Nuclear Magnetic Resonance Solvent Relaxation in Concentrated Polymer Solutions

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ABSTRACT: ^{1}H and ^{2}D NMR relaxation times T_1 and T_2 of C_6H_6 and C_6D_6 have been measured in concentrated benzene solutions of isotactic PMMA. We find that T_1 is independent, but T_2 is dependent upon the molecular weight of the polymer. A possible explanation is discussed in terms of a simple model that accounts for fluctuations in the environment of the solvent molecules.

I. Introduction

Nuclear relaxation has been studied in many polymer/solvent systems. These include (a) genuine polymer solutions, e.g., polyisobutylene/benzene;[1] and (b) systems where the solvent is sorbed by a polymer matrix, e.g., collagen/water.[2] Several reviews of this work have appeared.[3–7]

On this basis of experiments, the following generalizations can be made. In dilute polymer solutions, the T_1 and T_2 of solvent nuclei are roughly identical, the extreme narrowing case. Both the solvent T_1 and T_2 decrease with increasing polymer concentration. However, T_2 drops much more than T_1. Solvent (T_1/T_2) ratios of order 100 are common at 30–50% polymer concentrations. T_1 decreases monotonically with increasing polymer concentration and remains well above its expected minimum value. The solvent T_1/T_2 difference is usually attributed to molecular exchange between "bound sites" on the polymer, where $T_2 \ll T_1$, and "free sites" in solution, where $T_1 = T_2$. Large T_1/T_2 ratios are also found when solvents are sorbed by polymers and a similar interpretation of solvent relaxation is made.[8]

The nature of "bound" and "free" solvent sites is rarely specified. In some cases, there is a reasonable basis for specific bonding between the solvent and a group on the polymer.[9] In other cases, one is left with a vague notion of sorption, and the unanswered question: What is a "free" solvent molecule in a 50% polymer solution?

The present article contains three main ideas. First, we report proton and deuteron T_1 and T_2 measurements for benzene in 30% solutions of isotactic poly(methyl methacrylate) (PMMA). Individually, these results confirm earlier findings[10,11] that the (T_1/T_2) ratio is large in this system. Collectively, they confirm the experiments of Anderson and Liu, who found a molecular weight dependence for the solvent T_2 at constant polymer concentration.[10] Second, we advance the idea of an anisotropic potential surface surrounding solvent molecules. Rather than "bound" and "free" molecules, we suggest that large (T_1/T_2) ratios may reflect the amount of anisotropy. The solvent molecules are always in the same condition, "bound" or "free", but experience different anisotropic potentials with respect to a laboratory coordinate system. Third, we show how fluctuations in asymmetry lead to a molecular weight dependent solvent T_2, while having little effect on T_1.

II. Experimental Section

Three samples of isotactic PMMA were used in our experiments that were obtained and characterized by GPC from Dr. W. Wunderlich of Röhm GmbH, Darmstadt. The molecular weight distributions were rather broad but the average weights M_w = 58 000, 220 000, and 123 000 were sufficiently different for our purpose.

For preparation of solutions, spectroscopically pure benzene and benzene-d_6 (99%) both from MERCK were used without further purification. Samples were prepared on a vacuum line directly in 10-mm diameter NMR tubes using the following procedure. Weighed quantities of PMMA and benzene were taken in separate tubes (to give 30% w/w solution of the polymer in benzene) and PMMA was degassed by pumping for several hours keeping the temperature around 120 °C. The solvent was degassed by four freeze–pump–thaw cycles. The degassed solvent was then allowed to distil over the degassed polymer and the tube was then sealed under vacuum. Low molecular weight polymers dissolved easily and gave a "homogeneous" solution within 15 min, whereas it was difficult to prepare homogeneous solutions in the case of the high molecular weight polymers. All sealed tubes were kept in an oven at 120 °C and the tubes were tilted upside down periodically for 2 days. In spite of these precautions the solvent tends to separate in small quantities at the surface in the high molecular weight samples resulting in a concentration gradient over the sample (see below).

Relaxation measurements were carried out using a Bruker SXP variable frequency pulse spectrometer. ^{1}H relaxation was measured at 90 MHz and ^{2}D at 13.6 MHz. For proton measurements the magnetic field was stabilized by an external proton lock. All measurements were made exactly on resonance.

