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Study of the Redox Process of Poly(5-amino-1-naphthol) Thin Film by *In Situ* Raman Spectroscopy

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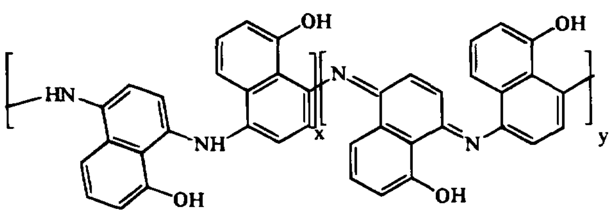
ABSTRACT

Poly(5-amino-l-naphthol) is a new conducting polymer, obtained by electropolymerization of 5-amino-l-naphthol. Raman spectroscopy confirms the structure which consists of amine (–NH–C) and imine (–N=C) links between naphthalene rings, characteristic of a polyaniline-like structure. Its redox properties were investigated in aqueous acid (pH 0) by *in situ* Raman spectroscopy. Some amine units are reversibly transformed into imine groups on oxidation.

Introduction

Poly(aminonaphthol) films were recently prepared by electrochemical polymerization in aqueous acid and acetonitrile solutions.[1,2] Poly(5-NH_2 1-NAP) and poly(5-NH_2 2-NAP) films synthesized by the electrochemical oxidation of 5-amino-1-naphthol (5-NH_2 1-NAP) and 5-amino-2-naphthol (5-NH_2 2-NAP) are conducting. Data from an *in situ* multiple internal reflection Fourier transform infrared spectroscopy (MIRFTIRS) study and x-ray photoelectron spectroscopy (XPS) analysis clearly showed that the electro-oxidization was selective and that electropolymerization occurred via coupling para to the NH_2 group.[1,2] These results were confirmed by frontier orbital calculations.[3] The film structure is of the polyaniline type, containing –OH groups in the chain (Scheme 1).



Poly (5-NH_2 1-NAP)

Scheme 1.

Poly(aminonaphthol) films show reversible, well-defined redox systems in aqueous acid.[1,2] Only one redox system is detected, contrary to polyaniline.[4,5] The redox process of these new conducting polymers, especially poly(5-NH_2 1-NAP) has been studied *in situ* by several spectroelectrochemical methods including probe beam deflection (PBD) and MIRFTIRS. Two different mechanisms were proposed, depending on whether the medium was organic or aqueous acid.[6]

Here, we have studied the electrochemical oxidation-reduction of poly(5-NH_2 1-NAP) at pH 0. This value was selected because the structural changes were more easily detected at this pH. We have also recorded for the first time *ex situ* Raman spectra of both monomer and polymer at different wavelengths. We show that during the oxidation-reduction process, the amine units are reversibly transformed to imine groups. The high C=N stretching frequency suggests weak delocalization of π electrons.

Experimental

Preparation of poly(aminonaphthol) films.—Polymer films were obtained by electrochemical polymerization on platinum electrodes. For Raman studies the electrodes were Pt-sputtered glass plates. For UV-visible studies, indium-tin oxide (ITO) plates (Donnelly Corporation) were used as electrodes.

Electrochemical polymerization was performed by potential cycling at a sweep rate of 50 mV s^{-1} for 15 min between 0 and 0.9 V during the first cycles, then the potential limit was progressively reduced to 0.7 V *vs.* saturated calomel electrode (SCE). The solutions consisted of aqueous 2 *M* $HClO_4$ containing 10^{-3} *M* of the monomer.

Experimental techniques.—UV-visible experiments were performed on a Varian 200 DMS spectrometer. Raman spectra excited with the laser line at 457.9 nm were recorded on a Dilor X-Y double monochromator spectrometer in the subtractive mode with a multichannel detector (1024 diodes cooled by Peltier effect). The laser line was provided by a Spectra-Physics (Model 165) argon ion laser (exciting wavelength λ_e = 457.9 nm) and from a Spectra-Physics helium-neon laser (exciting wavelength λ_e = 623.8 nm). In both cases the light power, measured at the sample was less than 10 mW. UV excitation Raman spectra (350.7 nm from a Spectra-Physics krypton ion laser) were recorded on a Jobin-Yvon double monochromator spectrometer. The light power was 20 mW. Raman spectra at 1064 nm were measured on a Fourier transform Raman spectrometer (Perkin-Elmer System 2000), the laser line being provided from an yttrium aluminum garnet) (YAG) laser. The output laser power was less than 10 mW.

