Nuclear Magnetic Relaxation of Polydimethylsiloxanes in Solution

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ABSTRACT: Nuclear magnetic relaxation of solutions of polydimethylsiloxanes have been investigated in several solvents and concentrations as a function of molecular weight. The spin–lattice relaxation time, T_1, is independent of concentration in the range studied, while the spin–spin relaxation time, T_2, is a function of concentration, the effect being more pronounced for materials of high molecular weight. T_2 and T_1 differ only slightly in the limit of zero concentration. The energies of activation of both T_1 and T_2 are found to be between 2000 and 2500 cal/mol.

Nuclear magnetic relaxation of polymers takes place because of molecular motion. If the polymer molecule contains hydrogen as the only magnetic nucleus, the principal mechanism of relaxation is through the time dependent magnetic interaction between pairs of nuclear dipoles. The time dependence of the dipole field is a consequence of Brownian motion in the material. A characteristic quality of nuclear magnetic relaxation is the short range of the interaction, the statistical weight given to the contribution of a given spin pair is inversely proportional to the sixth power of the distance separating the spins.[1,2] Consequently, magnetic relaxation is a probe of molecular motion on a local scale; distances greater than 5 Å normally have an insignificant effect on the relaxation times.

The materials reported on here are polydimethylsiloxane (PDS) solutions, the magnetic nuclei present are methyl hydrogen atoms. The distance between a pair of hydrogen atoms on the same methyl group is so much shorter than the distance between hydrogen atoms on different methyl groups that the latter interactions may be completely neglected in calculating magnetic relaxation. This simplification makes it possible to set up an elementary model to use in the interpretation of the relaxation study.

The spin–lattice (T_1) and spin–spin (T_2) relaxation times are equal to a linear superposition of the Fourier transforms, $J^k(\omega)$, of autocorrelation functions, $G^k(\tau)$, of the fluctuating magnetic field.[2] In these equations,

$$T_1^{-1} = (9\gamma^4h^2/8)[J^1(\omega) + J^2(2\omega)] \qquad (1a)$$

$$T_2^{-1} = (9\gamma^4h^2/8)[(1/4)J^0(0) + (5/2)J^1(\omega) + (1/4)J^2(2\omega)] \qquad (1b)$$

$$J^k(\omega) = \int_{-\infty}^{\infty} G^k(\tau)\exp(-i\omega\tau)\,d\tau \qquad (1c)$$

γ is the magnetogyric ratio, h is Planck's constant divided by 2π, and ω is the resonant frequency of the proton.

The relaxation times obtained experimentally are averages over all hydrogen atoms on the polymer. Strictly speaking, one would expect a difference in relaxation times for those atoms near the end of the polymer chain. For sufficiently long chains the fractional contribution of end groups is negligible, and it will be assumed here that the measured relaxation times are the same for all hydrogen atoms. Experimental support for this assumption is found in the exponential decay in both T_1 and T_2 experiments.

The motion of a chemical group on a polymer molecule may be described in terms of the normal modes of motion of the molecule. However, a normal mode representation applicable to local motions of a polymer chain has not been found. In lieu of an exact model, we have formulated a simple picture based on the local geometry of a PDS molecule. This is similar in kind, but not in detail, to the procedure adopted in an earlier investigation of polyethylene oxide.[3]

A CH_3 group bound to Si, which in turn is bound to oxygen atoms, is taken to be representative of the polymer molecule. The motion of the hydrogen atoms is presumed to take place by two mechanisms—(a) rotation of the CH_3 group about the Si–C bond axis and (b) angular reorientation of the Si–C bond. The CH_3 rotation about the Si–C bond is characterized by a single rate constant since this rotational motion may take place without the cooperative motion of the rest of the chain molecule.

Borrowing from an earlier analysis of PDS,[4] and neglecting the dipole interactions between H atoms on different methyl groups, one can write

$$G^k(t) = (\chi(k)/b^6)Q(t)[1 + 3\exp(-t/\tau_0)] \qquad (2a)$$

$$\chi(0) = \frac{2}{5},\ \chi(1) = \frac{1}{15},\ \chi(2) = \frac{4}{15} \qquad (2b)$$

In this equation b is the distance between two hydrogen atoms on a methyl group, τ_0 is the characteristic hopping rate of a hydrogen atom between three equivalent rotameric–isomeric positions of the CH_3 group, and $Q(t)$ represents the time dependent reorientation of the Si–C bond.