T_2 measurements were done using the Carr-Purcell sequence in its Gill-Meiboom version. In all samples the spin–echo train was characterized by a single exponential decay. Correction for self-diffusion was made similar to the prescription of Haeberlen et al.[12] T_1 measurements were made using the 90–90 °C method.

In the high M_w polymers, it was noticed that the value of T_1 and T_2 depended on the position of the sample tube in the rf coil. We believe that these samples are not truly homogeneous and report the values of the relaxation measurements in the upper, middle, and lower regions separately. T_1 and T_2 measurements were also made of the pure solvents which corresponded with the reported values in the literature.[12] All results are summarised in Table I.

III. Theory

We now outline a "fluctuating surface" model to account for the experimental findings. A realistic, three-dimensional treatment of these ideas should be extremely complex, for we deal with coupled, concurrent fluctuations of two processes in time. However, the following model encompasses the main ideas.[13]

We begin with the influence of an asymmetric potential of the NMR line width and on relaxation. Consider only the potential surface shown on the left in Figure 1. We treat a *representative* molecule that has only two allowed directions, an "A" orientation, where a resonant nucleus experiences dipolar field H_L, and a "B" orientation, where it sees field $(-H_L)$. The depths of the two minima differ by potential energy Δ. We also require Q, the steady state probability that the molecule is in "A": $Q = \{1 + \exp(-\Delta/RT)\}^{-1}$. The mean-square local field is $\langle H^2\rangle = QH_L{}^2 + (1-Q)H_L{}^2 = H_L{}^2$. This corresponds to the rigid-lattice second moment, S_{RL}. Note that S_{RL} is independent of Δ, the energy difference between the minima. We can also compute the average local field $\langle H\rangle = QH_L + (1-Q)(-H_L) = H_L(2Q-1)$, and the mean-square deviation $D = \langle H^2\rangle - \langle H\rangle^2 = 4H_L{}^2Q(1-Q)$. Assume "jumps" or transitions between the minima with rate con-

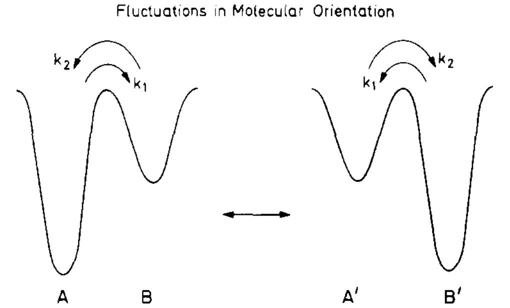

Figure 1. Assumed potential energy diagram for "fluctuating surface" model.

stants k_1 and k_2, respectively. This generates a correlation function

$$\begin{aligned}\phi(t) &= \langle H(0)H(t)\rangle \\ &= \{\langle H^2\rangle - \langle H\rangle^2\}\exp\{-(k_1+k_2)t\} + \langle H\rangle^2 \qquad (1) \\ &= 4H_L{}^2Q(1-Q)\exp\{-(k_1+k_2)t\} + H_L{}^2(2Q-1)^2\end{aligned}$$

The NMR second moment and relaxation are related to this correlation function. If $(k_1 + k_2) \gg \gamma H_L$, the experimental second moment takes on its motionally narrowed value, $\langle H\rangle^2$; note that this equals zero only when $\Delta = 0$, $Q = (1/2)$. When this is not the case, the incompletely averaged second moment corresponds to a residual line width and a short T_2. The depth of the T_1 minimum is proportional to $4H_L{}^2Q(1 - Q)$, which has a maximum (the T_1 minimum value is a minimum) when $\Delta = 0$, $Q = (1/2)$. These and other aspects of NMR reaxation *in an asymmetric potential* are discussed in an earlier paper.[14]

It is worthwhile to pause for a moment and reflect on the physical meaning of an asymmetric potential. In the extreme limit where Δ is very large, it might correspond to bonding between the solvent molecule and its surroundings, a bonding that depends on the relative orientation of the molecule and its environment. In the other limit, where Δ is small, the asymmetry might correspond to a molecular cavity that exerts some steric influence on the probable orientation of a solvent molecule. This can admit very rapid reorientational motions; $(k_1 + k_2)$ can satisfy extreme narrowing conditions, for example. However, if $\langle H\rangle$ is not averaged to zero, one obtains a nonzero second moment and a short T_2.

