restricted in the ion-exchange resin with smaller mesh size. The activation energies of 14–16 kJ/mol compare favorably with the activation energy of 13.1 kJ/mol obtained from measurements of correlation times for 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (Tempamine$^+$) exchanged into zeolites.[21]

The EPR spectra were simulated by using the slow-tumbling program of Freed derived from the stochastic Liouville equation. The magnetic parameters used in the simulation were determined from a rigid-limit computer simulation. A_z values of 36.0 ± 0.1 G were obtained for the two resins. These values are typical of systems with hydrogen bonds. From a simulation of the EPR spectrum we can calculate the rotational correlation time of the spin-probe. In order to get an estimate of the effect of viscosity on the EPR spectra, we compared our spectra with the variable-temperature, 9.5-GHz spectra of Tempo in glycerol[31] and obtained a calibration curve to approximate the viscosity inside the resin interior.

In the high-temperature region, the slope of τ_R vs η/T is a straight line with a slope of 1.6×10^{-8} s K P^{-1}. From the slope κ is determined to be 0.016. The smallness of κ implies that the anisotropic part of the intermolecular potential is negligible. κ values are known to be small for PD-Tempone in jojoba oil and MBBA, and for ClO_2 in a variety of neat liquids[33] where the solute size is small in comparison to the solvent size. The small κ value is consistent with clathrate-type vacancies and reflects the big difference in the size of the solute molecules when compared to that of the solvent molecules. This interpretation can also be applied to the ion-exchange resins and implies that the nitroxide spin-probe is rotating in a clathrate-type environment within the interior of the ion-exchange resin.

The EPR line shapes of Tempo in Dowex 44324 (mesh 20–50) and Dowex 44339 (mesh 200–400) were virtually identical, indicating that no surface effects were observed over this range of resin size.

Acknowledgment. This work was supported by King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia, as Research Project CY/ESR/30.

Registry No. TEMPO, 2564-83-2; Dowex 44324, 113703-88-1; Dowex 44339, 113703-89-2.

Deuterium NMR Study of the Molecular Motion of Azoxybenzene Embedded in a Solid Poly(methyl methacrylate) Host

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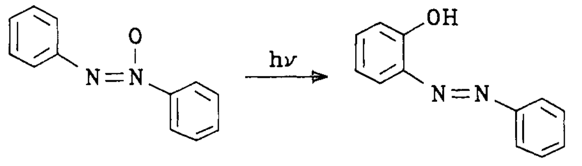
(Received: August 14, 1987; In Final Form: December 14, 1987)

Wide-line deuterium NMR has been used to study the motion of specifically labeled azo- and azoxybenzene solutes in poly(methyl methacrylate) (PMMA) over the temperature range −155 to 110 °C. In this temperature range the appearance of the spectra changes from that characteristic of static behavior on the NMR time scale to isotropic motion even 20 °C below the glass transition temperature. At room temperature the observed behavior is consistent with the independent reorientation of the individual phenyl rings about a twofold symmetry axis rather than the reorientation of the entire molecule. At all intermediate temperatures the spectra show contributions from different components: semiquantatively these components arise from more or less mobile molecules within the polymer matrix. Attempts to reproduce the spectra by theoretical simulation indicate that the solute molecules reside in a range of sites within the matrix and that, at any temperature, the spectrum is dominated by contributions from molecules whose motion is either extremely fast or very slow compared with the strength of the deuterium nuclear quadrupolar interaction. From a comparison of simulated and experimental spectra obtained as a function of time following complete saturation of the deuterium resonance, it is possible to estimate that the width of the distribution is approximately 2.5 orders of magnitude and that the center of the distribution follows an Arrhenius temperature relationship with an activation energy of approximately 40 kJ/mol.

Introduction

Previous studies in our laboratory have been concerned with the photorearrangement of azoxyarenes (**1**) to hydroxyarenes (**2**)



1 2

in poly(methyl methacrylate) (PMMA) solutions.[1,2] The quantum yield shows variations even in fluid solutions. The rearrangement of **1** to **2** occurs with a quantum yield of ca. 2×10^{-2} in ethanol;[3] in ethyl acetate, which should be a good model for PMMA, it was found to be 4×10^{-3}, and the quantum yield in PMMA was 8×10^{-4}.[2] From this information, there appeared to be some effect on the quantum yield due to changing the molecular environment from ethyl acetate to PMMA in addition to any effect of solvent polarity. It seemed reasonable to ascribe this difference to a reduction in molecular mobility in the viscous polymer matrix, and it was in an attempt to understand this phenomenon quantitatively that the present study was undertaken. However, even prior to this investigation, a different perspective on molecular mobility was evident in observations on a related system: the kinetics of the thermal cis-to-trans isomerization of azobenzene. In that case, the kinetics of isomerization in a nonpolar fluid solution were almost identical with those in PMMA.[4,5] (E_a = 87

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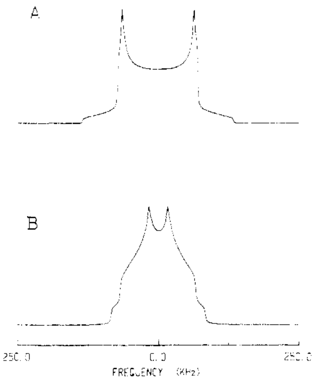

Figure 1. Two examples of simulations of deuterium quadrupolar split NMR spectra: (A) static quadrupolar spectrum for a deuteron attached to an aromatic ring where $e^2qQ/h = 179$ kHz and $\eta = 0.05$. (b) quadrupolar spectrum for rapid twofold reorientation about an axis oriented at 60° to the C–D bond direction; the effective $e^2qQ/h = 112$ kHz and $\eta = 0.6$. To compare these simulations with experimental spectra obtained using the quadrupolar echo technique, we applied the appropriate reduction of the intensity in the wings of the spectra.

kJ/mol in isooctane and 88 kJ/mol in PMMA), suggesting that the motion of the molecules was not unduly restricted. Resolving the dichotomy of these kinetic results with the photochemical observation on the reaction of **1** to **2** gave a second objective to the present work.

