Spectroscopic and Electrochemical Study of the Redox Process of Poly(2,2'-dithiodianiline)

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The redox process undergone by the electrochemically synthesized poly(2,2'-dithiodianiline), poly(DTDA), has been examined in acetonitrile-water mixtures by electrochemical and spectroscopic techniques. The spectroscopic properties of this material are equivalent to those exhibited by the chemically synthesized one. The polymeric structure displays a ladder structure, with S-S bonds serving as interconnections between two adjacent polyaniline chains. The kinetic reversibility of the $RS-SR \rightleftharpoons 2RS^{\cdot-}$ reaction is very poor for the DTDA monomer species, and this irreversibility is retained in the polymeric material. According to the results presented, the hypothesis that poly(DTDA) could display a high energy density due to the simultaneity of the leucoemeraldine $\rightleftharpoons$ emeraldine and dithiolate $\rightleftharpoons$ disulfide electrochemical transformations does not seem justified.

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During the past two decades, the family of organic disulfide compounds has been investigated as promising positive electrodes for high-energy density lithium batteries.¹⁻⁶ However, commercial systems are making use of diverse lithium intercalation materials as actual positive electrodes.⁷ The generic nature of organic disulfide compounds jointly with their low cost, low toxicity, high theoretical energy density, and low operating temperature make these materials particularly promising for energy storage devices. In addition, other chemical properties such as their stability, redox behavior, and kinetic reversibility can be modified by the appropriate choice of the organic groups linked to the disulfide moiety $RS-SR'$. Contrary to these expectations, Liu et al. reported the occurrence of a large separation between the anodic and cathodic peak potentials for different organic disulfides.⁵ From these results it follows that, as a general rule, slow electrode reaction rates should be inherent to these kinds of materials. Later, Naoi et al.^{8,9} proposed that the involved redox processes should become more reversible in order to make the application of disulfide compounds to electrodes in energy storage devices feasible. It was then realized that the use of proper electrocatalysts would be essential to improve the performance of the charging-discharging process. For instance, it was claimed that electropolymerized polyaniline was able to enhance the redox process of 2,5-dimercapto-1,3,4-thiadiazole (DMcT).⁹ On carbon electrodes the peak separation was found to be as large as 1.5 V. However, it was reduced to just 0.5 V when the electron transfer was done on a polyaniline filmed electrode. The improvement was attributed to the formation of adducts between S atoms in DMcT and N sites in polyaniline.

The model of disulfides was further extended by introducing polysulfides as a new group of organic-polymeric energy storage materials. Because polysulfides contain many S atoms in their structure, it was expected that these materials could exhibit higher energy density than single disulfides.¹⁰ Particularly, it was reported that the tetrasulfide compound prepared by reaction of SCl_2 with DMcT was able to possess double-energy density than DMcT alone. Also, it was observed that the redox processes of disulfide monomers, oligomers, and polymers are accompanied by structural changes of the material that lower the charge retention efficiency and make it strongly dependent on the conformation of the obtained polymer.^{10,11} In order to overcome the conformational effect on the cleavage and recombination of S-S bonds, it was suggested that the electroactive material should have a confined polymer structure interconnected with S-S bonds. Poly(2,2'-dithiodianiline), poly(DTDA), was presented in the late nineties and the first years of

the current decade as a new conducting polymer having S-S bonds confined between polyaniline chains.¹²⁻¹⁴ This particular configuration was claimed to be at the origin of the high-energy density obtained when compared to that of polyaniline. It was proposed that the redox reaction of aniline-anilinium (i.e., the π -conjugated system) takes place at almost the same potential as that of thiolate-disulfide.^{12,13}

In our laboratory we are interested in electrodes modified with poly(DTDA) because they can be used as an organic matrix to host active metal, particularly copper, particles. These new organic-inorganic hybrid materials containing Cu atoms were employed for the analytical determination of certain amino acids such as γ -aminobutyric acid,¹⁵ which is an important inhibitory neurotransmitter and a component of drinking wines. Our results showed that the electropolymerization process of DTDA is analogous to that shown by Naoi et al.^{12,13} under similar experimental conditions. However, some preliminary results suggested that the cleavage of disulfide bonds could take place at potentials far away from those related to the aniline-anilinium transition. In this paper we report the electrochemical and spectroscopic characterization of poly(DTDA), paying special attention to the redox processes related to the cleavage and recombination of the S-S bond. The structure of the DTDA

Scheme 1.

monomer is depicted in Scheme 1.

