Proton Magnetic Resonance Self-Diffusion Studies of Poly(ethylene oxide) and Polydimethylsiloxane Solutions

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ABSTRACT: Self-diffusion coefficients of poly(ethylene oxide) and polydimethylsiloxane have been determined by pulsed nmr methods. Samples with molecular weights ranging between 10^2 and 10^6 were studied in solutions containing 0.5–100% polymer. The functional dependence of polymer self-diffusion upon concentration varies with molecular weight. In low molecular weight samples, ln *D* is roughly proportional to polymer concentration. In solutions containing high molecular weight polymers, plots of ln *D* *vs.* concentration exhibit a marked upward curvature. The self-diffusion coefficients and reciprocal viscosities of the low molecular weight bulk polymers vary as $M^{-1.7}$. However, the self-diffusion coefficients do not exhibit the marked change in molecular weight dependence shown by the viscosities at higher molecular weights. This indicates that polymer entanglements influence self-diffusion and viscosity differently. The variation of polymer self-diffusion in going from a good to a bad solvent is less pronounced than the corresponding change in reduced viscosity.

Diffusion processes in bulk polymers and their solutions have attracted considerable interest during the past few decades. The diffusion of solvents into and through bulk polymers has been studied extensively. Many investigations of polymer diffusion in dilute solutions have been reported, and theories relating diffusion coefficients to polymer dimensions, viscosity, and sedimentation have been developed.[1,2]

Diffusion studies on concentrated polymer solutions have commonly followed the transport of the polymer into a solvent or into a more dilute solution. Interpretation of these results is complicated. Diffusion in such systems depends on the gradient of activity with concentration, a quantity which must be determined independently. Correction for this yields the mutual diffusion coefficient, a parameter involving the translational mobility (self-diffusion coefficients) of polymer and solvent, as well as the mass flow of the polymer. Consequently, the inherent translational mobility of the polymer is viewed indirectly in these experiments.[1,3]

The translational mobility of a molecule in the absence of concentration gradients is characterized by its self-diffusion coefficient. This, rather than the mutual diffusion coefficient, would seem to be the central parameter relevant to polymer translation in concentrated solutions. However, owing to experimental difficulties, few self-diffusion measurements of concentrated polymer solutions have been reported.[4,5]

Here we report a comprehensive self-diffusion study of polydimethylsiloxane and poly(ethylene oxide) in solutions containing 0.5–100% polymer. The measurements employed the pulsed-field-gradient modification of the nmr spin-echo technique.[6] Self-diffusion measurements are carried out more conveniently and rapidly by the nmr method than by the alternative technique using radioactive tracers. However, the nmr method is restricted to fairly large self-diffusion coefficients. Self-diffusion coefficients smaller than 10^{-9} cm^2/sec can be measured by nmr only in extremely favorable cases (where $T_2{}^2T_1 > \sim 10^{-4}$ sec^3).

Experimental Section

Sharply fractionated samples of polydimethylsiloxane (PDS) were obtained from O. K. Johannsen and R. Buch of the Dow Corning Co. They were used without subsequent purification. Some physical properties of these materials as determined in the Dow Corning Laboratory are summarized in Table I.

Samples of poly(ethylene oxide) (PEO) were obtained from Union Carbide Co. and from Hoechst AG. The low molecular weight samples had low polydispersity ($\bar{M}_w/\bar{M}_n \leq 1.1$) and were studied without further treatment. The high molecular weight PEO samples, which initially had a ($\bar{M}_w/\bar{M}_n$) ratio of order 30, were fractionated by selective precipitation. Final molecular weights and polydispersities were determined by viscometry, gel-phase chromatography,[7] and near-end-group analysis by nmr.[8] The results are given in Table II. The final polydispersity of these high molecular weight PEO samples left much to be desired; it was accepted because of the difficulty in fractionating this polymer.

The polymer solutions were prepared by mixing known amounts of solvent and polymer in standard nmr tubes. The tubes were then sealed and kept at 50–60° for 3–15 hr. A few samples were prepared without heating. No difference in the results was observed. Owing to the limited solubility of PEO in CCl_4, these measurements were made on supercooled solutions. The PEO samples were dissolved in CCl_4 at 60–70° and measured immediately after thermal equilibration at 33° in the nmr probe. PEO is degraded in CCl_4; therefore, all measurements on the PEO–CCl_4 system were performed within 2 days of sample preparation.

The proton spin-echo studies were performed on a Varian DA-60 spectrometer modified for pulsed rf output.[9] Rf pulses of order 2–4 msec were used. Most of the measurements were made with the 90–180° sequence. Rf pulse separation times were usually 100–150 msec. Rectangular field gradient pulses were applied immediately following each rf pulse. The pulses ranged up to 27 msec in length and their amplitude varied up to 100 G/cm. The most viscous solutions required use of the "stimulated echo" method,[10] employing three 90° pulses. This method was also used on several of the less viscous samples to ensure consistency in the results.

