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Effect of Elevated Temperature on the Reactivity and Structure of Polyaniline

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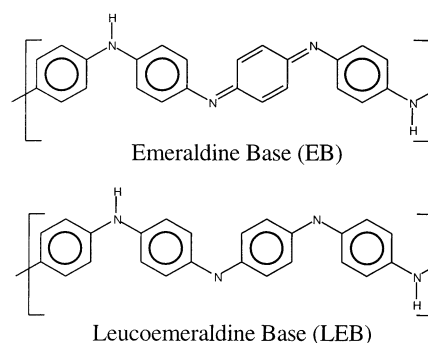
ABSTRACT: The structure and oxidation state of emeraldine base polyaniline (PANI) in *N*-methylpyrrolidinone solutions that have been heated to 120–190 °C have been characterized by solid-state NMR, UV/vis, FTIR, and GPC. The spectroscopic studies reveal that the polymer is completely converted to its fully reduced leucoemeraldine form after heating at 175–190 °C for only 2 h, and bubbling oxygen gas through the solutions after heating results in partial reoxidation of the polymer. Cross-links, consisting of phenazine structures, have been identified in PANI films cast from heated NMP solutions by ¹⁵N interrupted decoupling solid-state NMR. After heating, the polymer is partially cross-linked with the cross-link density increasing with annealing temperature, and the non-cross-linked regions are the reoxidizable portions of the polymer. A mechanism by which the cross-linking reaction of PANI leads to the polymer reduction is discussed.

Introduction

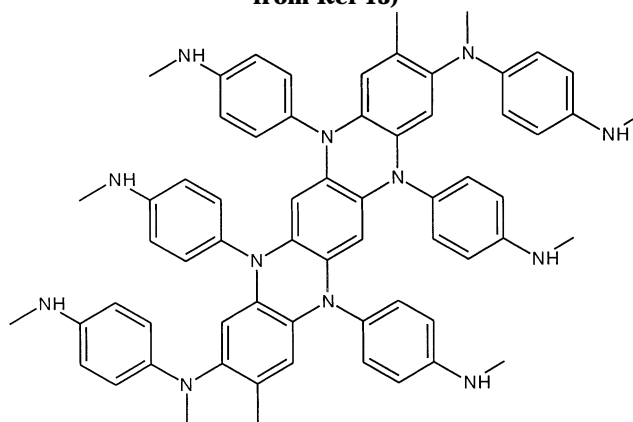
Among conducting polymers, polyaniline (PANI) has significant importance because of its ease of processability, good environmental stability, and high conductivity. The half-oxidized emeraldine base (EB) form of PANI can be doped into a highly conducting material. Upon reduction, the EB form of PANI is converted into the fully reduced leucoemeraldine (LEB) form of the base (Scheme 1). PANI is usually synthesized in the emeraldine base form, and this polymer can be processed readily into thin films, fibers, and elastomers^{1–4} and has shown great potential for many applications including rechargeable batteries, light-emitting diodes, molecular sensors, and gas separation membranes.^{5–8} Of the solvents used to dissolve the EB form of PANI, *N*-methyl-2-pyrrolidinone (NMP) is predominant, and PANI films and fibers are routinely processed from relatively concentrated solutions in NMP.⁹ With the high boiling point (202 °C) of NMP, along with the hydrogen-bonding interaction of the C=O group in NMP with the amine groups in PANI, elevated temperature treatments are commonly used to remove the solvent during the processing of PANI materials.¹⁰ Hence, it is scientifically and industrially important to examine the solution characteristics of PANI at different temperatures.

In the solid state, heating the PANI powder has a significant impact on the structure, morphology, and dynamics. Thermogravimetric analysis of PANI has shown that the EB form is stable up to ~450 °C, and thermal degradation of the polymer takes place above this temperature.^{11,12} Also, it has been reported that when PANI powder is annealed above 150 °C, cross-linking between PANI chains occurs.^{13–20} The studies supporting cross-linking of PANI include differential scanning calorimetric and dynamic mechanical analysis,^{10b,14,15} gel permeation chromatography,¹⁶ FTIR spectroscopy,^{10b,14,17,18} solubility,^{14,17,19} and electron paramagnetic resonance.¹⁹ It has been proposed by Scherr

Scheme 1



Scheme 2. Structure of Cross-Linked PANI (Adapted from Ref 13)



et al.¹³ that the cross-linking reaction proceeds between imine nitrogens and the quinoid rings, resulting in a two-dimensional “phenazine” type structure for PANI (Scheme 2). However, in these previous studies of annealed PANI samples the putative tertiary amine nitrogen formed during the cross-linking reaction had not been observed directly. In our recent solid-state NMR characterizations of annealed PANI powder, we have observed the tertiary nitrogens generated by the cross-link formation between chains, supporting the model of Scheme 2.²⁰

