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Ring Flips as a Probe of the Structure of Polyanilines

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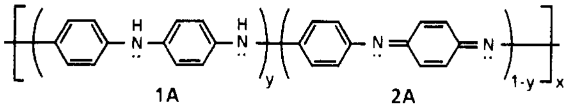
ABSTRACT: Deuterium solid–echo and carbon magic angle spinning NMR measurements have been performed in order to investigate the structure and dynamics of insulating and conducting forms of polyaniline. For all of the polymers studied, the primary motion of the chains from room temperature to over 400 K is phenyl ring 180° flipping, which is commonly observed in the amorphous regions of polymers. Deuteron spin alignment and carbon spin–lattice relaxation data show that there is a very broad distribution of correlation times for ring flips, extending from less than 10^{-7} s to at least 1 s. However, the deuterium spectra can be deconvoluted into two line-shape components, attributable to fast and slow flippers, and the ratio of these components is shown to be a convenient indicator of the polymer dynamics and a sensitive probe of free volume. For the conducting salt form, emeraldine hydrochloride, approximately one-third as many rings can be classified as fast flippers as for the emeraldine base. The decrease in the number of fast flippers is caused by partial π-character of the ring–nitrogen bonds and/or steric interactions with adjacent chloride counterions. This result is shown to be consistent with a structure for the salt containing poly(semiquinone radical cation) segments and residual reduced units.

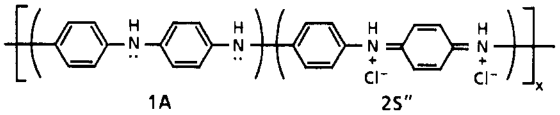
Introduction

Polyaniline has been the subject of considerable scientific inquiry because of its unique electrical behavior and its potential as an environmentally stable conducting polymer. It is synthesized by the electrochemical or chemical oxidative polymerization of aniline and can exist as a number of unique structures, characterized by the oxidation state, i.e., the ratio of amine to imine nitrogens, and the extent of protonation.[1-3] These different structures can be interconverted by acid/base or oxidation/reduction treatment. Six basic repeat unit building blocks have been proposed from which the different forms of polyaniline are composed.[2] They are designated by 1 = reduced or 2 = oxidized, followed by A = amine or imine base, S′ = monoprotonated salt, or S″ = diprotonated salt. The unprotonated forms of polyaniline consist of reduced base units, 1A, and oxidized base units, 2A, as follows:



(I)

where the oxidation state of the polymer increases with decreasing values of y ($0 \leq y \leq 1$). Claims have been made that polyaniline polymers having the following compositions (and others) have been isolated: the fully reduced leucoemeraldine base ($y = 1$), the half-oxidized emeraldine base ($y = 0.5$), and the fully oxidized pernigraniline base ($y = 0$).[2] Protonation of the base forms leads to polymers whose conductivity depends upon the ratio of reduced and oxidized units as well as the extent of protonation. Of particular interest is the highest conductivity form, the emeraldine salt, which has an idealized composition corresponding to an equal number of 1A and 2S″ units:



(II)

Structural characterization of the various forms of polyaniline has been limited because, like most conducting polymers, they are largely insoluble in common organic solvents. A number of spectroscopic studies have been carried out, however, in the solid state. X-ray diffraction measurements of emeraldine base and emeraldine hydrobromide salt indicate these forms of polyaniline to be completely amorphous.[4] Raman studies of emeraldine base have identified the presence of para-disubstituted benzene and quinone diimine moieties and, taken together with infrared spectra, have provided evidence for a head-to-tail polymerization of aniline, with no ortho incorporation of phenylenediamine groups.[5] The same conclusion was reached by comparison of the infrared spectrum of emeraldine base with that of a regiospecifically synthesized polymer.[6] Difficulties have been encountered in establishing the polyaniline secondary structure, such as sequence distribution and chain conformations, because of broad line widths measured in ^{13}C NMR[7,8] and photoemission[9] spectra. Possible reasons for the low spectroscopic resolution are compositional defects, a distribution of torsion angles between adjacent rings, variations in syn and anti conformational arrangements about the benzenoid

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rings or cisoid and transoid configurations about the quinoid rings, variations in the sequencing of benzenoid and quinoid units, thermally induced molecular motions, the possibility of rotations or flips of benzenoid rings about their 1,4 axes, and for the conducting salts, a nonuniform charge and/or spin distribution.

Despite broad (8–12 ppm) lines, ^{13}C cross-polarization magic angle spinning nuclear magnetic resonance (CPMAS NMR) spectra of the emeraldine base resolve localized benzenoid and quinoid ring structures,[7,8] indicating that extensive electron delocalization along the backbone does not occur. Recent ^{13}C studies have determined that the emeraldine base consists primarily of a well-defined microstructure of *alternating* 1A and 2A units, although the polymer is slightly overoxidized ($y = 0.46$).[10] In this paper we use solid-state deuterium NMR to give further insight into the structure of polyanilines. ^2H NMR has been previously applied to characterize the molecular dynamics of solid polymers.[11,12] Line shapes and relaxation behavior can be analyzed in terms of specific motions over a very wide range of correlation times.[11,12] In particular, phenyl ring 180° flipping, common to many polymers,[11] is readily identified from the ^2H spectra of ring-deuterated polyanilines. It will be shown for the base forms of polyaniline that the number of rapidly flipping rings is a measure of the free volume available to the polymer chains. From these ^2H spectra and the ^2H and ^{13}C relaxation measurements, we obtain structural and dynamical properties for three forms of polyaniline—leucoemeraldine base, emeraldine base, and the emeraldine HCl salt.

