Concurrent reduction and modification of polyaniline emeraldine base with pyrrolidine and other nucleophiles

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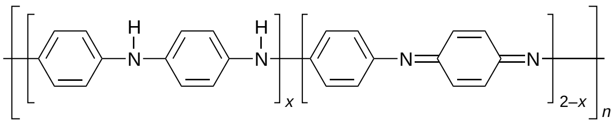
Polyaniline emeraldine base 1 can be easily modified by pyrrolidine and other nucleophiles, *e.g.* piperidine, morpholine, alkane-1-thiols and mercaptoacetic acid, presumably *via* a concurrent reduction and substitution mechanism.

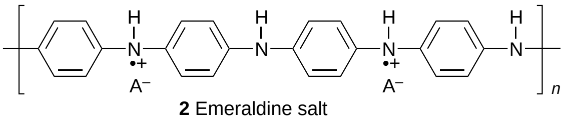
Among other conducting polymers, polyanilines are of particular interest in light of their unique electro-optical properties and market potential.[1,2] Although undoped (neutral) polyaniline, *i.e.* the emeraldine base **1** (Scheme 1), can be solution processed more easily than other conducting polymers, doped (conductive) polyanilines, *i.e.* the emeraldine salts **2**, cannot be processed easily. The difficulty encountered in solution processing the emeraldine salts **2** has recently been alleviated by an *in situ* de-doping and re-doping process,[3,4] and also by a counter-ion induced solubility approach.[4–6] In our previous attempt to develop the *in situ* de-doping and re-doping solution processing chemistry,[7] we found that many Lewis base solvents, *e.g.* pyrrolidine, piperidine and morpholine, are highly effective solvents for emeraldine salts[8] and emeraldine base.[9] Highly conductive coatings with good optical quality can be directly prepared from the fresh pyrrolidine solutions of emeraldine base **1** or emeraldine salts **2**. In those previous works, we also found some mysterious aging phenomena happened to those cyclic amine solutions. The polyaniline coatings prepared from such aged solutions were somehow less conductive.

In this work, we explore the nature of this aging chemistry to find possible means for prevention. These results actually suggest a very interesting concurrent reduction and substitution chemistry between polyaniline and nucleophiles. This new chemistry provides a facile approach for modifying a polyaniline backbone with various electron-donating groups, *e.g.* amino, alkylthio and alkoxy.

When polyaniline emeraldine base **1** was stirred in pyrrolidine for 96 h, the solution's colour gradually changed from blue to purple, and finally to purple–brown. The resultant polymer was precipitated with a large amount of Et_2O, collected, rinsed with copious amounts of acetone, and then dried at 90 °C under dynamic vacuum for 12 h to remove any solvent residues. The obtained polymer sample was free of the strong odour of pyrrolidine and had no weight loss up to 130 °C by thermogravimetric analysis. The solid state ^{13}C CPMAS (cross-polarization magic angle spinning) NMR spectrum of the resultant polymer, Fig. 1, strongly suggests that emeraldine base **1** has been reduced and the pyrrolidino substituents subsequently added. The new sp^3 carbon signals at *ca.* δ 25 and 52 are similar to those chemical shifts of pyrrolidine,† confirming the presence of pyrrolidino fragments. Correspondingly, a decrease in the peak intensity of *ca.* δ 157 (the characteristic peaks of the imine quinoid rings assigned by Kaplan *et al.*[10]) and an increase at *ca.* δ 135 and 120 (characteristic peaks of the amine benzenoid rings[10]) confirmed the reduction of polyaniline. These results suggest that some of the imine quinoid rings are converted to amine benzenoid rings while introducing pyrrolidino substituents. Except for no sp^3 carbons, similar NMR signal variation behaviour in the aromatic region [Fig. 1(*d*)] was observed when emeraldine base **1** was reduced by hydrazine to form leucoemeraldine base **3**. Our NMR results clearly indicated that the amounts of new sp^3 carbons and the degrees of reduction of emeraldine base **1** simultaneously increased with reaction time. Thus, the above results strongly suggest that the reduction and substitution events were actually concurrent.