In situ Raman experiments were performed by coupling electrochemical techniques with the Raman spectrometer by means of the specially designed cell previously described.[7]

In these *in situ* Raman experiments, the working electrodes were poly(5-NH_2 1-NAP) film-coated Pt electrodes. The electrolytic medium was aqueous 2 *M* HCl. The film-coated electrode was polarized at the desired potential for about 4 min, this time being necessary for spectra acquisition.

Results and Discussion

UV-visible results.—To determine the optimal excitation frequency, UV-visible absorption spectra were recorded for films deposited on ITO electrodes. Figure 1 shows the

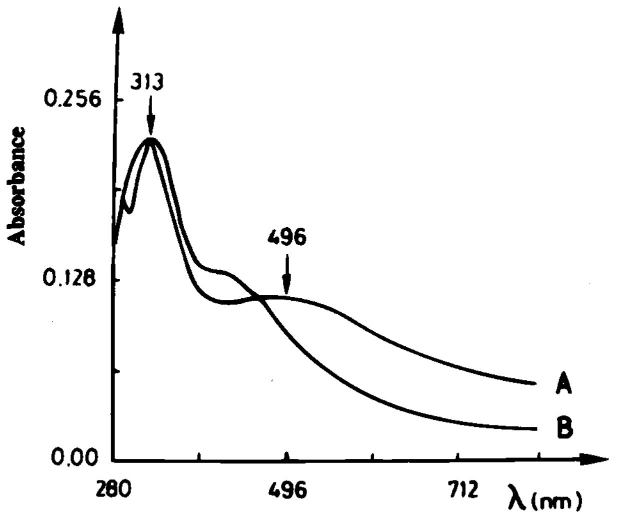


Fig. 1. UV-visible spectra recorded during the polarization of a poly(5-NH_2 1-NAP) film in 2 *M* $HClO_4$ solution at two different potentials: (A) +0.5 V, (B) −0.5 V. The film was prepared from a 10^{-3} *M* monomer + 2 *M* $HClO_4$ solution by cyclic voltammetry.

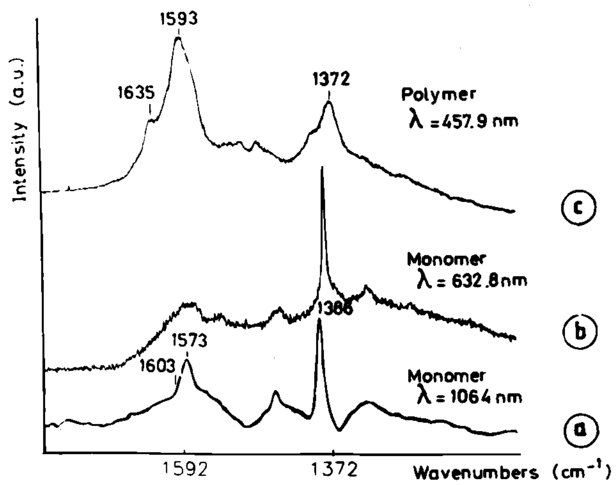


Fig. 2. *Ex situ* Raman spectra of (a) 5-NH_2 1-NAP at λ = 1064 nm; (b) 5-NH_2 1-NAP at λ = 632.8 nm; and (c) poly(5-NH_2 1-NAP) film recorded with 457.9 nm excitation. The film was prepared from a 10^{-3} *M* monomer + 2 *M* $HClO_4$ solution by cyclic voltammetry.

in situ UV-visible spectra of poly(5-NH_2 1-NAP) film immersed in 2 *M* $HClO_4$ at various applied potentials. At −0.5 V the polymer film in its reduced state is light yellow and shows one absorption band ~313 nm. The shoulder at 442 nm is probably from benzenoid rings. At +0.5 V, in the oxidized state the polymer film turns dark green with the appearance of a new broad absorption band having a maximum ~496 nm. The 496 nm band may be related to the formation of polarons or quinone-imine transitions, as proposed for polyaniline.[8-10] The band at 313 nm is present in the film in both forms. It may be ascribed to the $\pi \rightarrow \pi^*$ electronic transition. Based on the UV-visible spectra, λ_e = 457.9 nm was chosen as the optimal excitation frequency since this wavelength is close to the isobestic point (464 nm). It allowed the recording of resonance Raman spectra of both oxidized and reduced forms of polymer films.