Experimental Section

Material Preparation. Polyanilines used in the current study were synthesized by methods previously described.[2,3,13] Emeraldine hydrochloride was prepared by oxidizing a 1 M aqueous HCl solution of aniline (or Aldrich 99+ atom % aniline-d_5, $C_6D_5NH_2$) with ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, at ~5 °C. The precipitate was washed with 1 M HCl and dried under vacuum. The emeraldine hydrochloride was converted to the base form by stirring with a dilute (0.1 M) aqeuous solution of NH_4OH, followed by repeated washing with 0.1 M aqueous NH_4OH and drying under vacuum. Leucoemeraldine base (hereinafter referred to as leucoemeraldine) was prepared by reduction of the emeraldine base with excess neat degassed hydrazine monohydrate for 48 h under static vacuum (initial pressure, 1 μmHg) with constant stirring. The light grey leucoemeraldine powder was isolated by vacuum removal of excess hydrazine monohydrate and dried under dynamic vacuum at 80 °C for 3 h. In order to avoid oxidation, leucoemeraldine samples were handled in an argon atmosphere, and NMR magic angle spinning was accomplished by using nitrogen rather than air as the driving gas. Deuterated polymers were weighed and loaded into 5-mm NMR tubes in a glovebox and then attached to a vacuum line for flame sealing.

NMR Spectroscopy. NMR spectra were obtained on a Bruker CXP spectrometer in a Cryomagnet Systems, Inc., 47-kG widebore superconducting magnet system. Solid-state ^2H NMR spectra were measured on ring-deuterated polyanilines at 30.7 MHz with a Cryomagnet Systems, Inc., high-power probe. The probe has a Q of ~100 and achieves 90° pulse widths of 2 μs with ~500-W power in a 5-mm sample tube. Data were acquired with quadrature detection using the quadrupolar-echo pulse sequence ($90^\circ_{\pm x}-\tau_1-90^\circ_y-\tau_1$–acquire–RD) with alternate scans added and subtracted in order to minimize distortions from probe acoustic ringing. Typically, the slowest relaxing deuterium component had a T_1 of a few seconds; consequently, recycle delays (RD) of 10–20 s, depending upon sample and temperature, were used. Data were acquired with a dwell of 0.2 μs per point (2.5-MHz acquisition bandwidth), and the free-induction decay was left-shifted 12 points (2.4 μs) in order to start at the echo peak. Selective observation of the more quickly relaxing component was achieved with five saturation pulses preceding the solid–echo sequence as follows: $(90^\circ-100\ \mathrm{ms})_5-90^\circ_{\pm x}-\tau_1-90^\circ_y-\tau_1$–acquire–RD. Deuterium spin–lattice relaxation times were measured by using the inversion recovery method ($180^\circ-\tau_0-90^\circ_{\pm x}-\tau_1-90^\circ_y-\tau_1$–acquire–RD), where τ_0 is the variable recovery time. In order to investigate slow motions, the spin alignment experiment[14] was carried out on emeraldine base. This technique utilizes the Jeener–Broekaert[15] three-pulse sequence ($90^\circ_{\pm x}-\tau_1-45^\circ_y-\tau_2-45^\circ_y-\tau_1$–acquire–RD), where τ_2, the alignment echo mixing period, was varied between 0.5 ms and 1 s. For slow molecular jump motions, the decay rate is a measure of the correlation time (i.e., the reciprocal of the jump frequency), up to the measurement limit of T_1.

^{13}C spin–lattice relaxation measurements at 50 MHz on natural ^1H abundance polyanilines employed the artifact suppression technique developed by Torchia.[16] Cross-polarization (CP) used 0.3 (emeraldine base), 0.5 (leucoemeraldine), or 0.8 (emeraldine hydrochloride) ms mixing times, high power ($H_1 = 50$ KHz) ^1H decoupling, and a recycle time of 1 s. Variable-temperature magic angle spinning (MAS) at ~4.2 KHz was performed in a Doty Scientific probe with 30–150 mg of each sample (depending upon availability) packed into 6-mm-o.d. sapphire rotors.

Deuterium Data Analysis. A Pascal program for the Bruker Aspect 3000 computer was written to calculate line shapes and store the theoretical spectra as data files for plotting and analysis by the Bruker DISMSL software package. Line shapes for rigid phenyl rings and for rings undergoing 180° flips about their 1,4-axes were calculated by using standard powder pattern line-shape equations.[17] Spectra so obtained were broadened slightly by using the smoothing function of the DISMSL software in order to account for additional dipolar line broadening of the experimental data. Calculated spectra were corrected for both the excitation bandwidth of the finite length radiofrequency pulses[18] as well as for the frequency response to our high-Q probe. The probe characteristics were experimentally obtained by measuring the signal intensity in response to resonant 90° pulses of a few drops of D_2O adsorbed into some hexamethylbenzene powder as a function of the probe center-tuned frequency, which was systematically varied. Using this transfer function, calculated deuterium line shapes were corrected for both the frequency-dependent response of the probe circuitry during signal detection and the frequency dependence, due to the probe bandwidth, of the 90° pulse length. Correction for probe frequency response results in a noticeable improvement of the predicted line shapes at the tails of the experimental spectra. Corrections for frequency-dependent signal loss due to motion during echo formation time, τ_1,[19] were not necessary to achieve good line-shape fits.

