

Monitoring of electroinitiated polymerization of aniline by Raman microprobe spectroscopy

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Abstract

It was observed that some water soluble products were formed during the electrochemical synthesis of polyaniline, and Raman spectroscopy can be used to detect those products. The amount of water soluble products increases with increasing electrolysis potential and the peak observed at 1620 cm^{-1} is characteristic for these products. Rinsing the polyaniline coated electrode with water even once removes the soluble products from the polymer, which indicates that care must be taken in polyaniline characterization studies during washing, solvation and doping–undoping processes. The transition of H_2SO_4 -doped polyaniline to undoped form by treating with 1.0 M NaOH takes place very rapidly in high yields which can be followed by in situ Raman spectroscopy. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The demand for new materials in high technology, made the conducting polymers attractive substances to be studied extensively [1–4]. Polyaniline (PANI) has become particularly popular due to its good electrical properties, air stability, low price of raw materials and its ease in synthesis by electrochemical and chemical techniques.

Chemical synthesis methods require a strong oxidant such as persulfates, perchlorates, and hydrogen peroxide [5–7]. Electrochemical techniques include potentiostatic, galvanostatic, and potential cycling methods [8–11]. PANI becomes insulating when treated with aqueous alkaline solution [1,7] or reduced electrochemically in aqueous acid solution [12]. Conversion to a conducting form can easily be accomplished by either protonation or electrochemical doping. The properties of PANI obtained electrochemically depend on the type of electrode, applied potential, temperature, and the type of doped-anion [13,14].

Various techniques have been employed, such as infrared spectroscopy [15,16], cyclic voltammetry [13], ^{13}C -NMR [17], to investigate the relations between the chemical structure of PANI and the conditions of polymerization.

Raman spectroscopy is a useful technique in elucidation of structure of polymers and has been recently used for PANI [18]. Raman spectra of polymer films obtained by electrolysis can easily be recorded without the need of removing the film from the electrode; this is an advantage over other analytical techniques.

It is possible to obtain in situ Raman spectra of the polymeric product formed on the electrode surface without disturbing the electrolysis course or damaging the polymeric film. It also enables one to take in situ spectra in short periods during the polymerization, even at early stages of reaction [18].

The use of Raman microprobe spectroscopy allows areas on the surface, as small as 1 mm^2 , to be studied [19]. The uniformity of the film can be observed directly by Raman spectroscopic imaging, a form of microscopy in which images of selected areas are recorded for light scattered in a selected Raman band [18,20]. Finally, the rate of polymerization can be followed by Raman studies of the solution [21].

In the present work, Raman spectra of H_2SO_4 -doped PANI synthesized at various potentials were taken. In situ Raman spectra of PANI formed on the electrode surface at various intervals were recorded and the undoping process was also monitored by in situ Raman spectra.

2. Experimental

Electrolysis was carried out in an H-type cell detailed

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previously [22]. Concentrations of aniline and H_2SO_4 were chosen as 0.1 and 1.0 M, respectively. The electrodes coated with PANI after being subjected to electrolysis at desired potential were taken out of solution and used directly in taking Raman spectra. A Princeton Applied Research (PAR) Model 362 scanning potentiostat was used throughout the study.

In situ Raman spectra were taken in a specially designed electrolysis cell described previously [18]. The working electrode was a 2-mm long Pt wire, and the cathode was a 20-mm long Pt wire coiled around the working electrode. A silver wire was used as a reference electrode. After the laser beam was focused on the surface of the working electrode with the aid of an optical microscope, the electrode was connected to the potentiostat which had been adjusted to apply 0.6 or 0.8 V to the working electrode. Raman spectra of the PANI forming on the Pt wire surface were obtained at various times during the electrolysis.

The in situ undoping process was monitored using the same cell. After the PANI coated electrode inserted to the cell filled with water, 1.0 M NaOH was injected into the cell and Raman spectra of the PANI on the electrode surface

were recorded at various intervals. Raman spectra were recorded using a Renishaw Ramascope (Model 2000) with a 25-mW He-Ne laser and a 50X objective. The maximum distance that the laser beam traveled through the solution to reach the polymer on the working electrode was 8 mm. The spectral and spatial resolutions were 2 cm^{-1} and $1\ \mu\text{m}$, respectively.