Experimental

The chemicals employed were of reagent grade. 2,2'-dithiodianiline monomer was supplied by Aldrich and used as received. The voltammetric experiments were conducted in 50% (v/v) acetonitrile/water mixtures making use of either 0.4 M $NaClO_4$ + 0.1 M $HClO_4$ or 0.5 M $NaClO_4$ as supporting electrolytes. The working electrode employed for the synthesis of the polymer films was a spherical polycrystalline platinum surface of about 4 mm². A platinum wire was employed as the counter electrode and the potentials were measured against a Ag/AgCl electrode which was im-

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mersed in the working solution through a Luggin capillary. Polymers for X-ray photoemission spectroscopy (XPS) measurements were grown on a mirror-polished Pt disk electrode. All electrolytic solutions were deaerated by bubbling N_2 before immersing the working electrode, and the N_2 atmosphere was maintained during the experiments.

A Nicolet Magna 850 spectrometer equipped with a DTGS detector was employed for the Fourier transform infrared (FTIR) experiments. The FTIR spectra were collected in the transmission mode (KBr) at a 4 cm^{-1} resolution. XPS spectra were recorded in a VG-Microtech Multilab 3000 electron spectrometer using a non-monochromatized Mg-K α (1253.6 eV) radiation source at 300 W. The pressure of the analysis chamber during the scans was about $5 \times 10^{-7}\text{ N m}^{-2}$ and the temperature was kept at 173 K. Photoelectron kinetic energies were measured in the fixed analyzer transmission mode at a pass energy of 50 eV. The intensities of the different contributions were obtained by integration of the corresponding peak area after the corresponding baseline correction and division by tabulated atomic sensitivity factors. The experimental curves were fitted with mixed Lorentz (30%)/Gaussian (70%) line-shape functions. All binding energies (BE) were referred to the line of the C 1s (284.6 eV) and recorded to an accuracy of $\pm 0.2\text{ eV}$. Raman spectra were obtained with a LabRam spectrometer from Jobin-Yvon Horiba. The slit and pinhole employed were 200 and 600 nm, respectively. The excitation line was provided by a 17 mW He-Ne laser at 632.8 nm. The laser beam was focused through a 50 times long-working distance objective (0.5 NA) into a $2\text{ }\mu\text{m}$ spot at the electrode surface. The spectrometer resolution was better than 3 cm^{-1} and the detector was a Peltier cooled charge-coupled device (CCD) (1064×256 pixels). Surface-enhanced Raman spectroscopy (SERS) experiments were performed using a gold activated electrode¹⁶ mounted on an electrochemical poly(tetrafluorethylene) PTFE cell designed to acquire in situ Raman spectra. A fused silica window separated the microscope objective from the electrolytic solution (0.4 M NaClO_4 in acetonitrile-water medium). A Pt wire was used as a counter electrode, whereas a saturated calomel electrode was used as a reference electrode contacting the working solution through a Luggin capillary. All the spectra shown in this paper are presented as obtained, with no further manipulation.