Results and Discussion

^2H NMR Line Shapes. For polymers with 1,4-disubstituted benzenoid rings in the backbone, 180° ring flips can occur, and the flipping populations and rates are a probe of local structure.[11,12,20–23] Such flips are absent in crystalline regions of semicrystalline polymers.[20] However, in amorphous regions of polymers, deuterium NMR line shapes characteristic of flipping as well as static rings are observed. This marked motional heterogeneity is taken as a manifestation of differences in packing at the different sites.[11,12] For amorphous polymers there is usually a very broad distribution of correlation times, extending as much as 6–10 orders of magnitude.[22] Furthermore, it is often necessary to incorporate rapid small-angle librations as well into simulations to fit the experimental spectra.[11,12,20,23] It is important to note that ring flipping may be influenced by factors other than local free volume. For example, π-bonding to quinoid moieties will prevent rotation. It has been suggested that for poly(butylene terephthalate) the partial double bond character of the carbonyl–aromatic bonds constrains flipping.[20] Also, for charged species, such as emeraldine hydrochloride, the electrostatic attraction of counterions may be important.

^2H spectra for the ring-deuterated emeraldine base as a function of temperature are plotted in Figure 1, which shows the fully relaxed spectra obtained with echo evolution times, τ_1, of 20 and 80 μs, as well as partially relaxed spectra with $\tau_1 = 20$ μs. Partial relaxation, achieved by

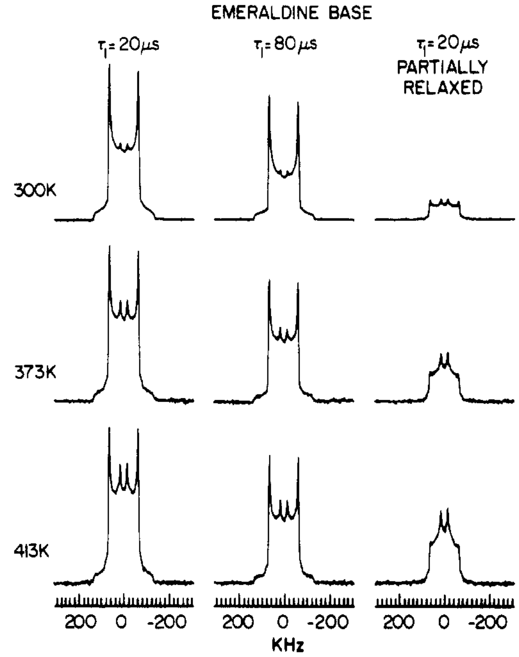


Figure 1. Deuteron spectra of ring-deuterated emeraldine base at T = 300, 373, and 413 K. At each temperture spectra are obtained with the two-pulse quadrupole echo sequence using echo delay times of τ_1 = 20 μs and τ_1 = 80 μs and with the presaturation sequence (see text) to obtain partially relaxed spectra. All spectra were measured with a repetition delay of 10 s. For T = 300 K, the number of scans = 6600, while for T = 373 and 413 K, the number of scans = 2300.

the presaturation experiment, suppresses the static powder pattern, and the spectra are dominated by a line shape characteristic of rings undergoing rapid 180° flips. The residual static component in the partially relaxed spectra can be entirely accounted for by incomplete saturation of the rigid deuterons. In Figure 2 the τ_1 = 20 μs data are deconvoluted into rigid and flipping ring components. Deconvolutions were accomplished by taking appropriate linear combinations of the simple solid–echo spectra and the spectra obtained by the presaturation experiment. The fraction of flipping rings obtained in this manner may be underestimated because of the shorter T_2 of the flipping component. However, the τ_1 = 80 μs spectra of Figure 1 show only a slight reduction in the line shape fraction attributable to the flipping rings when compared to the τ_1 = 20 μs spectra, indicating T_2 distortions to be minimal. Calculated spectra, using a quadrupole coupling constant ($e^2qQ/\hbar$) of 178 KHz for both the flipping and nonflipping components, are plotted in Figure 2 for the T = 413 K data.

As seen in Figure 2, the rigid and flipping component line shapes are nearly independent of temperature, although their relative intensities vary. This observation holds for all three polymers and indicates that deuterium line shapes can be conveniently described in terms of rings that undergo rapid flips (time interval between flips, $\tau_c < 10^{-7}$ s) and rings that flip slowly ($\tau_c > 10^{-4}$ s), if at all. This is not to say that there is not a continuous distribution of flip rates. In fact, ^{2}H and ^{13}C relaxation data (below) prove that there is a very wide distribution. Because of deuteron signal reduction due to intermediate regime motion (10^{-7} s $< \tau_c < 10^{-4}$ s) during the echo formation time, τ_1,[19,22,24] it is often difficult to distinguish a very broad distribution of correlation times from a bimodal superposition of very rapid and very slow motions. For emeraldine base, signal reduction factors based on total spectral integration have been computed. After accounting for signal loss with increasing temperature due to the Boltzmann factor, it was found that from 303 to 413 K, signal intensity loss was only ~4%. The absolute signal reduction factors may be higher, but since there is little additional signal reduction over the temperature range accessed, the simple determination of the ratio of fast to slow flippers is a good approximation of the polymer dynamics.

