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^{15}N NMR OF POLYANILINE

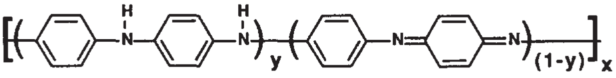
A.F. RICHTER, A. RAY, K.V. RAMANATHAN, S.K. MANOHAR, G.T. FURST, S.J. OPELLA AND A.G. MACDIARMID
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323 (USA)
A.J. EPSTEIN
Department of Physics and Department of Chemistry, The Ohio State University, Columbus, OH 43210-1106 (USA)

ABSTRACT

^{15}N NMR spectroscopy has been utilized as a structural probe for the leuco- and "emeraldine" base forms of polyaniline. Preliminary results suggest that the emeraldine base polymer exists as an alternating copolymer of oxidized and reduced units. End-groups are not detected at the experimental level of sensitivity.

INTRODUCTION

The term "polyaniline" is descriptive of a class of conducting polymers derived from the base of general composition



, $0 \leq y \leq 1$

Reduced ("1A") unit
Oxidized ("2A") unit

The chemical, electronic, magnetic and mechanical properties of the polymer are sensitive to several variables. These include:

(i) The average oxidation state, defined by the term (1-y) in the above general formula [1].

(ii) The level of protonation, which has been shown to change the material of oxidation state (1-y)~0.5 from an insulator ($\sigma \sim 10^{-8}$ S/cm) when doped at pH~7 to a conductor ($\sigma \sim 1$ S/cm) when doped at pH~0 [2,3].

(iii) Substitution of hydrogen atoms by alkyl groups on the $-C_6H_4-$ rings [4].

(iv) Substitution of hydrogen atoms on $-N(H)-$ sites by alkyl groups or addition of alkyl groups to $-N=$ sites [5].

(v) Molecular weight and morphology.

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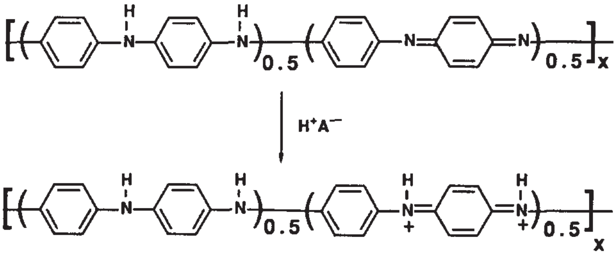
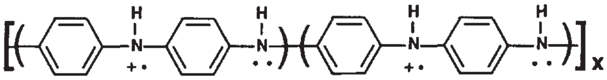
Protonation of the nitrogen atoms at pH~0 leads to a conducting form of the polymer having (1-y)~0.5. This "protonic acid" doping process is believed to be dominated by the reaction



EPR [6] and magnetic susceptibility [7] data suggest that the protonated polymer exists mainly as the semiquinone radical cation



In this formal structure, the unpaired spins are believed to reside mainly on the nitrogen atoms. It may be noted that the nitrogen atoms are also the reactive sites for "pseudo-protonic" [5] doping processes, where, for example, a "positive" methyl group instead of a proton adds to the imine sites. Thus, ^{15}N NMR is expected to be a sensitive and useful probe of the structure and chemistry of the polyanilines. We report here some early results in this context as an indicator of the potential value of the method.

EXPERIMENTAL

^{15}N aniline (ICN Biomedicals) was distilled on a vacuum line and used either directly or at ~50% enrichment by co-distilling with ^{14}N-aniline (Fisher Scientific).

Synthesis of "emeraldine" base

Conventional Technique(CT)

Polymerization was carried out in 1M HCl using $(NH_4)_2S_2O_8$ as has been described elsewhere [8] to yield "emeraldine" hydrochloride, (1-y)~0.5. This was deprotonated in air using 0.1M NH_4OH. The base form thus prepared is generally found to have an oxidation state of (1-y)~0.6 [1].

Phase-Transfer Technique(PTT)

In this method, aniline was dissolved in CH_2Cl_2 containing a catalytic amount of tetrabutylammonium perchlorate. A solution of $(NH_4)_2S_2O_8$ in aqueous 1M HCl was added to this, taking care not to mix the layers [9]. The polymer formed at the interface and was subsequently collected by filtration of the two-phase mixture. Subsequent deprotonation with 0.1M NH_4OH was carried out as previously described [8], except that all operations were performed in a glove bag under argon.

Inert-atmosphere syntheses of "emeraldine" base have been found to yield products having (1-y) values ~0.4 [1].

