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Reaction of polyaniline with NMP at elevated temperatures

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Heating a dilute solution of polyaniline emeraldine base in 1-methyl-2 pyrrolidinone under nitrogen at elevated temperatures resulted in the reduction of PANI to its leucoemeraldine state. The product was identified by infra-red, ultraviolet–visible, and X-ray photoelectron spectroscopy, and characterized by cyclic voltammetry and gel permeation chromatography. © 1997 Elsevier Science Ltd.

INTRODUCTION

Conducting polymers have attracted significant attention in recent decades, due to their potential applications, especially in the electronic industry. Among these polymers, poly(aniline) (PANI) has emerged as the most promising candidate for commercial applications[1-3], mostly because of its environmental stability in doped and undoped form. PANI is unique among the conducting polymers in that its electrical conductivity can reversibly be changed by protonation (doping) of the imine nitrogens of the polymer chain. Unlike most conjugated polymers, moreover, PANI is not completely intractable. Of the solvents used to dissolve PANI in its undoped form, 1-methylpyrrolidinone (NMP) is prominent, and many studies on spectroscopy[4], doping[5] and stretch orientation[6], have been carried out either on NMP solutions of PANI or on PANI films derived from NMP solutions. In this paper we examine the reactions of PANI in NMP solution at moderately high temperatures, which result in reduction of PANI to its leucoemeraldine form. Identification of the reduced product is based on comparative spectroscopy—Fourier transform infra-red (*FT*i.r.), ultraviolet–visible (u.v.–vis), and X-ray photoelectron (X.p.s.)—along with cyclic voltammetry (CV) and oxidation of the product to the pernigraniline and emeraldine states.

EXPERIMENTAL

General: u.v.–vis–near infra-red (n.i.r.) absorption spectra were recorded on a Perkin Elmer Lambda 9 spectrometer. *FT*i.r. spectra were recorded on a Nicolet 710 instrument. X.p.s. were recorded on a Surface Science Laboratories small spot X.p.s. with monochromatized A1K X-ray radiation. The carbon 1s binding energy (BE) of 285.0 eV (–CH_x type carbon atoms) was used as an internal BE reference. G.p.c. analyses were carried out by LARK Enterprises, Webster, MA on a Toyo Soda TSK SW column using NMP as eluent and polystyrene as standard. CV was carried out on an EG&G PAR 273 potentiostat, using a 7 mm Pt working electrode, Pt mesh counter electrode, and a saturated calomel reference electrode (SCE).

Emeraldine base (PANI) was prepared by the procedure described by MacDiarmid *et al.*[7]. The reactions were carried out on solutions of PANI (0.5–1% solid) in anhydrous NMP under a stream of nitrogen. After 2 h of heating at 160–180°C, the deep blue colour of PANI solution disappears, and the solution becomes grey-brown. The solution was then cooled, and excess NMP was distilled under vacuum so that a 5% solution of the product in NMP was obtained. The concentrated solution was then filtered through a 0.5 μm filter. Samples for u.v. and i.r. spectroscopy were prepared by spin-coating of the filtered solution on quartz and sodium chloride disks, respectively, and dried on a hot plate at 95°C for 15 min. The sample for g.p.c. was prepared by precipitation of the concentrated NMP solution of the product in deionized water under nitrogen and filtration. It was then sent to Lark Enterprises in a sealed vial for dissolution in purged NMP and injection on the g.p.c. column. For CV, thin films of reduced product were coated on a platinum electrode from 0.5% solution and dried in vacuum at 60°C with a nitrogen purge overnight.