1 Emeraldine base (x = 1)
3 Leucoemeraldine base (x = 2)
4 Pernigraniline base (x = 0)



2 Emeraldine salt

Scheme 1

The IR spectroscopic results in Fig. 2 also verify the presence of pyrrolidino substituents. The intensity of the newly appeared sp^3 C–H stretching peaks among 2800–3000 cm^{-1}, as caused by the pyrrolidino attachment, increased with the reaction time.

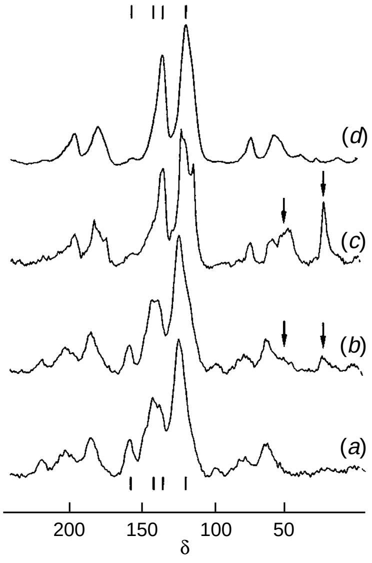


Fig. 1 Solid state ^{13}C CPMAS NMR spectra for various polyanilines measured at 50.3 MHz at a spinning speed of about 3 kHz. The NMR spectrum (*a*) is for emeraldine base; (*b*) and (*c*) are for emeraldine bases after reacting with pyrrolidine for 10 min and 96 h, respectively; and (*d*) is for leucoemeraldine base. Vertical bars are placed at δ 157, 143, 135 and 120. Arrow marks are placed at δ 52 and 25.

Also, the relative degrees of reduction of the resulted polyanilines increased simultaneously with reaction time, as indicated by the increase in intensity at around 1500 cm^{-1} (C=C stretching vibration of amine benzenoid rings) relative to that at 1600 cm^{-1} (C=C stretching vibration of imine quinoid rings).[11] The new peaks at 960 cm^{-1} and the shoulder at 925 cm^{-1} might be caused by the newly formed 1,2,4-trisubstituted benzene ring.[12] The reduction phenomenon of emeraldine base **1** induced by pyrrolidine has also been confirmed by UV–VIS spectroscopy. The fact that polyaniline emeraldine **1** was slowly reduced by pyrrolidine toward the less conductive leucoemeraldine form explains why the polyaniline coatings prepared from the aged solutions were less conductive.

The same concurrent reduction and substitution chemistry is applicable to other cyclic amine systems, *e.g.* piperidine and morpholine. In both cases, ^{13}C CPMAS NMR and IR spectroscopy confirmed that the resultant polymers (after thoroughly washed and dried) were partially reduced and substituted with piperidino and morpholino fragments, respectively. The ^{13}C NMR for the piperidine-treated polyaniline showed new sp^3 carbons at *ca.* δ 25 and 52 and those for the morpholine-treated polyaniline at *ca.* δ 52 and 68, similar to those chemical shifts of piperidine and morpholine, respectively.† A model compound, *N*,*N*′-diphenylphenylene-1,4-diimine, also reacted with pyrrolidine *via* the same reductive substitution chemistry, yielding a pyrrolidino-substituted *N*,*N*′-diphenylphenylene-1,4-diamine.‡

This chemistry can also be extended to other nucleophile systems, *e.g.* thiols and alcohols. Our preliminary results indicate that alkanethiols, such as dodecane-1-thiol and butane-1-thiol, react at a much higher rate (*ca.* 1000 times faster) than amines. Since dodecane-1-thiol contains greater number of sp^3 carbons, the IR spectrum for the dodecanethiol-treated polyaniline, Fig. 2(*d*), showed much stronger sp^3 C–H stretching vibration signals among 2800–3000 cm^{-1}. Although the above polymer was identified by elemental analysis to contain 20.7 mol% of dodecylthio group basing on aniline repeat unit, it was free of any odour of thiol. The cyclic voltammograms of the resultant polymers did not behave any more like the unsubstituted polyaniline, but rather resembled to the polyanilines substituted with electron-donating groups, such as polyanisidine and polyphenetidine. The nature of the S atoms in the sample was characterized by X-ray photoelectron spectroscopy. The S 2p line was measured to be at 163.5 eV, confirming the formation of sulfide, but not disulfide or thiol.§ These dodecylthio-substituted leucoemeraldine bases can be converted back to their corresponding emeraldine forms by oxidaton with *m*-chloroperoxybenzoic acid. Additional dodecylthio groups can be attached by repeating the reductive substitution chemistry with dodecane-1-thiol. We have found that the multiple reduction–oxidation modification cycles can be most conveniently carried out by an electrochemical process. In another example, we have also succeeded in attaching mercaptoacetic acid to the backbone of polyaniline, forming a self-doping polyaniline. The carboxylic acid groups remained at the polyaniline backbones even after thorough de-doping treatments with bases.