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While the impact of heating on NMP solutions of PANI has been studied by several groups in recent years, quite different results have been observed. Lee et al.²¹ report that when a dilute NMP solution of PANI is heated to $\sim 150^\circ\text{C}$ for 2 h, complete cross-linking between PANI chains occurs (Scheme 2). Films of the fully cross-linked material are reported to be cast from the NMP solutions. However, several studies have shown that completely cross-linked PANI is insoluble in NMP.^{14,17,19} In contrast to these results, Afzali et al.²³ have reported that when a 0.5–1 wt % solution of PANI in NMP is heated to 160–180 $^\circ\text{C}$, complete reduction of PANI chains from the EB form to the LEB form occurs and that there is little or no cross-linking. The solvent, NMP, is proposed to be the reductant in this system. On the basis of UV/vis data and decreasing solubility, Tan et al.²² have reported that EB PANI solutions in NMP undergo increasing amounts of cross-linking with increasing processing temperature. These contrasting reports indicate that the chemical/structural changes caused by elevated temperature treatment of PANI/NMP solutions are still not well-defined.

An understanding of the chemistry that occurs in heated NMP solutions of PANI is then critical in determining the optimal or allowable ranges of the various processing parameters. This report details our results from the characterization of the composition and oxidation state of PANI after annealing NMP solutions of the polymer over the temperature range 125–190 $^\circ\text{C}$. The systems have been studied by UV/vis, FTIR, solid-state NMR (SSNMR), and GPC in an effort to determine the chemistry occurring and its extent. Our studies of PANI from heated NMP solutions indicate that a combination of cross-linking and reduction occurs.

Experimental Section

Materials. Aniline was purchased from Aldrich and doubly distilled under vacuum and kept in a refrigerator prior to use. ^{15}N -labeled aniline, 1-methyl-2-pyrrolidone (NMP), and hydrazine (35 wt % of aqueous solution) were purchased from Aldrich and used without further purification.

Preparation of ^{15}N -Labeled PANI. ^{15}N -labeled EB PANI was prepared by taking a 1:1 molar ratio of ^{15}N -labeled aniline and unlabeled aniline (used after double distillation under vacuum) and polymerized by oxidizing an acidic aqueous solution (1 N HCl solution) with ammonium persulfate as the oxidant at 0–5 $^\circ\text{C}$.²⁴ The weight-average molecular weight of the polymer obtained is 55 000, and the polydispersity is 3.0.

Synthesis of Leucoemeraldine PANI. The completely reduced leucoemeraldine base form of polyaniline was prepared by reduction of emeraldine base PANI with aqueous hydrazine.²⁵ EB powder was added to an excess amount of 35 wt % of aqueous hydrazine and stirred for 24 h. The pale blue powder was then filtered, washed with deionized water, and dried in a vacuum oven at 50 $^\circ\text{C}$ for 16 h. The powder was stored in a refrigerator under argon atmosphere. Reoxidation of the LB polymer was performed by bubbling oxygen gas for 24 h through a 1 wt % solution of the polymer in NMP.

PANI–NMP Solutions. A 1 wt % solution of PANI in NMP was heated under vacuum at temperatures ranging from 125 to 195 $^\circ\text{C}$ under a nitrogen atmosphere for 2 h. PANI films were cast from a portion of that solution by placing the solution in a vacuum oven at 60 $^\circ\text{C}$ for 15 h. The remaining portion of the solution was reoxidized by bubbling oxygen gas through the solution for 24 h at room temperature.²⁶ Films were cast from this solution by drying in a vacuum oven at 60 $^\circ\text{C}$ for 15 h. The PANI/NMP solutions or the films cast from these solutions are labeled Δ (solution temperature), and after re-oxidation with oxygen gas they are labeled Δ (solution temperature)-OX.

EB and LEB films were prepared by stirring 1 wt % solutions of PANI in NMP for 24 h and then removing the solvent in a vacuum oven at 60 $^\circ\text{C}$ for 15 h. In the case of the LB film, prior to dissolving the polymer, the solvent was purged with N_2 .

UV/Vis. The UV/vis spectra were collected on a Shimadzu UV-1601 UV/vis spectrophotometer. Samples were drawn from the PANI/NMP solutions under a N_2 atmosphere, and the spectra were recorded immediately.

FTIR. The FTIR spectra were obtained on a Nicolet model NEXUS 870 from thin PANI films cast on KBr disks. The films were dried by placing the disks in a vacuum oven at 50 $^\circ\text{C}$ for 15 h.