Ex situ Raman results.—We recorded spectra of both monomer and polymer in the dry state before the *in situ* experiments to compare the main bands and the general shape of the spectra. The polymer spectrum was recorded at λ = 457.9 nm while the monomer spectra were recorded at 632.8 and 1064 nm. At 457.9 nm the high fluorescence of the monomer leads to unresolved Raman spectra.

Monomer.—Figure 2 presents spectra of both the polymer and the monomer. The monomer spectrum was recorded at λ = 632.8 nm and λ = 1064 nm with extremely low laser power (see Experimental section). That the same bands are observed proves that the spectra are real sample spectra and not those of photochemical products generated by the destruction of the sample by the laser beam.

An intense line is detected at 1386 cm^{-1} when the spectrum is recorded at 1064 nm. This mode, characteristic of naphthalene derivatives,[11] has been attributed to C–C ring stretching vibrations. Two others peaks, of medium intensity, are detected at 1573 and 1603 cm^{-1}, and are probably due to C=C ring stretching vibrations ($C{=}C_{aromatic}$).[11]

Polymer.—The Raman spectrum of electrodeposited poly(5-NH_2 1-NAP) film in its oxidized form with 457.9 nm laser line excitation is presented in Fig. 2c. As for the monomer spectrum, the predominant bands are situated ~1600 and 1370 cm^{-1}. The strong 1593 cm^{-1} band is assigned to $C{=}C_{aromatic}$ stretch, while the shoulder at 1635 cm^{-1} may be assigned to C=N stretch, indicating the presence of imine groups. This value, which is in good agreement with data published in the literature,[11] indicates that the C=N bond has considerable double-bond character due to weak delocalization in the chain. The Raman pattern in this range is similar to infrared results observed previously,[1] *i.e.*, a strong $C{=}C_{aromatic}$ stretching band at 1581 cm^{-1} and a marked shoulder at 1664 cm^{-1} assigned to C=N stretch.

In the second range, a fairly strong band at 1372 cm^{-1} is detected. By comparison with the monomer spectrum, it is difficult to attribute this band either to C–N or C–C ring stretching vibrations. As seen below, on the basis of the *in situ* results this band may be assigned essentially to C–N stretching vibrations.

Resonance Raman spectra of electrodeposited poly(5-NH_2 1-NAP) film in its oxidized form were also obtained with 350.7 nm excitation. This wavelength, close to the $\pi \rightarrow \pi^*$ UV absorption band of the naphthalene rings, seems to enhance the Raman lines of naphthalene nuclei. The spectrum (Fig. 3) shows a very strong, sharp band at *ca.* 1610 cm^{-1} along with a broad band at 1375 cm^{-1}. However, the Raman pattern is less well resolved than that recorded with 457.9 nm excitation (Fig. 2c).

Study of the redox process of poly(5-NH_2 1-NAP) film by in situ Raman spectroscopy.—Raman spectra with 457.9 nm excitation of the film during its polarization at pH 0 medium were obtained at three potentials: +0.025, +0.3, and +0.7 V *vs.* SCE (Fig. 4). These values were deter-