RESULTS AND DISCUSSION

Comparative spectroscopy

The u.v.–vis spectrum of the PANI which was heated under nitrogen in NMP showed only the π–π^* absorption peak at 330 nm (see *Figure 1*). The exciton transition peak at 610 nm had all but disappeared. Although there had been a report[5] that upon heating a very dilute solution of PANI in NMP up to 100°C the intensity of the exciton transition band decreases, to our knowledge there is no report of complete disappearance of this peak simply by heating PANI in NMP. During the course of our investigations, we soon found out that the reaction is complete only when the heating is carried out under a stream of nitrogen. When air is not excluded during the heating process, the PANI solution retains its deep blue colour at the end of 2–3 h, and the absorption peak at 610 nm is present in the u.v. spectrum, albeit at a lower intensity. The thin film of the reduced product, which has

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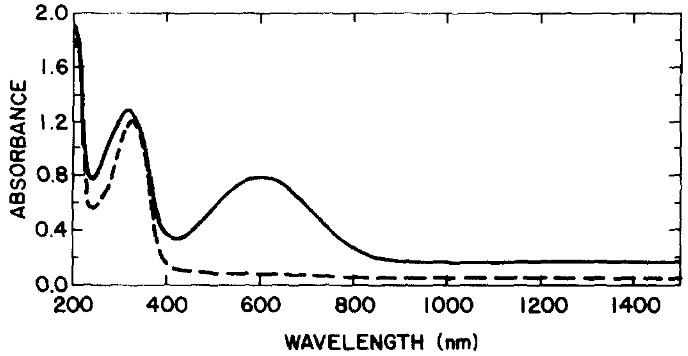

Figure 1 U.v.–vis spectra of PANI. ——, Emeraldine base as spun from NMP solution; ----, after heating in NMP

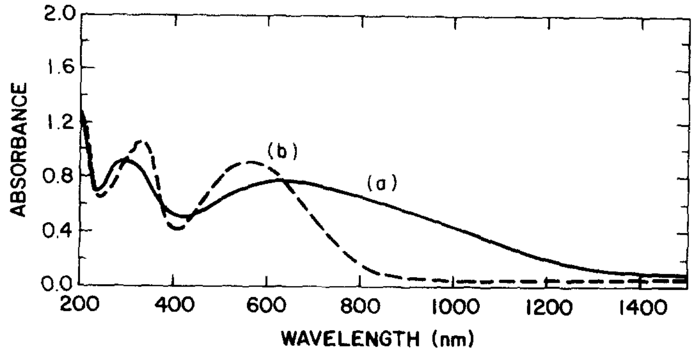

Figure 2 U.v.–vis spectra of NMP-treated PANI films after further treatment. (a) After immersion in ammonium persulfate/HCl. (b) After treatment of film from (a) with dilute ammonium hydroxide

a greyish colour, is stable under nitrogen; however in air it slowly oxidizes, its colour changing to yellow-green after a few days. When a thin film of the sample was immersed in dilute hydrochloric acid, there was no change of colour; the u.v. spectrum showed the appearance of a very weak absorption at about 400 nm, which is present in doped emeraldine base. However, when the reduced product was immersed in a solution of ammonium persulfate in dilute hydrochloric acid, the grey colour changed instantaneously to green, and then immediately to blue. The u.v.–vis absorption of this blue compound (*Figure 2*) is similar to that of acid-doped pernigraniline, as reported earlier[8]. Immersion of the latter in 0.5% ammonium hydroxide solution for 1 h resulted in a purple compound whose u.v. absorption spectrum (*Figure 2*) shows two peaks at 320 and 550 nm, similar to that of pernigraniline reported by Sun *et al.*[8]. Finally, when the purple compound was immersed in 10% hydrochloric acid for 24 h, the colour changed to emeraldine green, and the u.v.–vis–n.i.r. spectrum showed disappearance of the absorption peak at 550 nm, replaced by a broad free carrier tail, which is the signature of the doped emeraldine base. This sample had a conductivity of 0.8–1.0 S cm^{-1} comparable to the starting PANI, with a conductivity of 1–1.5 S cm^{-1}.