A common method for the study of motion at the molecular or submolecular level is wide-line nuclear magnetic resonance (NMR).[6] In the present context deuterium is the preferred nucleus for several reasons: (1) It can be easily introduced at specific sites in the molecule. (2) It has spin $I = 1$, and the resulting quadrupolar interaction reflects the time-averaged site symmetry. (3) Measurements of the spin–lattice relaxation time can determine the time scales of the molecular motions with the aid of a suitable theoretical model. (4) The spectral line widths (~170–200 kHz) are in a convenient range for modern Fourier transform spectrometers. (5) Broadening of the spectrum due to dipolar interactions with surrounding spins is small (0–1 kHz). In summary, deuterons act as an excellent probe of the local environment at specific molecular sites.

For preliminary studies, 2,2′,4,4′,6,6′-hexadeuterioazoxybenzene in PMMA was examined over the temperature range +100 to −155 °C. At the upper temperature limit, a narrow line (~5 kHz) was seen, but as the temperature was lowered below the glass transition temperature of PMMA (106 °C) the spectrum changed. At ca. 75 °C the spectrum had the appearance of two overlapping quadrupolar split powder patterns; one with a quadrupolar splitting $\nu_Q \sim 30$ kHz and the other with $\nu_Q \sim 130$ kHz. The spectrum appeared to be a superposition of the two spectra shown in Figure 1. As the temperature was lowered, the doublet having $\nu_Q \sim 130$ kHz gained in intensity at the expense of the inner doublet. Two explanations of these observations are possible. First, there could be azoxybenzene molecules in two different environments. This could occur in a bulk polymerized sample if some of the solute molecules are held immobile in highly polymerized regions of the polymer sample ($\nu_Q \sim 130$ kHz), while other molecules are reorienting about a twofold symmetry axis in pockets of unpolymerized methyl methacrylate. Second, the solute molecules may be undergoing rotation about a preferred axis. By analogy with observations on deuteriated polystyrene,[7] the rotation axis might pass through C(1) and C(4) of each phenyl ring, with each ring reorienting independently. Alternatively, the molecule as a whole may reorient about an axis passing through the 4,4′ positions. In either case, deuterons that lie off the axis (e.g., ortho ^{2}H) would show motion as the temperature was raised, while the line widths of those that lie close to the axis (para ^{2}H) would not reflect the additional motional freedom gained by the temperature increase.

To understand the motional behavior of these systems, we have synthesized specifically deuteriated azoxybenzenes and have studied their behavior in PMMA over a wide temperature range. Specifically deuteriated 3,3′-azobenzene was also synthesized to compare the ^{2}H NMR results from this symmetric molecule with those from the asymmetric azoxybenzenes. The results to be presented here are consistent with the solute molecules being in environments where motion occurs about a twofold axis through a single phenyl ring. However, the individual molecules are located in a variety of different sites in the host PMMA, giving rise to a distribution of flipping rates.

Experimental Section

Materials. Preparation of 2,2′,4,4′,6,6′-Hexadeuterioazoxybenzene. Aniline hydrochloride (5 g) was heated to reflux with D_2O (50 mL) overnight. Following neutralization, the aniline was extracted into CCl_4 and dried, and the solvent removed. The resulting incompletely trideuteriated aniline was purified by distillation from Zn dust and subsequently oxidized to azoxybenzene by using H_2O_2 (4 mL) in glacial acetic acid (25 mL).

Symmetrically Deuteriated Azoxybenzenes. The substituted nitroaniline (5 g) was dissolved with warming in a mixture of 12 mL of concentrated D_2SO_4 in D_2O (MSD Isotopes) and 22 mL of D_2O. The mixture was then cooled rapidly in a salt/ice slurry; the sulfate salt precipitated as a creamy amorphous solid. A previously cooled solution of sodium nitrite in D_2O (5.5 g in 15 mL) was then added in 1-mL increments until a test mixture (2 drops of reaction mixture/4 drops of H_2O) yielded an immediate blue on starch iodide paper. Care was taken to introduce the $NaNO_2/D_2O$ solution beneath the surface of the reaction mixture to avoid loss of nitrite by oxidative processes.

The diazotization mixture was allowed to stand on ice for approximately 10 min and then chilled hypophosphorous acid (35 mL; 35% w/v) was added in 1-mL portions ($T < 5$ °C), again with the additions being made beneath the surface of the mixture. Once the addition was complete, the flask was lightly stoppered and allowed to reach room temperature overnight, yielding a dark red-brown solution.

Approximately 100–150 mL of tap water was added to the reaction mixture, which was then filtered with gentle suction to remove solid byproducts and extracted with five 25-mL portions of CH_2Cl_2. The combined organic portions were washed with saturated sodium bicarbonate (3 × 25 mL) and then with water, dried over $MgSO_4$, and filtered, and the CH_2Cl_2 was removed under reduced pressure. The oily residue was then loaded onto a 1-in. × 4-in. column of neutral alumina and eluted with CH_2Cl_2 (200 mL).