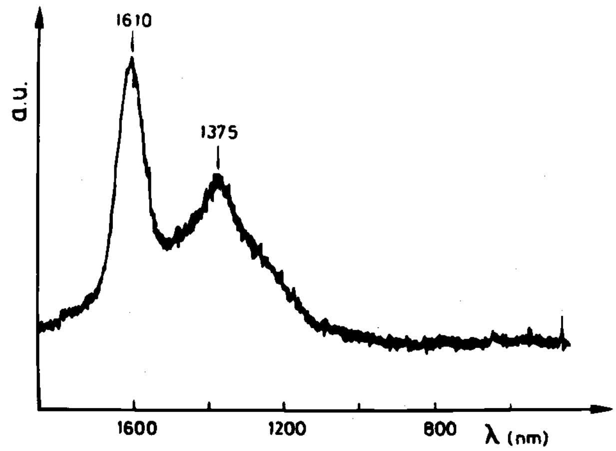


Fig. 3. *Ex situ* Raman spectrum of poly(5-NH_2 1-NAP) film recorded with 350.7 nm excitation. The film was prepared from a 10^{-3} *M* monomer + 2 *M* $HClO_4$ solution by cyclic voltammetry.

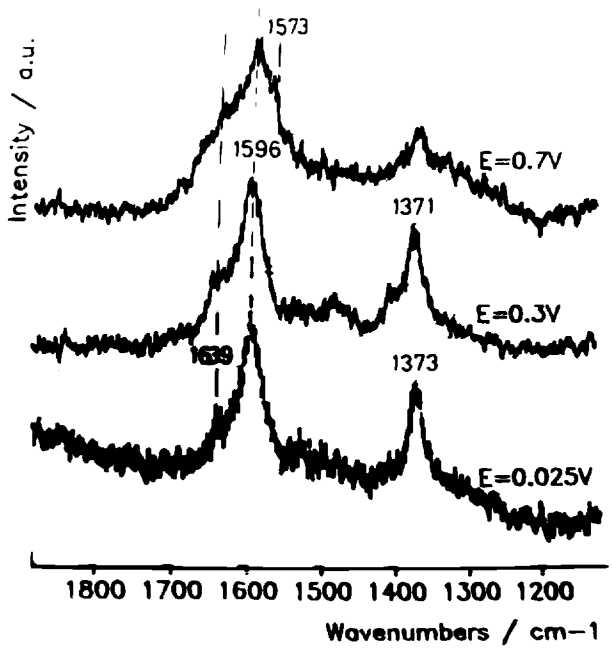


Fig. 4. *In situ* Raman spectra obtained during the polarization of poly(5-NH_2 1-NAP) film at pH 0 and +0.025, +0.3, +0.7 V *vs.* SCE. The film was prepared from a 10^{-3} *M* monomer + 2 *M* $HClO_4$ solution by cyclic voltammetry.

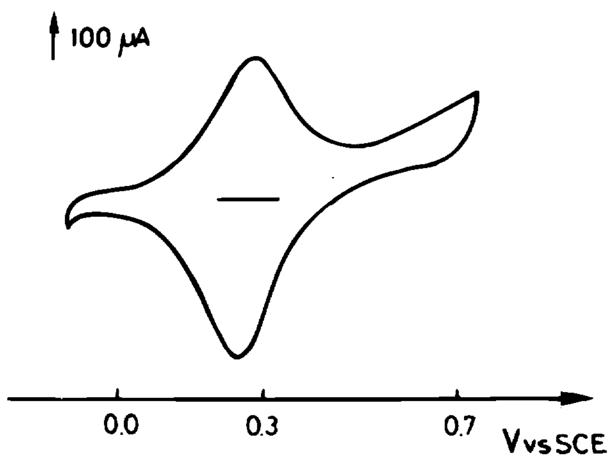


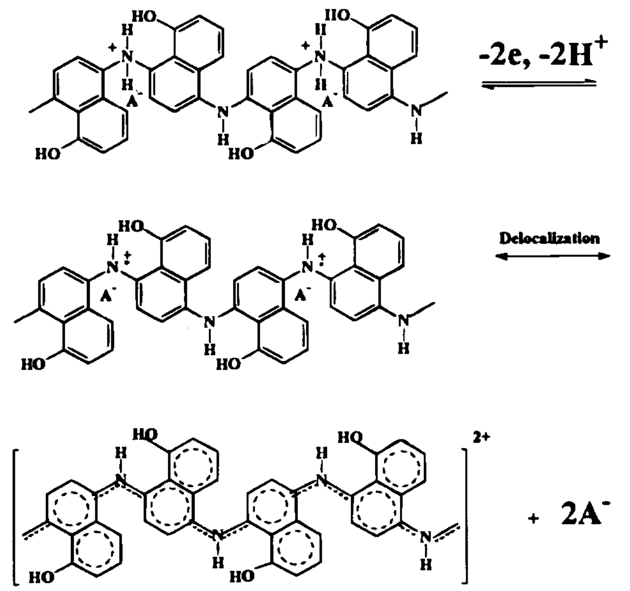
Fig. 5. Cyclic voltammetric response of a poly(5-NH_2 1-NAP) film-coated Pt electrode (film prepared in 2 *M* $HClO_4$). Medium: 2 *M* HCl; scan rate: 5 mV s^{-1}; electrode surface 2.16 cm^2.