The i.r. spectrum of the reduced product is also very revealing, and matches that of leucoemeraldine[9]. The absorption band at 1600 cm^{-1} ($\nu_{C=N}$), which is very strong in emeraldine base, has completely disappeared, and a weak absorption at 1606 cm^{-1} (aromatic C=C stretching) is visible (see *Figure 3*). In addition, the absorption peak for 1,4-disubstituted phenyl which appears at 830 cm^{-1} for emeraldine base, is shifted to a higher wavelength (819 cm^{-1}), again consistent with the i.r. spectrum reported for leucoemeraldine[9]. Finally, an additional weak peak at 1667 cm^{-1} (*Figure 3*) is present in the i.r. spectrum. This peak, which coincides with the carbonyl absorption peak of NMP, becomes weaker when heated at 140°C in a vacuum, but does not completely disappear, even when the sample is immersed in chloroform under nitrogen for 48 h. This result, combined with the fact that a broad peak is present at 2900–3000 cm^{-1} region where C–H absorption occurs, suggests that, at least in small amounts, some NMP moieties have been attached to the polymer backbone.

In order for the emeraldine base form of PANI to be reduced, obviously another molecule must be oxidized. Lacking any other candidates, we looked at the chemistry of NMP and related compounds. There are several references which indicate that hydrogen atoms can be abstracted from NMP and other lactams. For example, aromatic ketones are photoreduced in the presence of NMP[10]. A quantitative analysis for aliphatic amides using oxidation at a platinum electrode has been reported[11]. For tertiary amides, the oxidation occurs at 1.35 V vs saturated calomel electrode, which is a considerably higher voltage than the emeraldine–leucoemeraldine couple observed in CV (see below). For this reason, we believe that the reaction observed in NMP at 160°C is not an electron transfer similar to that observed electrochemically at room temperature, but more likely a hydrogen atom transfer from NMP to PANI.

In this regard, it is of interest that the dehydro analogue of NMP is known[12]. It occurs as an equilibrium mixture of isomers, 1,5-dihydro-2H-pyrrol-3-one and 1,3-dihydro-2H-pyrrol-3-one (dehydroNMP). To investigate the possibility that dehydroNMP may be playing a role in the PANI–NMP thermal chemistry, we repeated its synthesis by oxidation of 1-methylpyrrole[12]. Using capillary gas chromatography, we were not able to detect dehydroNMP in a PANI solution in NMP after heating, except perhaps at the trace levels that it seems to be present in NMP. It is worth noting, however, that the predominant isomer of dehydroNMP is a cyclic analogue of acrylamide, and therefore it might very well be polymerized by or copolymerized with PANI at the temperature at which the emeraldine base is converted to leucoemeraldine in NMP. This possibility would explain the observation that the recovered PANI shows an NMP-like carbonyl absorption in the i.r. which cannot be removed by extraction (see above). As a check on this hypothesis, we added various amounts of dehydroNMP to PANI solutions in dimethylsulfoxide before heating. The dehydroNMP was consumed, and the material recovered after distilling off the solvent showed an i.r. spectrum consistent with dehydroNMP incorporation into the PANI.

Cyclic voltammetry

Cyclic voltammetry was carried out to directly measure the oxidation state of the reduced material via a measurement of the open circuit voltage (OCV) and to compare the CV spectrum with that of standard PANI. A sample was cast onto a Pt working electrode by flooding the Pt surface with 0.5% solution of PANI heated in NMP and shaking off excess liquid. This was dried at 60°C overnight in vacuum with a slight nitrogen purge. After cooling, the sample was removed and immersed in 1 M HCl under bubbling N_2, connected to the potentiostat, and the OCV measured. The OCV for different samples of the NMP-treated PANI ranged from a high of 0.19 V to a low of 0.13 V (vs SCE). This indicates that the sample was in an oxidation state more reduced than emeraldine, either leucoemeraldine or proto-emeraldine. When the sample with the OCV of 0.13 was allowed to stand under bubbling of N_2 for 3 h, the OCV drifted to 0.19 V. This shift was very rapid at first, slowing considerably within minutes.

To further test the oxidation state of the NMP-treated PANI, a fresh sample was immersed in electrolyte and an applied potential was scanned in the positive direction, beginning at the OCV of 0.19 V. A broad non-symmetrical oxidation peak was observed at 0.36 V. The direction was reversed at 0.5 V and a symmetric reduction peak was observed at 0.14 V. This scan was again reversed at −0.1 V and cycled to +0.5 V, this time showing a larger and symmetric oxidation peak at 0.23 V, which did not shift with further cycling. This clearly showed that the NMP-treated PANI was initially in an oxidation state more reduced than emeraldine.