After evaporation of the CH_2Cl_2, the residue was transferred to a 10-mL round-bottom flask and distilled, affording ca. 2 g of pure nitrobenzene-d_1. The deuteriated azoxybenzenes were prepared from the corresponding deuteriated nitrobenzenes by thallium reduction[8] and recrystallized from absolute ethanol. NMR (400 MHz, $CDCl_3$): 2,2′-dideuterioazoxybenzene δ 7.35–7.6 (m, meta + para, rel intensity 3.0), 8.15–8.35 (m, ortho, rel intensity 1.1); 3,3′-dideuterioazoxybenzene δ 7.35–7.6 (m, meta + para, rel intensity 1.0), 8.15–8.35 (m, ortho, rel intensity 1.2); 4,4′-dideuterioazoxybenzene δ 7.45–7.55 (t, meta, rel intensity 1.0), 8.15–8.35 (m, ortho, rel intensity 1.1).

*Preparation of 3,3′-Dideuterioazobenzene (**6**).* This compound was prepared from 3,3′-dideuterioazoxybenzene by the method of Vogel,[9] only by using one-twentieth of the scale stated. Prior to recrystallization, the crude azobenzene was chromatographed on neutral alumina (1-in. × 4-in. column), eluting with CH_2Cl_2. Collection and concentration of the orange band afforded an

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orange–red oil. Recrystallization from a 1:12 mixture of H_2O/95% ethanol gave 0.13 g of **6**: mp 58.5–60 °C; NMR (400 MHz, $CDCl_3$) δ 7.45–7.6 (m, meta + para rel intensity 1.1), 7.9–7.95 (m, ortho, rel intensity 1.0).

Polymerization of the Deuterium-Labeled Sample into PMMA. The monomer was purified by removing the inhibitor with aqueous NaOH/NaCl solution,[10] dried ($CaCl_2$), and filtered. Labeled azoxybenzene (or azobenzene) (150 mg) was dissolved in 1 mL of the purified monomer, and a few milligrams of benzoyl peroxide were added as an initiator. The mixture was put into a Pyrex tube (i.d. 8 mm, o.d. 10 mm), corked, and placed in the dark in an oil bath at 50 °C. The temperature was increased over the course of 1 week to 80 °C and then maintained in the dark at 80 °C for another 2 weeks. The polymerized sample was removed from the bath, the tube was broken, and the polymer pellet was removed.

NMR Measurements. The deuterium NMR spectra were obtained by using a home-built spectrometer and a superconducting magnet operating at 6.3 T (270 MHz for protons). The NMR signal was collected by using a digital oscilloscope (Nicolet Model 2090) that was interfaced to an IBM/pc. Software written specifically for the spectrometer not only allowed the collection of the free induction decay signal and subsequent Fourier transformation to obtain the spectrum but also control of the sample temperature and pulsing of the spectrometer so that data collection over the period of several days could take place under computer control. The quadrupolar echo[11] pulse sequence

$$(\pi/2)_x\text{–}\tau\text{–}(\pi/2)_y\text{–}\tau\text{–acquire}$$

was used to obtain the spectra. Because of the broad NMR lines found particularly at low temperatures, it was often necessary to use spectral widths as large as 500 kHz, and special care was taken to minimize[12] the distortion of the spectra. Typically the $\pi/2$ pulse width was 3 μs and the separation between the pulses, τ, was 45 μs. Even with radio frequency pulses as short as 3 μs, the intensity of the signal in the wings of the spectra was significantly reduced from the true value.[13] Several simulations of the experimental spectra were carried out, and for a fair comparison to be made, the simulated intensity in the wings was given the same reduction as predicted for the experimental spectra on the basis of the applied pulse width. Spin–lattice relaxation time measurements were made by initially saturating the entire broad-line spectrum by using a sequence of 10–20 short (2 μs) pulses[14] and then waiting a variable length of time before measuring the amplitude of the nuclear signal. Measurements of the signal amplitude were made by using the quadrupolar echo technique for typically 15 different delay times between the saturating sequence and the subsequent quadrupolar echo.

The sample was held within a thick-walled copper container to eliminate any temperature gradients. The sample temperature could be read to within 0.1 °C and was electronically regulated to approximately 0.2 °C over the period of time needed to obtain a spectrum or relaxation time measurement.

Deuterium NMR Spectra. The nuclear Zeeman and electric quadrupole interactions determined the observed deuterium NMR spectral line shape. Because the Zeeman energy is very much larger than the quadrupolar energy for deuterons, the nuclear energy levels need to be determined only to first order in the quadrupolar interaction. The shifts in the Zeeman energy levels due to the static part of the quadrupolar interaction are

$$E_m = (\hbar\omega_Q/6)[3m^2 - I(I+1)] \tag{1}$$

where the strength of the quadrupolar interaction is

$$\omega_Q = [3e^2qQ/(4I(2I-1)\hbar)][(3\cos^2\Theta - 1)/2 + \eta(\sin^2\Theta\cos 2\Phi)/2] \tag{2}$$

The orientation of the principal axis of the electric field gradient (EFG) tensor with respect to the applied magnetic field is given by the angles Θ and Φ. In the principal axis system the EFG tensor (V_{ij}, $i,j = x,y,z$) can be described in terms of two parameters:

$$eq = V_{zz} \qquad \eta = (V_{xx} - V_{yy})/V_{zz} \tag{3}$$

where $V_{zz} > V_{xx} > V_{yy}$. The parameters eq and η are the maximum component of the EFG tensor and the asymmetry parameter. The parameter eQ is the nuclear quadrupole moment, and e^2qQ/h is the quadrupolar coupling constant. When the EFG is at a particular orientation with respect to the applied static magnetic field for all the ^2H nuclei, the NMR spectrum is a doublet whose components are separated by the quadrupolar splitting:

$$\Delta\nu_Q = \omega_Q/2\pi \tag{4}$$

In a powder sample all values of Θ and Φ occur, giving rise to the characteristic quadrupolar powder pattern spectrum. Two examples are shown in Figure 1.

