

Electrochemical and in situ Raman spectroscopic study on the stability of poly(*N*-methylaniline)

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Abstract The stability of poly(*N*-methylaniline) (PNMA) as electrode material has been studied in aqueous solutions of sulfuric acid with the use of electrochemical and in situ Raman spectroscopic techniques. It has been shown that the electrochemical decomposition of electrodeposited PNMA films follows a first-order reaction kinetics. The decomposition rate constants vary between 1.2×10^{-5} and $2.0 \times 10^{-3} \text{ s}^{-1}$ for electrode potential varying between 0.2 and 1.0 V vs Ag/AgCl, respectively. In situ Raman spectroscopy has been applied in obtaining kinetic data at selected electrode potentials, and good correlation of these data with the corresponding data obtained by cyclic voltammetry has been found. As compared to polyaniline, the decomposition of PNMA proceeds at nearly the same rate at electrode potentials not exceeding 0.5 V. The decomposition of PNMA proceeds faster within the potential limits of 0.5 to 0.8 V and slower at electrode potentials exceeding 0.8 V as compared to polyaniline.

Keywords Polyaniline · Poly(*N*-methylaniline) · Decomposition · Kinetics · Raman spectroscopy · Spectroelectrochemistry

Introduction

Polyaniline and its derivatives are widely studied due to numerous expected applications of these materials in electrochemistry-related fields like sensors, batteries and energy conversion systems. For many applications, the stability of these materials is of primary interest. It is well known that polyaniline undergoes irreversible destruction processes in aqueous electrolytes, especially at higher anodic potentials [1, 2]. Although the pathways of anodic decomposition of polyaniline are relatively well studied, little attention has been paid to the kinetics of these processes. Earlier, we studied the net kinetics for electrochemical degradation of polyaniline in acidic solutions [3–5]. It has been shown by cyclic voltammetry and ultraviolet-visible (UV-Vis) spectroscopy that electrochemical decomposition of aniline follows a first kinetic reaction order, whereas the decomposition rate constants depend greatly on electrode potential used, varying within broad limits from about 4×10^{-5} to $3 \times 10^{-3} \text{ s}^{-1}$ for electrode potential varying from 0.3 to 1.0 V vs Ag/AgCl reference, respectively.

Little is known about the stability of polyaniline derivatives. Among many derivatives of the polyaniline family, poly(*N*-methylaniline) (PNMA) is of enhanced interest. Although the electric conductivity of PNMA is lower by about one order of magnitude than that of polyaniline, this polymer retains its conductivity as well as electrochemical redox activity even in slightly acidic and pH-neutral solutions, whereas the parent polyaniline almost loses its conductivity and redox activity at solution pH exceeding 4. In their early work, Yano et al. [6] claimed a higher stability of PNMA compared to polyaniline. The present work has been aimed to the kinetic study of the electrochemical decomposition of PNMA with the use of

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traditional electrochemical techniques, as well as Raman spectroscopy.

Experimental

PI-50-1 model potentiostat, arranged with PR-8 model programmer, was used throughout the experiments. Raman spectroelectrochemical experiments have been performed in a three-electrode cell. A circular gold electrode of about 5 mm in diameter, press-fitted into a Teflon rod, was used as a working electrode for the Raman spectroelectrochemical experiments, whereas a platinum wire electrode, about 0.5 mm in diameter and 5 mm in length, was used as a working electrode in the electrochemical experiments. A platinum wire and a saturated Ag/AgCl electrode were used as counter and reference electrodes, respectively. All potential values reported refer to the saturated Ag/AgCl electrode. The working electrode was placed at about 2 mm distance from the cell window, and a Kr-ion laser (model Innova 90-K, Coherent) beam at 647.1 nm, with the power restricted to 40 mW, was incident on the surface at about 60 ° and focused to a spot of 1 mm² in area. The experiments were performed in 90 ° scattering geometry. The laser plasma lines were attenuated by means of an interference filter. The scattered light was analyzed by a *f*/2.5 custom-built spectrometer equipped with 600 lines/mm grating and detected by a thermoelectrically cooled at –70 °C charge-coupled device camera (model Spec-10:256E, Princeton Instruments). The integration time was 1 s. Each spectrum was recorded by accumulation of 100 scans. The cutoff edge filter (model 659AELP, Omega Optical) was put in front of the spectrograph to eliminate Rayleigh scattering from the electrode. To reduce photo- and thermoeffects, the spectroelectrochemical cell, together with the electrodes, was moved linearly with respect to the laser beam with a rate of about 20 mm/s [7]. The Raman frequencies were calibrated using the toluene spectrum.