Another fresh sample was scanned in the negative direction beginning at the OCV (0.18 V). A reduction peak was observed at 0.09 V. The scan was reversed at −0.1 V, and an oxidation peak was seen at 0.17 V on this and all subsequent cycles. The reduction peak on the second cycle shifted to 0.12 V, and was considerably more intense. This indicates that the sample was in an oxidation state more oxidized than leucoemeraldine.

From these two results, we can narrow the oxidation state of the NMP-treated material to two possibilities. First, reaction with hot NMP may reduce the polyaniline to a protoemeraldine state (between leucoemeraldine and emeraldine states). Secondly, the hot NMP may convert the PANI to the leucoemeraldine state which may rapidly oxidize to the protoemeraldine state during the first seconds of sample immersion in the HCl electrolyte for OCV measurement. As the measurements were not performed under drybox conditions, some air is introduced to the measurement cell during sample positioning. The very thin nature of the sample films and the demonstrably rapid re-oxidation in the presence of oxygen and electrolyte makes this a realistic possibility.

When the NMP-treated PANI was cycled continuously at 50 mV s^{-1} between −0.10 V and +0.85 V, the $E_{1/2}$ (average of the oxidation and reduction peak positions) of the first redox couple, associated with the emeraldine (E) to leucoemeraldine (L) transition was 0.18. The $E_{1/2}$ of the second peak, the emeraldine to pernigraniline transition (P) was measured at 0.66 V (*Figure 4*—see *Table 1*). For untreated PANI, $E_{1/2}$ of the E to L redox couple was 0.20 V, and that of the E to P redox couple was 0.86 V (*Figure 4*). The E to L transition is very similar in the native and treated materials within experimental error. The shift of the E to P transition to a lower potential in the treated material is an indication of some degradation or chemical modification. This is similar to shifts observed in polyaniline materials with pendant side groups, and may constitute evidence for some side-chain substitution taking place.

In summary, the OCV and CV measurements clearly

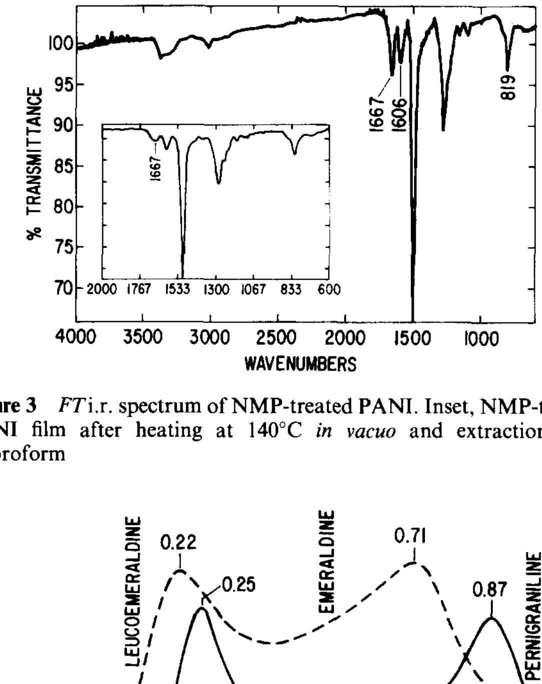

Figure 3 *FT*i.r. spectrum of NMP-treated PANI. Inset, NMP-treated PANI film after heating at 140°C *in vacuo* and extraction with chloroform

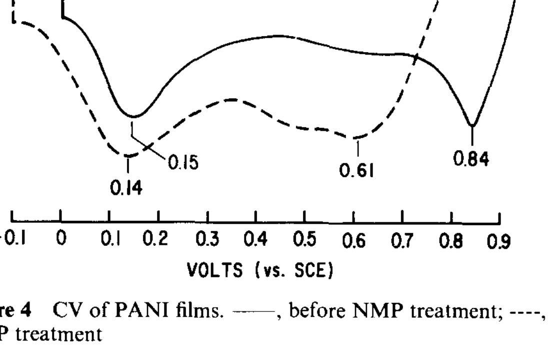

Figure 4 CV of PANI films. ——, before NMP treatment; ----, after NMP treatment

Table 1 CV results (V vs SCE)

Sample	Open circuit (average)	$E_{1/2}$ (leucoemeraldine to emeraldine)	$E_{1/2}$ (emeraldine to pernigraniline)
Native PANI	0.55	0.20	0.85
Hot NMP treated PANI	0.17	0.18	0.66

indicate that the emeraldine base is chemically reduced by hot NMP. It is only the extent of reduction which is not unambiguously determined by these electrochemical measurements.

