III–$CHCl_3$ show clearly the presence and effect of hydrogen bonding of I to the polymer. To a good approximation probe I behaves as if it were covalently bonded to PMMA. In DMF probe I was expected to hydrogen bond to the solvent with increasing solvent concentration. The extreme similarity between these data and PMMA–I′ makes any detailed interpretation impossible.

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References and Notes

(1) On leave of absence from Institute Ruđer Bošković, Zagreb, Yugoslavia.
(2) (a) Z. Veksli and W. G. Miller, *Macromolecules,* **10,** 686 (1977); (b) J. Fujita and A. Kishimoto, *J. Chem. Phys.,* **34,** 393 (1961).
(3) A. L. Buchachenko, A. L. Kovarskii, and A. M. Wasserman, *Adv. Polym. Sci.,* 26 (1976).
(4) P. Tormala and J. J. Lindberg, "Structural Studies of Macromolecules by Spectroscopic Methods", K. J. Ivin, Ed., Wiley, New York, N.Y., 1976, pp 255–272.
(5) P. L. Kumler and R. F. Boyer, *Macromolecules,* **9,** 903 (1976).
(6) E. L. Wee and W. G. Miller, *J. Phys. Chem.,* **77,** 182 (1973).
(7) C. C. Wu and W. G. Miller, *Macromolecules,* in press.
(8) R. P. Mason, C. F. Polnaszek, and J. H. Freed, *J. Phys. Chem.,* **78,** 1324 (1974).
(9) A. L. Kovarskii, Thesis, IKhF AN SSR, Moscow, 1972.
(10) R. P. Mason and J. H. Freed, *J. Phys. Chem.,* **78,** 132 (1974).
(11) R. P. Mason, E. B. Giavedoni, and A. P. Delmasso, *Biochemistry,* in press.
(12) A. T. Bullock, G. G. Cameron, and P. M. Smith, *Eur. Polym. J.,* **11,** 617 (1975).
(13) D. Kivelson, *J. Chem. Phys.,* **33,** 1094 (1960).
(14) K. J. Liu and R. J. Ullman, *J. Chem. Phys.,* **48,** 1158 (1968).
(15) J. F. Anderson and K. J. Liu, *J. Chem. Phys.,* **49,** 2850 (1968).
(16) W. G. Rothschild, *Macromolecules,* **5,** 37 (1972).
(17) F. Heatley and J. H. Scrivens, *Polymer,* **16,** 489 (1975).
(18) W. G. Rothschild, *Macromolecules,* **1,** 43 (1968).
(19) G. P. Rabold, *J. Polym. Sci., Part A-1,* **7,** 1203 (1969).
(20) N. Kusumoto, M. Yonezawa, and Y. Motozato, *Polymer,* **15,** 793 (1974).
(21) A. T. Bullock, G. G. Cameron, and P. M. Smith, *Eur. Polym. J.,* **11,** 617 (1975).

Diffusion of *n*-Alkanes in Poly(dimethylsiloxanes)

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ABSTRACT: Plots of *n*-alkane carbon number against diffusional friction coefficient in two dimethylsiloxanes of different molecular weight (4×10^5 and 3.5×10^4) intersect. It is proposed that diffusion of shorter *n*-alkanes is governed by free volume which is greater in the higher molecular weight polymer, while diffusion of the longer *n*-alkanes is governed by segmental relaxation speed which is greater in the lower polymer. The specific volume of the higher polymer at 100 °C is 1.102 and the coefficient of expansion is 9.98×10^{-4} $cm^3/cm^3/°C$ over the range 30 to 250 °C. The nonlinearity of the friction coefficient with *n*-alkane carbon number is confirmed.

Unusually high diffusion coefficients for *n*-alkanes in the highly viscous poly(dimethylsiloxane) gum (General Electric "SE-30") (9.5×10^6 cSt at 25 °C, mol wt = 4×10^5) relative to less viscous poly(dimethylsiloxanes) have been noted by Butler and Hawkes[1] and Kong and Hawkes.[2,3] Their work with SE-30 and General Electric "SF-96-2000" (2000 cSt at 25 °C, mol wt = 3.5×10^4) has been repeated using a more rigorous equation[4] for determining diffusion coefficients from chromatographic data. In addition, their work has been extended to include diffusivities of some higher molecular weight *n*-alkanes which they had been unable to determine.