Synthesis of leucoemeraldine base, (1-y)~0

~150 mg. of "emeraldine" base(CT), synthesized as described above, was treated with ~10 mL of hydrazine hydrate (Aldrich). Reduction of imine units can be described by the net reaction

The evolved nitrogen was periodically removed by freeze-pump-thaw cycles on the vacuum line. The heterogeneous mixture was allowed to stir for ~72 hours and unreacted hydrazine was subsequently pumped off. A pale grey free-flowing powder resulted.

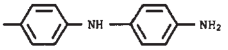
Solid State NMR

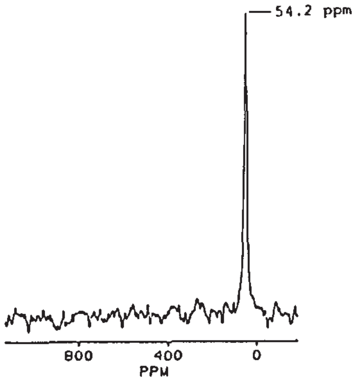
Measurements on powders were carried out on a custom-built 150 MHz (^{15}N frequency = 15.24 MHz) instrument using magic angle spinning at 2.5 KHz. Cross-polarization was used to enhance the sensitivity. An optional delay of 50 µsecs could be applied before observation of the ^{15}N FID. This depleted the polarization of nitrogen species directly bonded to H atoms. Such cross-depolarization decreases the intensity of such -N(H)- species and can thus be used to distinguish them from imine, -N=, nitrogens which are relatively unaffected by the delay. $(NH_4)_2SO_4$ was used as an external reference for chemical shifts.

Solution NMR

Solution experiments were performed on a Bruker WP 200SY (^{15}N frequency = 20.28 MHz) instrument using a 3:1 mixture of N-methylpyrrolidinone and d_6-dimethylsulfoxide as the solvent system. ^{15}N aniline was used as an approximate external reference, taken to be at 29.0 ppm downfield of $(NH_4)_2SO_4$ in order to permit comparison with the solid-state studies. An inverse-gated decoupling pulse sequence was used to minimize the effect of a possible small negative Nuclear Overhauser Effect.

RESULTS AND DISCUSSION

A solid-state spectrum of leucoemeraldine base, (1-y)~0, is shown in Fig. 1. A single resonance is seen at 54.2 pm downfield from $(NH_4)_2SO_4$. The spectrum of the model compound p-aminodiphenylamine, , is shown in Fig.2. Comparison of these spectra shows that leucoemeraldine base does not contain any detectable end-group population (expected at ~37 ppm) on the ^{15}N level of



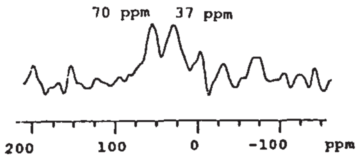
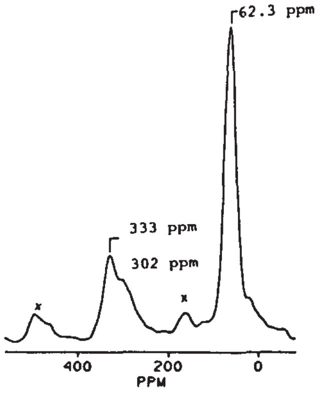


Fig. 1. Solid-state ^{15}N NMR spectrum of leucoemeraldine base; Fig. 2. Solid-state ^{15}N NMR spectrum of p-aminodiphenylamine.

sensitivity. The 54.2 ppm signal arises from -N(H)- groups separated by p-phenylene moieties.

Using this information, it is possible to analyze the spectra of "emeraldine" base forms of polyaniline, where (1-y)~0.5. Figs. 3 and 4 compare a solid-state spectrum of "emeraldine" base (CT) with a solution spectrum of "emeraldine" base (PTT) respectively.



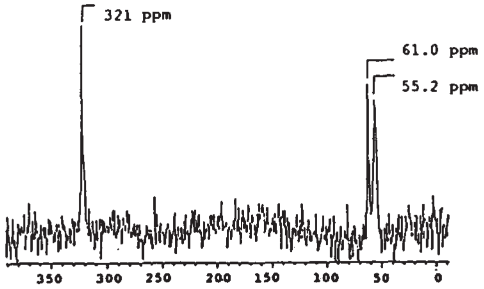
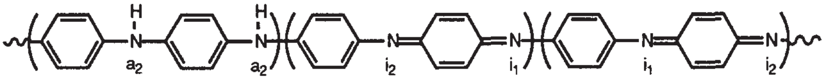