For deuterons bonded to carbons on an aromatic ring, the electric field gradient is almost axially symmetric along the C–D bond. For example, in solid benzene at low temperature, the quadrupolar coupling constant is 177 kHz and the asymmetry parameter is 0.041,[15] while in solid phenylalanine at −173 °C, e^2qQ/h = 180 kHz and η = 0.05.[16] If there is any significant line broadening due to the dipolar interaction between the nuclear spins or due to molecular motion, the nonzero asymmetry parameter is very difficult to detect from the powder pattern spectrum (see Figure 1A).

If there is any motion of the C–D bond with respect to the direction of the applied magnetic field, both the observed coupling constant and asymmetry parameter are affected.[17-21] For the case where the static electric field gradient is axially symmetric the factor $(3\cos^2\Theta - 1)/2$ in eq 2 must be replaced[22] by

$$(3\cos^2\beta - 1)(3\cos^2\delta - 1)/4 + 3[\sin 2\beta\sin 2\delta\cos(\Gamma + \sigma) + \sin^2\beta\sin^2\delta\cos 2(\Gamma + \sigma)] \tag{5}$$

where β is the angle between the C–D bond and the axis about which the reorientation takes place. The angles δ and Γ define the orientation of the flipping axis in the laboratory frame of reference, while σ is the flipping angle. When the molecular motion is rapid compared with the spectral width, it is only necessary to average eq 5 over the possible values of the flipping angle σ. In these circumstances an effective coupling constant and asymmetry parameter can be defined. When the motion about the axis of reorientation has threefold or higher symmetry, the effective asymmetry parameter is 0 and the resulting powder pattern spectrum shows axial symmetry. In the special case of twofold reorientation,[16,23-28] an asymmetric pattern results, and

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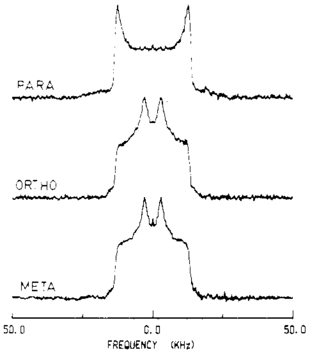

Figure 2. Experimental NMR spectra for deuterons selectively placed at the three different positions on the aromatic ring. The spectra were obtained by using the quadrupolar echo sequence with 3.0-μs pulses and a pulse separation of 50 μs at 20 °C.

an asymmetry parameter can be defined in addition to the quadrupolar coupling constant. The flipping of a six-membered ring about the para axis leads to asymmetric powder patterns for deuterons in the ortho and meta positions as shown in Figure 1B. The effective coupling constant is reduced from the static value by a factor of 0.625 and the effective asymmetry parameter is 0.6.

Results and Discussion

Deuterium NMR Spectra at Room Temperature. Figure 2 shows the deuterium NMR spectra taken at room temperature for three different samples containing azoxybenzene molecules selectively deuteriated in the three positions around the ring. The para spectrum appears to be nearly axially symmetric, with a quadrupolar coupling constant equal to 180 kHz, a value expected for a rigid C–D bond attached to an aromatic ring. It is not possible to determine the asymmetry parameter because of broadening of the peaks, probably due to the dipolar interaction with surrounding protons. The ortho and meta compounds give asymmetric spectra that can be simulated by using a twofold reorientation model in which the motion takes place about an axis inclined at an angle of 60° to the C–D bond. The simulated spectrum is shown in Figure 1B. The immediate conclusion is that at room temperature there is rapid reorientation of the phenyl rings about a twofold axis. However, the NMR spectra do not allow the distinction between reorientation of the molecule as a whole (where the twofold axis passes through the 4,4′ positions and hence almost through the 4,4′ deuterium substituents) and the alternative motion of a single phenyl ring relative to the rest of the molecule.

Spectra of 3,3′-dideuterioazobenzene at room temperature and below are indistinguishable from those for either the ortho- or meta-deuteriated azoxybenzene samples. The two phenyl rings are equivalent in azobenzene but not in the asymmetric azoxybenzene molecule. In the PMMA host, however, the similarity of the spectra over a wide temperature range suggests that the motion of the two phenyl rings is the same in either molecule.

Molecular orbital calculations were carried out in an attempt to estimate the activation barrier for the single phenyl "flip" process. This was done by calculating the difference in energy between the fully planar molecule and a geometry in which one phenyl ring was rotated 90° out of the plane. With use of the geometry corresponding to the crystal structure,[29] both the MNDO and the extended Hückel methods indicated an activation energy for phenyl rotation of <3 kJ/mol, which is negligible. Changes of ±5° in the N=N–C and C–C–N bond angles afforded similar results, showing that the barrier is not sensitive to the initial geometry. While we place little reliance on the actual value calculated for the barrier, the prediction of a small barrier to phenyl rotation is consistent with the observation that in solution the phenyl groups of ortho-substituted azobenzenes rotate easily to minimize steric hindrance, i.e., without substantial loss of conjugation energy.[30] Consequently, we believe that the calculations are at least consistent with the observed NMR behavior being due to the phenyl flipping motion.