Before each experimental set, the gold working electrode was cleaned for 1 h in a piranha solution (a mixture of 30% hydrogen peroxide solution and concentrated sulfuric acid, 3:1 by volume). Electrosynthesis of PNMA at the electrode surface was performed in a separate three-electrode cell either by potential cycling for 30 min at 0.1 V/s within the scan limits of 0.0 to 1.0 V or by continuous electrolysis for 30 min at a controlled potential of 1.0 V in 0.5-M solution of sulfuric acid containing 0.05 M of *N*-methylaniline (Fluka). After that, the electrode was rinsed and transferred into a three-electrode spectroelectrochemical cell. For stability tests, the PNMA-modified electrode was kept in supporting electrolyte at an appropriate potential, and either cyclic voltammograms or Raman spectra were recorded at definite time intervals.

Results and discussion

Two traditional procedures have been used in preparing PNMA films—potential cycling within the window of 0.0 to 1.0 V and electrolysis at a controlled potential of 1.0 V. Electrochemical polymerization of *N*-methylaniline is known to be a complex process consisting essentially of two steps, viz. electrochemical (anodic) generation of reactive species like radical cations and the next chemical polymerization. As distinct from the parent aniline, the reactive species generated by anodic oxidation of *N*-methylaniline or other *N*-alkylanilines appear to be less active in polymerization processes as evidenced by UV-Vis spectroscopy [8–10]. Therefore, electropolymerization should be provided for a relatively long time, sufficient to obtain polymer films suitable for decomposition study. On the other hand, a long duration of electropolymerization means that a definite content of degradation products should be present in a final polymer film, as both electropolymerization and decomposition processes occur in parallel at a sufficiently high electrode potential [11]. Thus, precisely speaking, the data reported below belong to a partially decomposed polymer.

In a solution of 0.5 M sulfuric acid, PNMA-modified platinum electrodes show a pair of anodic and cathodic peaks with the midpoint potential $(E_{pa} + E_{pc})/2 = 0.47 \pm 0.03$ V and the peak separation $(E_{pa} - E_{pc}) = 0.15$ V at a potential scan rate of 0.1 V/s. The midpoint potential value obtained coincides with the corresponding value reported earlier [12, 13]. Under the conditions used, the prepared PNMA films show the redox capacity of 10–15 mC/cm² as obtained from cyclic voltammetry study. For electropolymerization of unsubstituted aniline, films of nearly the same redox capacity (and thus of nearly the same thickness) can be obtained at a substantially shorter time of polymerization, e.g. at approximately 10 min of potential cycling under nearly same other conditions (instead of 30 min needed for electropolymerization of *N*-methylaniline). This shows a lower activity of reactive species of *N*-methylaniline formed during anodic oxidation.

Although holding the PNMA modified electrode at a definite potential in a solution of sulfuric acid, both anodic and cathodic peaks, as well as the redox capacity of a polymer layer, diminish as a result of progressive decomposition of the polymer layer. Figure 1 (top) shows the decrease in anodic peak current for PNMA electrode prepared by potential cycling procedure as obtained at different electrode potentials. Following a presumed first-order kinetics for degradation process, the data obtained were treated in the coordinates ($\ln I_{pa}$, t) according to first-order reaction equation:

$$\ln I_{pa} = k \cdot t$$

where I_{pa} denotes anodic peak current, t is reaction time, and k is first-order reaction rate constant.

