The deviations from Kirkwood–Riseman theory for PM and PDMS at short chain lengths probably originates in the assumptions of point centers of friction and a solvent continuum. However modification of the Oseen tensor to account for finite segment sizes cannot explain the observed variation of $\zeta$ with solvent. Hence, one is forced to conclude that solvent structure must be taken into account in some way, and, in the absence of improved hydrodynamic theories, semiempirical correlations provide a reasonable rationale of such behavior.

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# On the Conformation of Peptides in Solution. Circular Dichroism Studies of *N*-Acetyl-L-alanine *N*-Methylamide and *N*-Acetyl-L-serine *N*-Methylamide

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ABSTRACT: The simplest model compounds which include the primary structural elements of polypeptides are the *N*-methylamides of *N*-acetyl-$\alpha$-amino acids. The conformation of such compounds has been the subject of extensive experimental and theoretical study. In the present investigation, an origin-independent matrix formalism has been used to calculate rotatory strengths for *N*-acetyl-L-alanine *N*-methylamide and *N*-acetyl-L-serine *N*-methylamide as a function of conformation. In an attempt to place limits on the nature of the conformers which are present in solution, the calculated rotatory strengths were compared with circular dichroism spectra which were measured under various experimental conditions. The results of this investigation indicate that many of the conformational energy calculations which have been reported in the literature seem to yield a reasonable representation of the conformation assumed by these molecules in nonpolar, but not polar media.

## Introduction

Historically, the conformation of proteins and polypeptides has been an important area of research, with the dipeptide model playing a pivotal role. Recent work in this laboratory has been directed toward the calculation of the optical properties of proteins and polypeptides as an aid to the study of macromolecular conformation in solution. As an adjunct to such studies, it has proven useful to investigate simple model systems which simulate the interactions responsible for the specialized properties of macromolecules. Among the simplest compounds which include the essential structural elements of a polypeptide backbone are the *N*-methylamides of *N*-acetylamino acids.

These compounds have been the subject of extensive theoretical analyses by a variety of conformational energy methods,[1-24] which have indicated that their preferred conformational states can be described with the aid of a limited number of spatial forms. However, there has been disagreement as to the number and exact nature of these species.

The preferred conformational state of these compounds in solution has also been the subject of numerous experimental studies utilizing techniques such as infrared spectroscopy,[23,25-35] proton nuclear magnetic resonance spectrometry,[24,25-27,36,37] Raman spectroscopy,[38,39] measurement of dipole moment,[40,41] ultraviolet absorption