The hindrance to methyl group rotation is known for a great many systems[5,6] though structures closely

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(1) C. P. Slichter, "Principles of Magnetic Resonance," Harper and Row, New York, N. Y., 1963, Chapters III and V.

(2) A. Abragam, "The Principles of Nuclear Magnetism," Oxford, Clarendon Press, Oxford, England, 1961, Chapter VIII.

(3) K. J. Liu and R. Ullman, *J. Chem. Phys.* **48**, 1158 (1968)

(4) R. Ullman, *ibid.*, **44**, 1558 (1966).

(5) W. H. Flygare, *Ann. Rev. Phys. Chem.*, **18**, 325 (1966).

(6) E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959).

allied to this polymer have not been studied. However, the barrier to rotation of the methyl groups of isobutylene is 2.2 kcal, and since the methyl groups on the siloxane are structurally akin but less hindered than on isobutylene, it is a safe assumption that the rotation of the hydrogen atoms about the Si–C bond is very rapid with respect to the shortest correlation time in an exponential expansion of $Q(t)$. Therefore, the final term in eq 2a plays a negligible role in relaxation, and eq 2a reduces to

$$G^k(t) = \frac{\chi(k)}{b^6}Q(t) \tag{3a}$$

$$Q(t) = \sum_p A_p \exp[-t/\tau_p] \tag{3b}$$

$$J^k(\omega) = \frac{2\chi(k)}{b^6}\sum_p \frac{A_p\tau_p}{1 + \omega^2\tau^2} \tag{3c}$$

A_p and τ_p are statistical weights and correlation times of the various modes of motion. Complete success would be obtained if the experiments made it possible to determine all A_p and τ_p. This is not a reasonable possibility under present circumstances, the best that can be expected is an estimate of some correlation times in terms of a simplified model.

Procedure

The samples of PDS and low molecular weight oligomers were obtained from O. K. Johannsen and R. Buch of the Dow-Corning Co. of Midland, Mich. Weight and number average molecular weights, determined by light scattering and osmometry at the Dow-Corning laboratories, are presented in Table I. The low molecular weight species are $(Si(CH_3)_2O)_3$, the cyclic trimer, $(Si(CH_3)_2O)_4$, the cyclic tetramer, and the linear molecule $(CH_3)_3SiO(Si(CH_3)_2O)_8Si(CH_3)_3$. The polymers and low molecular weight oligomers were dissolved in the solvents benzene, deuteriobenzene, carbon tetrachloride, chlorobenzene, and deuteriocyclohexane. The concentrations were varied from 1 g/100 ml of solvent to 20 g/100 ml of solvent. They were placed in standard nmr tubes, frozen, degassed, and thawed several times to remove the last traces of oxygen, and then sealed.

TABLE I
MOLECULAR WEIGHTS OF POLYDIMETHYLSILOXANE SAMPLES

Sample no.	M_w	M_n
S1	1.82×10^6	
S2	8.01×10^5	
S3	1.17×10^5	8.66×10^4
S4	4.05×10^4	3.58×10^4
S5		4.62×10^3

The T_1 measurements were carried out by adiabatic fast passage with sampling. The earlier experiments were done on an A-60 Varian nmr spectrometer, specially adapted for this purpose;[7] later determinations were carried out on a DA-60 Varian nmr spectrometer similarly modified. A few experiments were performed using a saturation–recovery technique.

T_2 measurements were made using a 90–180–180 Carr–Purcell spin–echo method. Cumulative errors in the pulse train were minimized using the Meiboom phase shift of the coherent pulse.[8] Both T_1 and T_2 determinations were time averaged when the signal was weak. In all experiments care was taken that only polymer protons were measured in the relaxation experiments. The hydrogen atoms in the solvents used were at resonance several hundred cycles from the methyl group on the polymer. The sampling sweep in the adiabatic passage experiments was 50 cycles wide and did not effect the solvent protons. The pulse experiments were conducted using weak pulses, typical values of the applied radiofrequency field being of the order of 30–40 mG. Signals from the off-resonance protons in the pulse experiments were eliminated by an active filter used in conjunction with phase-sensitive detection.