mined from the redox response of poly(5-NH_2 1-NAP) film (Fig. 5). At 0.7 V the film is completely oxidized. Consequently, greater structural changes are expected at this potential than at 0.3 V. In an attempt to obtain the completely reduced form, the potential was set at −0.15 V. Unfortunately, this undoped state is strongly fluorescent and leads to unresolved Raman spectra.

The pattern of the spectrum recorded at +0.025 V is similar to the *ex situ* Raman spectrum (Fig. 2c). The two strong dominant bands at 1596 and 1373 cm^{-1} may be assigned to $C{=}C_{aromatic}$ and C–N stretch, respectively. A small band at 1639 cm^{-1} may indicate the presence of imine groups with strong C=N double-bond character.

When the film is polarized at +0.3 V, the potential corresponding to the oxidation peak of the polymer, the 1373 cm^{-1} band decreases in intensity while the 1639 cm^{-1} band increases. At +0.7 V, the 1639 cm^{-1} band continues to increase and a shoulder appears at 1573 cm^{-1}. Thus, besides the band at 1639 cm^{-1}, assigned to imine bond stretching, the key bands detected at +0.7 V are situated at 1596 and 1573 cm^{-1}. They could be assigned to the stretching vibrations of benzenoid (1596 cm^{-1}) and quinoid rings (1573 cm^{-1}).[12,13] The presence of the peak at 1573 cm^{-1} seems to indicate that delocalization increases from 0.3 to 0.7 V. At 0.7 V the band around 1370 cm^{-1} is very weak while that at 1639 cm^{-1} (C=N stretch) is strong. It can be assumed that during the oxidation process some amine groups are transformed into imine groups. The process is reversible on reduction. When the potential is switched back to 0.3 V the Raman spectrum obtained is the same as that first recorded at this potential; the 1639 cm^{-1} band decreases in intensity while the 1371 cm^{-1} one increases. From these data, it seems likely that the *ca.* 1370 cm^{-1} band in the polymer is due mainly to C–N stretch of amine groups.

The above Raman data are consistent with the redox mechanism of poly(5-NH_2 1-NAP) at pH 0 which has been proposed previously on the basis of a PBD study.[6] In aqueous acid, protons are the predominant species for the charge compensation process. The deprotonated salt loses two electrons and two protons, forming a radical cation. Relaxation and delocalization of the electrons lead to a polaronic state which exhibits semiquinoid character.[14] (Scheme 2).



Scheme 2.

Conclusion

Raman spectroscopy experiments were performed with 5-amino-1-naphthol monomer and the resulting polymer in the dry state. This study was consistent with previous work on poly(5-NH_2 1-NAP) film, suggesting that the film consisted of amine (–NH–C) and imine (–N=C) units.

The electrochemical oxidation-reduction of poly(5-NH_2 1-NAP) film has been studied *in situ* in aqueous solution at pH 0. The structural changes detected suggest that certain amine units are transformed into imine groups on oxidation. On reduction, the process is reversible. The redox mechanism in aqueous acid involves the proton but not the dopant anion. This is consistent with data obtained by a PBD study of the poly(5-NH_2 1-NAP) redox process.