We now turn to the case with a fluctuation mechanism for temporally averaging the instantaneous anisotropic potential. For simplicity, we assume that the environment jumps between primed and unprimed states as shown in Figure 1 while reorientation corresponds to A ↔ B and A′ ↔ B′ transitions. The environmental transitions are decoupled from the reorientational transition. Thus, we obtain a four-site exchange

$$\begin{tikzcd}
\mathrm{A} \arrow[r, shift left, "k_3"] \arrow[d, shift right, swap, "k_1"] & \mathrm{A'} \arrow[l, shift left, "k_4"] \arrow[d, shift right, swap, "k_2"] \\
\mathrm{B} \arrow[u, shift right, swap, "k_2"] \arrow[r, shift left, "k_4"] & \mathrm{B'} \arrow[l, shift left, "k_3"] \arrow[u, shift right, swap, "k_1"]
\end{tikzcd}$$

where transitions A ⇄ B′ and A′ ⇄ B are neglected. The relations between steady state probabilities and rate constants $p_A/p_B = p_{B'}/p_{A'} = k_2/k_1$, $p_A/p_{A'} = p_{B'}/p_B = k_4/k_3$, $p_A + p_{B'} + p_{A'} + p_B = 1$, and $p_A + p_B = p_{A'} + p_{B'}$ yield $p_A = p_{B'} = Q/2$, $p_B = p_{A'} = (1 - Q)/2$, and $(k_1/k_2) = (k_3/k_4)$. Because of the last relation, we have three independent k_1 values rather than four.

In order to obtain the local field correlation function we have to solve rate equations (master equation) that can be formulated as

Table I
^{1}H and ^{2}D Solvent Relaxation Times (s) in 30% w/w PMMA Benzene Solutions

	^{1}H relaxation times		^{2}D relaxation times	
M_w	T_1	T_2	T_1	T_2
58 000	5.8	1.0	0.66	0.62
220 000	4.8	2.3		
4 123 000[a]	10.2	0.1	0.81	0.45
	8.1	0.07	0.67	0.38
	6.8	0.05	0.41	0.30
Benzene	18.5	16.8	1.5	1.5

[a] The three sets of values refer to measurements made in the upper, middle, and lower regions of the sample tube, respectively.

$$\frac{\mathrm{d}}{\mathrm{d}t}(A - B') = -(k_1 + k_3)(A - B') + (k_2 - k_4)(B - A')$$

$$\frac{\mathrm{d}}{\mathrm{d}t}(B - A') = (k_1 - k_3)(A - B') - (k_2 + k_4)(B - A') \qquad (2)$$

where, e.g., A is the probability of finding the molecule in the unprimed environment and in the A orientation at time t. The local field fluctuates between H_L and $-H_L$ where $H_L = H_L(A) = H_L(A') = -H_L(B) = -H_L(B')$. Thus the correlation function has the form

$$\begin{aligned}\phi(t) &= \langle H(0)H(t)\rangle \\ &= \sum_i p_iH_i \sum_k P_k(t/P_i(0) = 1)H_k\end{aligned}$$

where p_i is the steady state probability defined above (i = A, B, A′, B′), and $P_k(t/P_i(0) = 1)$ is the probability of finding state k at time t when state i occurred at time $t = 0$. The latter is obtained from the solution of eq 2 subject to the appropriate initial condition. The result is

$$\begin{aligned}\phi(t) = H_L{}^2(R_+ - R_-)^{-1}\{&(1 - R_+)[Q(1 - R_-) - 1]e^{-\lambda_+t} \\ &+ (1 - R_-)[1 - Q(1 - R_+)]e^{-\lambda_-t}\} \qquad (3)\end{aligned}$$

$$\lambda_\pm = \tfrac{1}{2}\{(k_1 + k_2 + k_3 + k_4) \pm [(k_1 + k_2 - k_3 - k_4)^2 + 4(k_1 - k_2)(k_3 - k_4)]^{1/2}\}$$

$$Q = \frac{k_2}{k_1 + k_2} = \frac{k_4}{k_3 + k_4}$$

$$R_\pm = \frac{k_1 + k_3 - \lambda_\pm}{k_2 - k_4}$$

Equation 3 can be evaluated numerically for given values of Q, k_1, and k_3. In the limit of slow potential fluctuations (k_1, $k_2 \gg k_3$, k_4) the correlation function becomes

