Reversible Quantum Confinement of Polarons by Reaction of Protonated Emeraldine with Nitric Oxide

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Received: June 5, 2009; Revised Manuscript Received: July 2, 2009

Nitric oxide (NO), a free radical, adds to green emeraldine acid, a polyradical and a one-dimensional polaronic conductor. As more NO is added, the segments through which protons and their associated unpaired electrons move, i.e., the polarons, are progressively shortened. This confinement of polarons is observed as a spectral progression from the parent green emeraldine acid, with an absorption maximum at 875 nm, to a series of blue polymers, their absorption maxima shifting progressively while decreasing in intensity with NO uptake to 670 nm, then turning colorless, with only a faint residual absorption at $\lambda_{max} = 625$ nm for the end member of the series which is insulating and no longer shows a voltammetric wave. The sequence is reversed in dilute HCl where the colorless and insulating polymer releases nitric oxide, the polaron is deconfined and the voltammetric wave reappears.

Nitric oxide (NO) is a stable free radical, combining rapidly with organic and inorganic radicals[1,2] and with transition metal complexes having unpaired electrons. Protonated emeraldine, referred to as emeraldine acid, is a cationic polyradical and a one-dimensional polaron conductor. The conduction is restricted to the main axis of the polymer; in three-dimensional hydrated emeraldine films electrons diffuse by redox conduction, i.e., by Marcus-type electron exchange between neighboring chains.[3] Protonation of emeraldine, referred to as doping, increases the hydration of the chains and thereby their mobility and the exchange of electrons.

In emeraldine the ratio of reduced amine nitrogens to oxidized imine nitrogens is about 1.0 (Scheme 1, top).[4] The nitrogens of emeraldine acid are cationic radicals;[5] their unpaired electrons and protons propagate as polarons. Being a polyradical, emeraldine acid reacts with NO to produce a series of polynitrosamines. The fully denitrosylated and nitrosated end members of the series are shown in Scheme 1. Because the polynitrosamines are weaker bases than emeraldine, the emeraldine acid is deprotonated as it reacts with NO, and because the nitrosated nitrogens block the propagation of the polarons, the polarons are progressively confined to shorter chain segments as the nitrosation progresses, while the polymer becomes increasingly insulating. The fully nitrosated emeraldine-derived polynitrosamine, like leucoemeraldine, is colorless and reduced. However, unlike leucoemeraldine, polynitrosamine cannot be oxidized in the given potential range because the necessary proton transfer reactions are not possible. Release of the NO by strong acids, i.e., the reprotonation, is accompanied by deconfinement of the polarons. The NO exposure caused green to blue to colorless sequence and the loss of electrochemical activity are reversed by HCl exposure.

Poly(2-acrylamido-2-methyl-1-propanesulfonic acid)-protonated polytoluidine (PoT-PAAMPSA) was synthesized as described for polyaniline by Loo and her colleagues[6–8] by

SCHEME 1: Reaction of NO with Emeraldine Acid (1) Whereby the Polynitrosamine (2) Is Formed
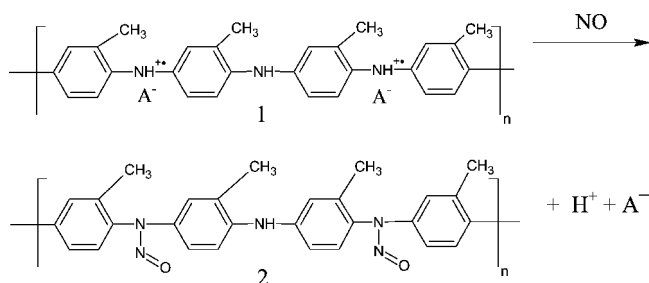
adding dropwise to the stirred and cooled solution of 1:1 molar ratio *o*-toluidine:acid monomer, ammonium peroxydisulfate (1:09 monomer to peroxydisulfate molar ratio). After 24 h, the emeraldine acid PoT-PAAMPSA was precipitated with acetone and collected, after drying, as green powder.

