

amples for imino carbonyls with the imino and amino hydrogens typically found in nucleic acids will be needed to determine whether there is a general quantitative correlation between ΔH and DIE for individual hydrogen bonds between nucleosides.

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Supplementary Material Available: Table showing dependence of δ (^{13}C) at C2 and C4 of protonated and deuterated **2** on temperature and concentration (1 page). Ordering information is given on any current masthead page.

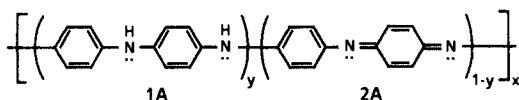
Solid-State ^{13}C NMR Characterization of Polyanilines

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Abstract: ^{13}C solid-state nuclear magnetic resonance measurements are reported for the leucoemeraldine base, emeraldine base, and emeraldine hydrochloride forms of polyaniline in order to characterize the structures of these three distinct polymers. Chemical shift assignments are facilitated by use of the cross-polarization technique to distinguish carbons with and without directly bonded hydrogens. Comparison of the spectra of emeraldine base with those of leucoemeraldine base and air-oxidized leucoemeraldine (which partially converts to emeraldine base) establishes that emeraldine base is essentially an alternating copolymer of reduced **1A** $[-(\text{C}_6\text{H}_4)\text{N}(\text{H})(\text{C}_6\text{H}_4)\text{N}(\text{H})-]$ and oxidized **2A** $[-(\text{C}_6\text{H}_4)\text{N}=(\text{C}_6\text{H}_4)=\text{N}-]$ repeat units. The 8–12 ppm spectral line widths measured for both emeraldine base and leucoemeraldine base are attributed to local fluctuations in conformational and configurational geometries, a distribution in chain packing, and compositional defects. ^{13}C spin-echo measurements establish that the 60 ppm wide line from the conducting emeraldine hydrochloride is *inhomogeneously* broadened. It is postulated that this line width is due to local variations in charge density along the polymer backbone arising from polymer structural heterogeneity.

Polyaniline has been the subject of considerable scientific inquiry because of its unique electrical behavior and its potential as an environmentally stable conducting polymer. Conductivity exhibits a strong dependence on solution pH,^{1–5} oxidation state^{3,6} and water content.^{3,7–10} Polyaniline 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. 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.¹ 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**, represented as follows



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 ($y = 0$).¹

Structural characterization of polyanilines has been limited because, like most conducting polymers, they are largely insoluble in common organic solvents. Raman studies of films 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.¹¹ The same conclusion was reached by comparison of the infrared spectrum of emeraldine base with that of a regio-

specifically synthesized polymer.¹² Cross-polarization magic angle spinning ^{13}C nuclear magnetic resonance (CPMAS NMR) spectra also resolve localized benzenoid and quinoid ring structures,^{13,14} indicating that extensive electron delocalization along the backbone does not occur. In this paper we extend these NMR results to demonstrate that emeraldine base is, in fact, an *alternating* copolymer of **1A** and **2A** units.

Protonation of the base forms of polyaniline 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 is the diprotonated emeraldine base. It has been postulated (although not universally accepted^{15,16}) that under strong acid conditions

- (1) Chiang, J.-C.; MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 193–205.
- (2) MacDiarmid, A. G.; Chiang, J.-C.; Richter, A. F.; Epstein, A. J. *Synth. Met.* **1987**, *18*, 285–290.
- (3) Focke, W. W.; Wnek, G. E.; Wei, Y. J. *Phys. Chem.* **1987**, *91*, 5813–5818.
- (4) MacDiarmid, A. G.; Chiang, J.-C.; Huang, W.-S.; Humphrey, B. D.; Somasiri, N. L. D. *Mol. Cryst. Liq. Cryst.* **1985**, *125*, 309–318.
- (5) MacDiarmid, A. G.; Chiang, J.-C.; Halpern, M.; Huang, W.-S.; Mu, S.-L.; Somasiri, N. L. D.; Wu, W.; Yaniger, S. I. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 173–180.
- (6) McManus, P. M.; Yang, S. C.; Cushman, R. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1556–1557.
- (7) Nechtschein, M.; Santier, C.; Travers, J. P.; Chroboczek, J.; Alix, A.; Ripert, M. *Synth. Met.* **1987**, *18*, 311–316.
- (8) Angelopoulos, M.; Ray, A.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1987**, *21*, 21–30.
- (9) Javadi, H.; Zuo, F.; Angelopoulos, M.; MacDiarmid, A. G.; Epstein, A. J. *Mol. Cryst. Liq. Cryst.*, in press.
- (10) Travers, J. P.; Nechtschein, M. *Synth. Met.* **1987**, *21*, 135–141.
- (11) Furukawa, Y.; Hara, T.; Hyodo, Y.; Harada, I. *Synth. Met.* **1986**, *16*, 189–198.
- (12) Wudl, F.; Angus, R. O., Jr.; Lu, F. L.; Allemand, P. M.; Vachon, D. J.; Nowak, M.; Liu, Z. X.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3677–3684.
- (13) Devreux, F.; Bidan, G.; Syed, A. A.; Tsintavis, C. *J. Phys.* **1985**, *46*, 1595–1601.
- (14) Hjertberg, T.; Salaneck, W. R.; Lundstrom, I.; Somasiri, N. L. D.; MacDiarmid, A. G. *J. Polym. Sci.: Polym. Lett. Ed.* **1985**, *23*, 503–508.
- (15) Hagiwara, T.; Demura, T.; Iwata, K. *Synth. Met.* **1987**, *18*, 317–322.
- (16) Genies, E. M.; Lapkowski, M.; Santier, C.; Vieil, E. *Synth. Met.* **1987**, *18*, 631–636.