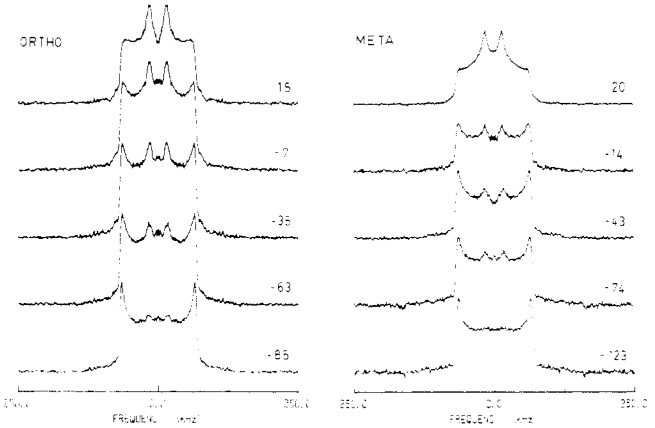

Figure 3. Experimental NMR spectra for selectively deuteriated samples as a function of temperature. At the high- and low-temperature extremes, the rapidly reorienting and static conditions are observed. The spectra at the intermediate temperatures appear to be superpositions of the two extremes, with the proportions of each changing as a function of temperature. Because the spectra are symmetric, folding about the center frequency has been applied to improve the signal-to-noise ratio.

A consideration of possible axes of twofold reorientation of the azoxybenzene molecule within the polymer matrix also suggests that the phenyl rings reorient separately. It is reasonable to assume that when the molecule flips through 180° it takes up a position in the polymer matrix that minimizes the volume occupied in the two possible orientations. The axis of reorientation is then at an angle of ~10° with respect to the para C–D bond. Although the motion of the para C–D bonds would still not be observable according to our simulations, the existence of an axis of this kind should have an observable effect on the spectra of the ortho and meta isomers, because each of the two ortho (or meta) deuterons becomes inequivalent when averaged over the motion. One of the pair (either meta or ortho) reorients so that the C–D bond is at ~47° with respect to the axis of reorientation while the other C–D bond is at an angle of ~68°. If such a model for the motion were correct, the deuterium NMR spectra would reflect the motion and be quite different from what is observed. On the basis of the above arguments, we favor the interpretation of the motion being due to the single phenyl reorientation process.

Deuterium NMR Spectra at Low Temperature. It is expected that as the temperature of the sample is reduced, the twofold reorientation of the azoxybenzene will slow. At sufficiently low temperatures, only the static deuteron quadrupolar powder pattern will be observed at all positions on the aromatic ring. Figure 3 shows representative spectra for deuterons at both the ortho and meta positions as a function of temperature in the region below 20 °C. In both cases there is a gradual evolution from the asymmetric spectra characteristic of rapid twofold reorientation to the static, nearly axially symmetric pattern, with the same width as that found for the para position. The spectra at the intermediate temperatures appear to be superpositions of the static spectra found at low temperature and the spectra from rapidly reorienting molecules found at high temperature.

In principle, details of the dynamics of molecular motion[31] can be determined from the powder patterns in the intermediate temperature region. Figure 4 displays a sequence of simulated spectra calculated for twofold reorientation[32] as a function of the rate of flipping of the ring. The spectra are appropriate for either the ortho or meta position where in each case the angle between

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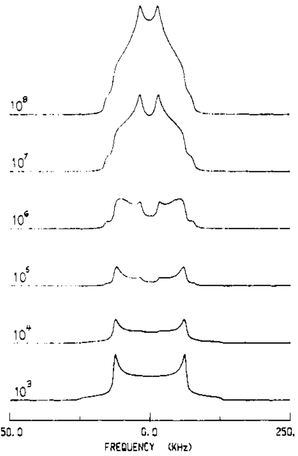

Figure 4. Simulations of deuterium NMR spectra derived from a model for twofold reorientation about the para axis as a function of the flipping rate constant, k, in s^{-1}. Notice the loss in intensity when $k \approx \omega_Q$.

the C–D bond and the axis of reorientation is 60°. So that the observed spectra may be compared with the simulated, the calculated spectra explicitly include the use of the quadrupolar echo pulse sequence with a separation between the pulses equal to 50 μs and of the distortion due to the finite width of the radio frequency pulses used to excite the nuclear spin system. Even so, there is little similarity between the observed and simulated spectra in the motional region between the static and rapidly reorienting cases. The characteristic loss in intensity seen when the rate of molecular motion is of the same order of magnitude as the strength of the quadrupolar interaction is not observed for azoxybenzene embedded in PMMA. The observed spectra therefore cannot be explained just in terms of twofold reorientation of the phenyl rings where all the molecules are assigned a single temperature-dependent jump rate.

Inspection of the spectra for both the ortho and meta positions in the intermediate temperature region suggests that the spectra are superpositions of the rapidly flipping and static spectra. A somewhat similar situation has been observed in L-phenyl-d_5-alanine,[33] where the percentage of fast-flipping component depended on the conditions of crystallization of the sample. As the temperature of the azoxybenzene sample is lowered, there appears to be a monotonic increase in the percentage of static as compared with rapidly flipping molecules. Since the percentage of crystalline as opposed to amorphous regions is not likely to be a function of temperature, at least in the temperature region below 20 °C, the observed superposition does not arise from the morphology of the sample. One possible explanation of the observed spectra is that the azoxybenzene molecules reside in a variety of sites provided by the host PMMA. The result is that the concept of a single flipping or jump rate describing the reorientation is not valid, but instead there is a distribution of jump rates. For each particular molecule there is a well-defined potential barrier to reorientation, and for that molecule the transformation from the rapidly flipping to static state occurs over a relatively small temperature interval. However, for the sample as a whole there is a distribution of molecular reorientation rates. In an attempt to simulate the observed spectra, a log Gaussian[34] distribution of jump rates having the form