Consistently with the expected polaron confinement (Scheme 2A−C), adding of 10 µL aliquots of NO-saturated solutions (∼2 mM) to the degassed PoT-PAAMPSA solution (2 mL volume, 0.01 wt %) caused the solution to turn from green through a series of blues to colorless (Figure 1). The spectra of the intermediate nitrosamines and the end member of the series are shown in Figure 2. The emeraldine PoT-PAAMPSA band at 875 nm is gradually down-shifted to 625 nm and then fades. When the pH of a highly acidic solution of the emeraldine is raised, changes resembling those upon NO uptake are observed in the absorption spectra. As the emeraldine acid is deprotonated, the polaron transitions-associated absorption maximum shifts from 875 to 700 nm or less and decreases in intensity. The spectral change is the basis for the use of polyaniline in optical pH sensing.[9,10] However, there are major differences between the changes induced by nitric oxide and those brought about by pH change. First, deprotonation upon nitrosation results of formation of a weaker base, not of a lesser proton concentration in the solution. Second, upon decreasing the acidity of the

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SCHEME 2: Confinement of the Polaron by NO Resulting in Diminished 875 nm Absorption by PoT-PAAMPSA
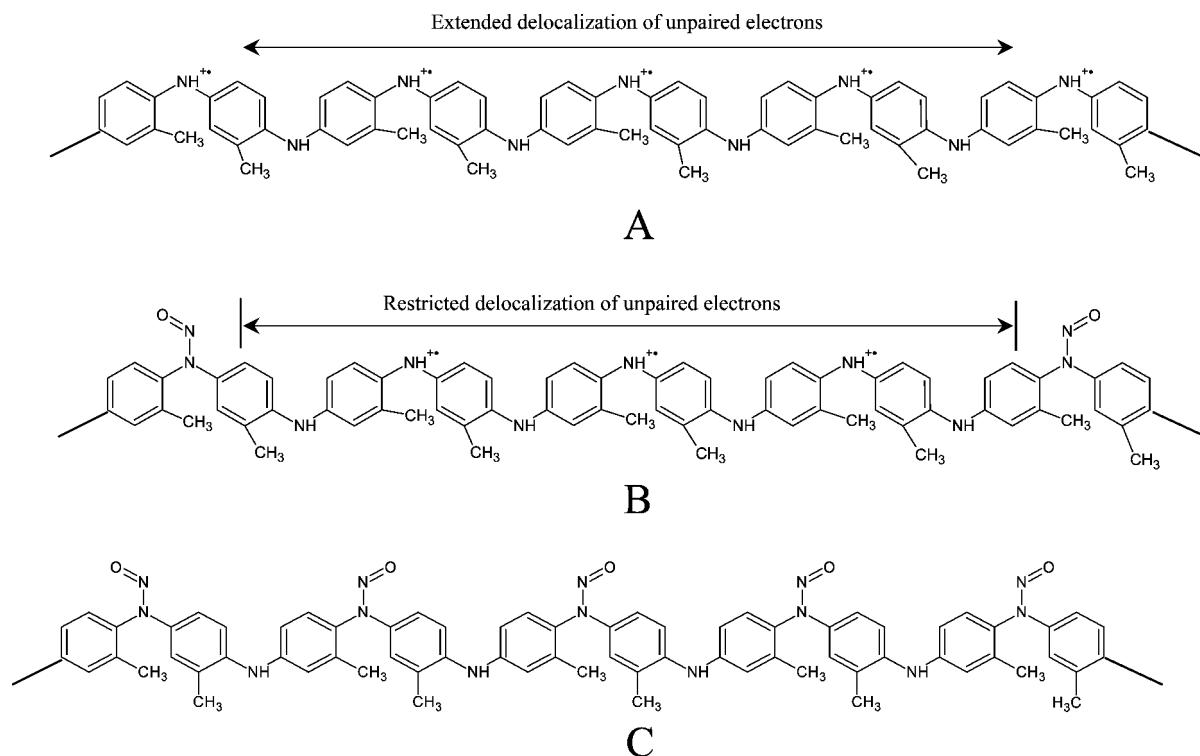
solution there is an increase in the intensity of the 600−650 nm exciton band, associated with the increase in the fraction of quinoid rings. A 600−650 nm exciton band does not appear, however, upon nitrosation. Third, the isosbestic point observed for the pH increase caused spectral change is not observed when the spectral changes are caused by adding NO.