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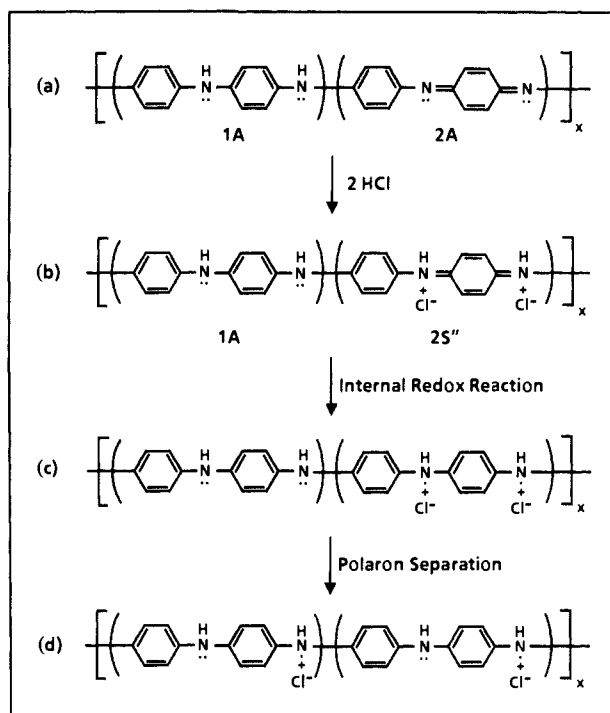


Figure 1. Scheme showing protonation of emeraldine base in HCl. (a) Emeraldine base. (b) Bipolarons centered on quinoid rings. (c) Localized polarons. (d) Separated polarons or polaron lattice.

the imine nitrogens of emeraldine base (Figure 1a) are preferentially protonated,¹ forming **2S'** units, which may be thought of as containing localized bipolarons centered on the quinoid rings (Figure 1b). EPR,^{2,12} magnetic susceptibility,^{2,17,18} and optical^{17,18} data have led to the suggestion that semiquinone radical cations (polarons) are formed (Figure 1c) by an internal redox reaction of the bipolarons.^{2,12} Direct synthesis of emeraldine hydrochloride by oxidizing aniline in acidic solution may not involve the protonated imine structure as an intermediate, but the final polymer is likely the same.¹⁹ There is disagreement over whether these polaron pairs separate because of coulomb repulsion to form metallic polaron lattice regions (Figure 1d)^{2,11,17} with conductivity limited by tunneling between these regions,^{17,18,20–22} or whether polaron formation results in a high density of localized states, conductivity being mainly due to intermolecular hopping.¹² X-ray photoelectron spectroscopy (XPS) N_{1s} and C_{1s} spectra,²³ supported by ^{13}C cross-polarization magic angle spinning (CPMAS) NMR,²⁴ show that most of the charge accompanying protonation resides on the nitrogen atoms, with very little on the carbons. In this paper a spin-echo experiment is used to demonstrate that the broad ^{13}C line width from emeraldine hydrochloride is entirely inhomogeneous, and although charge may be somewhat delocalized along the polymer backbone, the chemical shift dispersion reflects a structural disorder which disrupts delocalization. This disorder