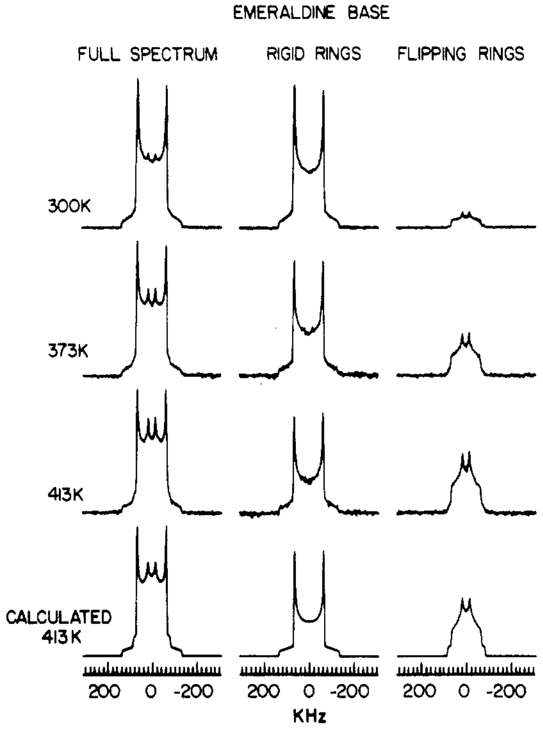


Figure 2. Deuteron spectra of ring-deuterated emeraldine base. Fully relaxed spectra are obtained with the quadrupole echo pulse sequence using the same experimental conditions as described for the left column of Figure 1. Rigid and flipping ring line-shape components are experimentally determined from appropriate linear combinations of the fully and partially relaxed spectra plotted in Figure 1. The calculated spectra for the T = 413 K data use a quadrupole coupling constant ($e^2qQ/\hbar$) of 178 KHz.

In Figures 3 and 4 the experimental spectra of ring-deuterated leucoemeraldine and emeraldine hydrochloride, respectively, are plotted as a function of temperature. Line shapes are identical with those of emeraldine base; at a given temperature only the relative contributions of the two components differ. Signal intensity reductions over the measured temperture range were ~12% and ~2% for leucoemeraldine and emeraldine hydrochloride, respectively.

Because the leucoemeraldine and emeraldine base polymers have a distribution in packing densities, it is reasonable that local free volume determines the rate of ring flipping. As temperature is raised, free volume increases, and rings are sterically less confined by neighboring chains. Therefore, flipping rates become faster and the number of fast flippers should increase, as is observed in the deuterium spectra of Figures 1–4. It has been shown that the free volume fraction, f, for a polymer glass can be expressed by a simple exponential relationship:[25,26]

$$f = Ae^{-\bar{\varepsilon}/kT}$$

where A is nearly constant, $\bar{\varepsilon}$ is the mean thermodynamic energy required for hole (i.e., free volume) formation, k is Boltzmann's constant, and T is temperature. Under the assumption of proportionality between the fraction of fast flippers and the fractional free volume, the slope of the Arrhenius plots of the fraction of fast flippers versus inverse temperature (Figure 5) should give the mean energy

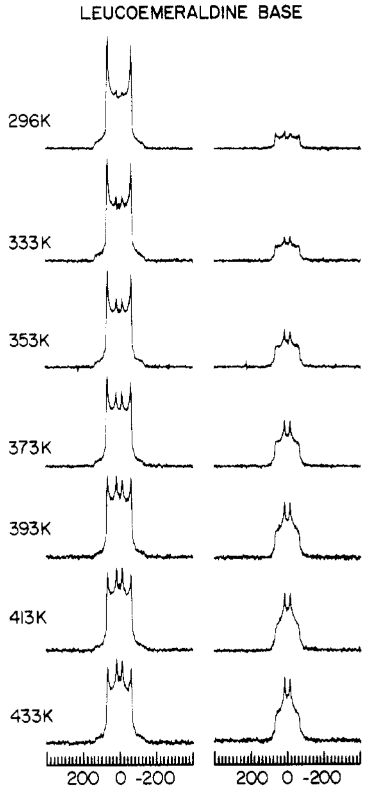


Figure 3. Deuteron spectra of ring-deuterated leucoemeraldine as a function of temperature. Left: fully relaxed spectra obtained from the two-pulse quadrupole echo sequence. Right: Partially relaxed spectra obtained by the presaturation pulse sequence. All spectra are obtained with an echo delay time $\tau_1 = 20$ μs, number of scans = 1000–2000, and a repetition delay of 12–20 s.