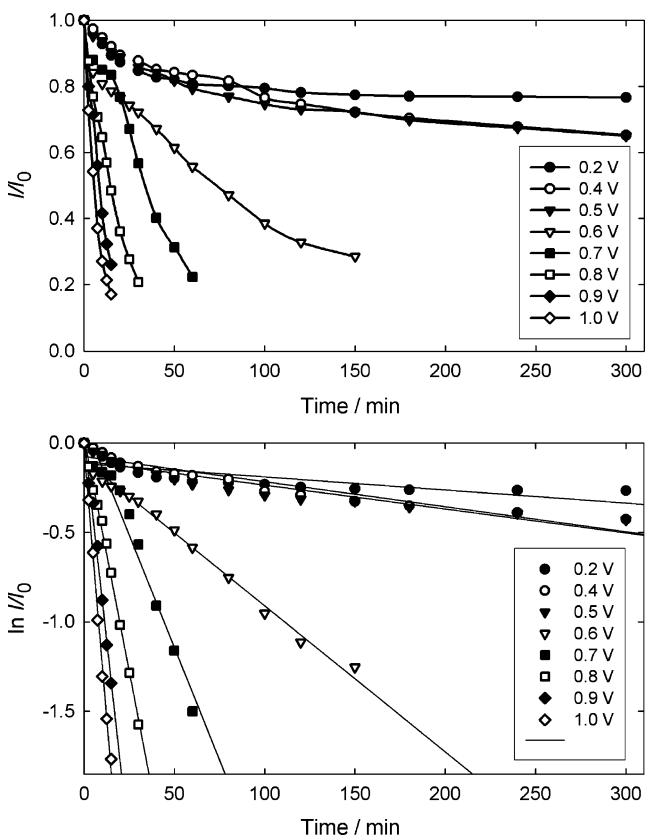


Fig. 1 Evolvement of a relative peak current as obtained for PNMA-modified electrode held in a solution of 0.5 M sulfuric acid at different electrode potential values (as indicated; *top*) and linearization of the data obtained in semilogarithmic coordinates (*bottom*). PNMA-modified electrode was prepared by potential cycling for 30 min at a scan rate of 100 mV/s within the limits of 0.0 to 1.0 V in a solution of 0.5 M sulfuric acid containing 0.05 M of *N*-methylaniline

The data obtained can be linearized in the coordinates ($\ln I_{pa}, t$) as shown in Fig. 1 (bottom). From the slope of the dependencies obtained, the decomposition rate constants can be obtained. The constants thus calculated are collected in Table 1. Within the potential window studied, the decomposition rate constants vary within two orders of magnitude from 1.22×10^{-5} to $2.01 \times 10^{-3} \text{ s}^{-1}$ for applied electrode potentials of 0.2 and 1.0 V, respectively. As with other conducting polymers (polyaniline or polypyrrole), the decomposition process occurs faster by extending the electrode potential to higher values, i.e. by an increasing degree of oxidation of a polymer film.

For PNMA films prepared by the use of a controlled potential electrolysis, again, a gradual decrease in anodic peak current is observed by holding the electrode at an anodic potential in a monomer-free solution (Fig. 2). Furthermore, the decomposition proceeds faster at a higher electrode potential. However, the kinetic data do not linearize satisfactorily in the first-order reaction coordinates. It seems likely that two or more different kinds of

PNMA are formed under controlled potential electrolysis conditions. These forms could differ in the degree of polymerization or in their film morphology and compactness. It is commonly accepted that more uniform and well-adherent films of polyaniline are formed by using a potential cycling procedure than by controlled potential electropolymerization. The different forms of PNMA could differ in their susceptibility to anodic treatment, yielding a net (I_{pa}, t) dependence of a higher kinetic order. More precisely, it is also seen for PNMA films prepared under potential cycling conditions that, at an initial stage of treatment, deviations from linearity in the first-order coordinates are observed, especially at lower electrode potentials, as depicted in Fig. 1 (bottom). In the latter case, however, the effect appears to be much less expressed compared to that observed for polymer films prepared by controlled potential electrolysis; thus, trustworthy values for the decomposition rate constants at different electrode potentials can be easily obtained, as summarized in Table 1.