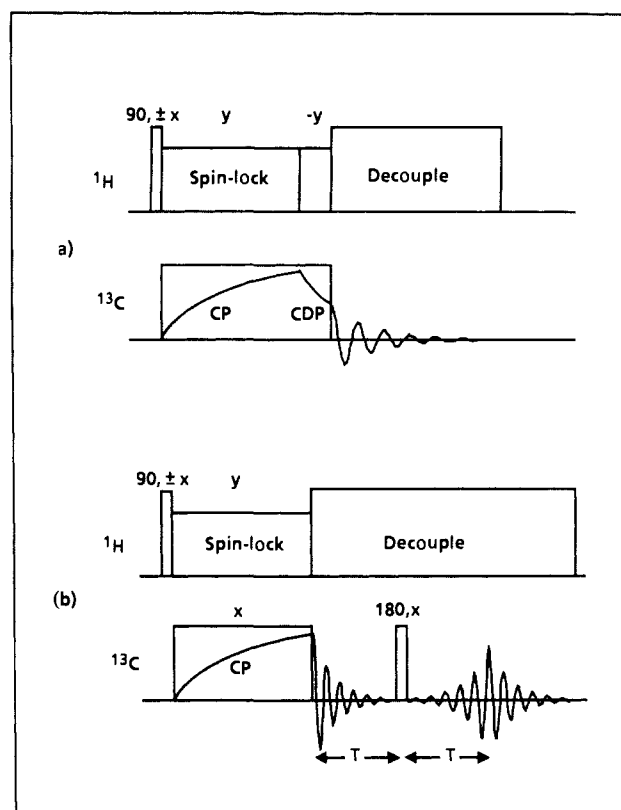


Figure 2. ^{13}C pulse sequences used in this paper. (a) Cross-depolarization technique (CDP) used to invert carbons with directly attached hydrogens. The 1H spin temperature reversal ($-y$) pulse is typically 50–100 μs . The standard CP experiment is identical except this pulse is omitted. (b) Single spin echo pulse sequence used to separate homogeneous and inhomogeneous contributions to the ^{13}C line width. The echo time, T , is stepped in 600- μs increments from 0 to 6 ms, and each acquisition is triggered at the end of the spin-lock time. The composite free induction decay is Fourier transformed to yield a spectrum whose individual peaks are homogeneously broadened while the overall envelope gives the inhomogeneous line width.

may also be responsible for the proposed segregation into metallic and insulating polymer regions,^{17,18,20–22} or alternatively, for the severe disruption of the metallic band structure into a high density of localized states.¹²

Experimental Section

Material Preparation. Polyanilines used in the current study were synthesized by methods previously described.^{1,2,19} 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 $\sim 5^\circ C$. 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) aqueous 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 $80^\circ C$ for 3 h. In order to avoid oxidation, leucoemeraldine samples were handled in an argon atmosphere, and NMR magic angle spinning was accomplished with nitrogen rather than air as the driving gas. Deuteriated polymers, required for spin counting and 2H NMR analysis (publication in preparation²⁵), were weighed and loaded into 5-mm NMR tubes in a glove box and then attached to a vacuum line for flame sealing.

NMR Spectroscopy. All solid-state NMR spectra were obtained on a Bruker CXP spectrometer operating at 200 MHz for 1H in a Cryomagnet Systems, Inc. 47 kGauss widebore superconducting magnet system. ^{13}C cross-polarization (CP) measurements at 50.3 MHz used

(17) Epstein, A. J.; Ginder, J. M.; Zuo, F.; Bigelow, R. W.; Woo, H.-S.; Tanner, D. B.; Richter, A. F.; Huang, W.-S.; MacDiarmid, A. G. *Synth. Met.* **1987**, *18*, 303–309.

(18) Ginder, J. M.; Richter, A. F.; MacDiarmid, A. G.; Epstein, A. J. *Solid State Commun.* **1987**, *63*, 97–101.

(19) MacDiarmid, A. G.; Chiang, J.-C.; Richter, A. F.; Somasiri, N. L. D.; Epstein, A. J. In *Conducting Polymers*; Alcácer, L., Ed.; Reidel Publications: Dordrecht, Holland, 1987; pp 105–120.

(20) Zuo, F.; Angelopoulos, M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1987**, *36*, 3475–3478.

(21) Epstein, A. J.; Ginder, J. M.; Richter, A. F.; MacDiarmid, A. G. In *Conducting Polymers*; Alcácer, L., Ed.; Reidel Publications: Dordrecht, Holland, 1987; pp 121–140.

(22) Epstein, A. J.; Ginder, J. M.; Zuo, F.; Woo, H.-S.; Tanner, D. B.; Richter, A. F.; Angelopoulos, M.; Huang, W.-S.; MacDiarmid, A. G. *Synth. Met.* **1987**, *21*, 63–70.

(23) Salaneck, W. R.; Lundstrom, I.; Hjertberg, T.; Duke, C. B.; Conwell, E. M.; Paton, A.; MacDiarmid, A. G.; Somasiri, N. L. D.; Huang, W. S.; Richter, A. F. *Synth. Met.* **1987**, *18*, 291–296.

(24) Stafström, S.; Sjögren, B.; Wennerström, O.; Hjertberg, T. *Synth. Met.* **1986**, *16*, 31–39.

(25) Kaplan, S.; Conwell, E. M.; Richter, A. F.; MacDiarmid, A. G., submitted.