Solid-State NMR. Solid-state NMR spectra were obtained by using a Varian Unityplus-200 (4.7 T) spectrometer with a Doty Scientific magic-angle-spinning (VTMAS) probe. The polymer films were packed into 7 mm silicone nitride rotors with Kel-F end caps. Spectra were acquired at sample spinning speeds of 3 kHz for ^{15}N NMR studies and 5 kHz for ^{13}C NMR studies, with a recycle delay of 1 s and cross-polarization (CP) contact time of 2 ms. All ^{15}N chemical shifts were referenced to double labeled $^{15}\text{NH}_4^{15}\text{NO}_3$ ($\delta^{15}\text{NH}_4^+ = 0$ ppm, $\delta^{15}\text{NO}_3^- = 352$ ppm), and all ^{13}C chemical shifts were referenced to hexamethylbenzene ($\delta\text{Me} = 17.3$ ppm).

Interrupted Decoupling. In this experiment the proton decoupling is turned off for a variable time during the evolution time of a standard Hahn-echo sequence. The removal of proton decoupling results in dephasing of the transverse magnetization and a subsequent loss in signal intensity. The rate of decrease of the signal intensity is dependent on the strength of the ^{15}N – ^1H dipolar coupling; for nitrogens more strongly coupled to protons the intensity will decrease more rapidly.

GPC Analysis. The molecular weight of the EB powder was determined by using a gel permeation chromatography (GPC) system consisting of an HPLC pump (Waters 2960) and two polystyrene columns. The column temperature was controlled at 50 $^\circ\text{C}$. A photodiode array (Waters 996) detector was used to determine the molecular weight. NMP containing 0.1 wt % LiCl was used as eluent, and polystyrene standards were used to calibrate the columns.

Results and Discussion

UV/Vis Spectroscopy. The UV/vis spectrum from EB PANI has a peak at 330 nm from the $\pi \rightarrow \pi^*$ transition in the benzenoid rings and a second peak at 640 nm from the quinoid ring (Figure 1A). The intensity of the peak at 330 nm (I_B) and the intensity of the 640 nm peak (I_Q) are approximately equal in the EB form (Table 1).^{27,28} Upon chemical reduction of PANI to the LEB form, the peak at 640 nm disappears (Figure 1A). When the NMP solution of LEB PANI is reoxidized by bubbling oxygen gas through the solution (ROLEB), I_B/I_Q returns to 1.3 (Table 1), and it is evident from the UV data that $\sim 90\%$ of the polymer has returned to the EB form (Figure 1). Exposure of the sample to molecular oxygen beyond 24 h caused no further changes in the UV/vis data. These results indicate that the transition from EB to LB and back to EB is almost completely reversible, as seen previously.²⁶

Heating a 1 wt % solution of EB PANI in NMP at 190 $^\circ\text{C}$ for 2 h resulted in the solution turning from blue to brown in color with a concomitant loss of the peak at 640 nm (Figure 1B), consistent with previous reports.^{21,23,29} Upon bubbling oxygen gas through the NMP solution, the solution color returned to blue along with a return of $\sim 50\%$ of the intensity of the peak at 640 nm (Figure 1B). Exposure of the heated solution to ambient atmosphere also caused a return of the 640 nm peak but at a significantly reduced rate. Similar results were obtained when PANI/NMP solutions were heated over the temperature range 125–175 $^\circ\text{C}$. While full reduction