Results and Discussion

Electrochemical synthesis of poly(DTDA).— Cyclic voltammetry curves recorded during the electrochemical polymerization of 1 mM DTDA on a Pt electrode are shown in Fig. 1a. The solvent employed was a 50% (v/v) acetonitrile-water mixture and the background electrolyte was 0.4 M $\text{NaClO}_4 + 0.1\text{ M HClO}_4$, which gives a pH value of about 1.5. The platinum working electrode was immersed at a controlled potential of 0.05 V in order to avoid the initial oxidation of the monomer species. After equilibration, the potential was swept in the positive direction up to 0.8 V. The onset of monomer oxidation takes place at about 0.4 V during the first forward scan. When the scan direction is reversed, a new cathodic peak appears centered at 0.27 V, whose voltammetric charge raises upon cycling. This cathodic peak is intimately related to the anodic one which develops at 0.35 V. The occurrence of such a growing couple points to the slow growth of an electroactive polymeric material on the electrode surface. Concurrently, the monomer oxidation current decreases from cycle to cycle and seems to shift toward more positive potential values. After 50 potential sweeps in the -0.1 to 0.8 V potential range, the platinum electrode modified with the electroactive poly(DTDA) film was withdrawn from the working solution, thoroughly rinsed with electrolytic solution, and transferred to a clean background electrolyte which was free of DTDA monomer. The cyclic voltammogram of the synthesized poly(DTDA) in the background electrolyte (Fig. 1b) displays a single reversible transition centered at 0.35 V, which accounts for the transformation of the fully reduced into the fully oxidized state

Figure 1. (a) Cyclic voltammograms recorded during the electropolymerization of 1 mM DTDA on a platinum electrode. The electrolyte was 0.4 M $\text{NaClO}_4 + 0.1\text{ M HClO}_4$ in 1:1 (v/v) acetonitrile-water solution. The arrows indicate the evolution of the voltammetric profile. (b) Voltammetric response recorded in a monomer-free background solution for the poly(DTDA) coated electrode. Scan rate 50 mV s^{-1} .

of the polymer. This voltammetric profile fits well with that obtained by Naoi et al. under similar experimental conditions.^{12,13}

FTIRS and XPS characterization of poly(DTDA).— The spectroscopic characterization of electrochemically synthesized poly(DTDA) was performed by means of Fourier transform infrared

Figure 2. Transmission FTIR spectrum collected in KBr for an electrochemically synthesized poly(DTDA). Resolution 4 cm^{-1} .

spectroscopy (FTIRS) and XPS. Figure 2 shows the infrared spectrum of this material obtained in the 700 to 2500 cm^{-1} frequency range. The main spectral characteristics are consistent with those obtained previously for a chemically synthesized poly(DTDA).^{17,18} The absorption bands between 1250 and 1300 cm^{-1} are assigned to the characteristic N-H bending and C-N stretching modes. The feature at 1157 cm^{-1} is assigned to the in-plane C-H bending in quinoid rings, whereas the bands at 1473 and 1617 cm^{-1} are associated with the C-C ring stretching in benzenoid and quinoid rings, respectively. This latter feature could also contain a contribution from the C=N stretching of imines in quinoid units. Finally, the band appearing at 752 cm^{-1} is related to the C-S bending, thus showing that this structure is preserved in the polymer backbone. From these results it follows that, together with the sulfur units, poly(DTDA) is composed of quinoid and benzenoid rings linked by amine-imine centers, very much like in polyaniline.

The wide-scan XP spectrum of electrodeposited poly(DTDA) displays photoemission lines originating from C 1s, N 1s, O 1s, Cl 2p, and S 2p core-level photoelectrons (Fig. 3a). No signal from the underlying Pt substrate is present, pointing to the growth of a uniform film of a higher thickness than the escape depth of Pt 4f photoelectrons through the polymer (i.e., about 100 Å , Ref. 19). The quantitative elemental composition of the surface film taken from corrected peak areas in narrow-scan spectra are summarized in Table I. The [S]/[N] area ratio is 0.95, which confirms that the stoichiometry of the monomer is preserved in the polymer film. Instead, the [N]/[C] ratio is slightly higher than 0.1, i.e., below the theoretical

Figure 3. X-ray photoelectron spectrum of poly(DTDA) electrochemically synthesized on Pt by repeated cycling in a $0.4\text{ M NaClO}_4 + 0.1\text{ M HClO}_4$ 1:1 (v/v) acetonitrile-water solution. (a) Wide-scan spectrum, (b) C 1s, (c) N 1s, and (d) S 2p.