0.5–2 ms mixing times, high power ($H_1 = 50$ kHz) ^1H decoupling, and recycle times of 1–5 s. Magic angle spinning (MAS) at 4.2–5.2 kHz was performed in a Doty Scientific probe with 30–150 mg of each sample (depending upon availability) packed into 6 mm od sapphire rotors. A one time angle adjustment was accomplished by maximizing the spinning sideband intensities of a sample of KBr.²⁶ Spectra are referenced to tetramethylsilane (TMS) by assigning the upfield peak of a minute quantity of adamantane added to each sample to 29.5 ppm.²⁷ Spectral assignment is facilitated by using the cross-depolarization (CDP) technique (Figure 2a) to distinguish between carbons with and without directly bonded hydrogens.^{28,29} After the cross-polarization mixing period and prior to carbon observation, the ^1H radiofrequency phase (i.e., ^1H spin temperature) is inverted for 50–100 μs . During this period carbon spins cross-polarize in the reverse direction, carbons with attached hydrogens the fastest and carbons without attached hydrogens the slowest. Cross-depolarization better distinguishes between these two types of carbon atoms than the commonly used delayed decoupling technique.³⁰ Furthermore, unlike delayed decoupling spectra, which have frequency dependent phase shifts, CDP spectra have identical phase to the corresponding simple CP spectrum. There is no need to apply 180° carbon refocusing pulses to restore phase coherence.³¹

The ^{13}C homogeneous line width of the emeraldine hydrochloride salt was determined by using a carbon spin echo pulse sequence (Figure 2b). Single echoes, measured for incremental pulse spacings, were summed to give a composite response, similar to the echo train produced by multiple 180° pulses in a Carr-Purcell or Meiboom-Gill pulse sequence.^{32,33} Although this experiment requires more time, it gives a reliable homogeneous line width because there is no possibility of line narrowing from the spin locking effect of a train of closely spaced pulses.³² Fourier transformation produces a sideband split pattern whose individual peaks are homogeneously broadened, while the overall envelope gives the inhomogeneous line width.

^1H spin counting was performed on ring-deuterated polymers prepared identically to the corresponding natural ^1H -abundance polymers of leucoemeraldine, emeraldine base, and the emeraldine hydrochloride. These measurements provide the average number of hydrogens attached to nitrogen, and together with elemental analysis they are important for defining the compositions of the polymers studied. Spin counting measurements were performed in a 5 mm hydrogen-free probehead with $Q = 35$, capable of a $\sim 2.5 \mu\text{s}$ 90° pulse with 350 W radio frequency power. Deadtime is $\sim 3.5 \mu\text{s}$. Hexamethylbenzene was a convenient calibration standard since it coincidentally has the same weight per mole of hydrogen as water, and thus adsorbed water does not lead to errors.

Solution ^1H spectra were measured at 500 MHz on the University of Rochester Chemistry Department's Varian VXR-500 spectrometer. Leucoemeraldine, emeraldine base, and the corresponding ring-deuterated samples were dissolved in a 1:3 mixture of DMSO- d_6 and *N*-methylpyrrolidinone. Solutions were prepared with 2% (wt/vol) solid polymer, but in some cases, only a fraction of the sample was soluble, precluding any quantitative considerations.

Results and Discussion

Figure 3 depicts ^{13}C cross-polarization magic angle spinning (CPMAS) and cross-depolarization (CDP) spectra of emeraldine base as well as difference spectra for mixing times of 0.5 and 2 ms. The CDP spectra selectively show non-protonated carbons with positive intensities, while the difference spectra have been calculated to show only the protonated carbons. (Note that we use the term *protonated* here to refer to carbons with attached hydrogens so as to avoid confusion with the term *protonated*, which, in this paper, refers to H^+ addition.) Previously published ^{13}C spectra of emeraldine base have identified the primary carbon resonances,^{13,14} but the present data also resolve longer range shifts which are due to neighboring benzenoid or quinoid groups. The more detailed assignments are made possible by the excellent discrimination of the CDP technique and the comparison with the leucoemeraldine spectra. A summary of chemical shift assignments is given in Table I.

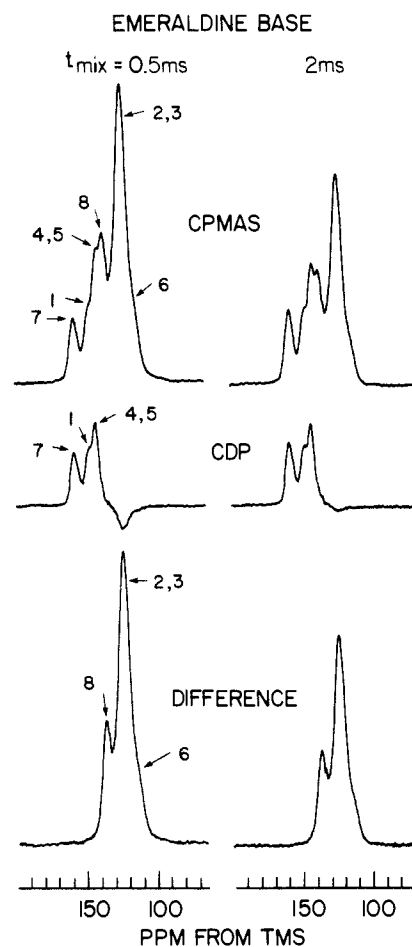


Figure 3. ^{13}C CP and CDP magic angle spinning spectra as well as the difference spectra of emeraldine base for cross-polarization mixing times of 0.5 and 2 ms. Spinning speed = 5.0 KHz, CDP time = 50 μs , recycle delay = 1.0 s. Number of scans = 48 000. Assignments correspond to the numbering scheme of Table I.