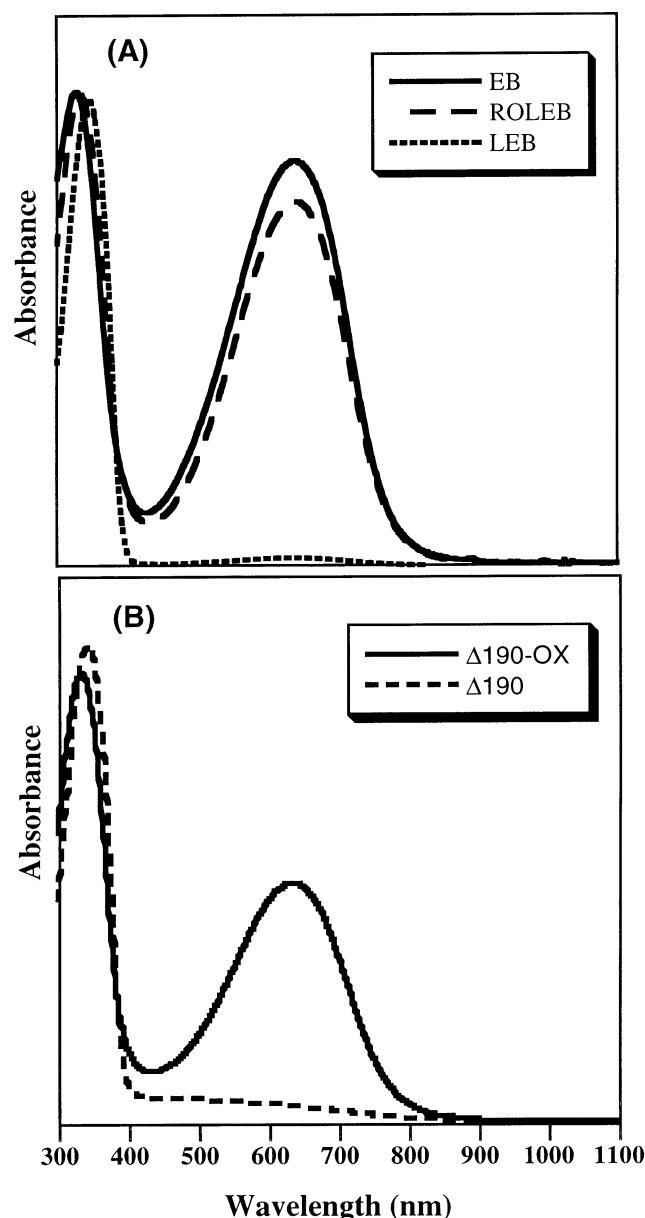


Figure 1. UV/vis spectra of PANI samples in NMP. (A) Emeraldine base PANI (EB); chemically reduced PANI before (LEB) and after (ROLEB) exposure to oxygen gas. (B) PANI/NMP solution heated to 190 °C for 2 h (Δ190) and after exposure to oxygen gas (Δ190-OX).

Table 1. Intensity Ratio of Peaks in the UV/Vis Spectrum from PANI/NMP Solutions Heated to Various Temperatures

sample	I_B/I_Q^a	sample	I_B/I_Q^a
EB	1.20	Δ175	b
LEB	b	Δ175-OX	1.8
ROLEB	1.3	Δ150	3.4
Δ190	b	Δ150-OX	1.6
Δ190-OX	1.9	Δ120	1.8
Δ180	b	Δ120-OX	1.4
Δ180-OX	2.1		

^a I_B is the intensity of the peak near 333 nm, and I_Q is the intensity of the peak near 636 nm. ^b I_Q is ~ 0 .

of the polymer is observed with annealing at 175 °C, the extent of reduction decreases with decreasing temperature (Table 1). For each sample, exposure to oxygen gas resulted in only a partial reoxidation of the polymer. To determine the impact of PANI concentration on the

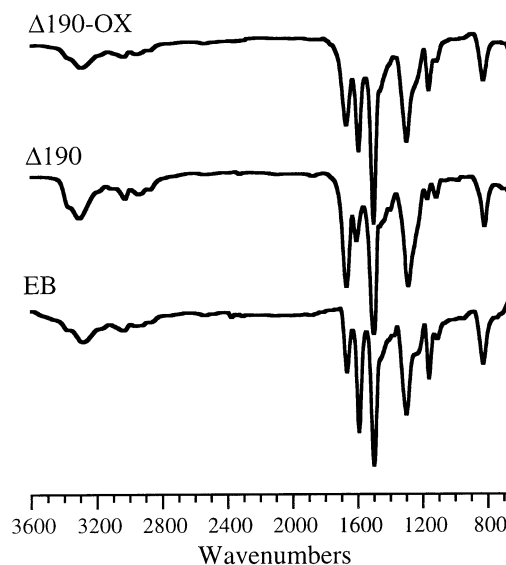


Figure 2. Infrared spectra of PANI cast from NMP solutions EB, Δ190, and Δ190-OX.

extent of reduction, a 0.01% EB PANI solution was heated to 180 °C for 2 h (Δ180). The UV/vis results (Table 1) are nearly identical to those observed for Δ190 (Table 1), a 1 wt % solution, showing that concentration has a minimal impact on the effects of heating over the concentration range studied.

Infrared Spectroscopy. The FTIR spectra from the EB film, a film cast from a PANI–NMP solution heated at 190 °C (Δ190) and a film cast from an NMP solution that has been heated to 190 °C and reoxidized (Δ190-OX), are shown in Figure 2. The IR spectrum from the EB film is consistent with that reported previously for this oxidation state of PANI.^{30,31} The FTIR spectrum of the Δ190 film is similar to those reported previously^{10b,14,17,18} for heat-treated PANI samples that have undergone cross-linking as well as being very similar to the IR spectrum from the LEB form of PANI. In the spectrum from the Δ190 film the peaks characteristic of the half-oxidized form of polyaniline (1590, 1297, and 1161 cm⁻¹) are absent or much reduced in intensity. After the reoxidation, as observed in the case of UV analysis, the peaks characteristic of the oxidized PANI have returned but at a decreased intensity. The FTIR data show that while the polymer is fully reduced with heating it can only be partially reoxidized. While the UV/vis and FTIR analyses are able to monitor the overall oxidation state of the polymer, these techniques have not been capable of determining whether PANI has also undergone any additional chemistry during the heating process.