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Electrocatalysis of Anodic Oxygen-Transfer Reactions: Oxidation of Cr(III) to Cr(VI) at Bi(V)-Doped PbO_2-Film Electrodes

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ABSTRACT

Voltammetric and coulometric results are described for the electrocatalytic oxidation of Cr(III) to Cr(VI) at the mixed bismuth(V)-lead(IV) dioxide film electrodes (designated Bi-PbO_2) that are electrodeposited from acidic solutions of Pb(II) containing Bi(III). A current efficiency of 99.2% (σ = 1.1%, N = 12) is obtained for galvanostatic generation of Cr(VI) at a preconditioned Bi-PbO_2 film electrode. Preconditioning of the Bi-PbO_2 film merely involves the generation of Cr(VI) which, based on scanning electron micrographs, is concluded tentatively to achieve chemical stripping of noncatalytic portions of the Bi-PbO_2 films to produce films having greater electrocatalytic activity for the desired reaction. Electrochemical stripping of the Bi-PbO_2 electrode had a similar preconditioning effect. Based on wavelength dispersive spectroscopy, electrochemical stripping resulted in an increase in surface Bi concentration of 33% relative to Pb.

Introduction

Much research in this laboratory has been directed to the electrocatalysis of anodic reactions that require the concomitant transfer of oxygen from H_2O to the oxidation product(s).[1-4] Our use of the term electrocatalysis is intended to imply involvement of specific surface sites within these anodic O-transfer mechanisms to increase the rate of the heterogeneous reactions. Compounds typically investigated include inorganic and organic substances that are not generally observed to be electrochemically active at the conventional anodes (Pt, Au, PbO_2, and C). Electrocatalytic activity has been substantially increased for various anodic O-transfer at β-PbO_2 film electrodes that are heavily doped with various altervalent metallic ions. It is concluded that anodic O-transfer mechanisms require the concomitant anodic discharge of H_2O to produce adsorbed hydroxyl radicals ($\cdot OH_{ads}$).[5] Therefore, the catalytic function of altervalent dopants in the doped metal oxide film electrodes is commonly attributed to a diminished overpotential for discharge of H_2O at the dopant sites. Furthermore, it is speculated that a moderately low surface coverage by dopant sites ($\theta < 0.5$) assures that the distance between $\cdot OH_{ads}$ species at adjacent dopant sites is sufficiently large to prevent them from combining to produce O_2, an undesirable side reaction that can diminish the current efficiency for the desired O-transfer reactions.

Publications have reported studies of the anodic oxidation of Cr(III) to Cr(VI) in the presence of various metallic cations[6-8] and organic compounds[9,10] using a wide variety of electrodes materials.[10-12] However, all reported values of the current efficiency for production of Cr(VI) are significantly below 100%.[13,14] This is the cause for needless expenditure of energy due to the evolution of O_2, a competing anodic reaction.

Chang and Johnson demonstrated that trace levels of Bi(III) (< *ca.* 10 μM) added to acidic solutions of dimethyl sulfoxide (DMSO) could result in significant electrocatalysis of DMSO oxidation to $DMSO_2$ at rotated PbO_2/Au electrodes.[4] This observation was attributed to the electrosorption of Bi(III) as Bi(V) on the pure PbO_2 surface. Chang and Johnson also observed that higher concentrations of Bi(III) (> *ca.* 10 μM) produced a momentary electrocatalytic activity followed by a loss of electrode activity.[4] This was explained by Larew *et al.* as the consequence of the formation of a monolayer of the electrosorbed Bi(V) which covered PbO_2 sites necessary for preadsorption of the DMSO.[15]

Research described here is motivated by the goal of automating the determination of chemical oxygen demand (COD) of polluted waters on the basis of an indirect coulometric procedure that utilizes an electrochemically generated oxidation mediator. Chromium(VI) is a powerful oxidizing agent, as indicated by the large standard reduction potential given by

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$E^o_{Cr(VI/III)} = 1.33 \text{ V } vs. \text{ normal hydrogen electrode (NHE)} \quad [1]$$

and this compound has been used frequently for oxidation of organic compounds.[16] The standard method for determination of COD in organically polluted waters utilizes Cr(VI) with back titration of excess oxidant using a standard solution of Fe(II).[17]

Experimental

Chemicals.—All chemicals were analytical reagent grade from Fisher Scientific, Alfa Products, or Aldrich

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