Table I. ^{13}C CPMAS Chemical Shifts^a of Emeraldine Base and Leucoemeraldine Base

carbon no.	emeraldine ^b ($y = 0.5$)	leucoemeraldine ($y = 1$)
1	145.7 \pm 1 ^c	
2, 3	123.1 \pm 0.5	
4	141.6 \pm 0.5 ^c	
5	141.6 \pm 0.5	136.3 \pm 0.5
6	115 \pm 2	118.3 \pm 0.5
7	157.3 \pm 0.5	
8	135.7 \pm 0.5 ^d	

^a PPM from TMS based upon the upfield resonance of adamantane assigned to 29.5 ppm. ^b Emeraldine base assignments assume alternating 1A and 2A units. ^c Assignments may be interchanged. ^d Half of the signal from C-8 may be obscured by C-2,3 at 123.1 ppm. See text.

The quinoid peaks, C-7 and C-8 (numbering convention accompanies Table I), are readily identified from their chemical shifts and intensities as the most deshielded peaks in the CDP and difference spectra, respectively, of Figure 3. In order to assign the phenyl ring peaks, it is instructive to compare the emeraldine base spectra with those of leucoemeraldine, which is essentially a substructure of the emeraldine polymer. Figure 4 depicts this comparison along with spectra of a partly oxidized leucoemeraldine sample. Leucoemeraldine has two peaks, a protonated carbon resonance centered at 118.3 ppm (12 ppm wide) and a nonprotonated carbon resonance centered at 136.3 ppm (10 ppm wide).

(26) Frye, J. S.; Maciel, G. E. *J. Magn. Reson.* **1982**, *48*, 125–131.

(27) Earl, W. L.; VanDerHart, D. L. *J. Magn. Reson.* **1982**, *48*, 35–54.

(28) Melchior, M. T. *22nd Experimental NMR Conference*, Asilomar, CA, 1981, Poster B29.

(29) Zumbulyadis, N. *J. Chem. Phys.* **1987**, *86*, 1162–1166.

(30) Opella, S. J.; Frey, M. H.; Cross, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 5854.

(31) Murphy, P. D. *J. Magn. Reson.* **1983**, *52*, 343–345.

(32) Garroway, A. N. *J. Magn. Reson.* **1977**, *28*, 365–371.

(33) Zilm, K. W., private communication.

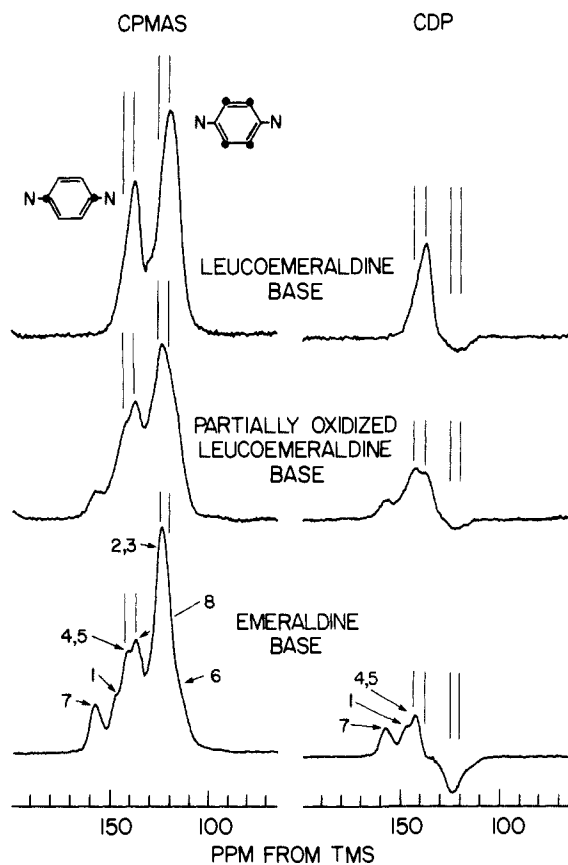


Figure 4. ^{13}C CP and CDP (CDP time = 100 μs) magic angle spinning spectra of (top) leucoemeraldine base, (center) leucoemeraldine oxidized at 80 $^{\circ}\text{C}$ and 100% relative humidity for 2 days, and (bottom) emeraldine base polymers. Top and center spectra: spinning speed = 4.2 kHz, number of scans = 20 000. Bottom spectra: spinning speed = 5.0 kHz, number of scans = 48 000. All spectra: mixing time = 0.5 ms, recycle delay = 1.0 s. Vertical bars are placed at 142, 136, 123, and 118 ppm. Assignments correspond to the numbering scheme of Table I.