Table I. Narrow-scan XPS quantitative data

Element	Atomic percentage (%)	Relative proportion of different atomic environments (%)		
C 1s	49.3	-C = C-/C-S		C-N/C = N/C-O
		71.2		28.8
N 1s	5.1	-NH-	N ⁺ (I)	N ⁺ (II)
		32.2	64.1	3.8
O 1s	32.1			
S 2p	4.8	-S-S-		S _{oxidized}
		91.0		9.0
Cl 2p	6.6			
Na 1s	2.1			

value for a polymer film with the proposed ladder structure. We attribute this deviation to the presence of adventitious hydrocarbon contamination.

The C 1s, N 1s, and S 2p high-resolution spectra for the electrosynthesized poly(DTDA) are shown in Fig. 3b-d. The C 1s peak can be fitted with a major peak at 284.0 eV and a minor peak at 285.3 eV. The main component is contributed chiefly by aromatic carbon (-C = C-) and some amount of adventitious carbon. The main peak should also have C-S groups associated with it. Despite a BE shift similar to C-O being expected due to the electronegative character of S, it has been reported that this shift is counteracted by the electron-donating character of the phenyl rings.²⁰ The secondary peak can be assigned to aromatic carbons bound to nitrogen.^{21,22} The C 1s BE of these nitrogen functionalities has been reported not to be unambiguously distinguishable from those for carbon singly bound to oxygen groups.²¹ Under the assumption that every N atom is bound to two carbons, the weight of C-N functionalities to the peak at 285.3 eV ($2[N]/[C_{285.3}]$) is estimated at 71%. An estimate of the contribution by C-O (assumed to be hydroxylated carbons) from the O 1s area previously corrected from perchlorate oxygen ($O_{ClO_4} = 4[Cl]$) gave nearly 40% of oxygenated functionalities. Thus, both calculations prove that C-N is the major contributor to the secondary C 1s peak. The N 1s spectrum displays a broad peak fitted with three components at 399.2, 401.2, and 403.1 eV. The BE peak below 400 eV can be ascribed to neutral amine (-NH-) nitrogen atoms, whereas the features above 400 eV correspond to positively charged nitrogens,²² resulting from complete protonation of quinoneimine sites. The ratio of positive N to neutral amine N exceeds that expected for a polyaniline-like chain in its emeraldine salt state (see Table I). In other words, the film obtained electrochemically is in a higher oxidation state than that synthesized via chemical oxidation.²³ Nevertheless, the electrochemically formed film is less degraded (hydrolyzed) than its chemical counterpart, because no XPS signal for oxidized carbon (C = O groups) appears in the C 1s spectrum. The Cl 2p line (not shown) features a $2p_{3/2}$ component at 207.4 eV. This signal is associated with electrolyte perchlorate ions remaining within the polymer. The $[Cl]/[N^+]$ area ratio is nearly 2, but this excess can be explained by taking into account the presence of Na⁺ at 1072 eV (see Fig. 3a). This suggests that part of the perchlorate ions compensates the positive charge residing on N atoms and the rest is in the form of NaClO₄ crystals inefficiently removed from the surface by rinsing. Finally, the S 2p signal (Fig. 3d) shows a main peak with tailing at the high BE side. The experimental photoemission curve can be fitted with two doublets, i.e., two different atomic sulfur environments, with $2p_{3/2}$ components peaking at 163.2 and 166.6 eV. The first one can be assigned to the disulfide link, while the second is related to partly oxidized sulfur, in agreement with previous results for the chemically synthesized polymer.²³

Testing the integrity of the S-S link against potential.— Once the poly(DTDA) has been characterized at both the atomic and molecular level, it seems of maximum interest to shed some more light

Figure 4. Voltammetric behavior of 1 mM DTDA on a platinum electrode in 0.4 M NaClO₄ acetonitrile-water medium. Polarization program: -0.4 V → +0.2 V → -1.25 V → +0.2 V. Scan rate 200 mV s⁻¹.

on the nature of the reversible redox transition occurring in the 0 to 0.5 V potential range in Fig. 1b. Particularly, the key issue is to ascertain whether or not the disulfide bond cleavage and the leuco-emeraldine to emeraldine conversion take place under the same voltammetric wave, as suggested by Naoi et al.^{12,13} However, we will first focus on the electrochemical behavior of the DTDA monomer. This presentation sequence is preferred because the results obtained for the monomer will help the interpretation of the polymer redox behavior.