The cyclic voltammogram of PANI was obtained in 1.0 M H_2SO_4 . The working electrode was a 2-mm long Pt wire, and the counter electrode was a 10-mm long Pt wire coiled around the working electrode. The reference electrode was $\text{Ag}^\circ/\text{Ag}^+$, in the form of an isolated Luggin capillary.

Undoped PANI samples were prepared by stirring H_2SO_4 -doped PANI in 1.0 M NaOH for 24 h, before being filtered, washed with water and dried in vacuum.

Conductivity of H_2SO_4 -doped PANI samples was measured using a standard four-probe method.

3. Results and discussion

Fig. 1 shows the Raman spectra of H_2SO_4 -doped PANI

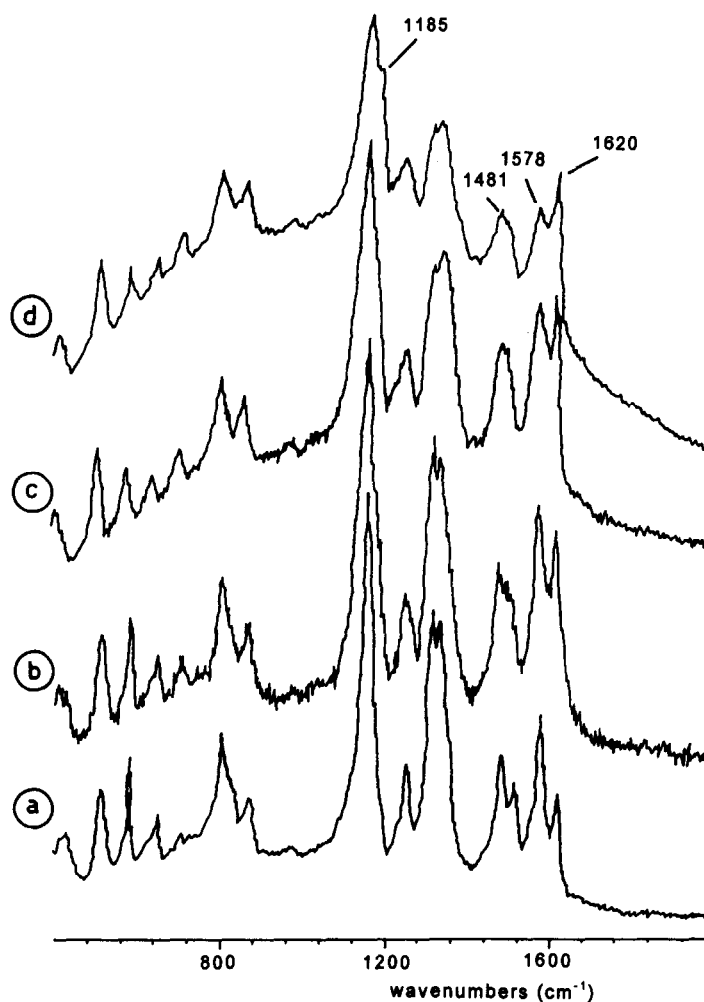


Fig. 1. Raman spectra of PANI obtained electrochemically in 1.0 M H_2SO_4 containing 0.1 M aniline at (a) 0.6 V; (b) 0.7 V; (c) 1.0 V; and (d) 1.5 V.

obtained at various potentials (0.6–1.5 V) at the end of 4 min of electrolysis. The spectrum obtained at 0.6 V (Fig. 1(a)) is a sharp line spectrum and peaks broaden as the potential is increased. This is due to superposition of multiple signals caused by different structural modes in longer polymer chains formed at higher potentials. The IR spectra of PANI were reported to show similar behaviour [23]. It is seen in the Raman spectra that the intensity of the peak observed at 1620 cm^{-1} increase with increasing potential. This peak is due to C=C stretching of *p*-disubstituted benzene [24,25]. Other main peaks are due to C=N stretching of a quinoid structure at 1481 cm^{-1} ; the peak at 1578 cm^{-1} was attributed to C=C stretching of a quinoid structure, as well as *p*-disubstitution of benzene rings [24,26].