$$P(k) = (h/(2\psi k)) \exp[-h^2(\ln (k/k_0))^2] \qquad (6)$$

was used. The parameter h determines the width of the distribution, while k_0 is the central jump frequency. By superimposition of the spectra[35] for twofold reorientation as shown in Figure 4 with the weighting determined by eq 6, simulations of spectra resulting from a distribution of jump frequencies were obtained as shown in Figure 5. A comparison of Figures 3 and 5 shows that the simulations are capable of reproducing the essential features of the experimental spectra. The exact width of the distribution could not be determined very precisely by a comparison of the experimental and simulated spectra since values of h between 0.1 and 0.2 all gave satisfactory results and only allow h to be bracketed within this range. If $h > 0.2$, the distribution is too narrow, and simulations similar to those shown in Figure 4 for jump rates of 10^5 and 10^6 s^{-1} result, contrary to experimental observation. As will be explained in more detail, if $h < 0.1$, the distribution is so wide that molecules with spin–lattice relaxation times near the T_1 minimum (where the jump rate $\approx 2.4 \times 10^8$ s^{-1}) always dominate the spectra, and the spectral shape changes little with changes in central jump frequency. A log Gaussian distribution with $h = 0.15$ has a full width at half maximum equal to ≈2.5 orders of magnitude.

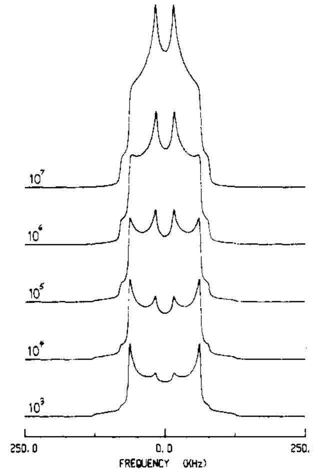

Figure 5. Simulations of the deuterium NMR spectra assuming a log Gaussian distribution of flipping rates. The width parameter, h, of the distribution was taken to be 0.15, and the central frequencies expressed in s^{-1} are indicated in the diagram.

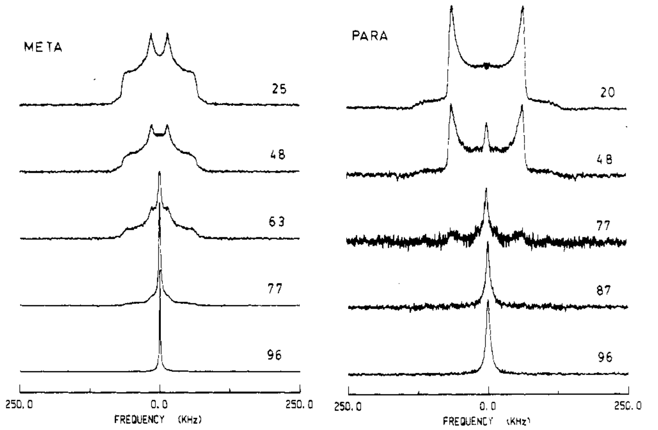

Figure 6. Experimental deuterium NMR spectra for the para and meta positions at temperatures approaching the glass transition. The narrowing of the spectra into a single narrow peak is indicative of rapid isotropic reorientation of the azoxybenzene molecule. Notice that this motion sets in well below the glass transition temperature, which is 106 °C for PMMA.

Simulations of the ortho spectra show that the central frequency, k_0, of the jump-rate distribution increases from 10^2 to 10^7 s^{-1} over the temperature range from −85 to 57 °C. The parameter k_0 has a roughly Arrhenius temperature dependence, and from a plot of ln k_0 versus reciprocal temperature an estimate of the activation energy of 40 ± 5 kJ/mol was obtained.

Deuterium NMR Spectra at High Temperature. As the temperature of the sample is increased toward the glass transition of the host PMMA (T_g = 106 °C), the deuterium quadrupolar powder pattern line shape for each position on the aromatic ring collapses into a single narrow peak as shown in Figure 6. The

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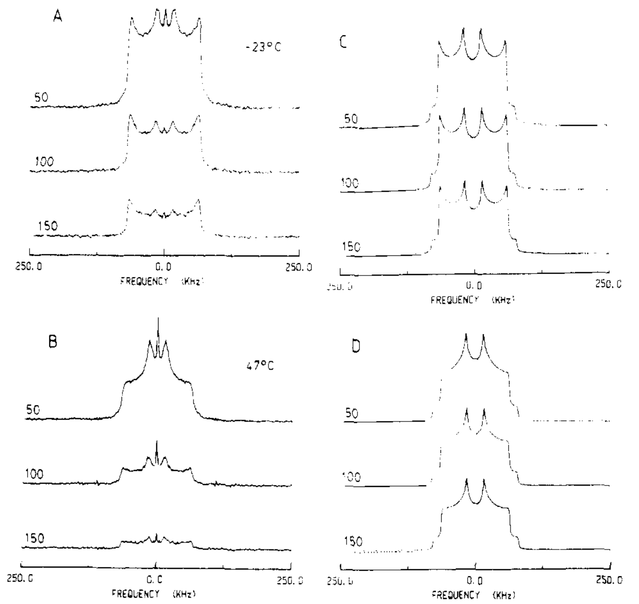

Figure 7. Simulations and experimental spectra obtained by using three different separations between the pulses in the quadrupolar echo sequence. The separations are expressed in microseconds, and the results for two temperatures are shown. The simulations use a log Gaussian distribution of jump rates with width parameter $h = 0.15$ and central jump frequencies indicated in the diagram. The simulations are unable to reproduce the rapid decay in the signal amplitude observed experimentally.

molecular motion of the azo- or azoxybenzene molecule just below and above the glass transition averages the electric field gradient at each of the deuteron sites to 0. Therefore, in the temperature region near the glass transition there is sufficient free volume within the host structure to allow the solute molecules to reorient isotropically. The collapse of the quadrupolar splitting into the narrow line probably indicates the onset of the glass transition in these samples. It is interesting to note that the isotropic reorientation begins 10–20 °C below the glass transition for pure PMMA. Because the bulk polymerization of the sample was carried out at ~84 °C, the samples were not completely polymerized.[36] The unreacted monomer acts as a plastisizer, reducing the effective glass transition temperature.