Solid-State NMR:¹³C CP/MAS. The ¹³C NMR spectra have been collected for PANI films that were cast from the NMP solutions of the polymer that were characterized by UV/vis. The ¹³C cross-polarization magic angle spinning (CP/MAS) spectra of EB film, LEB film, and ROLEB film are shown in Figure 3. The spectra from the EB and LEB films are nearly the same as those reported previously,^{32–34} showing that the solvent removal process used has little impact on the oxidation state or structure of the polymer. The spectrum from EB PANI has peaks at 123 ppm from the protonated aromatic carbons, peaks near 140 ppm from nonprotonated aromatic carbons and the protonated carbons of the quinoid ring, and a peak at 158 ppm from the imine carbon. The spectrum from LEB PANI is

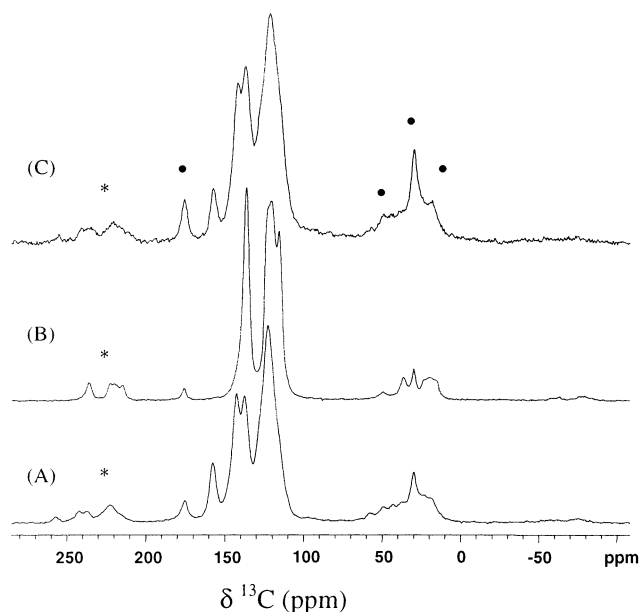


Figure 3. ^{13}C CP/MAS spectra from films cast from NMP solutions (A) EB, (B) LEB, and (c) ROLEB: (●) peaks from NMP; (*) spinning sidebands.

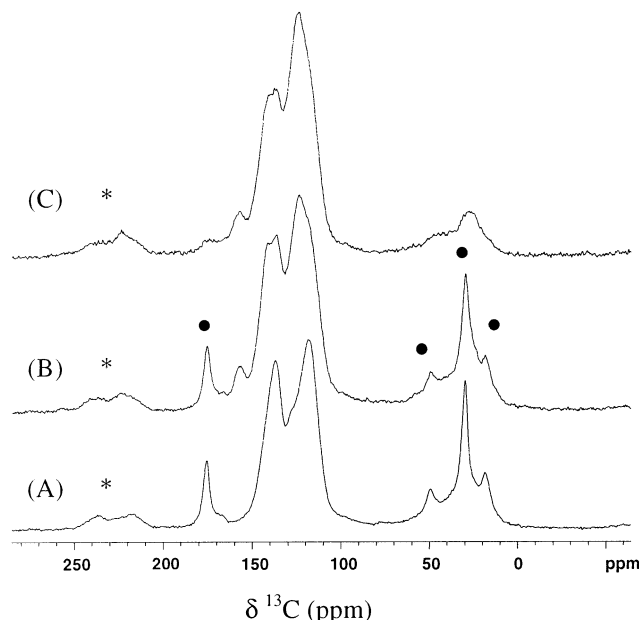


Figure 4. ^{13}C CPMAS spectra of films cast from NMP solutions (A) $\Delta 190$, (B) $\Delta 190\text{-OX}$, and (C) $\Delta 190\text{-OX}$ after methanol extraction: (●) peaks from NMP; (*) spinning sidebands.

much simpler with a peak at 118 ppm from the protonated aromatic carbons and a peak at 135 ppm from the nonprotonated aromatic carbons. Consistent with the UV/vis and FTIR data, the spectrum from the ROLEB film shows characteristics of the material containing a small amount of polymer still in the LEB oxidation state, resulting from incomplete reoxidation. The ^{13}C NMR spectra show no indication of any chemical reactivity occurring during the room temperature REDOX cycling of the polymer; the absence of reactivity has also been observed by Wei et al.²⁶ There is also some retention of NMP in each of the films.