The spectra given in Fig. 1 were obtained directly from the electrode surface without being subject to any washing or drying of PANI coating the surface.

Fig. 2 shows the Raman spectra of PANI obtained at 1.0 and 1.5 V before and after rinsing the PANI coated electrode with water once. The intensity of the peak at 1620 cm^{-1} was observed to show a significant decrease after being rinsed with water.

In Fig. 3 the cyclic voltammogram of PANI obtained electrochemically in 1.0 M H_2SO_4 containing 0.1 M aniline at 0.8 V is given. The middle cyclic voltammetry peaks observed at 0.26 and 0.45 V are an indication of PANI degradation. It corresponds to the redox reactions of dimers such as hydrazobenzene, benzidine,

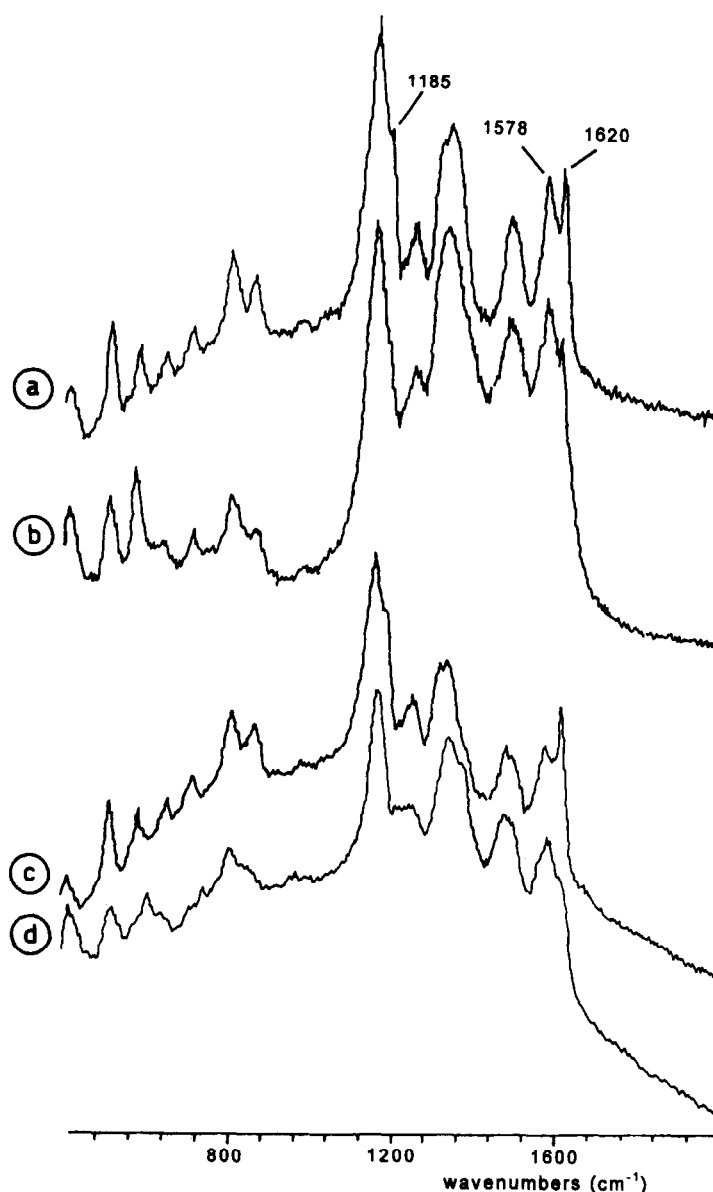


Fig. 2. Raman spectra of PANI (a) obtained electrochemically in 1.0 M H_2SO_4 containing 0.1 M aniline at 1.0 V; and (b) the sample in (a) rinsed with water once; (c) obtained electrochemically in 1.0 M H_2SO_4 containing 0.1 M aniline at 1.5 V; and (d) the sample in (c) rinsed with water once.

