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N-SUBSTITUTED DERIVATIVES OF POLYANILINE

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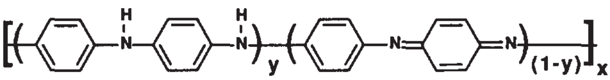
ABSTRACT

Fully N-methylated polyaniline was obtained analytically pure by the oxidative polymerization of $C_6H_5N(CH_3)(H)$ with $(NH_4)_2S_2O_8$ in 1.0M aqueous HCl. The resulting black-green polymer (σ ~10^{-4} S/cm) was shown to have a similar backbone structure to parent polyaniline, and upon heating, lost HCl and H_2O, yielding a black-brown solid, ($\sigma < 10^{-8}$ S/cm) containing ~14% oxidized groups. "Pseudo-protonic" acid doping of "emeraldine" base with neat $(CH_3)_2SO_4$ yielded polymers whose extent of doping could be monitored continuously. The ~50% methylated "emeraldine" base (σ = ~10^{-2} S/cm) had a χ_{Pauli} approximately half that of 50% proton doped "emeraldine" base, consistent with the symmetry-breaking effect of the methyl groups.

INTRODUCTION

The parent polyaniline bases of general composition



where y can in principle range from y=1 to y=0 have been studied extensively during the last three years, with most investigations having been performed on the "emeraldine" oxidation state where y~0.5 [1]. We believe the polymer consists principally of approximately equal numbers of oxidized and reduced groups and can be protonated by aqueous acids at the imine nitrogen atoms to yield a polysemiquinone radical cation (σ ~1-5 S/cm), [1,2] viz.,

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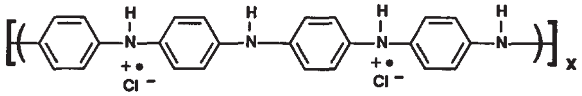
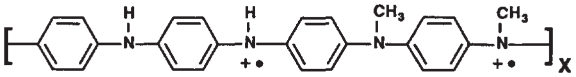


We have shown previously [3] in preliminary studies that the imine nitrogen atoms can also apparently undergo "pseudo-protonic' acid doping by e.g. methyl groups to yield a polymer containing both -N(H)- and -N(CH_3)- groups viz.,



shown here in the extreme polaronic form.

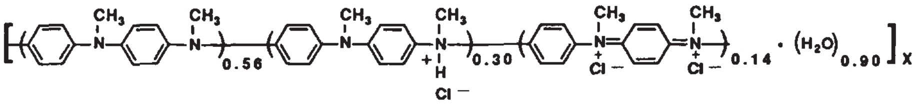
Of particular interest is the synthesis and characterization of a polymer where methyl groups are attached to all the nitrogen atoms so that its properties can be compared with those of the polymer in which H atoms are attached to all nitrogen atoms and with those of the polymer in which half the nitrogen atoms have attached H atoms and half have attached methyl groups. Previous studies [4] on the completely N-methylated polymer, synthesized by the chemical or electrochemical polymerization of $(C_6H_5)N(CH_3)(H)$ have not reported elemental analyses or detailed characterization of the materials.

The objectives of the present investigation were to (i) synthesize completely N-methylated polyanilines by the chemical oxidative polymerization of $(C_6H_5)N(CH_3)(H)$; (ii) synthesize polyaniline doped by $(CH_3)_2SO_4$ in the approximate emeraldine oxidation state containing approximately equal numbers of N(H) and N(CH_3) groups, and (iii) obtain evidence to assist in elucidating the constitution of the polymers synthesized.

EXPERIMENTAL

Synthesis of Protonated 14% Oxidized Poly(N-methyl)aniline

Polymerization of $(C_6H_5)N(CH_3)(H)$ in 1M aqueous HCl with $(NH_4)_2S_2O_8$ yielded a black-green insoluble powder (σ ~10^{-4} S/cm) which when filtered, re-equilibrated with 1.0M aqueous HCl for 24 hours followed by drying under dynamic vacuum for 24 hours at room temperature gave an elemental analysis [5] corresponding to



depicted in the bipolaronic form for clarity.