G.p.c. of the reduced product and the emeraldine base starting material is shown in *Figure 5a*. For the reduced product, a bimodal curve with high molecular weight portion of about 50% was obtained using NMP elution. In contrast, the high molecular weight portion of the curve for emeraldine base is about 8% of the total area. The apparent M_W of the NMP-reduced PANI in the low molecular weight fraction is somewhat lower than the corresponding fraction in emeraldine base. As has been observed previously for PANI and other polymers[13,14], the addition of 0.5% LiCl to the NMP solution of the polymers resulted in a unimodal molecular weight distribution (*Figure 5b*), indicating that the high M_W fraction was caused by polymer aggregation. Again, the average molecular weight for the NMP-reduced product is somewhat lower than that of emeraldine base. Because the effect of the NMP thermal treatment on the hydrodynamic volume of PANI is unknown, an absolute comparison of molecular weights before and after the treatment is not possible. The g.p.c. data, however, clearly indicate that there is little, if any, crosslinking between polyaniline chains during the thermal reduction of the latter in NMP.

Surface analysis

Analysis of NMP-reduced emeraldine base by X.p.s. clearly showed the reduction of the polymer, most strikingly in the collapse of the varied N1s binding energies of emeraldine base to one amine-type nitrogen binding energy in the NMP-reduced film (see *Tables 2* and *3*). The X.p.s. analysis of PANI is complicated by the presence of species, such as oxygen, not accounted for by the structure commonly given. *Tables 2* and *3* give peak assignments for all of the high resolution data except for trace elements*.

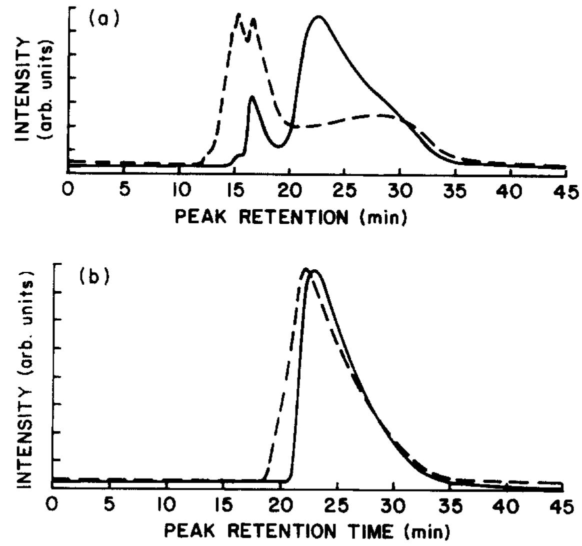

Figure 5 G.p.c. of PANI. (a) In NMP; ——, before NMP treatment; ----, after NMP treatment. (b) In NMP/0.5% LiCl: ----, before NMP treatment; ——, after NMP treatment

Table 2 High resolution X.p.s. data for elements found on leucoemeraldine surface

Element	Binding energy (eV)	Concentration (at %)	Literature assignment	Ref.
C1s	285.0	77	CH_x	15,16
	286.2	20	C–N, C–O	16,17
	288.0	4	C=O	16,17
O1s	532.0	52	Si–O–, C=O	15,16,20
	533.5	48	C–O–	16,17
N1s	399.9	100	–NH	16,21–23

Carbon 1s data for the NMP-treated PANI film in *Table 2* shows three peaks: the lowest BE peak is associated with carbon atoms not bonded to oxygen or nitrogen. The peak at 286.2 eV is due to C–N– and C–O– type species, while the last peak at 288.0 eV is associated with a C=O type carbon environment. The oxygen 1s X.p.s. data has two peaks, one at 532.0 eV associated with Si–O (B2p at 103.9 eV, i.e. SiO_2)[20] and C=O species, and one at 533.5 eV due to a C–O– type oxygen environment. The presence of the C=O species is likely due to a small amount of residual NMP[24]. The source of the C–O– type oxygen species is not clear, but C–O– is also found in a pressed pellet of the emeraldine base as synthesized, i.e. without exposure to NMP. It is therefore probable that this species is a result of the polyaniline synthesis.