It is of primary interest to compare the stability of PNMA and polyaniline in terms of their susceptibility to electrochemical treatment. In our earlier studies, we presented the first-order decomposition rate constants for polyaniline films, as well as their dependence on electrode potential under nearly same conditions as those used in the present work [4, 5]. Figure 3 shows the dependence of decomposition rate constants as a function of applied electrode potential both for PNMA, as obtained in the present work, and for polyaniline, as adopted from [4]. It is seen that at electrode potentials not exceeding 0.5 V (i.e. up to the midpoint potential for PNMA redox couple), the rate constants for both polymers nearly coincide. Within the potential range of 0.5 to 0.8 V, PNMA appears to be less stable than polyaniline. At 0.8 V, the stability of both polymers appears to be nearly equal, whereas at electrode potentials exceeding 0.8 V, PNMA is more stable compared

Table 1 First-order rate constants for electrochemical decomposition of poly(*N*-methylaniline) as obtained in a solution of 0.5 M or 0.1 M sulfuric acid at different electrode potentials (E)

E (V)	Rate constants (s^{-1}) as obtained by		
	Cyclic voltammetry (0.5 M H_2SO_4)	Raman spectroscopy	
		(0.5 M H_2SO_4)	(0.1 M H_2SO_4)
0.2	$(1.22 \pm 0.26) \times 10^{-5}$		
0.4	$(2.33 \pm 0.20) \times 10^{-5}$		
0.5	$(2.24 \pm 0.25) \times 10^{-5}$		
0.6	$(1.36 \pm 0.04) \times 10^{-4}$	$(1.07 \pm 0.10) \times 10^{-4}$	$(0.61 \pm 0.11) \times 10^{-4}$
0.7	$(4.19 \pm 0.28) \times 10^{-4}$		
0.8	$(8.72 \pm 0.22) \times 10^{-4}$	$(9.60 \pm 1.74) \times 10^{-4}$	$(2.80 \pm 0.28) \times 10^{-4}$
0.9	$(1.52 \pm 0.07) \times 10^{-3}$		
1.0	$(2.01 \pm 0.08) \times 10^{-3}$		

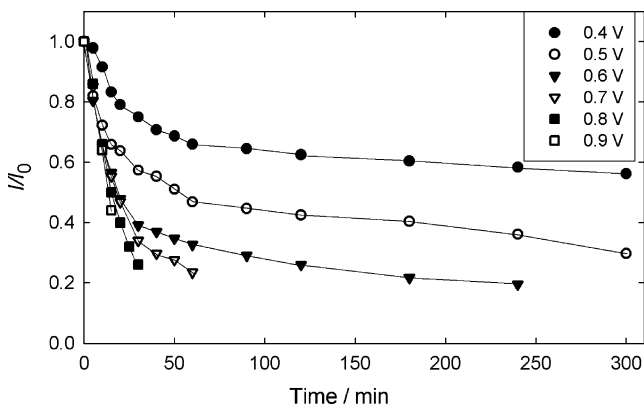


Fig. 2 Same as in Fig. 1, obtained for PNMA-modified electrode prepared by application of a controlled potential of 1.0 V for 30 min in a solution of 0.5 M sulfuric acid containing 0.05 M of *N*-methylaniline

to polyaniline. Because of a higher steepness of (k , E) dependence for polyaniline, the decomposition of PNMA proceeds slower at a higher electrode potential as compared to polyaniline. At $E=0.9$ V, the decomposition rate for polyaniline appears to be twofold higher than for PNMA.