There are also major differences in the spectral changes preceding the formation of the colorless leucoemeraldine by reduction of emeraldine and the formation of the also colorless highly nitrosated product of emeraldine acid formed by adding an excess of NO. The reduction of emeraldine to leucoemeraldine is discontinuous; i.e., there is no evidence for the presence of any intermediate macromolecule.[11] Because at any degree of reduction only two species, one reduced, one not reduced, are present, there is a well-defined isosbestic point in all partially

reduced solutions. In contrast, the confinement of polarons produces a continuum of macromolecules, differing in their degree of nitrosation; hence the intensity of the polaron band decreases before fading away as its energy is up-shifted and there is no isosbestic point. The NO addition-caused spectral changes thus resemble those that were observed when discrete emeraldine acids of diminishing chain length were synthesized, the energies of their polaron bands increasing upon decreasing their chain lengths.[12]

For IR spectroscopy, films of the polynitrosamine derived of PoT-PAAMPSA were spin-coated onto silicon wafers. Figure 3a compares the infrared spectra of the colorless polynitrosamine derived of emeraldine acid with that of green emeraldine acid. In nitrosamines the $N{=}O$ stretching frequency is at 1450−1500
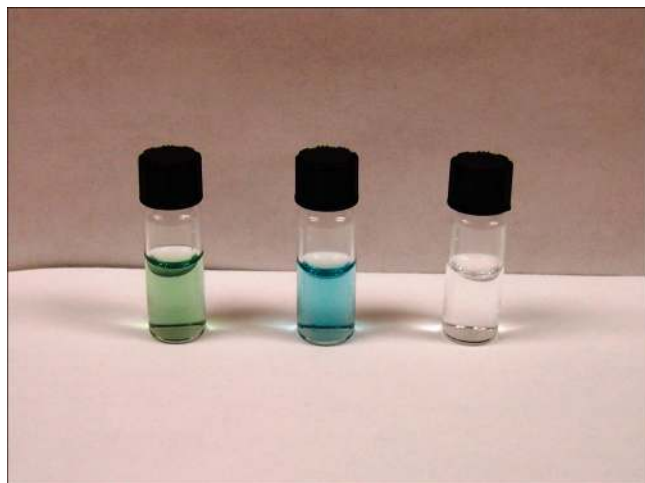

Figure 1. Color changes upon nitrosation of PoT-PAAMPSA: initially green solution (left); solution after bubbling NO for 3 min (center); solution after bubbling NO for 15 min (right).
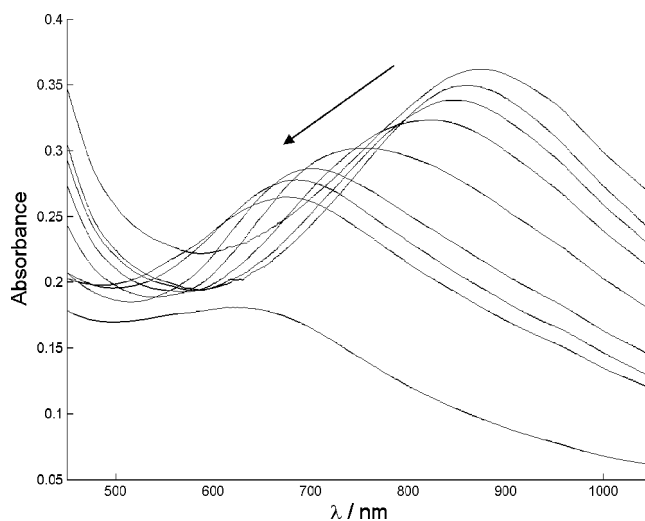
Figure 2. Progressive change in the spectrum of a 0.01 wt % solution (2 mL) of PoT-PAAMPSA (initially λ_{max} = 875 nm) when 10 μL aliquots of a saturated NO solution are added.