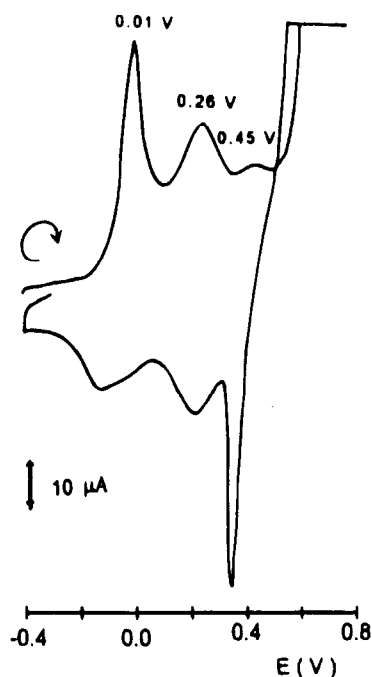


Fig. 3. Cyclic voltammogram of PANI obtained in 1.0 M H_2SO_4 containing 0.1 M aniline at 0.8 V. Recorded in 1.0 M H_2SO_4 at a scan rate of 50 mV/s

N-phenyl-*p*-phenylenediamine, along with oligomers and the degradation products of PANI including *p*-aminophenol, quinoneimines and *p*-benzoquinone/hydroquinone pairs [27].

The synthesis of PANI at potentials higher than 0.6 V causes degradation of PANI film formed on the electrode surface and this degradation rate increases with increasing potential [27,28]. In addition, at high potentials, the amount of soluble products increases and polymer yield decreases [27]. Polymer yield determined gravimetrically after 4 min of electrolysis at 0.8 and 1.5 V were 0.016 and 0.011 g, respectively, also indicating that high polymerization potentials cause degradation.

Abe et al. [29] in their Raman spectroscopy studies on PANI reported that the peak ratio of 1620/1578 could be used as the measure of the amount of soluble PANI in *N*-dimethyl pyrrolidinone, thus the ratio of the peak intensity at 1620 cm^{-1} to that at 1578 cm^{-1} for the soluble PANI was higher than that for the insoluble PANI. They also emphasized that another peak exists at 1185 cm^{-1} which appears only in the spectrum of the soluble part of PANI.

It can be seen from Fig. 1 that as the potential increases, the peak at 1620 cm^{-1} intensifies. The peak at 1185 cm^{-1} , which is another characteristic peak for the soluble products in PANI [18], becomes much more evident at polymerization potentials of 1.0 and 1.5 V. Fig. 3 shows that the peak at 1185 cm^{-1} vanishes and the intensity of the peak at 1620 cm^{-1} decreases when the PANI coated electrode is rinsed once with water.

These results given above show that the water soluble products (probably in salt form) in PANI increase at higher potentials and the presence of water soluble products in PANI can be monitored by Raman spectroscopy. They may either be dimers, oligomers, degradation products of PANI or very low molecular weight PANI formed due to radical cations densely present at high potentials [27–29].

In another experiment, *in situ* Raman spectra of 1.0 M H_2SO_4 containing 0.1 M aniline were recorded in short intervals starting from the initiation of electrolysis at 0.8 V (Fig. 4).

In the 10th second of the polymerization (Fig. 4(a)), the peak ratio of 1620/1578 was slightly higher compared to those observed at further stages of electrolysis. As expected, in early stages of electrolysis various soluble dimers (or partially dimers and very low molecular weight polymer) can be formed, and those dimers formed during the initial stages of aniline oxidation are capable of growing into longer PANI chains [30]. In further stages of the electrolysis other peaks, characteristic for PANI, became apparent.