Fig. 3. Solid-state ^{15}N NMR spectrum of "emeraldine" base(CT), "x" denotes spinning sidebands; Fig. 4. Solution ^{15}N NMR spectrum of "emeraldine" base(PTT)

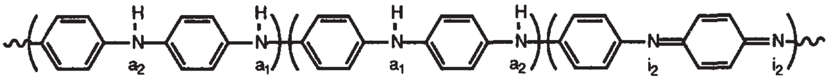
Examination of the relative intensities of the ~1500 and ~1600 cm^{-1} peaks [10] in the infrared spectra of the CT and PTT "emeraldine" base samples suggests that the CT material is more oxidized than the PTT. This is also confirmed by a comparison of their UV/visible spectra in aqueous 80% acetic acid [1].

Two imine-type resonances (in the range 300-330 ppm) and only one in the secondary aromatic amine, -N(H)- region (expected at 50-70 ppm) are seen for the CT sample (Fig. 3). Cross-depolarization studies are consistent with the 62.3 ppm signal being associated with N atoms which are directly bonded to protons. The spectrum is suggestive of a *unique* environment for the -NH- species, but at least two different environments for the -N= species. This is consistent with a structure of the type



where some imine-imine sequences exist for a polymer having $(1-y)>0.5$. "Type 1" resonances refer to homopolymeric diads; "type 2" to copolymeric diads; and 'a' and 'i' stand for amine and imine respectively. The -NH- signals for such structures are expected to be different from that for leucoemeraldine base, which has *only* a_1 diads, as can be seen experimentally, viz., 62.3 ppm for the "a_2" species of the CT "emeraldine" base polymer and 54.2 ppm for the leucoemeraldine base (a_1).

However, it can be seen (Fig. 4) that the PTT sample has two resonances in the amine region and one in the imine region. Using the same logic as for the CT sample, this observation is consistent with a $(1-y)$ value<0.5, where the imine units are isolated from each other but some contiguous amine-amine regions are present, viz.,



By comparison with Fig. 1, one can readily assign the 55.2 ppm signal of PTT "emeraldine" base to the a_1 species; the 61.0 ppm resonance corresponds to the a_2 species (seen at 62.3 ppm in the CT case). An i_2 peak can be readily identified at 321 ppm.

Since no i_1 peaks are seen in the under-oxidized PTT sample and no a_1 peaks are observed in the "over-oxidized" material, it would appear that when $(1-y)=0.5$ *exactly*, the spectrum of the base would consist of only 2 signals; an i_2 diad in the imine region and an a_2 diad in the amine region. It follows that for this special case, the polymer would tend to be composed mainly of *alternating* amine

(1A) and imine(2A) units, as has been suggested previously [11]. This permits us to make a qualitative prediction (shown in Table 1) of the spectral features anticipated for "true" emeraldine base, where (1-y) is *exactly* 0.5.

TABLE 1

Sample	(1-y) value	Chemical Shift (ppm)			
		a_1	a_2	i_1	i_2
leucoemeraldine	0	54.2	-	-	-
"emeraldine" base (PTT: under-oxidized)	<0.5	55.2	61.0	-	321
"emeraldine" base (CT: over-oxidized)	>0.5	-	62.3	333	302 shoulder
emeraldine base *(predicted)*	0.5	-	~62	-	~321

The above results are consistent with the CT "emeraldine" base being over-oxidized, i.e. (1-y)>0.5 and with the PTT sample being under-oxidized i.e. (1-y)<0.5. However, it should be stressed that in this discussion, a solid-state spectrum of the CT polymer is being compared with a solution spectrum of the PTT polymer. Studies are presently being carried out in which solid-state spectra of these two kinds of "emeraldine" base are compared and their respective solution spectra are also compared.

It is important to note that possible effects of geometric isomerism are not accounted for by this interpretation of the NMR data. Although cis-trans isomerism about the rigid quinoid rings of polyaniline has been detected in ^{13}C NMR [12], the N atoms may be too far from the sites of isomeric geometry to be substantially affected. However, the possibility cannot be eliminated until appropriate model compound studies have been carried out. We are currently examining this issue in our laboratory.

CONCLUSIONS

Preliminary ^{15}N NMR studies on "emeraldine" base suggest that the polymer exists as an alternating system of oxidized and reduced repeat units. Clustering of *only* those units which are present in larger number is observed in samples having oxidation states (1-y)~0.5. There is no evidence for end-group, $-NH_2$, species, suggesting that small-chain oligomers are not present in detectable quantities. ^{15}N NMR appears to be a promising technique for probing the structure of polyaniline.

ACKNOWLEDGEMENTS

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