There are two main kinds of electrochemical (anodic) decomposition of conducting polymers [1]. First, an anodic treatment could lead to some irreversible chemical changes in the polymer structure. As a result, the polymer layer loses its electric conductivity and electrochemical redox activity, although it remains bound to the electrode surface (modification mechanism). Alternatively, low molecular weight compounds can be produced during anodic treatment when

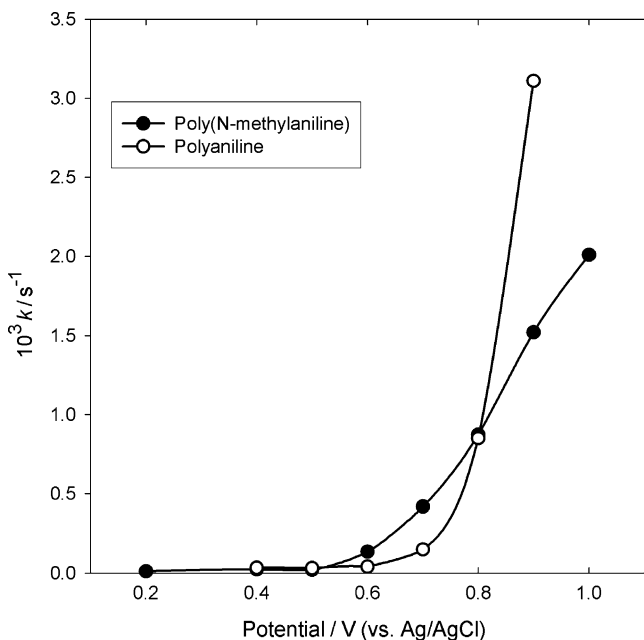


Fig. 3 Dependence of first-order decomposition rate constants for poly(*N*-methylaniline) on electrode potential as obtained in a solution of 0.5 M sulfuric acid. For comparison, the data for polyaniline adopted from [4] are shown

they diffuse out of a polymer layer into a surrounding solution. As a result, the electrode surface becomes free of any polymer layer after a sufficiently long and intense anodic treatment (destruction mechanism). Obviously, electrochemical experiments based on time-dependent changes of anodic peak current or even redox capacity cannot distinguish between these two mechanisms; thus, other independent techniques are needed. In the present work, we used time-resolved Raman spectroelectrochemistry. Surface-enhanced and resonant Raman spectroelectrochemistry is often used for the static study of conducting polymers of the polyaniline family [14–20]. Recently, we showed the usefulness of this technique in the dynamic (time-dependent) study of some processes taking place at polyaniline-modified electrodes [21, 22].

Figures 4 and 5 show in situ Raman spectra, obtained with 647.1 nm Kr-ion laser excitation from PNMA-modified gold electrode under a variety of conditions. Raman bands of oxidized segments are resonantly enhanced at this excitation wavelength [16]. For as-prepared PNMA films, a set of specific Raman bands is observed. The bands observed could be assigned based on the known data [14–20] and are presented in Table 2. Basically, the

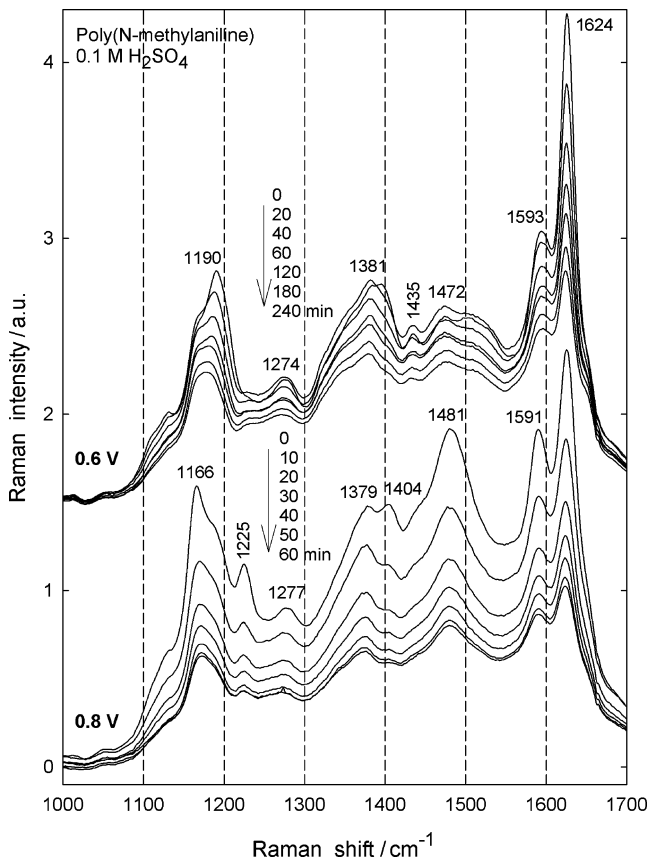


Fig. 4 Raman spectra from poly(*N*-methylaniline)-modified electrode as obtained in a solution of 0.1 M sulfuric acid by holding the electrode at a definite potential of 0.6 or 0.8 V for definite time periods (as indicated)