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(1) See, for example, J. Crank and G. S. Park, Ed., "Diffusion in Polymers," Academic Press, New York, N. Y., 1968, Chapter 1.

(2) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XIV.

(3) H. Fujita, *Fortschr. Hochpolym.-Forsch.*, **3**, 1 (1962).

(4) F. Bueche, W. M. Cashin, and P. Debye, *J. Chem. Phys.*, **20**, 1956 (1952), used tracer-tagged polymers to measure self-diffusion in polystyrene solutions and bulk poly(*n*-butyl acrylate). Over a limited range of molecular weight, concentration, and temperature they found the product $\eta D/c$ to be constant.

(5) A few measurements of polymer self-diffusion using spin-echo nmr have also been reported by (a) D. W. McCall and C. M. Huggins, *Appl. Phys. Lett.*, **7**, 153 (1965); (b) B. D. Boss, E. O. Stejskal, and J. D. Ferry, *J. Phys. Chem.*, **71**, 1501 (1967); (c) B. Gross, Dissertation, Technische Hochschule, Aachen, 1970.

(6) E. O. Stejskal and J. E. Tanner, *J. Chem. Phys.*, **42**, 288 (1965).

(7) M. Zinbo and J. L. Parsons, *J. Chromatogr.*, **55**, 55 (1971).

(8) J. E. Tanner and K. J. Liu, *Makromol. Chem.*, **142**, 309 (1971).

(9) J. E. Anderson, J. Steele, and A. Warnick, *Rev. Sci. Instrum.*, **38**, 1139 (1967).

(10) J. E. Tanner, *J. Chem. Phys.* **52**, 2523 (1970).

TABLE I
MOLECULAR WEIGHTS OF PDS

Designation	Property $\bar{M}_n$	 $\bar{M}_w$
PDS 1		746
PDS 2	4.6×10^3	
PDS 3	3.6×10^4	4.1×10^4
PDS 4	8.7×10^4	1.2×10^5
PDS 5		8.0×10^5

TABLE II
MOLECULAR WEIGHTS OF PEO

		Property and method		
Designation	Starting material	$\bar{M}_n$ (nmr)	$\bar{M}_w$ (viscosity)	$\bar{M}_w/\bar{M}_n$[a]
PEO 1	Carbowax 600	590		
PEO 2	Carbowax 6000	7300		1.04
PEO 3	PEGHM 100		28,000[a]	1.3
PEO 4	Polyox WSRN-750		120,000	2.4
PEO 5	Polyox WSRN-750		870,000	2.0
PEO 6	Polyox WSR-301		3,000,000	2.2

[a] Gel-phase chromatography.

An aluminum nmr probe was used in this work. Eddy currents, generated in the aluminum by removal of the field gradient, influence the echo amplitude if the second rf pulse (or the echo) occurs within 30 msec after the end of the field gradient pulse. For this reason at least 40 msec, and usually much longer times, was allowed between these pulses.

Measurements were performed at 33 ± 2°. The results were calculated relative to the diffusion coefficient of water, which is 2.7×10^{-5} cm^2/sec at this temperature.

Viscosities of solutions of PEO 1, PEO 2, and PEO 5 were measured at 33° in capillary flow viscometers.

Discussion

The pmr diffusion experiment measures the spatial displacement of protons during a time interval Δt. Typical Δt values are of the order of 0.1 sec; it is experimentally difficult to go to much shorter, or to much longer, times. High molecular weight polymers exhibit pmr self-diffusion coefficients of the order of 10^{-9} cm^2/sec in concentrated solutions. This means that polymer protons traverse a mean distance of 1.4×10^3 Å in 0.1 sec. Since this distance approaches the dimensions of a polymer coil, one must question whether segmental displacements and/or rotation of polymer molecules could influence pmr diffusion results. Both of these mechanisms clearly change the spatial positions of polymer protons during Δt. We note that the spatial displacement of polymer protons by such nontranslational processes is limited to distances comparable to the radius of gyration, the maximum value of which is 300–500 Å. Moreover, the effects of spatial displacements on spin-echo results are proportional to the square of the distance moved. Consequently, from consideration of the Δt values used in the present experiments, and the experimental self-diffusion coefficients, it appears that segmental displacement and polymer rotation play no important role in the present results. However, it seems possible to improve the pmr experiment to the point where these effects can be studied. The use of shorter diffusion times, obtainable employing gradient pulses of alternating sign,[11] could make such studies feasible.