Calculation of Friction Coefficients

The friction coefficient for a molecule at vanishingly small concentrations in the bulk of a polymer can be calculated using the equation

$$\zeta_1 = kT/D \qquad (1)$$

where k is the Boltzmann constant and D is the diffusivity of the penetrant. The diffusivities of a series of *n*-alkanes in SE-30 and SF-96-2000 at various temperatures have been determined,[4] and the friction coefficients calculated from eq 1 are listed in Table I.

Auerbach et al.[5] have suggested that the friction coefficient for *n*-alkanes in polymers is approximately linear with the chain length of the *n*-alkane. This was not found to be the case for *n*-alkanes in a variety of polysiloxanes[3] and is also inconsistent with the data in Table I which are plotted in Figures 1 and 2 and are clearly nonlinear.

The friction coefficient for a monomer unit of a polymer, ζ_0, has been shown by Ferry[6] to be approximately equal to ζ_1 for a penetrating molecule of the same size. This proposal can be shown to be consistent with data calculated here by extrapolating the log ζ_1 values at 100 °C for the lowest two *n*-alkanes in Table I linearly down to *n*-pentane. The results of this extrapolation are shown in Table II along with the ζ_0 value listed by Ferry[6] for a monomer unit for a poly(dimethylsiloxane).

Density and Expansion Coefficient of SE-30

The unusually high diffusivity of a few *n*-alkanes in SE-30 has been noted previously[1–3] and it has been suggested[3] that these high diffusivities (low ζ_1) are due to the higher free volume present in SE-30 which is evidenced by its lower density relative to the lower molecular weight poly(dimethylsiloxanes).

While a literature value was available,[1] the unusual diffusion characteristics of *n*-alkanes in SE-30 seemed to warrant an independent determination of its density and thermal expansion coefficient. Accordingly, the density of SE-30 was measured between 30 and 250 °C using a stainless steel density bottle and the results are listed in Table III.

The thermal expansion coefficient was determined by a linear regression analysis of the specific volume listed in Table III, against temperature, and resulted in the following equation for specific volume ν in cm^3/g where T is in °C, 1.002 is the specific volume at 0 °C, and 9.98×10^{-4} is therefore the thermal expansion coefficient.

Table I
Friction Coefficients for n-alkanes in SE-30 and SF-96-2000

	$\zeta_1 \times 10^9$, dyn s/cm					
	SE-30				SF-96-2000	
	50 °C	100 °C	150 °C	200 °C	50 °C	100 °C
n-Heptane	6.09				8.07	
n-Octane	7.52	4.12			9.45	4.95
n-Nonane	10.1	4.48			11.3	5.75
n-Decane	14.3	5.47			14.3	6.41
n-Undecane	23.6	6.47	3.26		19.4	7.42
n-Dodecane	46.4	9.49	3.95		30.8	9.04
n-Tridecane	92.4	15.7	4.79		53.5	11.1
n-Tetradecane		25.4	6.12	3.25		14.5
n-Hexadecane		67.2	10.0	3.91		36.8
n-Octadecane		256	23.4	5.43		114
n-Docosane			129	15.3		
n-Tetracosane				26.2		
n-Octacosane				148		

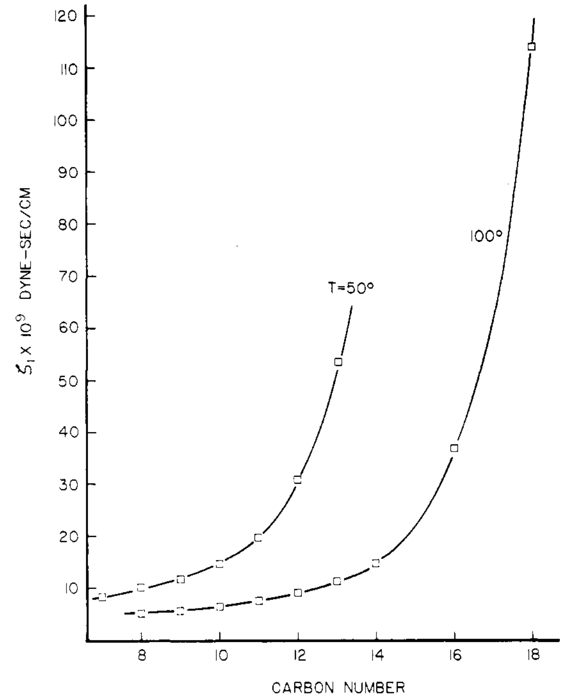

Figure 1. Translational friction coefficients for n-alkanes in SE-30

$$\nu = 1.002 + 9.98 \times 10^{-4}T \qquad (2)$$

The correlation coefficient, R, for the regression was 0.998 and the standard error for the expansion coefficient was 1.6×10^{-5} cm^3/cm^3/°C.

