

# Polymer Films on Electrodes. 28. Scanning Electrochemical Microscopy Study of Electron Transfer at Poly(alkylterthiophene) Films

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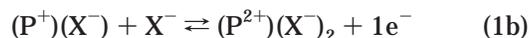
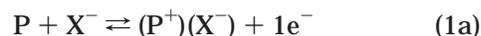
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The electrochemical doping and undoping processes of poly-(3,3''-didodecyl-2,2':5',2''-terthiophene) (poly(33''DDTT)) were studied by scanning electrochemical microscopy (SECM) to characterize the electron transfer of the polymer with a redox mediator in solution when the polymer was at different oxidation levels. SECM showed that electron exchange processes of oxidized poly(33''DDTT) were localized at the polymer/solution interface rather than inside the film. Poly(33''DDTT) in the neutral state did not allow the permeation of redox species to the underlying metal and behaved like a completely passivating film. A modified expression for the effective electron-transfer rate constant,  $k_{\text{eff}}$ , was obtained by grouping the terms concerned with charge transport across the polymeric film, and the values of  $k_{\text{eff}}$  were calculated from SECM approach curves. The values of  $k_{\text{eff}}$  for the electron transfer between poly(33''DDTT) film and methyl viologen ( $\text{MV}^{+/2+}$ ) as the redox couple ranged between  $10^{-5}$  and  $10^{-1}$   $\text{cm s}^{-1}$ , depending on polymer thickness, substrate potential, and MV concentration. Under the proper experimental conditions,  $k_{\text{eff}}$  could be directly correlated with the conductance of the polymer film, where poly(33''DDTT) thin films in the conducting state showed a metallic character.

## Introduction

The electrochemical processes of polymer modified electrodes (PMEs) have been the subject of extensive studies<sup>1</sup> and reviews<sup>2</sup> due to the complexity of the phenomena involved in such systems and their potential impact on technology.<sup>3</sup> Among electroactive polymers, electronically conducting polymers (CPs); i.e., conjugated systems, such as polyheteroaromatics, polyacetylenes, and polyphenylenes, represent an especially interesting class because of their high electrical conductivity in the oxidized state.<sup>4</sup> CPs switch in a reversible way from an insulating to a conductive state

when they undergo the oxidation reactions



where P represents a few monomeric units of the polymeric chain (typically 3 or 4) and  $\text{X}^-$  represents the counterion balancing the polymeric charge; the conductive state of the polymer is characterized by the presence of polaronic ( $\text{P}^+$ ) and bipolaronic ( $\text{P}^{2+}$ ) sites in the chain.<sup>5</sup> The polymeric system examined here is poly(3,3''-didodecyl-2,2':5',2''-terthiophene) (poly(33''DDTT)), electrochemically synthesized and oxidized, and  $\text{X}^- = \text{PF}_6^-$ . The interest in long-chain alkylated polythiophenes arises from their good electrical properties, chemical stability, and processability in most common organic solvents.<sup>6,7</sup> The starting monomer 33''DDTT (Figure 1) was chosen for the regioregularity of the resulting polymers and the absence of head-to-head interactions

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(1) (a) *Electroactive Polymer Electrochemistry—Fundamentals*; Lyons, M. E. G., Ed.; Plenum Press: New York, 1994; