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Heterogeneous segmental dynamics of poly(*p*-phenyleneterephthalamide)

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The segmental dynamics of the *p*-phenylenediamine rings of poly(*p*-phenyleneterephthalamide) (PPTA) have been examined via two-dimensional exchange solid state ^{2}H n.m.r. spectroscopy. Fully and partially relaxed experiments were performed over the temperature range −119°C to 75°C. Two populations of phenylene rings can be differentiated by their spin-lattice relaxation times and are associated with sites at the crystallite surfaces and the crystallite interiors; each population is found to be quite heterogeneous over the temperature range examined.

(Keywords: PPTA; segmental dynamics; two-dimensional n.m.r.)

INTRODUCTION

The morphology of poly(*p*-phenyleneterephthalamide) (PPTA)[1,2] has been the subject of a large number of investigations utilizing a number of approaches[3,4] such as X-ray diffraction[5–11], electron microscopy[12–14], infrared spectroscopy[15,16], Raman spectroscopy[17,18] and n.m.r. spectroscopy[19–29]. As a result, a very detailed picture of the morphology of this polymer has been developed. Recently the segmental dynamics of the *p*-phenylenediamine rings[24], terephthalamide rings[25–27] and amide sites[3,28] have been investigated over a wide temperature range by means of one-dimensional (1D) quadrupole echo ^{2}H n.m.r. methods[29]. In combination with structural studies via X-ray diffraction and transmission electron microscopy, the dynamic structure of PPTA has been characterized on a length scale of 1–100 Å in terms of sites associated either with the surfaces of crystallites (or alternatively crystal packing defect planes) or the interior of the crystallites (more perfectly formed planes). The dynamic structure of PPTA is heterogeneous not only in the sense that sites located at crystallite surfaces exhibit enhanced mobility relative to those located in the crystallite interiors, but that a distribution of mobilities reflecting the imperfect structural consolidation during the processing of PPTA exists within each population. In this paper we report the use of two-dimensional (2D) exchange solid state ^{2}H n.m.r. spectroscopy[30] to investigate more thoroughly the dynamics of the *p*-phenylenediamine rings.

One-dimensional quadrupole echo ^{2}H n.m.r. experiments and two-dimensional exchange solid state ^{2}H n.m.r. experiments produce complementary information[31]. The 1D spectra display lineshape distortions and intensity reductions if the correlation time of the motion is comparable to the width of the spectrum, i.e. for correlation times of 10^{-7} s $< \tau_c < 10^{-3}$ s (intermediate-exchange regime). Lineshape distortions are observed as a function of the spacing between the quadrature radio frequency pulses and information as to the timescale and the geometry of the motion is deduced through comparison with computer simulations of the lineshapes. The 2D spectra are especially suited to the study of slower motions with correlation times longer than 10^{-3} s, where the 1D lineshapes are insensitive to the motional process[32]. Slow molecular reorientations occurring during the mixing time of the 2D experiment generate off-diagonal intensity in the 2D plane. The shape of the off-diagonal intensity provides information on the geometry of the motion; the mixing time dependence of the intensity reflects the timescale of the motion. (The usual range of mixing times is from ~ 1 ms to an upper limit determined by the spin-lattice relaxation time.)

Interpretation of 2D spectra can be complex either when the exchange process is no longer in the slow-motion limit or when some of the components of the spectra have spin-lattice relaxation times comparable to the mixing time. In the slow-motion limit one can assume that molecular orientations only change during the mixing time and not during the much shorter evolution and detection periods. The 2D spectrum then represents a two-time distribution function tracing the molecular orientations before and after the mixing time[33,34]. For somewhat faster motions this interpretation is no longer valid since less well defined frequencies are correlated in the 2D spectrum[35]. At first this leads to a broadening of the off-diagonal pattern until, for shorter correlation times, the exchange signal vanishes completely and the spectrum of the motionally averaged lineshape is displayed along the diagonal of the 2D spectrum (fast-motion limit). Information on the timescale of the motion can nevertheless still be obtained by means of lineshape simulations[36]. The lineshape displayed along

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the diagonal of the 2D plane, for the case of discrete jump motions such as flipping phenylene rings, is identical to the 1D lineshape provided that spin-lattice relaxation during the mixing time has not altered the lineshape. Note that for motions characterized by a single correlation time in the intermediate-exchange regime, spreading the spectral information into two dimensions offers no advantage over 1D methods since the 2D spectra are independent of the mixing time. However, for the case of motions characterized by a distribution of correlation times, where the overall lineshape is a weighted superposition of single correlation time lineshapes, the variation of the intensity of the exchange signal with the mixing time supplies additional information not provided by 1D lineshapes.

Spin-lattice (T_1) relaxation is most effective for molecular motions which have a significant component of their spectral density function near the Larmor frequency (10^{-8} s). Therefore the motional process responsible for the T_1 relaxation is most likely not the motional process leading to the exchange pattern in the 2D spectrum and the lineshape distortions in 1D spectra. Spin-lattice relaxation is dominated by motions with very short correlation times, e.g. rapid restricted angle fluctuations (librational motions). These motional processes may cause anisotropic T_1 relaxation which consequentially is responsible for the changes in the 2D lineshape as a function of the mixing time. Of particular importance is the case where the spin-lattice relaxation is characterized by two (or more) relaxation times, where one of the components is of the order of the mixing time used in the 2D experiment and the other(s) being much longer. The lineshape contribution associated with the shorter relaxation time then vanishes completely from the 2D spectrum. This may be desirable, for example, to separate the lineshapes of the amorphous and crystalline domains in a semicrystalline material, or it may be particularly troublesome in the case of a motional process characterized by a broad distribution of correlation times. Here, for sufficiently short correlation times a significant population of molecules with correlation times of the order of the inverse of the Larmor frequency exists and the motion under study becomes itself T_1 active. This usually results in a decreasing contribution of the fast-exchange limit lineshape to the overall 2D lineshape with increasing mixing time; this situation is quite difficult to account for quantitatively in lineshape simulations.

EXPERIMENTAL AND CALCULATIONAL PROCEDURES

N.m.r. measurements

Fully and partially relaxed 2D spectra were obtained over the temperature range −119°C to 75°C with a Bruker MSL 200 n.m.r. spectrometer operating at a resonance frequency of 30.72 MHz and utilizing a 5 mm solenoid coil and a $\pi/2$ radio frequency pulse length of 2.6 μs. The temperature was controlled by a Bruker B-VT 1000 unit which had been previously calibrated.

Fully relaxed 2D spectra were acquired with a four-pulse sequence[30] or with a newly developed five-pulse sequence[37]. Partially relaxed spectra were acquired via saturation recovery by utilization of a pulse train of three $\pi/2$ pulses followed by a delay to allow for partial recovery of the magnetization prior to the four-pulse or five-pulse sequence. A typical data set for the time domain signals was 128 complex points in the t_2 dimension and 40 points in the t_1 dimension. To capture the complete spectral range a digitization rate of 1.6 μs was used in the t_2 dimension (with sequential data acquisition), whereas the increment in t_1 was 3.2 μs. Quadrature detection in both dimensions was achieved by acquiring two data sets and processing following the procedure of States *et al.*[38]. Prior to the second Fourier transform, the t_1 data sets were zero filled to yield a symmetric spectrum of dimension 128 × 128 points.

Spin-lattice relaxation of the selectively deuterated diamine rings was strongly non-exponential and could be decomposed in the time domain into two components whose relaxation times differed by at least a factor of 20 over the temperature range −78°C to 110°C. The amplitude of the long T_1 component below room temperature is near 70–80% and decreases with increasing temperature above room temperature. Values of T_1, calculated from the evolution of the total magnetization as a function of the recovery delay, were determined by least squares fitting of the data to a sum of two exponential functions corresponding to a fast-relaxing component ($T_{1\,\mathrm{short}}$) and a slow-relaxing component ($T_{1\,\mathrm{long}}$). In the measurement of fully relaxed 2D spectra the recycle delay time was varied so that it was at least five times the spin-lattice relaxation time of the slowest-relaxing component ($T_{1\,\mathrm{long}}$) in the spectrum at a given temperature; for the partially relaxed experiments the recycle delay time was five times the spin-lattice relaxation time of the faster-relaxing component ($T_{1\,\mathrm{short}}$). At ambient temperature $T_{1\,\mathrm{short}} \approx 20$ ms and $T_{1\,\mathrm{long}} \approx 2.3$ s.

The synthesis of diamine ring perdeuterated PPTA has been previously described[24].

N.m.r. lineshape simulation

Two-dimensional lineshapes were calculated for discrete, equal population two-site jumps (π-flips) about the 1,4-diamine ring axis[35]. The simulations included the effect of molecular motion during the evolution and detection periods on the 2D time domain signals calculated for the four-pulse and five-pulse sequences. Rapid restricted angle fluctuations (librations) which were found to be important in the simulation of the 1D lineshapes[24] were not taken into account here. Distributions of correlation times were introduced by specifying a mean correlation time $\langle \tau_c \rangle$ and standard deviation (σ) for a log–Gaussian, population-weighted summation of a basis set of lineshapes. This basis set consisted of lineshapes ($\eta = 0$; $e^2qQ/h = 170$ kHz) for each mixing time used in the experiment and for correlation times in the range $10^{-8}\,\mathrm{s} < \tau_c < 1000\,\mathrm{s}$ (five per decade); for correlation times outside these limits the spectra for $\tau_c = 10^{-8}$ s and $\tau_c = 1000$ s were used. Initial values for the mean correlation time and standard deviation of the correlation time distribution were estimated from a previous study of 1D lineshapes for a π-flip model of motion[24].

RESULTS AND DISCUSSION

The dynamic structure of PPTA is quite complex. The 1D lineshapes for the amide sites may be attributed to a major component (~75%) associated with relatively rigid amide sites and a minor component (~25%) associated with mobile amide sites which execute large-angle reorientations[3] over the range −183°C to 238°C. X-Ray diffraction shows that the crystallite size in the lateral dimension for as-polymerized PPTA is ~35Å. This small size requires that a large fraction (~40%) of all amide sites must reside on crystallite surfaces and hence ~20% of all amide sites in the entire crystal are not capable of forming a hydrogen bond. The minor population of amide sites that can execute large-angle jumps is associated mainly with the non-hydrogen-bonded sites on the crystal surfaces. This interpretation is supported by the finding that approximately 30–40% of the NH sites of as-polymerized PPTA are exchanged to ND upon exposure to D_2O; this observation correlates with the fraction of amide sites on the surface of crystallites. The differentiation of amide mobility is therefore identified as deriving primarily from incompletely hydrogen-bonded sites located at crystallite surfaces, and to a lesser extent from defect regions in the highly crystalline polymer. Additional evidence for the presence of the two dynamically differentiated populations for the amide, terephthalamide and diamine sites is available from the temperature dependence of the fractional populations of the $T_{1\,\mathrm{long}}$ components in the spin-lattice relaxation data. Over the temperature range −183°C to 74°C, the fractional populations of the $T_{1\,\mathrm{long}}$ components are in the region of 75 ± 10%; at higher temperatures (up to 238°C) the populations are gradually reduced to ~50% by the presence of considerable motion in nearby terephthalamide and diamine rings.

Further insight into the heterogeneity of the dynamic structure can be obtained by examination of the fully relaxed 1D lineshape data for the terephthalamide[27] and diamine ring sites[24]. These data reveal that the ring dynamics (π-flip) are characterized by a broad distribution of correlation times, indicating that in addition to the fairly simple picture described above (crystallite surface vs. crystallite interior), each population must contain a variety of dynamic environments. It appears that the heterogeneity of the dynamic structure reflects not only the small lateral dimensions of the crystallites, but also the concomitant proximity of all chains to a crystallite surface and hence a substantial probability of structural imperfections through a substantial portion of the crystallite.

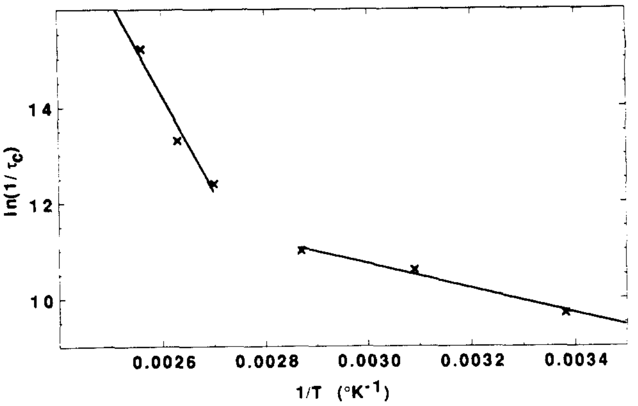

Figure 1 Logarithms of the inverse mean correlation times of an inhomogeneous log–Gaussian distribution of correlation times vs. inverse temperature for the π-flip motion of the diamine rings of poly(*p*-phenyleneterephthalamide). The data are separated into two temperature regimes: the low-temperature regime is dominated by the dynamics of the crystallite surface (activation energy of ~5 kcal mol^{-1}) and the high-temperature regime is dominated by the dynamics of the crystallite interior (activation energy of ~40 kcal mol^{-1})

Figure 1 shows a logarithmic plot of the inverse mean correlation time for π-flipping as a function of inverse temperature for the diamine rings of PPTA over the temperature range 23–121°C; these data were previously determined from the analysis of 1D lineshapes[24]. Fitted lines in the plot are intended to represent the separation of the data into two temperature regimes. The values of the activation energies for each fitted line, 5 kcal mol^{-1} for the low-temperature data and 40 kcal mol^{-1} for the high-temperature data, illustrate the substantial dynamic difference between the two temperature regimes. This behaviour is attributable to two populations, where the low-temperature regime is dominated by the dynamics of the crystallite surface (or defect regions) and the high-temperature regime is dominated by the dynamics of the crystallite interior. Although it is possible to generate magnetization selectively for the more mobile (crystallite surface) domains by using a delay in the saturation recovery sequence equal to five times the value of the smaller spin-lattice relaxation time ($T_{1\,\mathrm{short}}$), the resulting 1D lineshapes are nearly the same for all temperatures below ambient. The lineshapes show relatively little variation from a rigid, Pake-like spectrum because the processes reflected in the lineshapes do not contribute to spin-lattice relaxation differentiation. Significant differences between fully and partially relaxed spectra are observed only at temperatures at and above ambient and are differentiated by an enhancement in the relative contribution of the motionally averaged lineshape.

Two-dimensional ^{2}H n.m.r. methods can be utilized to expand the range of correlation times previously examined by 1D ^{2}H n.m.r. methods. However, at low temperatures the T_1 values of the slow-relaxing component become very long (several seconds) and prohibit the acquisition of fully relaxed 2D exchange spectra owing to the extremely long acquisition times required. Partially relaxed 2D experiments, however, are experimentally feasible and allow the phenylene ring dynamics of the minor population (crystallite surface) to be characterized below room temperature. Spectra were measured as a function of the mixing time (1 ms, 10 ms and, where possible, 100 ms) in the temperature range 23°C to −119°C in decrements of ~20°C. The observation of off-diagonal intensity in all of these spectra and the change in the intensity as a function of the mixing time (together with the presence of a small amount of motionally averaged lineshape) demonstrate that the phenylene ring dynamics at the crystallite surfaces are indeed characterized by a broad distribution of correlation times, as already expected from the simulation of the 1D lineshapes. The off-diagonal intensity is caused by phenylene rings flipping slowly with correlation times from ~10 μs to around the order of the mixing time. However, no elliptical ridges caused by the discrete jump motion are visible in the spectra owing to insufficiently short radio frequency pulses. Consequently, no information about the geometry of the flipping process can be obtained from the 2D experimental lineshapes and emphasis is then placed on obtaining information on

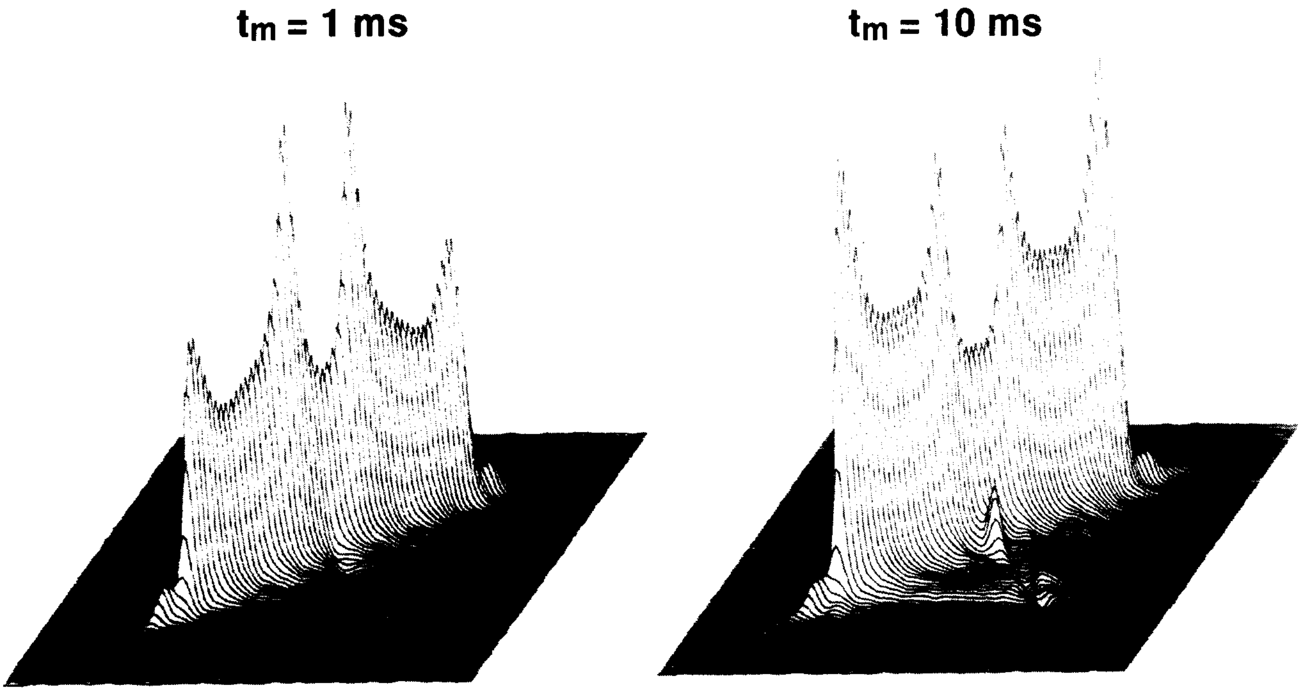

Figure 2 Ambient-temperature partially relaxed 2D solid state ^{2}H n.m.r. spectra of the diamine rings of poly(*p*-phenyleneterephthalamide) acquired with a mixing time of 1 ms (left) and 10 ms (right). The total spectral width is 313 kHz in both dimensions

its timescale. The analysis of the 2D spectra in the intermediate-exchange regime is possible only through comparison of simulated lineshapes with the experimental 2D lineshapes. Both 1D and 2D lineshapes depend not only on the width of the distribution of correlation times but also on the product of the distribution function and the quadrupole echo reduction factor curve.

Figure 2 illustrates partially relaxed 2D spectra at 23°C for mixing times of 1 ms and 10 ms. Examination of the diagonal portions of the spectra for the two mixing times indicates that the central section of the lineshape, associated with the rapidly π-flipping component, has been diminished as the mixing time was increased from 1 ms to 10 ms. This effect is due to the π-flipping component of the lineshape having a shorter T_1 relaxation time than the rest of the spectrum. The most plausible explanation for this behaviour is that the π-flip motion itself is responsible for the more rapid relaxation. Owing to the broad distribution of correlation times for the π-flip motion, a significant population of molecules with correlation times of the order of the inverse Larmor frequency exists and hence the π-flip motion itself becomes T_1 active for a portion of the distribution. This behaviour illustrates that the more rapidly relaxing T_1 component selected in this experiment does itself have a number of components with differing relaxation rates. Further comparison of the two spectra in *Figure 2* reveals that essentially no off-diagonal intensity is observed at a mixing time of 1 ms, but some is detectable at 10 ms (note that almost full exchange intensity, for all mixing times, is expected from the 1D results illustrated in *Figure 1*). This observation could be attributed to a strongly asymmetric or bimodal distribution of correlation times, but it is more likely simply a manifestation of the inability to detect the fairly weak exchange signal (off the diagonal) until the intensity of the rapidly flipping component (on the diagonal) has been attenuated through rapid spin-lattice relaxation during the mixing time. A semiquantitative interpretation of the partially relaxed 2D spectra finds that the width of the distribution of correlation times increases from ~1.5 decades at 23°C to ~2.5 decades at −119°C.

Figure 3 illustrates fully relaxed 2D spectra at 23°C for mixing times of 10 ms and 125 ms. Fully relaxed 2D experiments were performed in the range 10–75°C to gain further insight into the ring dynamics of the more slowly relaxing component in the higher-temperature regime of *Figure 1*. The spectrum acquired with a mixing time of 10 ms contains some contribution from the more rapidly relaxing component as well as a large contribution from the more slowly relaxing component; however, the spectrum acquired with a mixing time of 125 ms represents only the more slowly relaxing component. Comparison of the 10 ms mixing time fully relaxed spectrum with the corresponding partially relaxed spectrum (see *Figure 2*) reveals a substantially smaller amount of the π-flipping lineshape along the diagonal in the fully relaxed spectrum; however, a quantitative interpretation is complicated by the differing amounts of spin-lattice relaxation of the π-flipping components that has taken place during the mixing time. Comparison of the diagonal components of the two fully relaxed spectra reveals that the intensity of the π-flipping component is only slightly reduced in the 125 ms mixing time spectrum relative to the 10 ms mixing time spectrum. This observation is consistent with the 10 ms mixing time spectrum containing only a very small residual contribution from the more rapidly relaxing spin-lattice relaxation component. Off-diagonal intensity is visible in both spectra, with the 125 ms mixing time spectrum having slightly more off-diagonal intensity. Since an extrapolation of the mean correlation times