The cyclic voltammogram recorded for 1 mM DTDA at a Pt electrode in 0.4 M NaClO₄ solution is shown in Fig. 4. The use of acidic conditions was avoided to make the potential of the hydrogen evolution as negative as possible. The potential was set initially at -0.45 V and subsequently swept up to +0.2 V. Finally, the scan direction was reversed down to -1.25 V. A high scan rate of 200 mV s⁻¹ was employed in order to minimize the diffusion of the possible products out of the electrode surroundings. No faradaic process appears during the first anodic sweep. Upon reversing the scan, one cathodic peak centered at -1.05 V appears partially overlapped with the hydrogen evolution reaction. This peak can be reasonably ascribed to the splitting of the S-S link to yield the corresponding dithiolate form. In the subsequent forward scan, a broad anodic feature at -0.2 V is recorded, which could be attributed to the recombination of the disulfide bond. Similar electrochemical behavior has been reported by others for different disulfide-thiolate redox couples, most of them being highly irreversible from a kinetic perspective.⁵ The present voltammetric data suggest that the cleavage-recombination of the disulfide bond is a kinetically irreversible process with a peak separation, ΔE_p , approaching 850 mV. Hence, the following overall reaction can be written for the electrode process of interest

where *R* refers to an aniline moiety and all the involved species remain in solution.

At this point it appears necessary to extend the study of the kinetic reversibility of the electrochemical splitting-recombination of the disulfide bond to the polymeric product poly(DTDA). In this

Scheme 2.

instance, R in Eq. 1 will represent an aniline unit located between two adjacent aminophenyl groups, rather than an isolated aniline moiety (see Scheme 2).

Figure 5 shows the characteristic voltammograms of a Pt electrode coated with a thin film of poly(DTDA), which was grown as in Fig. 1, rinsed, and transferred to a clean cell containing 0.4 M NaClO₄ in acetonitrile-water medium. As in the monomer study, the coated electrode was immersed at -0.4 V and polarized up to 0.2 V to check for the absence of any faradaic process in this potential range. The scan was then reversed and the potential was swept down to different negative limit potentials. The effect caused by the negative limit potential on the voltammetric response of poly(DTDA) was then examined. It appears clear (Fig. 5) that the polarization of poly(DTDA) to a potential more positive than -1.1 V has no effect on the redox state of the polymer. By contrast, when the negative limit potential is extended below -1.1 V (Fig. 5d and e), a high cathodic current is recorded during the negative-going sweep related mainly, although not exclusively (see below), to the hydrogen evolution reaction. In addition, an anodic peak centered at -0.3 V appears in the subsequent forward scan. Because the voltammetric charge associated with this feature clearly rises as the lower potential limit is made more negative, it can be inferred that a poly(DTDA) reduction product is formed at potentials within the hydrogen evolution region and reoxidized at more positive values. Both the shape and the potential range within this anodic peak are similar to those recorded for the monomer species in Fig. 4. Moreover, the extremely high peak separation that should be expected from the voltammetric profile in Fig. 5 (not lower than 800 mV) also points to the occurrence of a kinetically irreversible cleavage of the S-S link within the polymeric material to yield the corresponding dithiolate form. To discard a possible participation of the polyaniline skeleton on the faradaic process assigned to the disulfide-dithiolate process, a pristine polyaniline film was submitted to the same polarization program as poly(DTDA) in Fig. 5. It was then observed that

Figure 5. Effect of the lower potential limit on the voltammetric response of a poly(DTDA) film synthesized as in Fig. 1. (a) -0.9 V; (b) -1.0 V; (c) -1.1 V; (d) -1.2 V; (e) -1.25 V. The voltammograms were obtained consecutively and the potential program employed was -0.4 V $\rightarrow$ $+0.2$ V $\rightarrow$ lower potential limit $\rightarrow$ $+0.2$ V. The background solution was 0.4 M NaClO₄ in (1:1) acetonitrile-water solvent. Scan rate 200 mV s⁻¹.

the polarization of polyaniline within the hydrogen evolution reaction did not cause the appearance of any anodic peak at more positive potentials in acetonitrile-water medium.