These chemical shifts are in agreement with solution values of 120.1 and 136.8 ppm, respectively, reported for the central phenyl ring of *N,N'*-diphenyl-1,4-phenylenediamine.³⁴ It follows that the barely resolved upfield shoulder at ~ 115 ppm in the emeraldine base spectrum is due to carbon C-6, which is most similar to the protiated carbon site in leucoemeraldine. The largest peak, which falls at 123.1 ppm, comprises C-2 and C-3. The asymmetric doublet at 145.7/141.6 ppm is assigned to distinct carbons, but it may originate from the effect of quadrupolar ^{14}N .³⁵ The former explanation is favored, however, since the measured separation of 210 Hz is larger than expected for the ^{14}N induced splitting of a phenyl-N carbon in a 50 kGauss magnetic field.³⁶ C-5 is assigned to 141.6 ppm by comparison with the nonprotiated carbons of leucoemeraldine. The tentative assignments of C-1 and C-4 at 145.7 and 141.6 ppm, respectively, may be interchanged. Separate peaks from each of the ortho carbons of the quinoid ring might be expected due to the nonlinear imine ($-\text{N}=\text{C}$) linkage and the torsion angle between the adjacent benzenoid and quinoid rings. Recent ^{13}C - ^1H heteronuclear correlated two-dimensional NMR experiments in solution on the trimer, *N,N'*-diphenyl-1,4-benzoquinonediimine,³⁷ demonstrate that peaks from the two quinoid carbons ortho to the same nitrogen are separated by ~ 12 ppm. This splitting suggests that the signal from half of the quinoid-ring carbons (C-8) in the emeraldine base may be obscured by the C-2,3 resonance at 123.1 ppm.

The C=N quinoid resonance (C-7) observed at 157.3 ppm is absent from the leucoemeraldine spectra. However, after heating at 80 $^{\circ}\text{C}$ for 2 days in 100% humidity air (Figure 4, center), the quinoid peak appears, and it is clear that oxidation has occurred, leading to the partial formation of emeraldine base. A similar result has been deduced from Raman and infrared spectroscopies.³⁸ It is plausible that, in the presence of water acting as a catalyst, oxygen extracts amine hydrogens to convert a 1A unit to a 2A unit. For our sample, oxidation is slow; even under severe conditions of heat and humidity for 2 days, only about 50% conversion occurred. However, sample color change from the initial light grey of leucoemeraldine to a dark green was evident after only $\sim 10\%$ conversion and to a dark blue shortly thereafter.

The nonprotiated carbon resonance (136.3 ppm) of leucoemeraldine diminishes in intensity in the partially oxidized material and is absent from emeraldine base. Blocks of 1A units are responsible for this resonance. The absence of spectral intensity at 136.3 ppm in the CDP spectrum of emeraldine base leads to the conclusion that all 1A units have 2A units as neighbors. Furthermore, from hydrogen spin counting measurements, the H/N ratio determined for ring-deuteriated emeraldine base is 0.46, i.e., the ratio of benzenoid to quinoid rings, B/Q, equals 2.7. This value is close to B/Q = 3, the ratio expected for equal numbers of 1A and 2A units. Taken together, these observations indicate that emeraldine base is primarily an *alternating* head-to-tail copolymer of 1A and 2A units. The 5.3 ppm shift difference between the nonprotiated leucoemeraldine carbons and C-5 of emeraldine suggests that chemical shifts are sensitive to sequencing of benzenoid and quinoid rings up to two rings removed. This result is reasonable, since π -bond conjugation can lead to long-range effects.

Hydrogen spin counting on ring-deuteriated leucoemeraldine gave unexpectedly high H/N ratios of 1.2–1.3. ^1H NMR solution spectra of natural ^1H -abundance material show a broad aromatic resonance at ~ 7 ppm, while spectra of the ring-deuteriated sample show three lower intensity impurity peaks (7.7 to 8.4 ppm), which may originate from a partial reaction (e.g., chain scission or H-substitution onto quinoid rings) of the hydrazine reducing agent with the emeraldine base, from which leucoemeraldine is prepared. On the other hand, the ^1H solution spectrum of natural ^1H -abundance emeraldine base has several peaks in the 7.0 to 7.4 ppm range, and the corresponding ring-deuteriated sample has, as expected, no aromatic peaks. Thus, although the emeraldine base sample is compositionally pure, the leucoemeraldine sample contains some impurities or compositional defects.