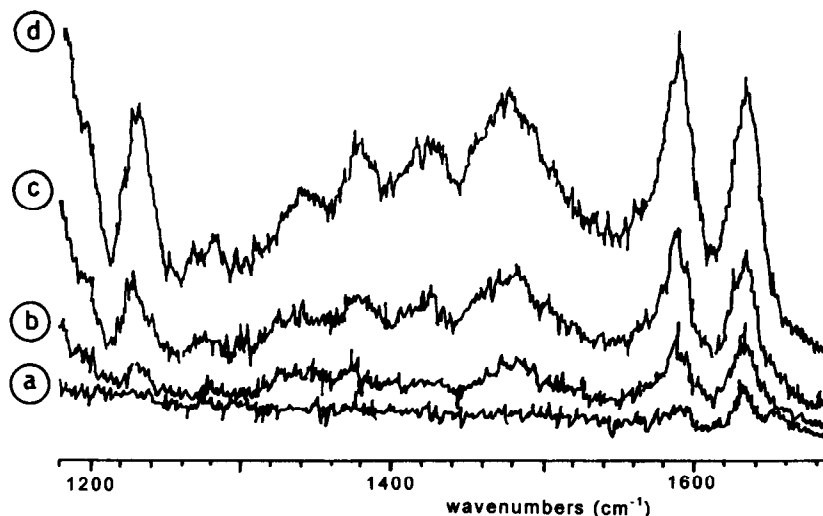


Fig. 4. The *in situ* Raman spectra obtained during the formation of PANI on the working electrode surface at 0.8 V after various periods of electrolysis as follows: (a) 10 s; (b) 20 s; (c) 40 s; and (d) 60 s.

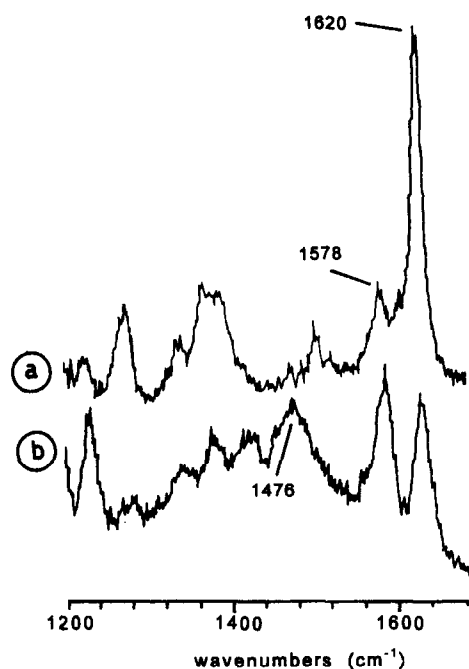


Fig. 5. The *in situ* Raman spectra of PANI recorded after a 40-s electrolysis time at (a) 0.6 V and (b) 0.8 V

Fig. 5 shows the *in situ* Raman spectra obtained at the 40th second of electrolysis, carried out at 0.6 and 0.8 V. In the case of polymerization at 0.6 V (Fig. 5(a)), due to low polymerization potential and rate, some of the characteristic peaks for PANI did not become apparent. The amount of

soluble products were high, which is indicated by the high intensity of the peak at 1620 cm^{-1} . Especially the intensity of the peak at 1476 cm^{-1} , which is indicative of the oxidized units (quinoid rings) [24,26], was very low due to low polymerization potential. The formation of oxidized units at 0.8 V or higher potentials progresses with a certain rate beginning from the initial stages of electrolysis, while at 0.6 V this rate is very low and the characteristic peaks of PANI can only be observed at latter stage of polymerization.

Fig. 6 shows the Raman spectra of the conducting forms of PANI and undoped PANI obtained by stirring H_2SO_4 -doped PANI with 1.0 M NaOH for 24 h. As seen in the spectra, prolonged washing and undoping procedure removes the soluble products from the polymer. Thus, the peak at 1620 cm^{-1} completely vanishes. Also, the well known Raman bands at 1320 and 1342 cm^{-1} in conducting form of PANI which characterizes protonation disappears in undoped form. However, short-term treatment of H_2SO_4 -doped PANI with water does not affect the intensity of these peaks, and therefore the conducting character of PANI (Fig. 2(b) and (d)).

An H_2SO_4 -doped PANI coated electrode was placed in a specially designed cell filled with water to follow undoping procedure with Ramascope. Then 1.0 M NaOH was injected into the cell, and the spectra of polymers were recorded in short time intervals. The results are seen in Fig. 7.