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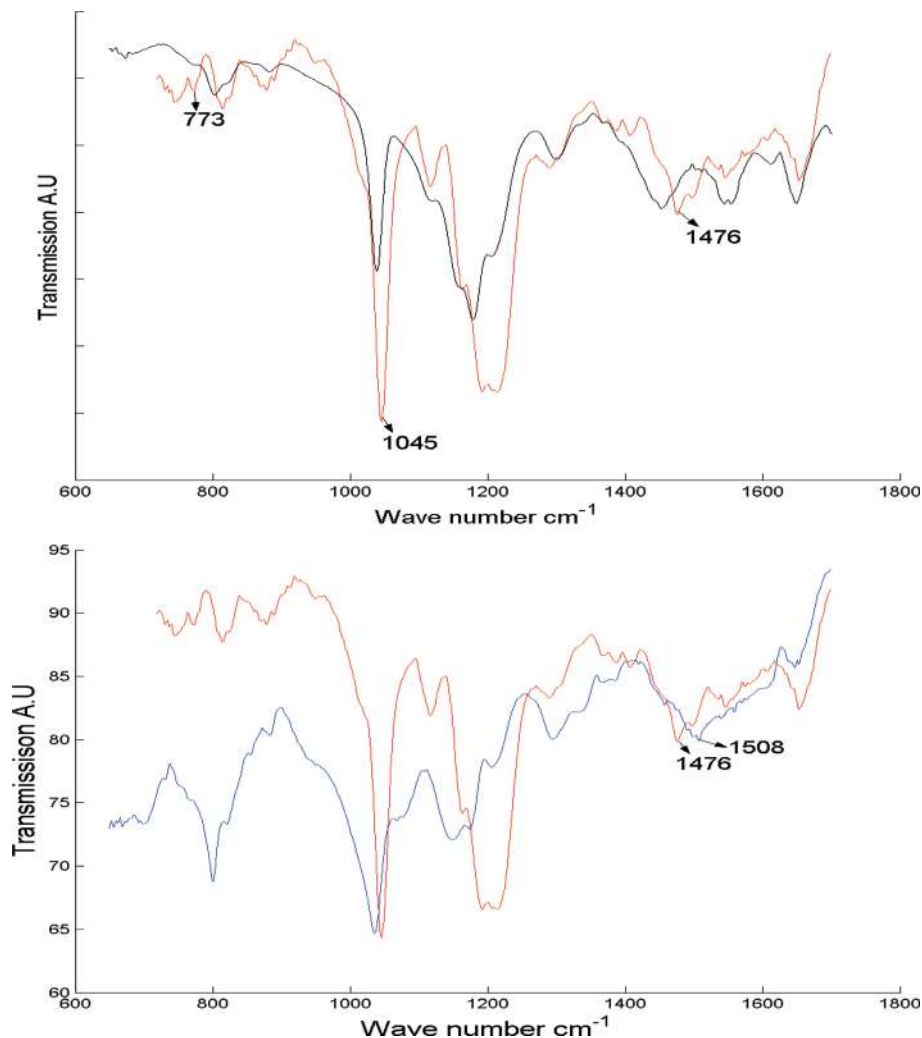
Figure 3. FT-IR spectra of PoT films. Top: unreacted PoT-PAAMPSA (black) and NO-reacted PoT- PAAMPSA (red). Bottom: fully NO-reacted PoT-PAAMPSA (red) and partially NO-reacted PoT-PAAMPSA (blue).
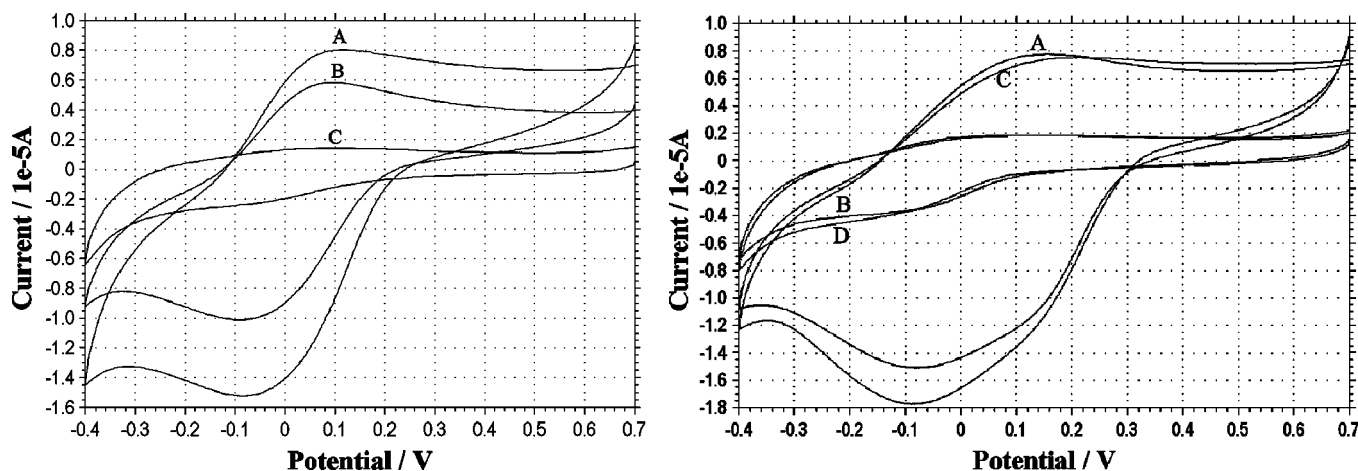
Figure 4. (a) Cyclic voltammograms of a PoT-PAAMPSA film on a glassy carbon electrode in a 0.1 M KCl solution. Scan rate: 100 mV/s. Voltammogram A: green emeraldine acid (0.005 wt % solution) coated on a 3 mm glassy carbon electrode. Voltammogram B: blue emeraldine acid (0.005 wt % emeraldine acid, to which 10 μL aliquots of saturated NO solutions had been added) coated on a 3 mm glassy carbon electrode. Voltammogram C: 0.005 wt % colorless polymer (formed by bubbling NO gas until the solution became colorless) coated on a 3 mm glassy carbon electrode. (b) Cyclic voltammograms of a PoT- PAAMPSA film on a glassy carbon electrode in a 0.1 M KCl solution. Scan rate: 100 mV/s. Voltammogram A: unreacted. Voltammogram B: after 1 min exposure to 1 atm NO. Voltammogram C: after exposure of the NO-reacted electrode to the vapor above a 2 M HCl solution for 30 s. Voltammogram D: after re-exposure to 1 atm NO for 1 min.