Results and Discussion

Experimental measurements of T_1 and T_2 of PDS polymers are presented in Table II. Briefly, the following was found.

1. T_1 of the polymer is the same in benzene and deuteriobenzene.
2. T_1 does not depend on concentration in the range studied (1–20%).
3. T_2 decreases with increasing concentration; the concentration dependence is much more pronounced for the high molecular weight materials.
4. T_1 and T_2 are only slightly sensitive to solvent in these experiments.
5. T_1 is independent of molecular weight for sufficiently high molecular weight.
6. The dependence of T_2 on molecular weight is small in the limit of infinite dilution. T_2 decreases with increasing concentration, this decrease is small for low molecular weight polymers, but is very pronounced for the high molecular weight materials.

Table III contains T_1 values for the oligomeric species studied. These are at least double that obtained for the polymers. Comparison of results obtained in benzene and deuteriobenzene shows that the effect of solvent motion on T_1 is significant in experiments with the cyclic trimer, but plays an insignificant part in the relaxation of the protons of the cyclic tetramer and the linear oligomer. T_1 of the oligomers is higher than that found for the polymer probably because of more rapid over-all rotation of the oligomer molecules. The rotation of the entire molecule does not play an important part in the relaxation of polymers of high molecular weight.

T_1 has been measured for several samples of the polymer over a range of temperature ranging from −36 to 74° in chlorobenzene and in other solvents over a narrower range in temperature. T_2 has been measured in carbon tetrachloride from −10 to 65°. The energies of activation computed from eq 4 are

$$\begin{Bmatrix} T_1 \\ T_2 \end{Bmatrix} = Ae^{-E/RT} \tag{4}$$

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[7] J. E. Anderson, J. Steele, and A. Warnick, *Rev. Sci. Instr.*, **38**, 1139 (1967).

[8] S. Meiboom and D. Gill, *ibid.*, **29**, 688 (1958).

TABLE II

T_1 AND T_2 VALUES OF PDS POLYMERS IN VARIOUS SOLVENTS AT 35°

Sample no.	Solvent	Concn	T_1	T_2
S1	C_6H_6	0.2	2.58	0.27
S1	C_6H_6	0.1	2.58	0.74
S1	C_6H_6	0.05	2.57	1.50
S2	C_6H_6	0.2	2.256	0.62
S2	C_6H_6	0.1	2.59	1.29
S2	C_6H_6	0.05	2.48	1.77
S4	C_6H_6	0.2	2.54	1.97
S4	C_6H_6	0.1	2.68	2.19
S4	C_6H_6	0.05	2.55	1.94
S5	C_6H_6	0.2	2.71	2.24
S5	C_6H_6	0.1	2.77	2.56
S5	C_6H_6	0.05	2.63	2.77
S1	C_6D_6	0.2	2.63	0.298
S1	C_6D_6	0.1		0.692
S1	C_6D_6	0.05		1.50
S1	C_6D_6	0.025	2.66	1.96
S1	C_6H_5Cl	0.2	2.22^a	0.32
S1	C_6H_5Cl	0.1		0.82
S1	C_6H_5Cl	0.05	2.38	1.57
S1	C_6H_5Cl	0.025	2.29^a	1.79
S2	C_6H_5Cl	0.08	2.18^a	
S3	C_6H_5Cl	0.2	2.36	
S5	C_6H_5Cl	0.2	2.78	
S5	C_6H_5Cl	0.05	2.52	
S1	C_6D_{12}	0.2	2.41	0.275
S1	C_6D_{12}	0.1		0.49
S1	C_6D_{12}	0.05		0.77
S3	C_6D_{12}	0.2	2.48	1.58
S3	C_6D_{12}	0.05	2.31	
S5	C_6D_{12}	0.2	2.70	2.26
S5	C_6D_{12}	0.1		2.15
S5	C_6D_{12}	0.05	2.70	
S1	CCl_4	0.2	2.44	0.21^a
S1	CCl_4	0.1		0.47^a
S1	CCl_4	0.05		1.12^a
S1	CCl_4	0.025		1.38^a
S1	CCl_4	0.01		1.43^a
S3	CCl_4	0.2		1.31^a
S3	CCl_4	0.1		1.53^a
S3	CCl_4	0.05		1.60^a
S4	CCl_4	0.2	2.32	1.54^a
S4	CCl_4	0.1		1.62^a
S4	CCl_4	0.05		1.70^a
S4	CCl_4	0.2		1.90^a
S4	CCl_4	0.1		2.02^a
S4	CCl_4	0.05		2.01^a
S4	CCl_4	0.025	2.24	