Figure 4 shows the ^{13}C NMR spectra from $\Delta 190$, $\Delta 190\text{-OX}$, and $\Delta 190\text{-OX}$ that has been extracted with methanol. In the spectrum from $\Delta 190$ the imine carbon

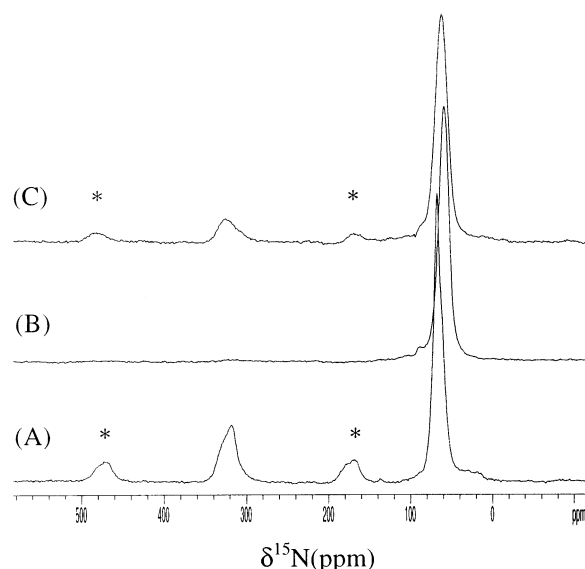


Figure 5. ^{15}N CP/MAS spectra of films cast from NMP solutions (A) EB, (B) $\Delta 190$, and (C) $\Delta 190\text{-OX}$. * = spinning sidebands.

peak at 158 ppm is absent, showing complete reduction of the polymer. The line widths observed for the $\Delta 190$ sample are significantly larger than those from the chemically reduced PANI (Figure 3B). The increase in line width indicates that there is an increase in the structural heterogeneity of the polymer in the $\Delta 190$ film. Upon reoxidation a portion of the intensity at 158 ppm returns, but the NMR spectrum shows that the polymer is still partially reduced. The ^{13}C spectrum from $\Delta 190\text{-OX}$ looks similar to the spectrum from partially cross-linked PANI powder samples we reported earlier.²⁰ While the methanol extraction removes nearly all the residual NMP, the extraction process has little impact on the spectrum of the polymer, Figure 4C. The ^{13}C chemical shifts observed in Figure 4 for $\Delta 190$ or $\Delta 190\text{-OX}$ are consistent with the presence of only aromatic amine species and NMP.

^{15}N CP/MAS Spectroscopy. The ^{15}N CPMAS spectra of EB, $\Delta 190$, and $\Delta 190\text{-OX}$ films are shown in Figure 5. In the ^{15}N spectrum from the EB film peaks are observed for imine (325 ppm) and amine (65 ppm) nitrogens. In the spectrum from the $\Delta 190$ film (Figure 5B), the imine nitrogens are absent as a result of full reduction of the polymer. Similar to the ^{13}C NMR data, the imine nitrogen signal is partially restored in the spectrum from the $\Delta 190\text{-OX}$ film cast from the reoxidized solution.

The occurrence of cross-linking of the polymer upon heating the NMP solution is anticipated to generate a structure similar to the structure observed for the cross-linked PANI powder (Scheme 2). In forming this compound, the imine nitrogens and the quinoid rings are converted to amine nitrogens and benzenoid rings, respectively. The chemical shift difference between the secondary aromatic amines and the tertiary aromatic amines is expected to be less than the experimental line width and not resolvable.³⁵ Isolation of the 3° amine peak, if present, can be achieved by taking advantage of the difference in the strength of the $^{15}\text{N}\text{--}^1\text{H}$ dipolar couplings for the two types of nitrogens. With a proton bonded to the 2° amine nitrogen the dipolar coupling is much stronger for this nitrogen than for the 3° amine, where the nitrogen is weakly coupled to protons that