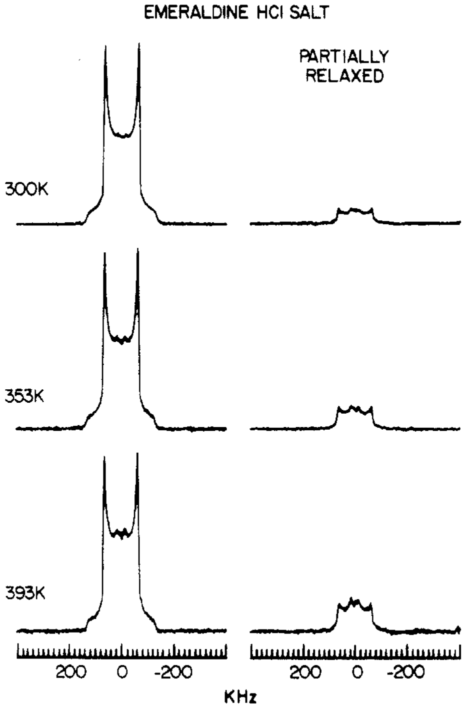


Figure 4. Deuteron spectra of ring-deuterated emeraldine hydrochloride as a function of temperature. Left: fully relaxed spectra obtained from the two-pulse quadrupole echo sequence. Right: Partially relaxed spectra obtained by the presaturation pulse sequence. All spectra used $\tau_1 = 20$ μs, number of scans = 3400, and a repetition delay of 12 s.

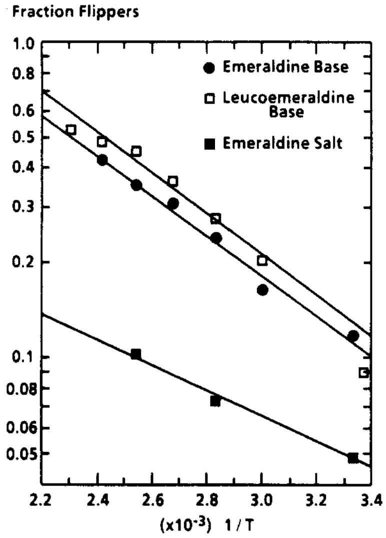
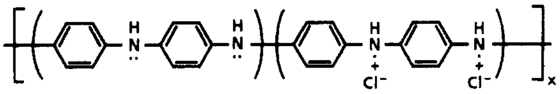


Figure 5. Semilogarithmic plot of the line-shape fraction attributed to rings undergoing rapid 180° flips as a function of inverse temperature for emeraldine base, leucoemeraldine, and emeraldine hydrochloride. Solid lines are linear least-square regression fits.

required to create sufficient free volume for rotation to occur. For the emeraldine and leucoemeraldine base forms $\bar{\varepsilon}$ derived from these plots is ~3.0 kcal/mol, which is consistent with hole energies determined from equation of state calculations for typical amorphous polymers.[27] This agreement supports the hypothesized relationship between the NMR measured number of fast flippers and free volume, at least over the measured temperature range. Since 1 of every 4 rings in the emeraldine base is quinoid and cannot flip, emeraldine base should have fewer flippers than leucoemeraldine, as was observed. A similar fraction of benzenoid rings flips in these two polymers, suggesting that chain packing is similar.

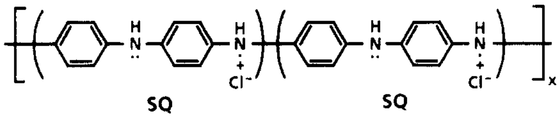
The emeraldine salt, on the other hand, has 30–40% as many flipping rings as the emeraldine base over the measured temperature range. This decrease in the number of flippers is attributable to either a direct steric interaction with the chloride counterions or to partial π-electron delocalization into the ring–nitrogen bonds. X-ray photoelectron valence band spectra show that protonation of the emeraldine base to form emeraldine hydrochloride is accompanied by a change in chain geometry.[28] This structural change is probably a manifestation of the partial π-character of approximately half of the ring–nitrogen bonds.

Emeraldine hydrochloride (II), schematically depicted above, likely rearranges via a proton-assisted spin-unpairing mechanism to form two polarons (semiquinone radical cations),[3,6,29] shown in III. It is believed that these



(III)

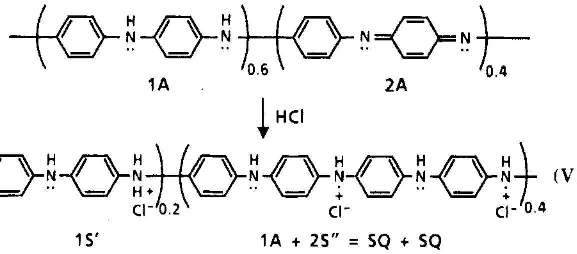
polaron pairs separate because of Coulomb repulsion to form the poly (semiquinone radical cation) structure IV,