The density and expansion coefficient for SE-30 are compared with the literature values[7] of some other poly(dimethylsiloxanes) in Table IV. One can see that the density of SE-30 is less than all of the poly(dimethylsiloxanes) listed, which implies a higher free volume for SE-30.

Effect of Free Volume and Viscosity on Friction Coefficients

By determining friction coefficients for a greater number of n-alkanes than Kong and Hawkes did for SE-30 and SF-96-2000 and by plotting ζ_1 against carbon number on the same graph, Figure 3, one observes that the data for the two polymers cross each other. As both polymers have identical chemical structures (end group differences being negligable) energy terms will be identical or nearly so in both polymers and the differences in friction coefficient must be the result of differences in the physical properties of the polymers.

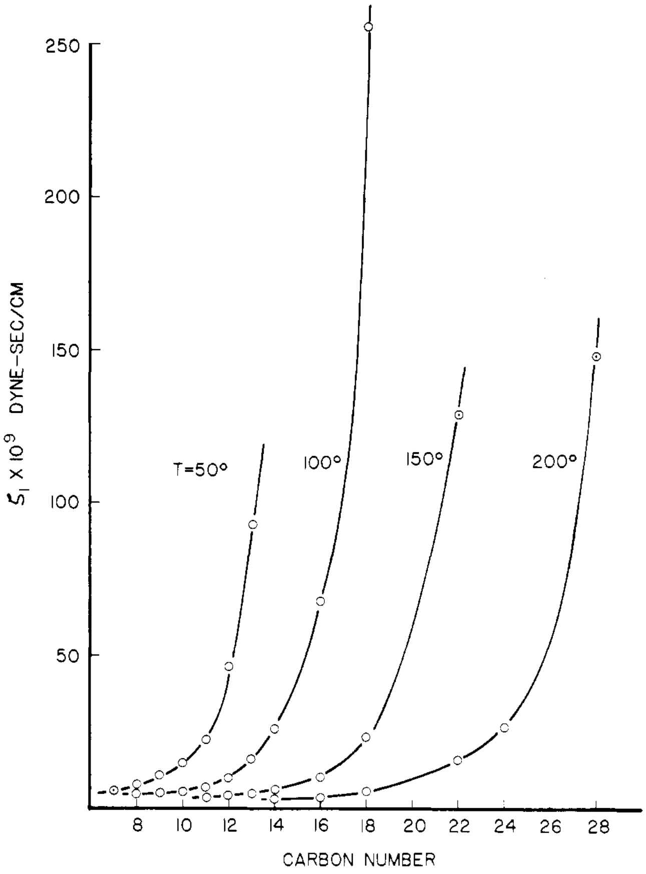

Figure 2. Translational friction coefficients for n-alkanes in SF-96-2000

The difference is easily explained for the lower n-alkanes as a result of the higher free volume of the higher polymer. As the size of the alkane increases, however, pockets of free volume become less accessible and diffusion must be assisted increasingly by thermal motions of the polymer chain. These may either be the natural motions of the polymer or may be induced by the motion of the alkane. Such motions are typical of high-frequency viscosity measurements[6] and it is known[8] that high-frequency viscosity is greater in the higher polymers although not so much higher as the regular viscosity obtained from flow measurements.

Table II
Comparison of Friction Coefficients at 100 °C

	Mol wt	ζ, dyn s/cm
n-pentane	72	
In SE-30		3.0×10^{-9}
In SF-96-2000		2.6×10^{-9}
Siloxane monomer unit	74	2.82×10^{-9}

Table III
Specific Volume of SE-30

$T \pm 1$ °C	ν, cm^3/g	$T \pm 1$ °C	ν, cm^3/g
30	1.0323	151	1.1492
50	1.0520	154	1.1555
70	1.0715	171	1.1653
90	1.0887	190	1.2006
110	1.1152	210	1.2085
130	1.1316	231	1.2137
133	1.1334	250	1.2523

Table IV
Properties of Poly(dimethylsiloxanes)

	SE-30	Viscasil 100 000	SF-96-2000	SF-96-200
Viscosity ctks at 25 °C	9.47×10^6	100 000	2000	200
Av mol wt MW	4.0×10^5	1.03×10^5	3.50×10^4	1.1×10^4
Sp gr at 25/25 °C	0.971^a	0.978	0.974	0.972
Coefficient of expansion	9.98×10^{-4}	9.25×10^{-4}	9.25×10^{-4}	9.25×10^{-4}

^{a} Calculated from eq 2 correcting for density of water at 25 °C.