cm^{-1}.[13,14] In the colorless polynitrosamine a 1476 cm^{-1} peak is observed; in the midrange blue polynitrosamine the peak is at 1508 cm^{-1} (Figure 3b).[15]

To assess the electron or polaron conduction-requiring electrochemical activity, a thin layer of PoT-PAAMPSA emeraldine acid was coated on a glassy carbon electrode (10 μL

of 0.005 wt % aqueous solution on a 3 mm diameter disk). While the green emeraldine acid film was electrochemically active, the film of the blue polymer was electrochemically less active and that of colorless polymer was electrochemically inactive (Figure 4a).

In the reverse polaron-deconfining reaction (1), the NO of the colorless polynitrosamine is hydrolytically released by 0.1 M HCl. The film on a carbon disk electrode is again electrochemically active (Figure 4b) and in solution the colorless polynitrosamine turns blue then emeraldine acid green.

$$>N-NO + H^+ \rightarrow >NH^{+\bullet} + NO \qquad (1)$$

That NO was released by the HCl was confirmed through the color change from red to yellow of sol−gel immobilized Fe (II) oxyhemoglobin (red),[16] which reacts with NO to produce Fe(III) methemoglobin (yellow) and nitrate.[17]

In summary, the combination of emeraldine acid with NO confines its polarons, while stripping of the NO with acid deconfines the polarons.

Note Added after Print Publication. This paper was published on the Web on July 10, 2009, and in the August 6, 2009, issue. An Acknowledgment section was added. The electronic version was corrected and reposted to the Web issue on August 21, 2009. An Addition and Correction was also published (DOI: 10.1021/jp9078103).

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JP905316D