$$\phi_{\mathrm{slow}}(t) = H_L{}^2[4Q(1 - Q)e^{-(k_1+k_2)t} + (2Q - 1)^2e^{-4k_3Qt}]$$

which coincides with eq 1 for a rigid potential if $4k_3Qt \ll 1$. Rapid potential fluctuations (k_1, $k_2 \ll k_3$, k_4) yield $\phi_{\mathrm{rapid}}(t) = H_L{}^2e^{-4k_1Qt}$ which coincides with eq 1 for the special case of a symmetric rigid potential, $Q = \frac{1}{2}$ and $k_1 = k_3$. Thus the molecule "sees" a symmetric average potential where the "reorientation rate" is $k' = 2k_1Q = 2k_1k_2(k_1 + k_2)^{-1}$.

IV. Discussion

Though our model treatment appears grossly oversimplified in comparison to reorientation of solvent molecules in real polymer solutions, it contains the essential features for explaining the peculiar T_1 and T_2 values in Table I and in ref 10. These results can be understood by assuming that the rate of potential fluctuations decreases with increasing polymer M_w. Presumably, this would arise from greater impediments to polymer mobility, impediments that are reflected in an increased solution viscosity and shortened polymer T_2 values as M_w is increased at constant composition.[4] Our observation that $T_1 \sim T_2$ in the low M_w polymer solutions would suggest more rapid potential fluctuations that tend to "symmetrize" the average potential. As shown in an earlier paper,[14] T_1 is relatively insensitive to an asymmetric potential. Since it is only sensitive to the nonsecular high-frequency components of molecular motion, it is insensitive to molecular weight changes unless $M_w < 10^4$.[15]

So far, nothing was said about particular spin relaxation mechanisms. Inspection of Table I shows that the proton T_2 is shortened by an order of magnitude if we compare low and high M_w solutions whereas the corresponding deuteron T_2 is shortened by a factor of 2. Since the deuteron is relaxed by the purely intramolecular quadrupole relaxation, the large effect for the proton T_2 seems to be dominated by an intermolecular mechanism. From our earlier study of PMMA–benzene solutions[10,16] the inter-benzene–polymer contribuion to the proton rate $1/T_1$ is about ⅓ of the total rate in 30% PMMA–benzene solutions. The inter-benzene–polymer contribution to $1/T_2$ should be larger and highly M_w dependent unless our measured T_2 values are influenced by different causes. It should be noted that the concentration gradient in the high M_w solution gives rise to a distribution of susceptibility shifts of the larmor frequencies. However, the resulting contribution to $1/T_2$ is very probably not larger than a few hertz and could only account for part of the short T_2. However, the experimental proton T_2 values differ in an unsystematic fashion for different PMMA samples (see Table I, and Figure 5 of ref 10) that is presently not fully understood.[17]

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Domain-Boundary Structure of Styrene–Isoprene Block Copolymer Films Cast from Solutions. 2. Quantitative Estimation of the Interfacial Thickness of Lamellar Microphase Systems[1]

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ABSTRACT: The characteristic parameters of the microdomain structure of alternating lamellae of polystyrene and polyisoprene A–B type block copolymers were estimated by small-angle x-ray scattering. Especially thickness of the domain-boundary interphase was quantitatively estimated by analyzing a systematic deviation of the scattering curves at large angle tail from the Porod's law. The experimental thicknesses of the domain and domain-boundary interphase were qualitatively in agreement with those predicted by current theories of statistical mechanics of the microdomain formation by Meier and Helfand. However, problems are still open to be clarified in quantitative comparisons of the experimentally observed thin interphase ranging from 19 to 22 Å with the thickness predicted by the current theories which assume relatively thick interphase or small value of the interaction parameter χ.

In the previous paper of this series,[2a] which will be called hereafter part 1, the microdomain structures of polystyrene–polyisoprene A–B type block copolymer films cast from toluene solutions were investigated by means of electron microscopic and small-angle x-ray scattering (SAXS) methods. The copolymers studied were those having chemical compositions giving rise to the domain structure of alternating lamellae of A and B components. It was demonstrated that the lamellae are highly oriented with their normals perpendicular to the bulk film surface (see Figures 1 to 3) and proposed that the meridional SAXS intensity distribution, i.e., the intensity distribution parallel to the lamellar normal, may be analyzed in terms of a scattering theory based upon one-dimensional paracrystal model of Blundell.[2b]