The characteristic conductance peaks at 1320 and 1342 cm^{-1} of PANI [24,26] (Fig. 7(a)) show a significant decrease in intensity after a short time (i.e. 10 s) following

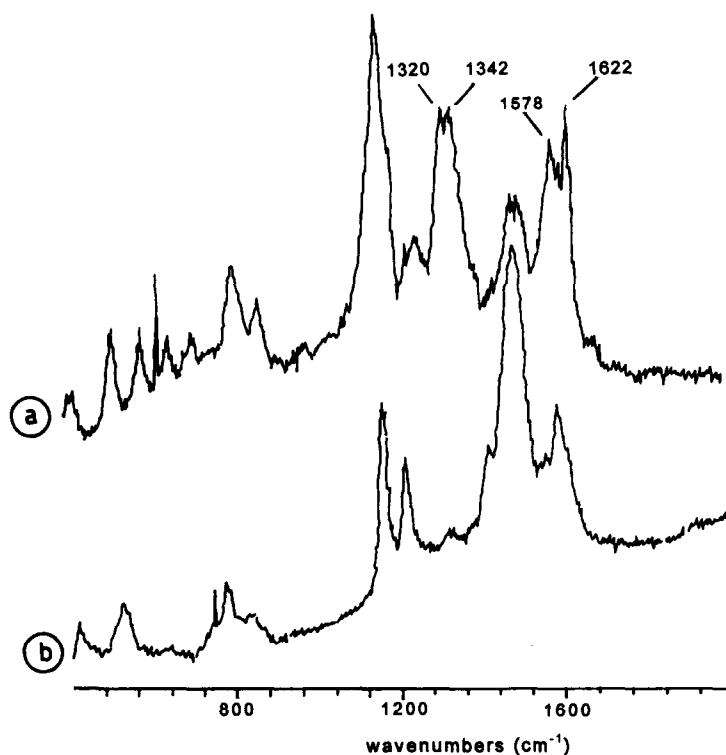


Fig. 6. Raman spectra of (a) PANI obtained electrochemically in 1.0 M H_2SO_4 containing 0.1 M aniline at 0.8 V and (b) undoped PANI prepared from the sample in (a) treating it with 1.0 M NaOH in water for 24 h.

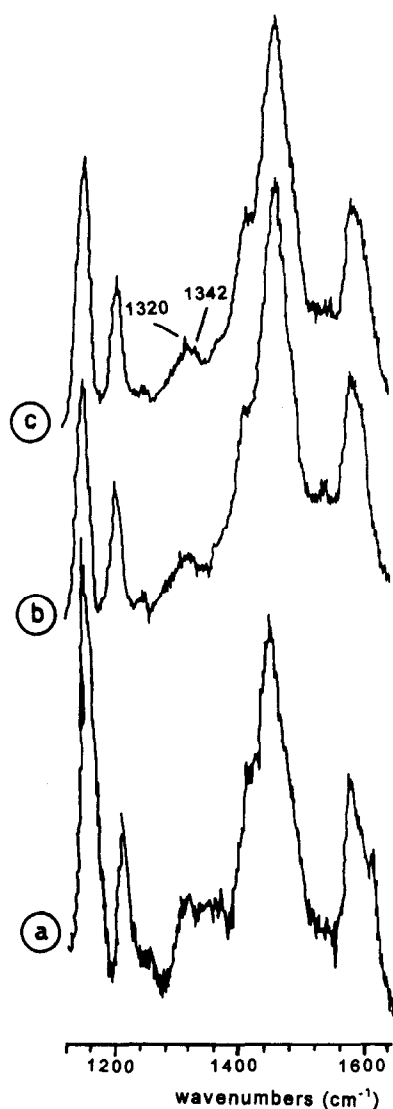


Fig. 7. The *in situ* Raman spectra recorded at (a) 10 s; (b) 20 s; and (c) 40 s during the undoping process. The PANI coated electrode was inserted in the cell filled with water and the undoping process was performed by injecting 1.0 M NaOH into the cell.

the addition of 1.0 M NaOH. They do not completely disappear, however, as in the case of H_2SO_4 -doped PANI treated with NaOH for a prolonged time (Fig. 6(b)).

The electrode was removed from the cell after 60 s and the PANI film coating was peeled off, and the conductivity of the undoped polymer sample was found to be lower than 10^{-6} S/cm. The original conductivity of H_2SO_4 -doped PANI was measured to be 0.2 S/cm. For undoping the doped PANI, it is generally treated with a base such as NaOH or NH_4OH for prolonged periods. Our results indicate that doped PANI is undoped to a significant extend for very short periods of base treatment.

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