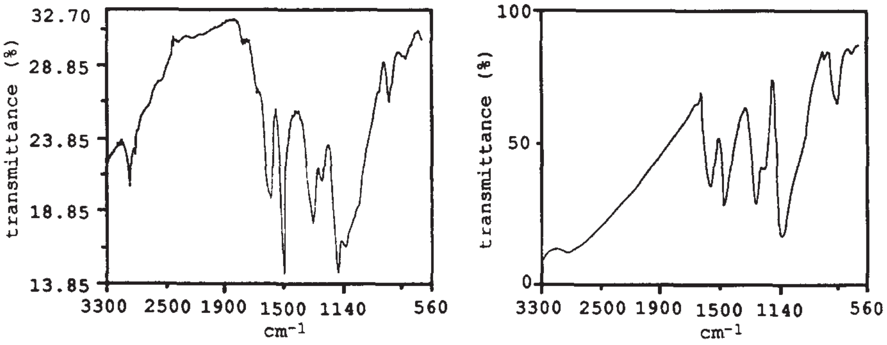
	C	H	N	Cl	O[b]	Total
Calc.[a]	68.00	6.50	11.33	8.33	5.83	100.00
Found	68.26	5.89	10.94	8.55	6.33	100.00

(a) Calc. for $C_{14}H_{16.10}N_2Cl_{0.56}O_{0.90}$

(b) Oxygen by difference.

The presence of some water in the polymer is understandable, since, as shown below, the material could not be heated to remove all water, as is customary in drying emeraldine•HCl [6] since heating removes HCl as well as water.

The IR spectrum of the polymer and emeraldine•HCl are given in Fig.1.

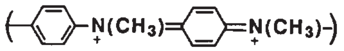
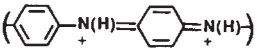


(a)

(b)

Fig. 1 (a) FT/IR spectrum (KBr) of protonated, 14% oxidized poly(N-methyl)aniline; (b) FT/IR spectrum (KBr) of emeraldine•HCl

As can be seen, the spectra are very similar, consistent with the protonated 14% oxidized poly(N-methyl)aniline having a similar backbone structure to emeraldine•HCl. In particular the following should be noted: (i) C-H stretching frequencies characteristic of $N-CH_3$ groups are clearly observed at 2925 cm^{-1} and 2855 cm^{-1}; (ii) from the 828 cm^{-1} peak characteristic of a para-substituted aromatic ring and from the very weak peak at 725 cm^{-1} characteristic of ortho or meta substitution, it appears that polymerization has proceeded in a "head to tail" fashion comparable to that in parent emeraldine•HCl and (iii) the greater relative intensity of the ~1500 cm^{-1} peak vs. the ~1600 cm^{-1} peak as compared to the relative intensities of the same two peaks in emeraldine•HCl [7] indicate that the polymer is in a less oxidized state than the corresponding emeraldine•HCl. This is consistent with the presence of only ~14% of oxidized

 groups in the polymer as compared to the ~50% of oxidized  groups (depicted in the bipolaronic form for simple comparison) in emeraldine•HCl. Its visible UV spectrum is given in Fig. 2 together with that of the protonated form of the parent emeraldine salt (formed by dissolving emeraldine base in 80% aqueous acetic acid.) Both solutions were filtered through a 2000Å micropore filter, to remove any particulate matter greater than 2000Å.

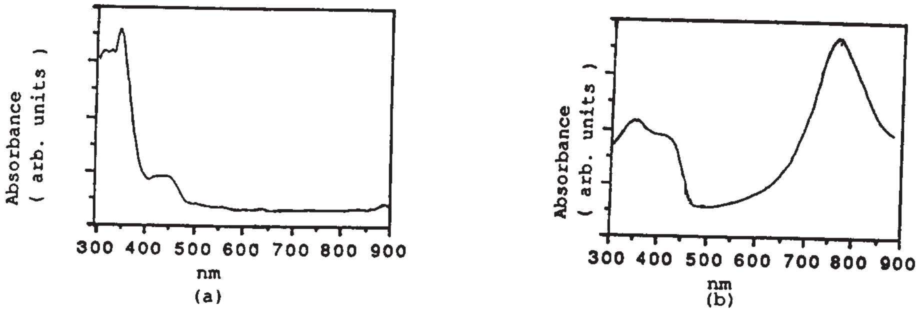
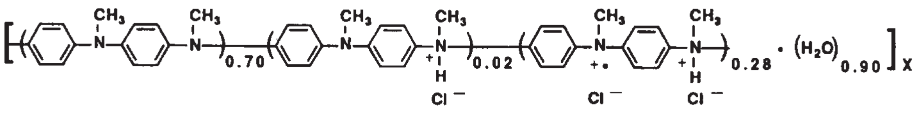


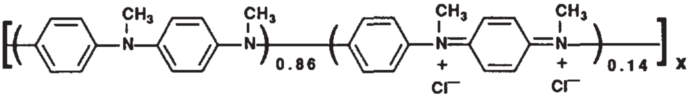
Fig. 2. (a) Spectrum of protonated, 14% oxidized poly(N-methyl)aniline in dimethylformamide; (b) spectrum of emeraldine•HOAc in 80% aq. acetic acid