As alluded to above, the NMP-treated film has a N1s singlet centred at 399.9 eV (*Figure 6*) assignable to an amine species which verifies the emeraldine base reduction to leucoemeraldine[24]. The Si-peak detected is due to SiO_2 based on the Si2p binding energy (BE) of 103.7 eV[20].

Emeraldine base pressed pellet samples (no exposure to NMP) were also analysed using X.p.s., and the high resolution X.p.s. data for carbon, oxygen and nitrogen are reported in *Table 3*. In the emeraldine base pellet, the N1s X.p.s. data are significantly richer than in the NMP-treated sample. The characteristic PANI N1s peaks are all detected, which is in stark contrast with the NMP-treated sample. The N1s data for the two types of samples are shown in *Figure 6*, which accentuates the difference between the two samples. It is clear that the

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* Survey scan analysis of the NMP-reduced film showed the presence of carbon, oxygen, nitrogen, and silicon and atomic percent composition of 78, 10, 10 and 2%, respectively. Silicon dioxide from the substrate may be the source of the latter.

Survey scan analysis of the untreated PANI pressed pellet detected carbon, oxygen, nitrogen, silicon, and fluorine on the surface with atomic percentage concentrations of 79, 8, 12, 2, and 1%, respectively. The trace amounts of Si and F were seen in two out of three samples. The source of these elements is not clear, but X.p.s. is extremely sensitive to surface contamination such as could be transferred from the surface of the pellet maker.

Table 3 High resolution X.p.s. data for elements found on emeraldine base pellet surface

Element	Binding energy (eV)	Concentration (at %)	Literature assignment	Ref.
C1s	285.0	67	CH_x	15,16
	286.2	24	C–N, C–O	16,17
	287.5	6	C=O	16,18,19
	289.7	3	O=C–O–	25
O1s	532.3	60	Si–O–, C=O	15,16,20
	533.5	34	C–O–	16,17
	536.1	6	H_2O	15
N1s	398.8	38	Imine	21,23
	399.9	42	Amine	16,21–23
	401.3	5	Cyclic, protonated imine	23
	403.0	8	Imine shake-up	23
	405.9	7	Amine shake-up	26

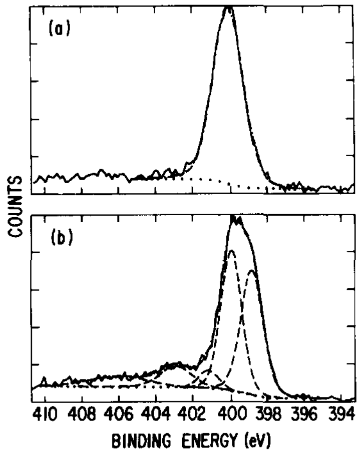

Figure 6 N1s X.p.s. data. (a) Spun film after NMP treatment. (b) Pressed pellet of emeraldine base

N1s chemical environment after NMP treatment is drastically simplified, resulting in a single peak centred at 399.9 eV, associated with amine.

All of the spectral data are completely consistent with the conclusion that PANI is reduced by NMP at moderate temperatures. This result is surprising because NMP is not normally thought of as a reducing agent. It indicates that the emeraldine base form of PANI is even more complex in its reactivity than previously suspected, and raises the question of what other solvents may have similar effects on its redox state. The reactivity of PANI with NMP should be taken into consideration by all who use NMP or solvents of similar structure for processing of PANI. Even if lower temperatures are used, it stands to reason that what occurs to completion at 160°C or above will occur to a partial extent at lower temperatures.

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