Raman spectroscopy is a powerful analytical tool which is particularly useful to investigate sulfide-related species. Hence, this technique has been employed to confirm the occurrence of the disulfide $\rightleftharpoons$ dithiolate electrochemical reaction in Fig. 5. The Raman spectrum of solid DTDA in the 400 – 600 cm⁻¹ frequency range is shown in Fig. 6a and displays two strong bands at 439 and 483 cm⁻¹. The existence of two Raman features in the frequency range between 400 and 540 cm⁻¹ for aromatic disulfides is due to the rotational isomerism, which is characteristic of this kind of compound.²⁴ These bands are clearly related to the S-S stretching in the monomeric species. In order to monitor the response of poly(DTDA) against potential, we made use of the in situ SERS technique. The polymer was synthesized on a surface-activated gold substrate¹⁶ under similar experimental conditions to those followed in Fig. 1a. Then, it was transferred to the spectroelectrochemical cell, which contained 0.4 M NaClO₄ in acetonitrile-water medium. The potential was set initially at 0.0 V and a SERS spectrum was acquired. Then, the potential was stepped sequentially in the negative direction and a new spectrum was collected for every step. The whole series of spectra is displayed in Fig. 6b. This figure shows a single S-S stretching peak at 483 cm⁻¹, which supports the preser-

Figure 6. (a) Raman spectrum recorded for the solid-state DTDA monomer species. (b) In situ SERS spectra collected as a function of the applied potential for a poly(DTDA) film immersed in 0.4 M NaClO₄ + (1:1) acetonitrile-water medium.

variation of disulfide structures at potentials ranging from 0.0 to -0.6 V. The absence of the absorption at 439 cm⁻¹ clearly shows that the rotational isomerism is impeded. Furthermore, the absorption intensity of the S-S stretching starts to decrease from -0.6 V and almost disappears at potentials below -0.9 V. Moreover, Raman spectra appear featureless within the diagnostic S-H stretch wavenumber region between 2500 and 2600 cm⁻¹, which indicates that sulfide sites are not significantly converted into the acid thiol forms at the working pH. These results, together with the voltammetric experiments described above, provide clear evidence that the electrochemical reduction of the disulfide bonds to yield thiolate centers are at the origin of the vanishing band.

Conclusions

The electrochemical oxidation of the disulfide compound 2,2'-dithiodianiline (DTDA) in acidic acetonitrile-water mixtures yields a polymeric product, poly(DTDA), on platinum and gold electrodes. The spectroscopic properties of this material are equivalent to those exhibited by the chemically synthesized one.

The disulfide link is preserved in the polymeric structure which could, at least apparently, display a ladder structure with S-S bonds serving as interconnections between two adjacent polyaniline

chains, as it was reported previously.¹²⁻¹⁴ Working at a high sweep rate under potentiodynamic conditions, the S-S bond can be reduced to the corresponding dithiolate and this latter species can be reoxidized to the disulfide again. In this case, the peak separation amounts to nearly 800 mV, which suggests that the kinetic reversibility of the $RS-SR \rightleftharpoons 2RS^-$ reaction is very poor. This result is in agreement with that obtained for the DTDA monomer in the present work and also with data reported for other disulfide compounds.

According to the results presented, the hypothesis that poly-(DTDA) could possess a high-energy density due to the simultaneity of the leucoemeraldine $\rightleftharpoons$ emeraldine and dithiolate $\rightleftharpoons$ disulfide electrochemical transformations seems not to be confirmed. So, it is suggested that the enhanced property may be due to some kind of conformational effect induced by the presence of the S-S links. More precisely, the disulfide bonds seem to force the adjacent polyaniline chains to adopt a more planar structure, which may result in a better exploitation of the redox characteristics than in pristine polyaniline.

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