Both compounds have absorbances at ~346 nm (~3.64 eV) characteristic of the interband transition. The weak peak at ~436 nm (~2.84 eV) characteristic of a polaronic transition may be compared with the peak at ~420 nm (~2.95 eV) in the more fully oxidized parent emeraldine salt. The low energy transition corresponding to the ~784 nm (~1.58 eV) peak in the parent emeraldine salt, if present, must fall below 900 nm (1.38 eV). These transitions, together with the presence of a significant number of Curie spins ($n_C = 4.66 \times 10^{-2}$ spins/2-ring) in the polymer, suggest that the configuration of the protonated poly(N-methyl)aniline compound given above should be modified possibly to include a contribution from a form such as



Synthesis of Deprotonated 14% Oxidized Poly(N-Methyl)aniline

When protonated poly(N-methyl)aniline was heated under dynamic vacuum at 90-100°C for ~3 hours, mass spectroscopic examination of the evolved gas up to mass 80 showed it consisted of HCl and water only. Elemental analysis [5] of the resulting black-brown powder ($\sigma \leqslant \sim 10^{-8}$ S/cm) corresponded to



	C	H	N	Cl	Total
Calc.[a]	76.38	6.36	12.73	4.52	100.00
Found	76.50	5.85	12.90	4.45[b]	99.70

(a) Calc. for $C_{14}H_{14}N_2Cl_{0.28}$

(b) Cl analysis performed by Micro-Analysis Inc., Wilmington, DE 19808

"Pseudo-Protonic" Acid Doping of Emeraldine Base with Dimethyl Sulfate

So that the extent of doping of emeraldine base with $(CH_3)_2SO_4$ could be monitored continuously during the doping process, a given weight of emeraldine base was stirred with neat $(CH_3)_2SO_4$ in the vacuum line at selected temperatures At periodic intervals all unreacted $(CH_3)_2SO_4$ was distilled from the reaction vessel under dynamic vacuum. From the increase in weight, assuming the only volatile material was unreacted $(CH_3)_2SO_4$, together with the weight of the emeraldine base employed, the gross elemental composition of the resulting product could be obtained. As can be seen from the analytical data below, excellent agreement was obtained for elemental compositions calculated from the weight increase and from conventional elemental analysis.

(1) 26.25% doped (i.e. N-methylated) polymer (~25°C):

Composition (wt%)	C	H	N
(a) From wt. increase	63.27	4.92	11.31
(b) From elemental analysis	63.29	5.81	11.87

(2) 56.94% doped (i.e. N-methylated) polymer (~50°C):

Composition (wt%)	C	H	N
(a) From wt. increase	52.90	4.70	8.65
(b) From elemental analysis	52.06	5.11	9.11

The 56.94% doping level could result from "emeraldine" base in which (1-y) ~0.57 [8].

The relationship between the conductivity (four-probe) of compressed pellets of the doped polymer as a function of doping percentage is given in Fig. 3. It should be noted that the conductivity of the undoped emeraldine base starting material is ~10^{-10} S/cm.

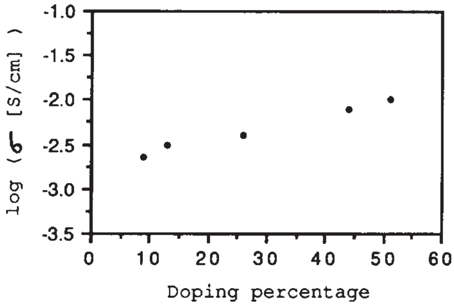
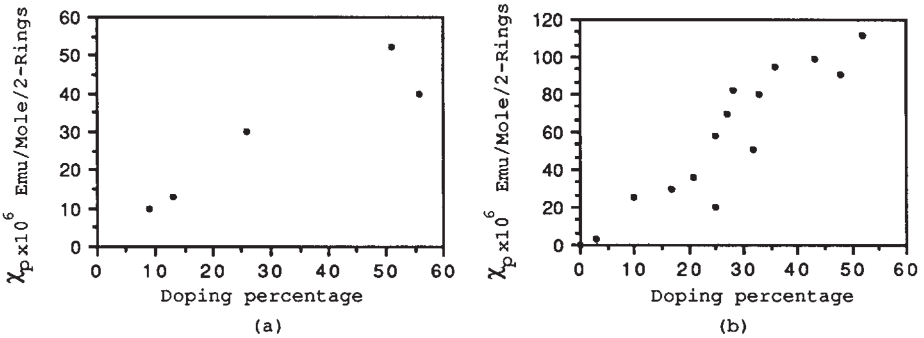


Fig. 3. Relationship between conductivity and percent doping of emeraldine base with dimethyl sulfate

The 50.90% doped polymer had a Curie susceptibility corresponding to 8.0×10^{-2} spins/two rings. The Pauli suceptibility, χ_p, of emeraldine base as a function of percent doping by $(CH_3)_2SO_4$ and by HCl [9] is given in Fig. 4.