Polymer diffusion in dilute solution is well understood. According to the theory of Flory,[2] the diffusion constant at infinite dilution is given by

$$D_0 = \frac{kT}{\eta_0 P M^{1/2}} \frac{M^{1/2}}{\langle r_0^2 \rangle^{1/2}} \frac{1}{\alpha} \tag{1}$$

where P is a numerical constant and η_0 is the solvent viscosity. $[M/\langle r_0^2 \rangle]^{1/2}$ is nearly independent of M and T. The solvent power is characterized by α, a quantity that varies as $M^{0.1}$ in a good solvent. Consequently, we expect the self-diffusion of PEO in CDCl$_3$ and the diffusion of PDS in hexamethyldisiloxane to vary as $M^{-0.6}$ at infinite dilution. These liquids are good solvents for the two polymers. The experimental data are consistent with this expectation. Note the close agreement between the present results for PEO and the results of previous studies by optical methods (Figure 1).

The concentration dependence of self-diffusion was similar for both polymers. In samples containing low molecular weight PEO or PDS, ln D is roughly proportional to polymer concentration. In solutions containing high molecular weight polymers, plots of ln D *vs.* concentration exhibit marked upward curvature (Figures 2 and 3). The functional relationship among self-diffusion, molecular weight, and concentration seems independent of the solvent power or the viscosity of the solvent used. These results indicate the molecular weight sensitivity of various polymer–polymer interactions, including chain-entanglement effects, which influence the variation of diffusion with concentration.

In this regard, it is noteworthy that the experimental self-diffusion coefficients of PEO 4 and PEO 5 appear to be concentration insensitive at high polymer concentrations. Although some upward curvature in plots of ln D *vs.* c seems reasonable in light of the other results, we believe that the complete leveling off of these curves is an experimental artifact resulting from the polydispersity of these samples. The solution viscosities of these PEO samples were observed to increase strongly with increasing polymer concentration in this region.[12] McCall and Huggins[5a] reported observations

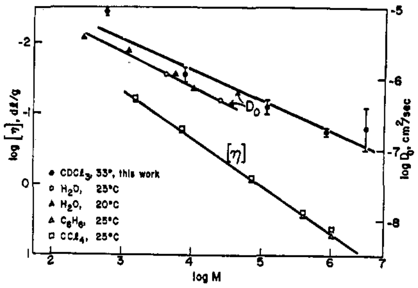

Figure 1. Intrinsic viscosities and diffusion coefficients of PEO at infinite dilution. For literature values, see ref 16, pp IV-33 and IV-100. Solvents indicated in legend. See Table II for molecular weight.

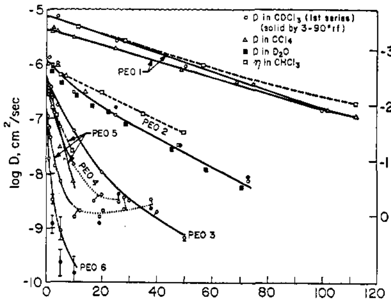

Figure 2. Self-diffusion and viscosity of PEO in solution.

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(11) B. Gross and R. Kosfeld, *Messtechnik*, 7/8, 171 (1969).

(12) The relative solution viscosities were observed rather crudely by tilting the nmr tubes and watching the relative rates of flow. The small amounts of fractionated PEO available precluded a more precise study of viscosity.

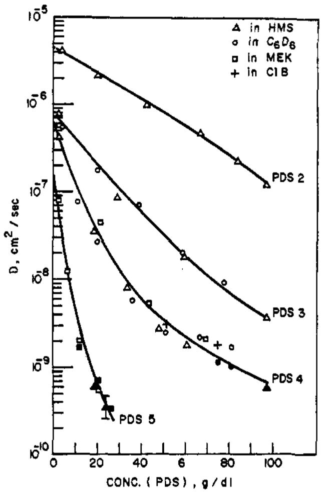

Figure 3. Self-diffusion of PDS in solution. Solvents indicated in legend. See Table I for molecular weight.

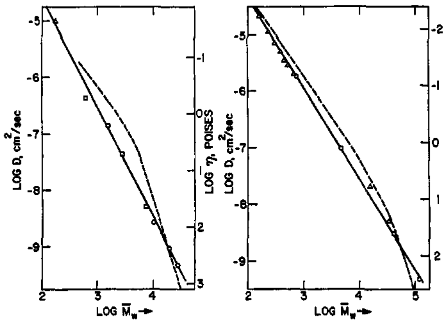

Figure 4. Self-diffusion (———) and viscosity (– – –) of PEO (left side) and PDS (right side) in bulk. Viscosities are taken from ref 17 and a private communication from Farbewerke Hoechst AG, 8261 Gendorfwerk, Germany. Measurements for PEO are in Carbowax (□) and in Hoechst material (○). The PDS measurements marked ○ are this work; those marked △ are from ref 5a.