three bands observed correspond to three kinds of C–N vibrations. From these, the band located at 1,225 cm⁻¹ corresponds to single-bonded C–N stretching vibrations characteristic for the amine site of the polymer. Stretching vibrations of double-bonded C = N molecular fragments, characteristic for imine sites in oxidized forms of PNMA, are observed at 1,472–1,475 cm⁻¹ at electrode potential of 0.6 V and shift up to 1,481 cm⁻¹ by extending the electrode potential up to 0.8 V, i.e. by an increase in the oxidation degree of a polymer. The band located around 1,380 cm⁻¹ corresponds to stretching vibrations of C~N⁺ molecular fragment containing an intermediate (between the first and the second) bond order that is characteristic for polaronic sites of the polymer backbone. The peak frequency of the C~N⁺ stretching band is blue-shifted by ~50 cm⁻¹ as compared with polyaniline film, indicating more localized nature of polarons in the PNMA polymer [23]. The bands centered around 1,590 and 1,625 cm⁻¹ correspond to stretching vibrations of C=C and C–C molecular fragments in quinoid and benzenoid rings of PNMA, respectively. Furthermore, the bands located at around 1,190 and 1,165 cm⁻¹, characteristic for C–H bending vibrations in leucoemeraldine and emeraldine forms of PNMA, respectively, are well expressed. From these, the band located at 1,190 cm⁻¹ diminishes in intensity, whereas the band at

Table 2 Characterization of vibrational bands of Raman spectra (cm⁻¹), obtained with excitation wavelength of 647.1 nm for poly(*N*-methylaniline) films in two different solutions and at different potentials

0.1 M H ₂ SO ₄		0.5 M H ₂ SO ₄		Assignment
0.6 V	0.8 V	0.6 V	0.8 V	
		1,130	1,130	
		1,166	1,165	C–H bending in emeraldine (9a)
1,190		1,205		C–H bending in leucoemeraldine salt (9a)
		1,225	1,225	C–N stretching (amine sites)
1,274	1,277	1,283	1,278	
1,381	1,379	1,383		C~N ⁺ stretching in polaronic form (polaronic sites)
		1,404	1,408	
1,435		1,436		
1,472	1,481	1,475	1,481	C=N stretching (imine sites)
1,593	1,591	1,591	1,589	C=C stretching in Q (8a)
1,624	1,624	1,627	1,626	C–C stretching in B (8a)

Assignments are based mainly on the known data [14–20]. The numbers given in parentheses, (8a) and (9a), refer to Wilson's notation of aromatic species vibration modes.

Tilde mark represents a chemical bond that is intermediate between a single and a double bond.