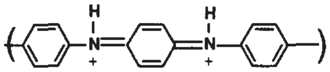
(a)

(b)

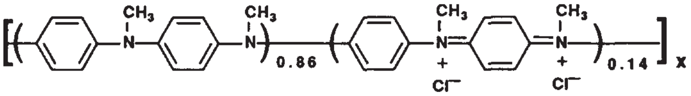
Fig. 4. (a) χ_p as a function of doping of emeraldine base by $(CH_3)_2SO_4$; (b) χ_p as a function of doping of emeraldine base by HCl [9].

Discussion

Oxidative polymerization of $C_6H_5N(CH_3)(H)$ under the experimental conditions employed results in the formation of a completely N-methylated protonated polyaniline whose constitution can be formulated from elemental analysis as discussed in the previous section. According to this formulation, the polymer is produced in a state containing ~14% of oxidized groups. This may be compared with the analogous synthesis of emeraldine•HCl, which is produced in a state containing

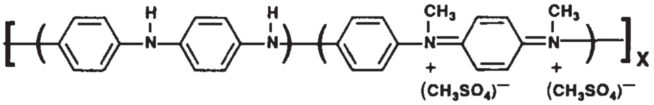
~50% of oxidized,  groups, written here, for simple comparison, in the bipolaronic form. There is no reason *per se*, to expect that the two polymers would necessarily be synthesized in the same oxidation state. It will be of interest to ascertain whether the ~50% oxidized polymer, if it can be synthesized, will have a larger conductivity than the present 14% oxidized material. It should be be noted that the conductivity of the fully protonated emeraldine base reaches a maximum when 50% of its constituent groups are in the oxidized form [10].

When the protonated 14% oxidized polymer is heated, all the water and HCl is removed to yield



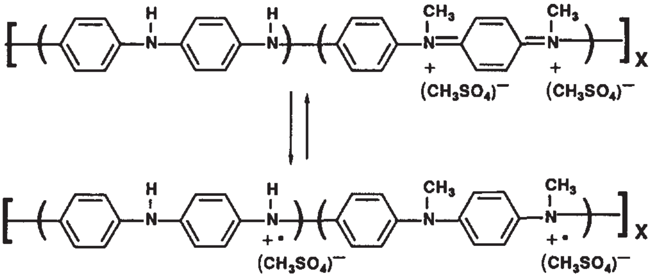
which has a $\sigma \sim 10^{-8}$ S/cm. A detailed analysis of the constitution of the deprotonated form of the 14% oxidized poly(N-methyl)aniline cannot be made until more complete magnetic data are available, although in view of its greatly reduced conductivity as compared to the protonated material, it appears it may exist primarily in the bipolaronic form depicted above. If this should be the case, it would appear that the oxidized and reduced repeat units of this polymer show little tendency to interact to form polarons. It has not yet been determined what changes in electronic and/or magnetic properties occur when this polymer is protonated; however it is apparent, that protonation plays a key role in at least the conductivity of the as-formed protonated form of the polymer.

It is believed that treatment of emeraldine base with $(CH_3)_2SO_4$ results in methylation of the imine nitrogen atoms to yield



depicted above for simplicity in the 50% bipolaronic doped form.

As can be seen from Figs. 4a,b, for similar levels of doping, the Pauli susceptibility for the methyl-doped "emeraldine" base is approximately half that of the proton-doped polymer; its conductivity (~10^{-2} S/cm) is also significantly less than that of the protonated polymer (~10^{0} S/cm). These data suggest a significantly greater contribution from the bipolaronic form in the methyl-doped polymer as compared to the proton-doped material, viz.,



due to the symmetry-breaking effect of the methyl groups.

It is apparent that the N-methylated derivatives of polyaniline represent a class of materials not only possessing a potentially rich unique chemistry and physics, but also that they display properties which will undoubtedly lead to a better understanding of the nature of the parent polyanilines.

ACKNOWLEDGEMENTS

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