similar to these in pmr diffusion studies of polydisperse PDS. They attributed their results to high polydispersity combined with T_2 values that decrease strongly with increasing molecular weight. Under these conditions, they showed that the nmr diffusion experiment gives high statistical weight to the diffusion of low molecular weight components, and that experimental diffusion coefficients should be anomalously large. We believe that similar reasoning can be applied to the PEO 4 and PEO 5 solutions at high polymer concentrations.[13]

We examined the relation between viscosity and diffusion predicted by the expression

$$\frac{\eta D}{c} = [\eta]\eta_0 D_0 = \frac{\phi k T}{P}\frac{\langle r_0^2\rangle}{M}\alpha^2$$

which was obtained from eq 1 in conjunction with the standard expression $[\eta] = \phi\langle r_0^2\rangle^{3/2}\alpha^3/M$.[2] P, ϕ, and $\langle r_0^2\rangle/M$ were obtained from literature values[2,14] and α was taken as unity. This yields values of $(\eta D/c)$ of 1.3×10^{-9} and 1.7×10^{-9} for PDS and PEO, respectively. The relative displacement of the viscosity and self-diffusion scales in Figures 2 and 4 are adjusted to satisfy this relation. The self-diffusion of low molecular weight PEO agrees reasonably well with that predicted from viscosity. Deviations occur at the higher molecular weight PEO 5, which may be due in part to the finite shear rate of the viscosity measurements.[15]

While viscosities of PDS in concentrated solution are not available, we may compare the total change from 0 to 100% polymer. For example, with $M = 40{,}000$, using values from Figures 3 and 4 and from ref 16 and 17, we find $[\eta]\eta_0 D_0 = 7.5 \times 10^{-8}$, and in bulk $\eta D/c = 1.2 \times 10^{-7}$ cm³. Thus the product of diffusion and viscosity changes by less than a factor of 2, while these quantities separately change by a factor of 200.

Self-diffusion and viscosity data on the bulk polymers were treated in the same way (Figure 4). For low molecular weight polymers, the experimental self-diffusion coefficients agree with those predicted from viscosity. Note that our self-diffusion results on PDS agree with those reported by McCall and Huggins.[5a] It is interesting to note the deviation between experimental and viscosity-predicted diffusion constants in bulk polymers of high molecular weight. It would appear that the self-diffusion coefficients of bulk PDS and PEO do not exhibit the marked change in molecular weight dependence typically shown by viscosities at high molecular weights[14] (see, however, ref 4). This indicates that polymer entanglements influence self-diffusion and viscosity differently.

Diffusion of low molecular weight PEO 1 is faster in $CDCl_3$, a good solvent, than in CCl_4, a poor solvent. In contrast, diffusion of high molecular weight PEO 5 is faster in CCl_4 than in $CDCl_3$. We attribute these observations to the combined effects of solvent viscosity and polymer solvation. The overall dimensions of low molecular weight PEO are relatively insensitive to good and bad solvents; consequently, this polymer diffuses more rapidly in $CDCl_3$ than in the more viscous CCl_4. At low polymer concentrations, the relative rates of diffusion are inversely proportional to the viscosities of the two solvents. The dimensions of high molecular weight PEO are much more sensitive to the solvent. In the good solvent, $CDCl_3$, the molecule is much more extended and thus encounters more resistance from the solvent. In the case of PEO 5 this effect apparently more than compensates for the lower viscosity of $CHCl_3$, so that diffusion is slower in this solvent than in CCl_4.

The variation of self-diffusion with solvent power is less pronounced than the corresponding variation in viscosity. This is shown dramatically in studies of salting out effects on self-diffusion. We found that the self-diffusion coefficients of dilute PEO 5 and PEO 6 in 0.5 M K_2SO_4–D_2O were 20% larger than those in D_2O. The intrinsic viscosities of corresponding solutions differ by 300–400%.[18] Differences between diffusion and viscosity with respect to solvent power were expected in dilute solution on the basis of Flory's work.[2] He has shown that the intrinsic viscosity is proportional to $M^{1/2+3\beta}$ and that the diffusion coefficient D_0 is proportional to $M^{-(1/2+\beta)}$ (β varies from 0 to 0.1 in going from a Θ solvent to a good solvent).

Acknowledgments. We are grateful to M. Zinbo and S. J. Hoffman for fractionating the PEO samples and performing the viscosity measurements and to R. Ullman for his valuable suggestions in the course of these experiments.

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(13) The large experimental T_2 values observed at low concentrations of PEO 4 and PEO 5 indicate that effect should not be important in these solutions.

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