A possible reaction mechanism is as follows. Protonation of the imine nitrogen could possibly promote the nucleophilic attack of pyrrolidine (and other nucleophiles) at the *meta*-position of the protonated quinoid ring, followed by a 1,3-proton shift of the *meta*-proton to the *para*-imine nitrogen and, ultimately, a conversion of the less stable quinoid ring to the more stable benzenoid.

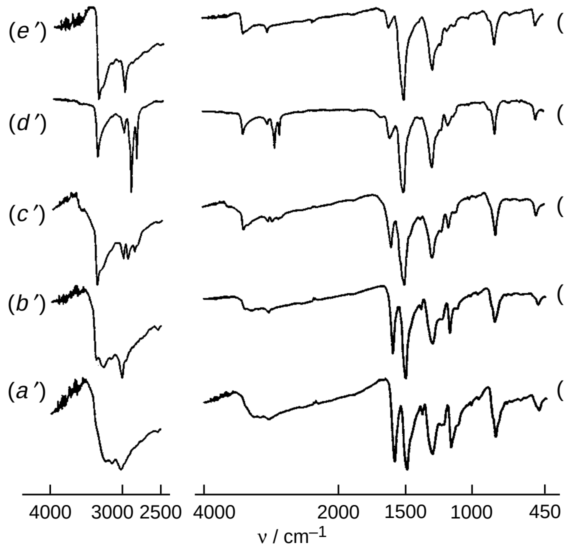


Fig. 2 IR spectra for various polyanilines are obtained in the transmission mode using KBr pellets at a nominal resolution of 8 cm^{-1} and co-adding 16 scans, IR trace (*a*) is for emeraldine base; (*b*) and (*c*) are for the emeraldine bases after reacting with pyrrolidine for 10 min and 96 h, respectively; and (*e*) is for leucoemeraldine base. Trace (*d*) is for the dodecanethiol-modified emeraldine base. Those corresponding blowup spectra for the 2500–4000 cm^{-1} regions (with arbitrary magnifications) are displayed in traces (*a*′)–(*e*′).

Footnotes

† For pyrrolidine, δ_C 25.64 and 47.20; for piperidine, δ_C 25.21, 27.32 and 47.53; for morpholine, δ_C 46.61 and 68.15.

‡ ^{13}C NMR data for pyrrolidino-substituted *N*,*N*′-diphenylphenylene-1,4-diamine, δ_C 24.8, 47.5, 112.3, 113.6, 117, 122.5, 128.9, 131.1, 143.7 and 146.5; for *N*,*N*′-diphenylphenylene-1,4-diamine, δ_C 115, 118.2, 119.6, 128.93, 136.4, and 144.8. For *N*,*N*′-diphenylphenylene-1,4-diimine, δ_C 120.25, 120.38, 124.35, 125.04, 125.08, 125.29, 136.39, 137.7, 149.8, 149.83, 157.84 and 157.9, complicated by the presence of both *E* and *Z* forms (ref. 13).

§ The S 2p line was reported to be 163.66 eV for poly(phenylene sulfide) and 163.50 eV for poly(ethylene sulfide); 164.4 eV for phenyl disulfide and 164.1 eV for butyl disulfide; 163.1 eV for thiophenol and 161–163 eV for alkanethiols (ref. 14).

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Received, 29th November 1996; Com. 6/08079K