[a] Calculated from the best straight line of a log T_1 *vs.* $1/T$ plot.

TABLE III

T_1 VALUES OF SOME OLIGOMERS OF PDS AT 35°

Material	Solvent	Concn	T_1
Cyclic trimer	C_6H_6	0.05	4.95
Cyclic trimer	C_6D_6	0.10	6.15
Cyclic trimer	C_6D_6	0.05	6.04
Cyclic trimer	CCl_4	0.10	5.35
Cyclic trimer	CCl_4	0.05	4.95
Cyclic tetramer	C_6H_6	0.10	4.52
Cyclic tetramer	C_6H_6	0.05	4.52
Cyclic tetramer	C_6D_6	0.05	4.56
Cyclic tetramer	CCl_4	0.10	4.55
Linear octamer	C_6H_6	0.10	4.47
Linear octamer	C_6H_6	0.05	4.32
Linear octamer	C_6D_6	0.05	4.56
Linear octamer	CCl_4	0.05	4.97

between 2 and 2.5 kcal/mol. No systematic differences were detected as a function of molecular weight between 4×10^3 and 1.8×10^6, or of concentration between 0.025 and 0.2 g/ml. The activation energies are lower than but consistent with the low values of energy of activation of viscous flow (3.65 kcal/mol) for PDS liquid.[9] It would appear that the low values of energy of activation in magnetic relaxation are a reflection of low potential barriers to intramolecular motion and of solvent viscosity on the rotational correlation time of polymer segments. The relative importance of these two effects is yet to be established.

In Figure 1, T_2^{-1} is plotted *vs.* concentration for several PDS samples. The intercept at zero concentration is slightly dependent on molecular weight. This dependence was predicted on the basis of a Zimm–Rouse model[10] (see eq 54 of ref 10). The magnitude of the molecular weight dependence is barely beyond experimental error; further studies are needed for an unequivocal demonstration of molecular weight dependence.

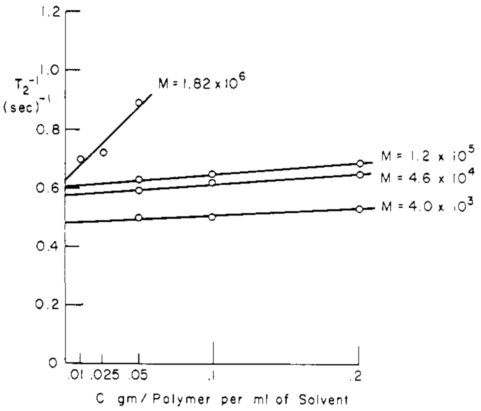

Figure 1. Dependence of T_2 of PDS on concentration and molecular weight in CCl_4 at 35°.

In the analysis of magnetic relaxation in terms of a spectrum of correlation times, it is possible to separate the correlation times into three general categories corresponding to $\omega\tau_p$ much less than, roughly equal to, or much greater than unity. If all τ_p are such that $\omega\tau_p$ is much less than one, $T_1 = T_2$. This seems to be almost true (for dilute solutions), and therefore it can be concluded that most of the correlation times satisfy this relationship. Second, T_2, particularly for the high molecular weight samples, is very sensitive to concentration, while T_1 does not vary at all. This can occur in these concentrated solutions if there exists a set of correlation times for which $\omega\tau_p \approx 1$ are insignificantly small, for if it were otherwise, a large variation

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(9) D. J. Plazek, W. Dannhauser, and J. D. Ferry, *J. Colloid Sci.*, **16**, 101 (1961).