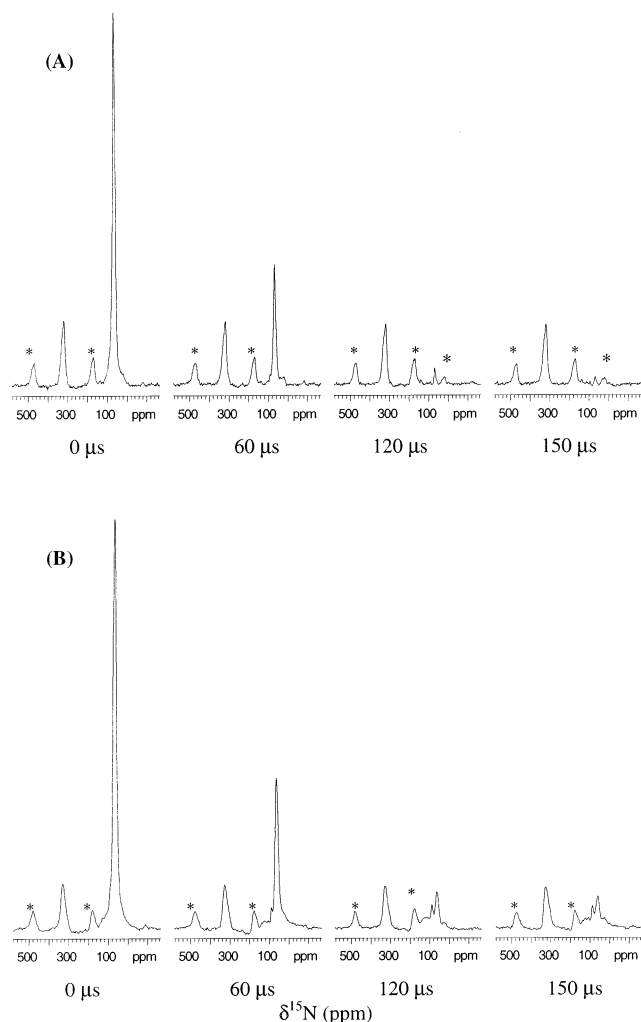


Figure 6. ^{15}N CP/MAS spectra acquired with variable time of interrupted proton decoupling. PANI films cast from NMP solution (A) EB and (B) $\Delta 190\text{-OX}$. The interrupted decoupling delay times are listed below each spectrum. * = spinning sidebands.

are spatially near the nitrogen but further away than a covalently bonded proton. The strength of the dipolar coupling can be probed by acquiring the ^{15}N NMR spectrum while also using the interrupted proton decoupling technique.³⁶ Turning off (interrupting) the proton decoupling results in a decrease in the signal intensity with the rate of signal loss being greater the larger is the dipolar coupling. The ^{15}N data for the EB and $\Delta 190\text{-OX}$ films with increasing interrupted decoupling times are shown in Figure 6. For the EB film, the amine nitrogen peak at 70 ppm decays completely in approximately 120 μs , whereas the intensity of the peak from the imine nitrogen, with no covalently bonded proton, has changed little even after 150 μs of interrupted decoupling. The small signals present near 70 ppm after 150 μs of interrupted decoupling arise both from a spinning sideband of the imine nitrogen signal and likely from a small population of defect sites generated during the polymer synthesis.³⁷ The signal intensity, then, from the 2° amines sites present in the PANI films will be absent after 120 μs of interrupted decoupling. The spectra from a similar analysis of the $\Delta 190\text{-OX}$ film are shown in Figure 6B. In this case, after 120 μs of interrupted decoupling, peaks at 70 and 90 ppm are present and show little additional change in

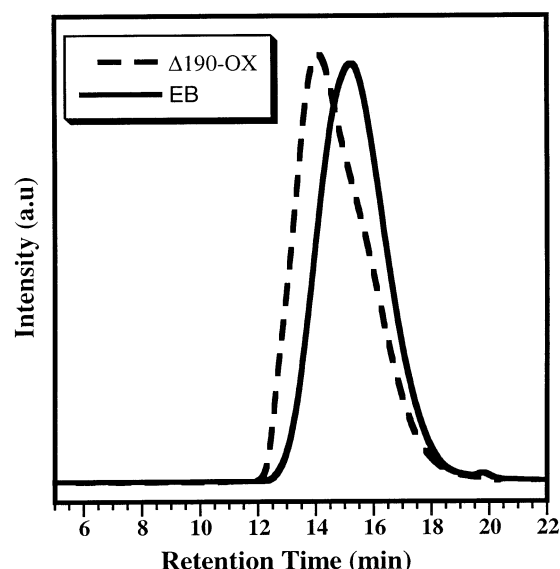
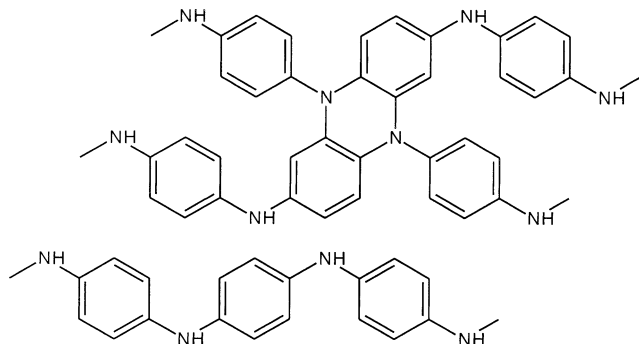


Figure 7. GPC chromatograms from PANI/NMP solutions of EB and $\Delta 190\text{-OX}$.

intensity even after 150 μs of interrupted decoupling. In our studies of the cross-linked PANI powder the tertiary nitrogens (Scheme 2) had a chemical shift of 70 ppm.²⁰ The peak at 70 ppm from the $\Delta 190\text{-OX}$ film, arising from a nonprotonated nitrogen, is also assigned to tertiary aromatic amine nitrogens. The identity of the species giving rise to the peak at 90 ppm has not been determined but must originate from a secondary reaction that occurs at elevated temperatures.