The ~ 10 ppm ^{13}C line widths of the leucoemeraldine and emeraldine base spectra are broader than the 2–7 ppm typically observed for amorphous polymers³⁹ and are attributed to a distribution of bond angles and chain packing. This hypothesis is consistent with ^2H measurements,²⁵ which suggest local fluctuations in free volume, and X-ray diffraction measurements,⁴⁰ which show emeraldine base to be completely amorphous. Quinoid-ring-centered triads can exist in cisoid or transoid geometries, which are nearly equal energy,^{41–43} and benzenoid-ring-centered triads may occur in syn or anti conformational arrangements. Furthermore, there may be a distribution of torsion angles between adjacent rings,²⁴ resulting in a variety of configurational and conformational organizations. Motional broadening cannot be a factor since ^{13}C line widths are independent of temperature up to 100 $^{\circ}\text{C}$.

The ^{13}C CPMAS spectrum of the HCl salt of emeraldine at 27 $^{\circ}\text{C}$ (Figure 5, top) is a single ~ 60 ppm broad unresolved

(38) Ohira, M.; Sakai, T.; Takeuchi, M.; Kobayashi, Y.; Tsuji, M. *Synth. Met.* **1987**, *18*, 347–352.

(39) VanderHart, D. L.; Earl, W. L.; Garroway, A. N. *J. Magn. Reson.* **1981**, *44*, 361–401.

(40) Annis, B. K.; Narten, A. H.; MacDiarmid, A. G.; Richter, A. F. *Synth. Met.* **1988**, *22*, 191–199.

(41) Conwell, E. M.; Duke, C. B.; Paton, A.; Jeyadev, S. *J. Chem. Phys.* **1988**, *88*, 3331–3337.

(42) Langer, J. J. *Synth. Met.* **1987**, *20*, 35–41.

(43) Hjertberg, T.; Sandberg, M.; Wennerström, O.; Langerstedt, I. *Synth. Met.* **1987**, *21*, 31–39.

(34) *Sadtler Standard Carbon-13 NMR Spectra*; Sadtler Research Laboratories: Philadelphia, PA.

(35) Naito, A.; Ganapathy, S.; McDowell, C. A. *J. Magn. Reson.* **1982**, *48*, 367–381.

(36) Olivieri, A. C.; Frydman, L.; Diaz, L. E. *J. Magn. Reson.* **1987**, *75*, 50–62.

(37) Sandberg, M.; Hjertberg, T., submitted.

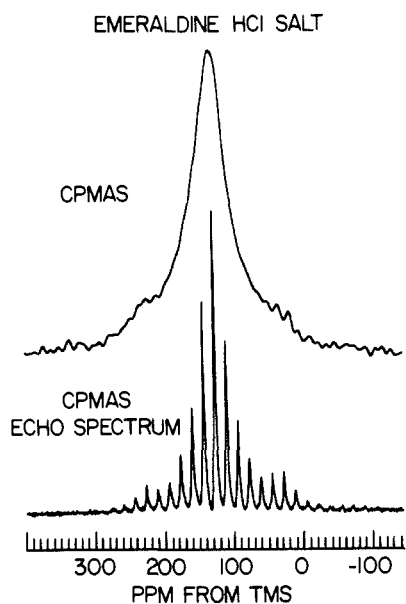


Figure 5. Top: ^{13}C CPMAS spectra of the emeraldine HCl salt. Spinning speed = 5.0 kHz, mixing time = 1 ms, recycle delay = 3 s, number of scans = 7200. Bottom: ^{13}C spin echo spectrum using the pulse sequence of Figure 2b. Spinning speed = 5.0 kHz, mixing time = 1 ms, recycle delay = 1 s, number of scans per echo = 7040.

resonance. This featureless signal has been reported earlier, and a number of possible line-broadening mechanisms have been cited.^{13,24,43} In the present work additional measurements were performed to assess the nature of the broadening. A spin echo pulse sequence was employed to separate the homogeneous and inhomogeneous contributions to the ^{13}C line width. The Fourier transform of a composite time-domain signal of ten individually acquired echoes with echo delays of $T = n\tau$ ($\tau = 600 \mu\text{s}$, $n = 0$ to 10) is plotted at the bottom of Figure 5. The overall envelope reflects the 60-ppm width of the simple cross-polarization free-induction decay. However, the homogeneous line width is only a few ppm, revealing that the ^{13}C spectrum of the emeraldine hydrochloride is *inhomogeneously* broadened as a result of a superposition of many overlapping narrow peaks from a heterogeneity of chemical environments. Therefore, the line width is not controlled by electron spin induced relaxation of ^{13}C nuclei, because this mechanism would lead to homogeneous broadening.