(IV)

where the charge is situated on alternate nitrogens.[3,29] There is disagreement over whether polaron formation (in structures III or IV) results in a high density of localized states, conductivity being mainly due to intermolecular hopping,[6] or whether structure IV represents metallic polaron lattice regions with conductivity limited by tunneling through defects between these regions.[3,29–32] In IV, the electron density distribution associated with the polarons will impart some π-character to at least one of the C–N bonds of each ring. This partial π-character and/or the steric interactions with adjacent chloride counterions should inhibit flipping. However, for the unseparated polaron structure of III, only three of every four rings would likely be frozen, while one ring could flip, given sufficient free volume. Therefore, the experimental determination that emeraldine hydrochloride has approximately one-third the number of fast flippers of the emeraldine base is consistent with structure III but not with structure IV. This conclusion is dependent upon the assumptions that rings adjacent to polaron centers cannot flip rapidly and that chain packing in the base and salt forms is similar. These assumptions are reasonable since the temperature dependence of the fraction of flippers in the salt form (Figure 5) has a slope corresponding to $\bar{\epsilon} \sim$ 2 kcal/mol, which is within experimental error of that measured for leucoemeraldine and emeraldine base. One would expect this value to be considerably higher if rings adjacent to polaron centers could also flip (because they require additional energy to do so).

Structure III, however, is not a realistic model for emeraldine hydrochloride, because polarons are not expected to remain strictly localized.[3,6] An alternative explanation for the ^{2}H NMR data is derived from recent redox[33] and volumetric[34] titration studies, suggesting that protonation of emeraldine base (which has been prepared and handled in air so that $y \sim 0.40$–0.46[10,33]) is simultaneously accompanied by reduction in oxidation state (due to hydrolysis) to $y \sim 0.6$[33] and that some amine nitrogens are protonated to convert 1A to 1S′ units.[34,35] If reduced groups constitute 60% of the protonated polymer, then redox rearrangement of equal numbers of 1A and 2S″ units to form poly (semiquinone radical cation) segments[35] would lead to structure V. With the assumption that rings in 1S′ units can flip (i.e., chlorides do not inhibit flipping) while those of the polaron segments cannot, structure V is then expected to have nearly 30% the number of flippers of the emeraldine base. Finally, structures III and V are both consistent with the elemental analysis determination of Cl/N = 0.5[13] and the NMR measured stoichiometry for the ring-deuterated salt of H/N = 1.0[10] (for structure III, H/N = 1.0; for structure V, H/N = 1.1). The present data are consistent with but do not prove structure V to be the correct representation of emeraldine hydrochloride. In any case, it has been demonstrated that the simplified picture of IV requires 1A (as in III) or 1S′ (as in V) "defects" to explain the observed population of flippers. The data say nothing about the distribution of such defects along the chains.



^{2}H Relaxation Behavior. Deuterium spin–lattice relaxation behavior of the static-line-shape component of emeraldine base (Figure 6) is a single exponential with T_1 = 1.9 s at 303 K and T_1 = 1.4 s at 373 K, while for the rapidly flipping ring component (not plotted) $T_1 \simeq$ 10–30 ms. The observation of distinct T_1 values means that those rings which flip fast and those which are static or flip slowly are not in a dynamic equilibrium, at least on a time scale of 1–2 s.[11] The question of a distribution of flipping times, which eludes a definitive statement from the line-shape analysis, has been addressed both by deuterium and carbon relaxation measurements, as will now be discussed.

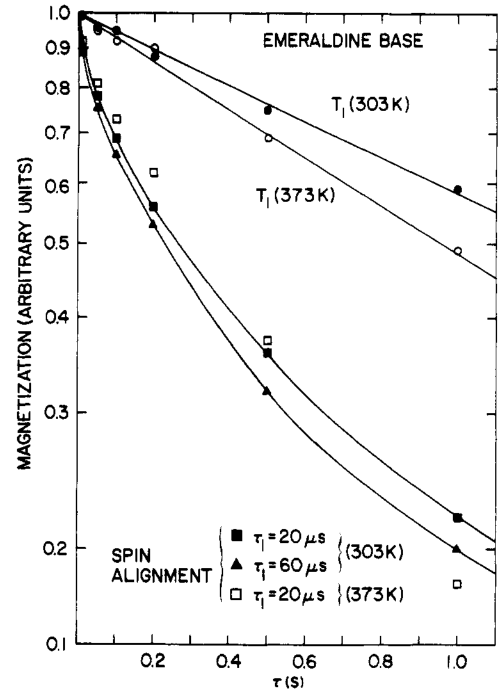


Figure 6. Deuteron spin–lattice (T_1) and spin alignment relaxation behavior for the static-line-shape component of ring-deuterated emeraldine base. T_1 data is plotted as $M(\infty) - M(\tau)$ versus τ where $\tau = \tau_0$, the spin–lattice inversion recovery delay. Spin alignment data are plotted as the alignment echo intensity versus $\tau = \tau_2$, the spin alignment mixing period.