Dependence of the Spectra on Pulse Separation in the Echo Sequence. Figure 7A displays experimental spectra for three different values of the separation between the two pulses in the quadrupolar echo sequence at two different temperatures. At the higher temperature the total signal amplitude decays more rapidly with separation, but in both cases the two peaks in the center of the pattern decay more rapidly than the edges of the spectra. In the situation where the twofold molecular reorientation occurs with a unique jump rate, k_u, the signal amplitude decays most rapidly when $k_u \approx \omega_Q$. At the extremes when $k_u \gg \omega_Q$ and $k_u \ll \omega_Q$, there is little change in the spectra with pulse separation for times of the order of 100 μs. Simulations of the spectra calculated by using a log Gaussian distribution of jump rates are shown in Figure 7B. A comparison of the simulations and experimental spectra in Figure 7 indicates that while changes in the spectral shape with pulse separation can be reproduced, the relative amplitudes of the simulated spectra do not agree with experiment. As noted previously, when there is a distribution of jump rates, the spectra appear as a superposition of spectra arising from the very rapidly and very slowly reorienting molecules. The simulations therefore are unable to reproduce the observed rapid decay of the signal with pulse separation. In particular the central peaks due to molecules having $k \gg \omega_Q$ do not decay rapidly enough to match experiment. The model for the molecular reorientation used in the simulations does not take into account the isotropic motion observed in the spectra at high temperature. The rapid decay of the spectra with pulse separation in the temperature region from 20 to 60 °C where $k \gg \omega_Q$ may be a result of the isotropic motion becoming an important relaxation mechanism.

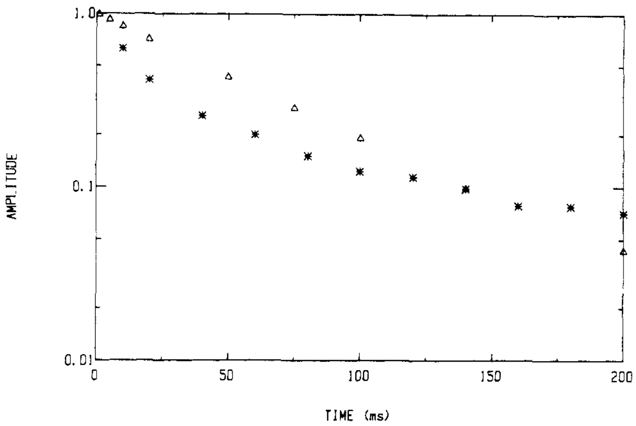

Figure 8. Comparison of experimental (*) and theoretical calculations (Δ) of the spin–lattice relaxation. The entire spectra were integrated as a measure of the signal amplitude. While the theory predicts a nonexponential decay, the deviation from an exponential behavior is small as compared with the experimental data taken from spectra for the ortho position at 15.0 °C.

Deuterium Relaxation Time Measurements. At all temperatures from −70 to 50 °C, the recovery of the equilibrium magnetization was found to be nonexponential, and spectra recorded at various times following complete saturation of the resonance had different line shapes. An example of the nonexponential recovery of the magnetization is indicated in Figure 8. Torchia and Szabo[37] have shown that nonexponential relaxation is characteristic of the recovery of the nuclear magnetization for a variety of models for molecular motion. This is because the relaxation rate depends explicitly on the orientation of the axis about which the motion takes place with respect to the applied magnetic field. In a powder sample, where all possible orientations of the axis occur, each segment of the powder pattern spectrum corresponds to a particular combination of the angles δ and Γ in eq 5. The experimentally determined relaxation time will depend on the portion of the NMR spectrum used as a measure of the NMR signal amplitude in the course of the measurements. For the two-site jump model, which is appropriate for the description of the reorientation of an aromatic ring, nonexponential recovery is expected to be observed except when the angle $\delta = 0°$ and $90°$ or when there is very rapid reorientation; $k \gg \omega_0$. To determine whether the observed nonexponential behavior was a result of the angular dependence of the relaxation, we simulated a sequence of spectra, each having a different delay time after the initial saturation of the resonance, taking into account the dependence of T_1 on the angles δ and Γ. The simulation assumed a single reorientation rate ($k_u = 10^7$ s^{-1}) for all molecules in the sample. At this jump rate $k_u \ll \omega_0$, and the theory predicts an angular dependence of T_1. Experimentally the entire spectrum was integrated and used as a measure of the NMR signal amplitude. The same procedure was applied to the simulated spectra, and the resulting data are shown in Figure 8. The deviation from exponential behavior is small over the first 1.5 orders of magnitude of the recovery of the equilibrium amplitude. The experimental data reveal a much more pronounced curvature on the semilogarithmic plot, suggesting that the observed nonexponential recovery must arise from a mechanism other that the intrinsic angular dependence of T_1.