The ^{13}C spectrum of emeraldine hydrochloride has a similar chemical shift range to that measured for the leucoemeraldine and emeraldine base forms, indicating that neither a distribution of Knight shifts nor isotropic contact shifts from paramagnetic centers governs the line width. Moreover, the latter interaction is strongly temperature dependent, but a spectrum of emeraldine hydrochloride measured at 90 °C is superimposable with the spectrum obtained at 27 °C (Figure 5, top). The pseudocontact shift, arising from the combined effects of electron spin–nuclear spin and electron orbit–nuclear spin dipolar couplings, may be operative.¹³ However, the small number of Curie spins present (1 per 100 rings)²² and the long residence time of these spins on the nitrogens²³ coupled with the $1/r^3$ dependence of the pseudocontact shift argues against its dominance. ^{13}C line widths may be exchange broadened by adsorbed moisture via proton-exchange-assisted charge transfer.^{3,7,10} However, this mechanism would lead to temperature dependent line shapes, which are not observed. The origin of the ^{13}C line broadening in emeraldine hydrochloride is most likely local variations in charge density along the polymer backbone. Although the charge resides mainly on the nitrogens, the charge density distribution associated with a polaron lattice extends over a number of polymer repeat units, and with a localized polaron over perhaps a few atomic distances. In either case the charge density distribution can influence the chemical shifts of the ring carbons. It is postulated that local variations in polymer structure (packing, conformations, etc.) can

perturb this charge distribution, leading to the observed spectral dispersion.

Aside from the broad ^{13}C line widths, there is additional spectroscopic evidence for structural heterogeneity in the salt form. X-ray diffraction measurements⁴⁰ of emeraldine hydrobromide indicate a completely amorphous polymer. Morphology of the salt is likely related to that of the emeraldine and leucoemeraldine base forms,²⁴ where the superposition of ^2H powder pattern line shapes characteristic of rigid non-rotating rings and rings undergoing rapid 180° flips about their 1,4 axes reveal fluctuations in local packing.²⁵ The emeraldine salt is observed to have approximately one-third as many flipping rings as the emeraldine base, attributable to either a direct steric interaction with the chloride counterions or to charge delocalization imparting some π -electron density to the ring–nitrogen bonds.²⁵ Mass spectra of species emitted from the emeraldine hydrochloride, coupled with simultaneous monitoring of electrical conductivity and X-ray photoelectron Cl (2p) and N (1s) spectra, suggest that in the vacuum dried salt, some protons of the imino nitrogens in $2\text{S}''$ units transfer to the amino nitrogens in 1A units, thus forming $1\text{S}'$ or $1\text{S}''$ units.⁴⁴ Recent redox⁴⁵ and volumetric⁴⁶ titration studies suggest that protonation of emeraldine base (which has been prepared and handled in air so that it is slightly over-oxidized⁴⁵) is simultaneously accompanied by reduction in oxidation state (due to hydrolysis) such that the product emeraldine hydrochloride consists of ~60% reduced units.⁴⁵ Amine nitrogens of the excess reduced (1A) groups may become protonated, forming $1\text{S}'$ units.^{46,47} The presence of $1\text{S}'$, $1\text{S}''$, or residual 1A units in the emeraldine hydrochloride would represent barriers that restrict charge delocalization, i.e., defects through which a polaron lattice could not extend. Finally, ^1H spin counting of the ring-deuteriated emeraldine salt yields a hydrogen to nitrogen ratio equal to 1.0, consistent with the chlorine to nitrogen ratio of 0.5 determined by elemental analysis,¹⁹ and in agreement with the expected stoichiometry of the emeraldine salt.

Conclusions

By comparison with the ^{13}C NMR spectra of pristine and partially oxidized leucoemeraldine, emeraldine base is shown to be an alternating copolymer of 1A and 2A units. The ~10 ppm ^{13}C line widths measured for the leucoemeraldine and emeraldine base reflect a high degree of structural heterogeneity. Local fluctuations in conformational and configurational geometries, a distribution in chain packing, as well as compositional defects all play a role. For the conducting emeraldine hydrochloride salt, the line width is inhomogeneously broadened so that a single unresolved 60-ppm resonance is observed. The secondary effect of structural variations perturbing the distribution of charge along the backbone of the polymer explains the additional chemical shift dispersion. From the present data it is not possible to distinguish between models of metallic polaron lattice regions separated by insulating (defect) regions or a high density of localized states, but the structural disorder implicit in the ^{13}C line width of emeraldine hydrochloride precludes extensive spin delocalization along the polymer chain.

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(44) Uvdal, K.; Hasan, M. A.; Nilsson, J. O.; Salaneck, W. R.; Lundstrom, I.; MacDiarmid, A. G.; Ray, A.; Angelopoulos, M. In *Proceedings of Winter School on Conducting Polymers*; Kuzmany, H., Mehring, M., Roth, S., Eds.; Springer-Verlag: Berlin, 1987.

(45) Asturias, G. E.; MacDiarmid, A. G.; Epstein, A. J., submitted.

(46) Menardo, C.; Genoud, F.; Nechtschein, M.; Travers, J. P.; Hani, P. In *Electronic Properties of Conjugated Polymers*; Kuzmany, H., et al., Eds.; Springer-Verlag: Berlin, 1987; p 244.

(47) Ray, A.; Richter, A. F.; MacDiarmid, A. G.; Epstein, A. J., submitted.