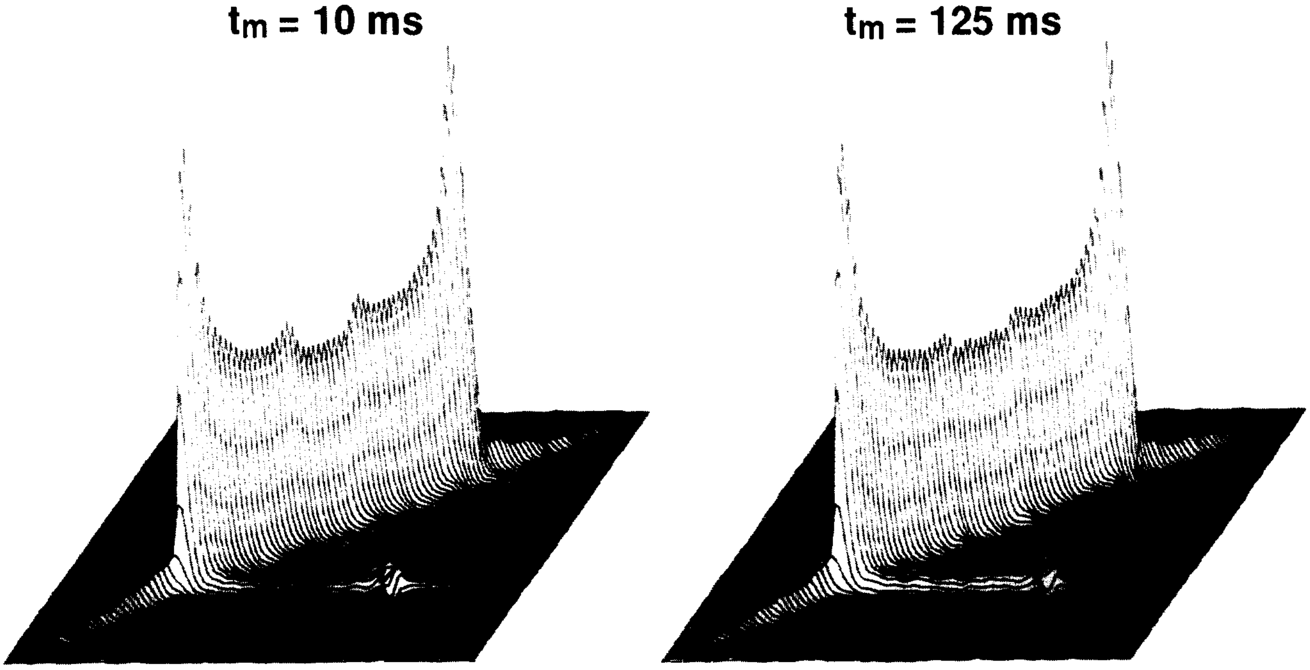

Figure 3 Ambient-temperature fully relaxed 2D solid state ^{2}H n.m.r. spectra of the diamine rings of poly(*p*-phenyleneterephthalamide) acquired with a mixing time of 10 ms (left) and 125 ms (right). The total spectral width is 313 kHz in both dimensions

from the high-temperature regime (*Figure 1*) to lower temperatures yields a value of ~200 ms at 23°C, the observation of exchange intensity as well as a motionally averaged lineshape in the 2D spectra directly demonstrates that the phenylene ring dynamics of the more slowly relaxing component are characterized by a broad distribution of correlation times. Although no quantitative interpretation of the 2D spectra was attempted, there is enough evidence to support the conclusion that the standard deviation of the distribution of correlation times for the more slowly relaxing component is at least 1.5 decades at 23°C; furthermore, data obtained at 10°C indicate that the width of the distribution increases as the temperature is decreased. Previous 1D ^{2}H n.m.r. results[24] for both populations found a composite distribution of correlation times with a standard deviation of 1.5 decades at 23°C.

CONCLUSIONS

A more complete description of the dynamics of the *p*-phenylenediamine rings in PPTA is provided by the use of two-dimensional exchange solid state ^{2}H n.m.r. spectroscopy. At ambient temperature, the mixing time dependence of the partially relaxed spectra illustrates that the more rapidly relaxing T_1 component selected in this experiment does itself have a number of components with differing relaxation rates and hence is quite heterogeneous. Furthermore, it is the π-flipping process itself which is responsible for the increase in the relative population of the short T_1 component with temperature. For this population, the width of the distribution of correlation times increases from ~1.5 decades at 23°C to ~2.5 decades at −119°C.

The observation of mixing time dependent exchange intensity as well as a motionally averaged lineshape in the fully relaxed 2D spectra directly demonstrates that the phenylene ring dynamics of the more slowly relaxing spin-lattice relaxation component are characterized by a broad distribution of correlation times. The width of the distribution of correlation times is found to be at least 1.5 decades at 23°C and increases as the temperature is decreased. Thus the two-dimensional exchange solid state ^{2}H n.m.r. experiments provide a more complete description of the heterogeneity of the dynamics of the *p*-phenylenediamine rings in PPTA than is available from one-dimensional quadrupole echo ^{2}H n.m.r. methods alone.

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