(10) R. Ullman, *J. Chem. Phys.*, **43**, 3161 (1965).

of T_2 with concentration would lead to a smaller but definite change in T_1. Therefore the function $J^1(\omega)$ and $J^2(2\omega)$ can be calculated from eq 3c by setting the denominator equal to one, and by retaining only the short correlation times ($\omega\tau_p \ll 1$), since the longer times make no contribution, and the times of intermediate duration have been shown to be of little or no importance. T_1 may be written

$$T_1^{-1} = \frac{3\gamma^4 h^2}{4b^6}\sum{}' A_p\tau_p \tag{5}$$

The prime on that summation signifies that the sum is taken over only those correlation times where $\omega\tau_p \ll 1$. The distance between two protons on a methyl group is designated by b. It is assumed that the C–H bond distance is 1.09 Å, and the hydrogen atoms are at the vertices of a regular tetrahedron. If $\Sigma' A_p\tau_p$ is replaced by an average time $\bar{\tau}$,[9] it is found that $\bar{\tau} = 3.6 \times 10^{-12}$ sec at room temperature, assuming that the room temperature value of T_1 is 2.5. The low value of $\bar{\tau}$ is consistent with the low energy barriers to rotation about the Si–O–Si bond.

The very abrupt drop in T_2 found in the polymer of highest molecular weight (1.8×10^6) at high concentration is the same as that found for high molecular weight polyethylene oxide.[3] It is apparent from geometric considerations as well as from measurements of viscosity of molten polymer[11] that the hindrance to motion of polymer molecules because of entanglements increases with increasing molecular weight. The dependence of T_2 at high concentration as a function of molecular weight is a projection of the effect of chain entanglement on small sections of the polymer molecule. The effect of entanglement appears at a higher concentration in T_2 measurement than in solution viscosity. Since T_2 is a projection of motion on a 5-Å scale, and viscosity measures the over-all translation and rotation of the polymer molecule, a quantitative difference between "critical entanglement" points is no surprise.

Nuclear magnetic relaxation times of bulk polydimethylsiloxanes have been studied in three other laboratories.[12–14] The results of these studies are not directly comparable with our own since the intermolecular effects play an important but undetermined role in the undiluted polymer. Kusumoto, *et al.*, find energies of activation for T_1 of 1.8 and 1.9 kcal/mol. Powles and Hartland find that the energy of activation *of T_2 is higher above 90° than below, and also that the* T_2 decay is nonexponential. This last result is in accord with the determination of McCall, *et al.*, who find that the energy of activation of T_1 is 2.3 kcal. This agrees with our experiments in solution. The energy of activation of T_2 is 3.4–3.7 kcal according to McCall, *et al.*, but it is not to be expected that T_2 for undiluted PDS is closely related to that of the isolated polymer molecule. T_2 changes very much with concentration, and some correlation times which are important in the bulk polymer are undoubtedly strongly dependent on intermolecular interactions.

The magnitudes of T_1 found by McCall, *et al.*, at room temperature are about 1 sec, substantially less than that obtained for the dilute solution. Since the energies of activation are about the same, this difference between the dilute solution (2.5 sec) and the bulk polymer can be attributed to steric hindrance caused by viscosity of the medium and by interpenetration of various polymer molecules. In other words the average correlation time of segmental rotation is increased by a factor of only 2.5 as measured by a method in the megacycle region. This is surprisingly small when it is considered that the bulk viscosity changes (particularly for the high molecular weight polymer) by several orders of magnitude. The simple proportionality between segmental rotational correlation times and bulk viscosity often found in low molecular weight liquids is nonexistent in bulk polymers or in polymer solutions. The constancy of T_1 over a wide range of molecular weight and solution concentration in the PDS system is additional confirmation of this fact.

Barlow, *et al.*, have studied viscoelastic relaxation of PDS fluids in the high frequency range (4–200 Mc).[15] The maximum in absorption is not reached, and the authors estimate that the maximum in the absorption curve is above 10^9 cycles. If the average correlation time, $\bar{\tau}$, is to be determined by that maximum, it is certainly less than 1.5×10^{-10} sec. This is consistent with our determination of $\bar{\tau}$ (3.6×10^{-12} sec), but is too rough an upper bound on $\bar{\tau}$ to be useful for a quantitative comparison.

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