To investigate the possibility of very slow ring flipping, deuteron spin alignment spectra[11,12,14] have been measured. In this experiment the Jeener–Broekaert three-pulse sequence ($90^\circ_{\pm x}$–τ_1–45°_y–τ_2–45°_y–τ_1–acquire–RD) is used to create deuteron spin alignment; i.e., deuterons are locked in a state of local quadrupolar order. During the mixing period, τ_2, spin alignment is subject to spin–lattice relaxation processes with a time constant T_{1Q}. Calculations[14,36] demonstrate that for isotropic motion characterized by a single correlation time, τ_c, in the limit of slow motion ($\omega_0\tau_c \gg 1$), $T_{1Q}/T_1 = {}^2/_3$, whereas for rapid motion ($\omega_0\tau_c \ll 1$), $T_{1Q}/T_1 = {}^5/_3$. Moreover, it can be shown that these limiting relationships are generally true, even for anisotropic motion. During the mixing period, τ_2, slow dynamic processes, with correlation times $\tau_c \geq \tau_1$, where τ_1 is the evolution period of the Jeener–Broekaert sequence, will change the quadrupole frequency and lead to further reduction of the spin alignment echo. Echo reduction is promoted by slow dynamic processes only; rapid motions ($\tau_c \ll \tau_1$) have no effect on the echo amplitude, since each deuteron sees the same averaged environment during the echo formation τ_1 period as during the initial evolution τ_1 period, independent of τ_2. In addition, the τ_1 dependence of the spin alignment response enables distinction between slow fixed angle rotational jumps and slow diffusive (i.e., continuous rotation or small random angle jump) motions. For fixed angle jumps, the spin alignment echo amplitude is nearly independent of τ_1 and decays with a time constant corresponding to the correlation time of the jump process to a limiting fractional intensity, which is the inverse of the number of sites (i.e., orientations) accessed. For diffusive motions the spin alignment echo decay is strongly

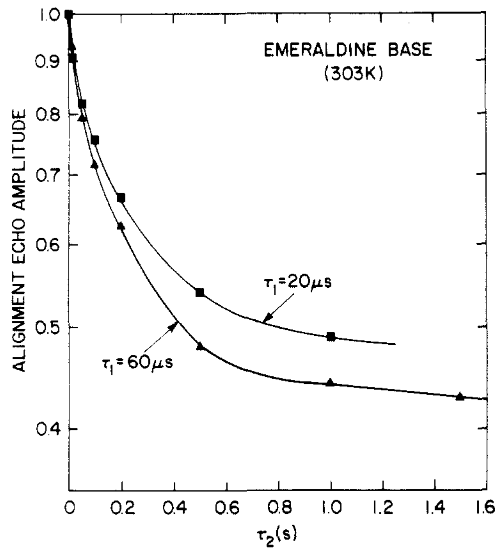


Figure 7. Deuteron spin alignment relaxation behavior of Figure 6, normalized to remove the effect of the spin-lattice relaxation contribution (see text).

enhanced by increasing τ_1 and decays to a limiting intensity depending upon τ_1 and the angular region to which the motion is confined.[12,14,37]

Spin alignment decays of the static-line-shape component of emeraldine base as a function of the spin alignment mixing time, τ_2, are plotted in Figure 6. The spin alignment echo amplitude decays significantly more rapidly than does T_1 relaxation, demonstrating the presence of slow motions. Deuteron line shapes are nearly independent of τ_2, and the spin alignment decay varies only slightly with τ_1, suggesting that fixed angle jumps, rather than diffusive motions, are dominant. In order to ascertain whether slow ring flips can explain the spin alignment response, the long mixing time behavior is examined. The T = 303 K spin alignment decays are replotted in Figure 7 after normalizing for signal loss due to the spin-lattice relaxation contribution, which, in the slow motion limit, can be approximated by $T_{1Q} = {}^2/_3T_1$. The long mixing time echo intensity is expected to reach a plateau value of $^1/_2$ for slow ring flips, but since one of four rings is quinoid and cannot rotate, a plateau value of ~0.6 is predicted. The τ_1 = 20 μs data level off at long mixing times (Figure 7) to a plateau value of nearly $^1/_2$, and the τ_1 = 80 μs data reach a slightly lower value. These results are consistent with two site jumps superimposed on a minor contribution from slow diffusive motions.[12,37] Since ring flips require far less local free volume than do conformational (e.g., syn/anti) reorientations, slow flips augmented by slow restricted-angle diffusive motions is the favored explanation for the spin alignment behavior of the static-line-shape component.

For emeraldine base, then, slow conformational jumps are not an important contributor to the polymer motions over the temperature range studied. Moreover, at the highest measured temperatures, the closeness of fit of the short T_1 component line shape to the calculated rapid ring flip pattern (Figure 2), using the same quadrupole coupling constant required to fit the rigid component line shape, precludes a significant contribution from other short correlation time ($\tau_c < 10^{-7}$ s) processes. Therefore, other than ring flipping, the polymer chains have little additional mobility, and the glass transition temperature is clearly above our measurement range. Differential scanning calorimetry traces of emeraldine base show no sign of any transition up to at least 440 K.

The marked dispersion in the spin alignment decay for the static-line-shape component (Figure 7) reflects a distribution of correlation times, with the initial slope corresponding to an average τ_c of ~100–200 ms. This result, together with the fact that rapidly flipping rings are simultaneously present, suggests that there is a continuous distribution of flip rates extending over at least 8 orders of magnitude. Line shapes due to rings that flip at intermediate rates are not observed because of signal reduction in this regime[22,24] and because the very broad distribution of correlation times diminishes the relative contribution of these deuterons to the overall spectra.