From Figure 9A it can be seen that there is a much slower recovery of the edges of the spectra as compared with the center of the spectra. This behavior can be understood if there is a distribution of flipping frequencies for the solute molecules in the PMMA host, as suggested by the analysis of the temperature dependence of the NMR spectra. The spin–lattice relaxation rate

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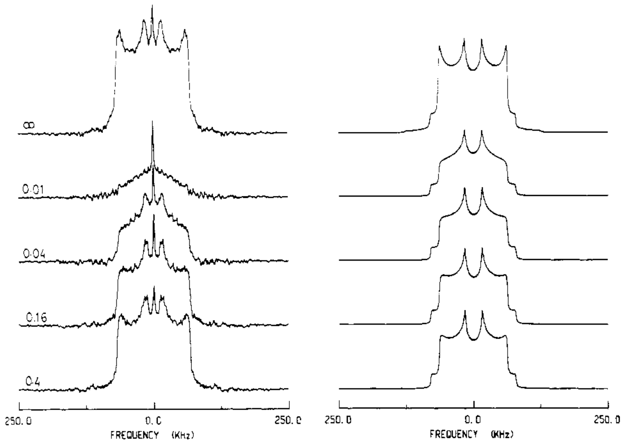

Figure 9. Comparison of simulations for the spin–lattice relaxation using a distribution of jump rates and experimental data. The experimental data are for the ortho-deuteriated sample at −16.0 °C. The delay times following saturation of the resonance are expressed in seconds. The simulations used a log Gaussian distribution of reorientation rates with a width parameter $h = 0.1$ and central frequency $k_0 = 10^4$ s^{-1}. While some features of the spectral line shapes could be reproduced, the delay times did not match the experimental values.

as a function of the molecular reorientation rate goes through a maximum when $k \approx \omega_0$ (2×10^8 s^{-1}) and decreases rapidly on either side of the maximum. The outside edges of the spectra arise from molecules having a slow jump rate ($k \approx 10^3$ s^{-1}) and long relaxation times, while the center comes from molecules with $k \approx 10^7$ s^{-1} and short relaxation times. Figure 9B is an example of a simulation of the recovery of the equilibrium amplitude with a distribution of jump rates. The simulation is able to reproduce the general trends in the evolution of the line shape. In particular, the more rapid recovery of the central region of the spectrum as compared with the outside edges is reproduced, but there are differences between the simulation and experimental results. The spectra shown in the simulation were chosen to match the experimental line shapes, but the delay times after the saturation of the resonance do not match the experimental values. The relaxation times used in the simulations were calculated by using the formula derived by Torchia and Szabo for two-site reorientation but averaged over the powder pattern. All attempts made by using the relaxation rates determined from theory and varying the width, h, and central jump frequency, k_0, of the jump-rate distribution were unable to match both the experimental line shapes and delay times. The inability to match the simulations with experiment may be an indication that the model for the molecular motion is not sufficiently refined. There are several avenues that could be explored, such as the addition of other spin–lattice relaxation mechanisms, the introduction of a temperature-dependent width to the jump-rate distribution, or the substitution of a more complex distribution function for the jump rates.

Conclusions

We have found that the ^{2}H NMR spectra of deuteriated azo- and azoxybenzene in PMMA are explicable in terms of twofold reorientation of the molecules in the polymer matrix rather than in terms of different molecules finding themselves in regions of the polymer that are more or less crystalline. We strongly favor assigning the reorientation process to motion of the individual phenyl rings about a twofold axis passing through C(1) and C(4). Because of the heterogeneity of the solute sites in the PMMA host, there is a wide distribution of reorientation rates for individual molecules at any temperature. Simulations of the spectra collected below 60 °C suggest that this distribution of reorientation rates is approximately 2.5 orders of magnitude, but the activation energy for reorientation of a phenyl ring in the "average" site is approximately 40 kJ/mol. Above 85 °C, a temperature still well below T_g of PMMA, completely isotropic motion is possible, and only a single narrow NMR resonance is observed.

Finally we return to the observations that gave the original impetus to this work. These were (1) the lowered quantum yield for the photorearrangement of azoxybenzene to 2-hydroxyazobenzene in PMMA compared with fluid solvents and (2) the similarity of the activation energy for the cis-to-trans isomerization of azobenzene in fluid solutions and in PMMA. The results here allow us to explain these phenomena in terms of their time scales. At room temperature, the reorientation rate of the individual phenyl rings is of the order of 10^7 s^{-1}. The lifetime of the reactive excited state of azoxybenzene can be deduced to be very short,[3] and so we conclude that on the time scale of the photochemical reaction, most molecules are held immobile in the PMMA matrix. Lack of motional freedom is likely to interfere with the approach of the azoxy oxygen atom to C(2) of the distant phenyl ring (the first step in the rearrangement). On the other hand, the thermal cis-to-trans isomerization of azobenzene is a slow process; it occurs only above room temperature ($k_{\text{cis-trans}} = 6.6 \times 10^{-5}$ s^{-1} at 60 °C). At this temperature the average azobenzene molecule is reorienting rapidly and is thus seen to be highly mobile. All configurations of the reactant will be sampled many times per second, and the necessary starting conformation for undergoing isomerization of the cis isomer should be easily accessible, particularly since it is known[38,39] that the actual mechanism of isomerization, involving inversion about one of the nitrogen atoms of the azo bridge, is not a sterically demanding process. At the temperature of isomerization ($T > 55$ °C), the PMMA matrix is sufficiently mobile that little hindrance to reorganization of the solute by the host should be expected.

Registry No. 6, 114059-65-3; azoxybenzene, 20972-43-4; 2,2′,4,4′,6,6′-hexadeuterioazoxybenzene, 114059-66-4; 2,2′-dideuterioazoxybenzene, 114059-67-5; 3,3′-dideuterioazoxybenzene, 114059-68-6; 4,4′-dideuterioazoxybenzene, 114059-69-7; azobenzene, 1080-16-6.

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