GPC Analysis. The GPC analysis of EB and $\Delta 190\text{-OX}$ samples in NMP are shown in Figure 7. The number-average and weight-average molecular weight of the parent polymer EB is 19 000 and 55 000, respectively, and the polydispersity is 3.0. The $\Delta 190\text{-OX}$ sample exhibits a 2-fold increase in the molecular weight with the number-average and weight-average molecular weight being 26 000 and 121 000, respectively, with a polydispersity of 4.6.

Reactivity and Structure of Polyaniline. Insights into the structure of PANI present in annealed NMP solutions can be gained from both the spectroscopic characterizations and the bulk physical properties of the polymer. Complete or nearly complete cross-linking of polyaniline leads to a material that has almost no solubility in NMP.^{14,17,19} If extensive cross-linking has occurred upon heating NMP solutions of PANI, as proposed by Lee et al.,²¹ then precipitation of the polymer should have been visible along with a significant increase in the average molecular weight. In each of the heated NMP solutions of PANI investigated, while the solution color did change from blue to brown from the reduction of the polymer, there was no evidence of precipitation or aggregation of the polymer. Also, only a modest change in molecular weight was measured by GPC. The UV/vis, FTIR, and NMR characterizations show full reduction of the polymer with annealing but only partial reoxidation in the presence of oxygen. As evidenced by the complete reoxidation of the chemically reduced PANI, in these polymer solutions oxygen would not be inhibited from interacting with all reduced sites within the polymer. Wei et al. have also observed full reoxidation of NMP solutions of LEB with oxygen gas.²⁶ The fact that PANI in annealed NMP solutions is not fully returned to the EB oxidation state indicates that

Scheme 3. Structure of PANI Generated in Heated NMP Solutions

a portion of the repeat units are chemically modified. The ¹⁵N SSNMR studies show that the reactivity of PANI in the NMP solutions results in the formation of tertiary aromatic amine sites. Similar NMR data have been reported for the cross-linking product from annealed PANI powder. Also, the ¹³C NMR spectra from PANI films cast from the heated NMP solutions are very similar to those from the cross-linked powder.²⁰ Heating NMP solutions of PANI then also results in the cross-linking of the polymer forming a phenazine structure at the cross-linking site similar to those shown in Scheme 2. In these samples only partial cross-linking occurs, giving rise to the 2-fold increase in the weight-average molecular weight, and the polymer retains enough mobility to remain soluble in NMP. The regions not involved in cross-linking are reduced during heating and then are readily reoxidized in solution with molecular oxygen. Combining the cross-linking with reduction, an average structure for PANI from heated NMP solutions is illustrated in Scheme 3. As the structure will vary along the chains, this structural heterogeneity accounts for the broadened line widths observed in the ¹³C NMR data.

The reduction of a portion of the polymer implies the presence of a reductant in the PANI/NMP solution. Afzali et al.,²³ who report that the polymer is fully reduced in heated NMP solutions but it does not undergo any significant amount of cross-linking, have proposed that NMP is the reductant. They were unable, however, to isolate any oxidized NMP in their solution and proposed that the oxidized solvent has reacted with the PANI. Our ¹³C solid-state NMR spectra of the PANI films also show the presence of NMP that cannot be removed by methanol extraction. However, the chemical shifts of the carbonyl peak, as well as those of the aliphatic carbons, are the same as those observed for PANI films cast from NMP solutions that have not been heated, showing that the trapped material is unreacted NMP.³⁸ We are unable to detect by any of our spectroscopic characterizations the presence of a retained reductant in the PANI films.

A possible candidate for the reductant of PANI in NMP solutions is the polymer itself. The cross-linking reaction between the imine nitrogens of one repeat unit with the quinoid ring of another, forming the phenazine structure, will also yield a hydrogen atom as a product. (This may be in the form of an electron and H⁺.) The hydrogen atom generated by cross-linking then will react with a quinoid group of an additional repeat unit, resulting in simple reduction of the polymer. Once a repeat unit is reduced, and it remains reduced as the heating is carried out under a nitrogen atmosphere, it

is then unable to participate in cross-linking. These repeat units are then reoxidized by molecular oxygen.

Conclusion

Application of a series of spectroscopic techniques has allowed a detailed characterization of PANI from NMP solutions of the polymer that have been heated to 125 °C. In these solutions the polymer undergoes a combination of cross-linking and reduction, with reoxidation to the EB form possible for the regions not involved in cross-linking. The spectroscopic studies have also yielded an average structure of the reacted polymer with a cross-linking product similar to that observed for cross-linked PANI powder. These results also illustrate that caution must be used when processing NMP solutions of PANI, as reactivity of the polymer occurs even at 125 °C. Long duration processing procedures conducted at more moderate temperatures are also likely to result in changes in the oxidation state and composition of PANI.

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