We propose therefore that the higher n-alkanes diffuse more freely in the lower polymer because of faster thermal motions of the polymer chain and that lower n-alkanes diffuse more freely in the higher polymer because of its greater free volume.

It is possible that there is some contribution from self-diffusion of the polymer but as this is of the order of 10^{-9} cm^2/s in the lower polymer and 10^{-10} in the higher[9] the effect on alkane diffusion coefficients near 10^{-5} is likely to be small.

The differences in the expansion coefficients noted in Table IV could be instrumental in proving these assertions in that, below 12 °C, SE-30 would be denser than the SF-96-200 (−17 °C for SF-96-2000) and diffusion of n-alkanes of any molecular weight should be slower in the SE-30. This will be the subject of a future experimental project.

The data on which Auerbach et al. based the assertion that ζ is linear with carbon number was mostly from penetrants with carbon numbers 1 to 5, which is lower than the shortest penetrants used here and their diffusion would, if the above explanation is correct, be controlled solely by the free volume effect and not at all by the relaxation time. This suggests that the linear relation would hold as a limiting case for short-chain penetrants.

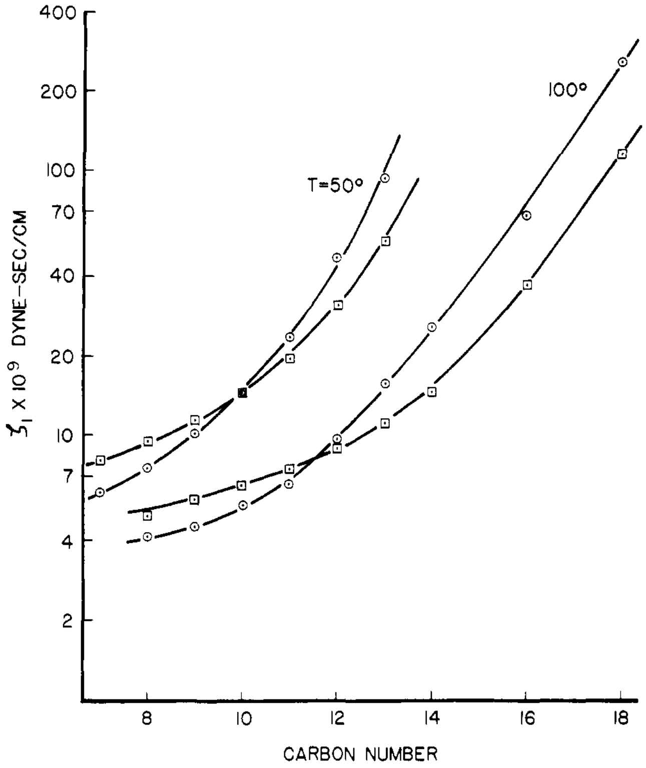

Figure 3. Translational friction coefficients for n-alkanes in two poly(dimethylsiloxanes): (⊙) SE-30; (⊡) SF-96-2000 at 50 and 100 °C.

More extensive data on better characterized polymers would provide a sensitive test of quantitative theories of diffusion: free volume can be varied by varying the molecular weight of the polymer without changing the chemical characteristics of the system or the temperature, and without using polymers below the critical molecular weight for entanglement or with substantial polymer-end or Flory–Huggins statistical effects.

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References and Notes

(1) L. Butler and S. J. Hawkes, *J. Chromatogr. Sci.*, **10**, 518 (1972).
(2) J. M. Kong and S. J. Hawkes, *J. Chromatogr. Sci.*, **14**, 279 (1976).
(3) J. M. Kong and S. J. Hawkes, *Macromolecules*, **8**, 685 (1975).
(4) W. G. Millen and S. J. Hawkes, *J. Chromatogr. Sci.*, **15**, 148 (1977).
(5) I. Auerbach, S. D. Gehman, W. R. Miller, and W. C. Kuryla, *J. Polym. Sci.*, **28**, 129 (1958).
(6) J. D. Ferry, "Viscoelastic Properties of Polymers", Wiley, New York, N.Y., 1970, Chapter 12.
(7) Technical Data Book, S-9B, General Electric Co., Silicone Products Department, Waterford, N.Y.,
(8) J. Lamb and P. Lindon, *J. Acoust. Soc. Am.*, **41**, 1032 (1967).
(9) J. E. Tanner, K-J. Liu, and J. E. Anderson, *Macromolecules*, **4**, 586 (1971).