B benzene-type ring, *Q* quinoid-type ring

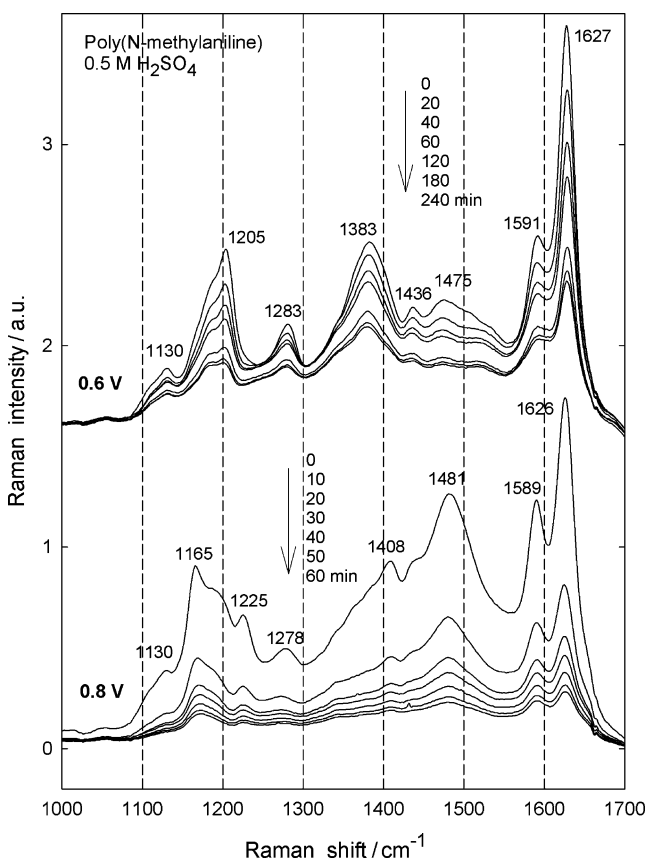


Fig. 5 Same as in Fig. 4, obtained in a solution of 0.5 M sulfuric acid

1,165 cm⁻¹ increases with the electrode potential shift from 0.6 to 0.8 V, indicating the growing content of oxidized sites with the potential shift to more positive values.

By holding of PNMA-modified electrode at a definite potential in a monomer-free electrolyte, a gradual decrease in all Raman bands occurs. It is seen in Figs. 4 and 5 that this decrease proceeds faster in more acidic solutions and at a higher electrode potential. The time dependence of the intensity of Raman bands can be satisfactorily linearized in

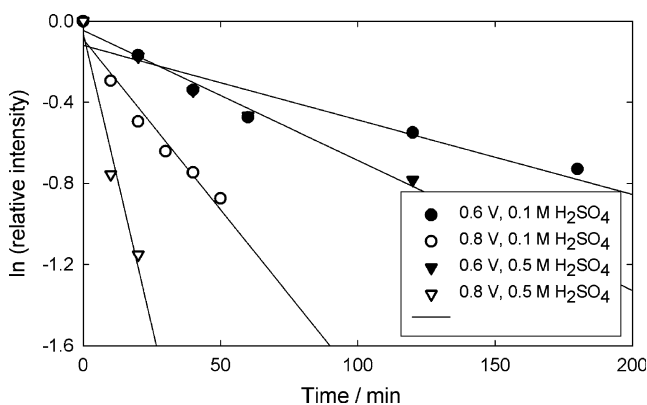


Fig. 6 Time dependence of a relative intensity for Raman band located at around 1,625 cm⁻¹ in semilogarithmic coordinates as obtained at electrode potential of 0.6 or 0.8 V in a solution containing 0.1 or 0.5 M of sulfuric acid (as indicated)

semilogarithmic coordinates, as shown in Fig. 6, indicating the first kinetic order for these processes. Therefore, the first-order decomposition rate constants can be easily obtained from these data. The data relating to the two potentials applied and two different electrolyte solutions are presented in Table 1. It is seen that the rate constant obtained in a solution of 0.5 M sulfuric acid by Raman spectroelectrochemistry at an operating potential of 0.6 V appears to be somewhat lower (by a factor of 1.27), whereas the rate constant at 0.8 V appears slightly higher (by a factor of 1.1) than the corresponding rate constant obtained from cyclic voltammetry. Keeping in mind the different natures of the two techniques used (cyclic voltammetry and Raman spectroscopy), a quite good correlation between the results obtained should be noted. This correlation suggests that, from the two possible decomposition mechanisms discussed above, the destruction mechanism seems to be more likely than the modification mechanism. Indeed, comparison of in situ Raman spectra obtained initially and after 240 min (Figs. 4 and 5) reveals very similar spectral pattern, indicating that the structure of the film does not change considerably. Furthermore, Raman spectroelectrochemical experiments show that the PNMA film tends to destroy and dissolve completely, leaving no spectroscopically detectable matter at the electrode surface in a sufficiently long electrochemical treatment.

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