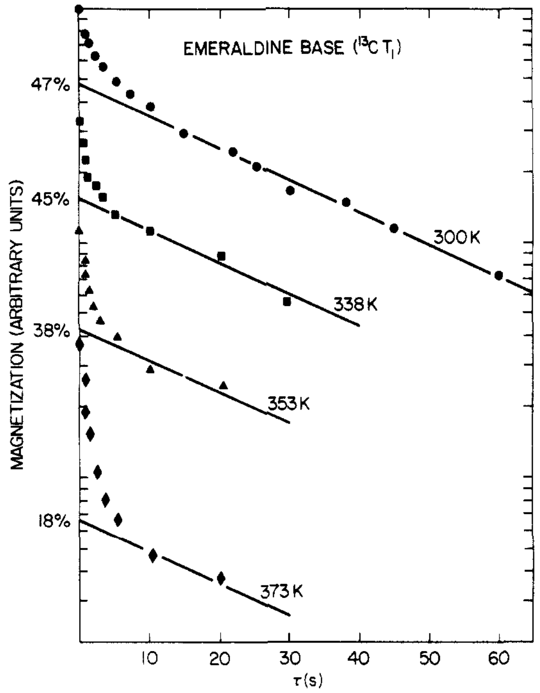


Figure 8. ^{13}C CP-MAS spin-lattice relaxation decay of the carbons with directly attached hydrogens for emeraldine base as a function of temperature. Plots are arbitrarily displaced vertically in order to avoid overlap. Percentages are indicated for the contribution of the long-time exponential component.

^{13}C Relaxation Behavior. ^{13}C spectra of polyanilines measured by cross-polarization magic angle spinning techniques have been reported previously.[7,8,10] In this paper, ^{13}C spin-lattice relaxation measurements have been obtained. Signal intensities from the C–H ring carbons versus τ, the spin-lattice recovery time, are plotted for emeraldine base in Figure 8. The recovery response shows a wide dispersion of relaxation times and provides further confirmation of a broad continuous distribution of phenyl ring flip rates. A similar behavior is observed for leucoemeraldine. The long time decay (attributable to the most rigid rings), with $T_1 \simeq$ 30 s for emeraldine base and $T_1 \simeq$ 70 s for leucoemeraldine, has only a slight temperature dependence, but the number of spins contributing to this component decreases dramatically with increasing temperature.

The spin-lattice responses of emeraldine hydrochloride at 296 and 363 K are shown in Figure 9. These decays are also nonexponential but nearly temperature independent, with relaxation times an order of magnitude shorter than for the nonconducting base forms of polyaniline. The temperature independence of the ^{13}C spin-lattice relaxation recovery is consistent with the ^{2}H spectra, which show that most rings do not flip and there is only a small increase in the contribution of flippers to the line shape over this temperature range. Efficient spin-lattice relaxation of the nonflipping rings is probably a result of charge fluctuations either from high-frequency low amplitude polymer chain motions which escape detection by

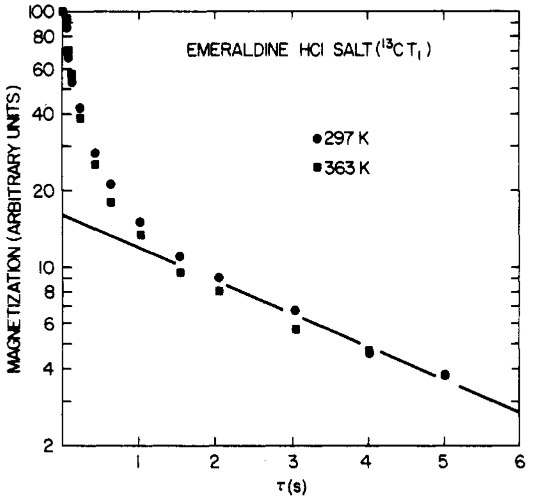


Figure 9. ^{13}C CP-MAS spin-lattice relaxation decay of emeraldine hydrochloride as a function of temperature.

^{2}H line shapes or from motions of the counterions. Unlike emeraldine base and leucoemeraldine, where the relaxation dispersion is caused by the distribution in flipping rates, it is hypothesized that for emeraldine hydrochloride the relaxation dispersion originates from local differences in charge density and/or the broad distribution of correlation times for these thermal motions. Variations in charge density have been previously cited as a possible source of the broad ^{13}C linewidth observed for emeraldine hydrochloride.[10]

Conclusions

Separation of deuterium spectra into flipping and rigid rings has provided a convenient approximation for the dynamics of polyaniline polymers, although deuteron spin alignment and carbon spin-lattice relaxation demonstrates that there is, in fact, a wide distribution of correlation times for ring flips. Temperature dependence of the fraction of benzenoid rings undergoing rapid 180° flips, calculated from ^{2}H spectra, reveals a wide distribution of local packing densities. From this data the mean energy for creation of free volume in the base forms is evaluated to be 3 kcal/mol. Close agreement with published energies for hole formation, determined by equation of state calculations on typical polymers, supports the hypothesized linear relationship between the ^{2}H-determined number of fast flippers and free volume. Finally, for the conducting emeraldine hydrochloride, the determination that about a third as many rings are fast flippers as compared with the emeraldine base is consistent with a structure containing unseparated polarons or with a more realistic one containing poly(semiquinone radical cation) segments and residual reduced units.

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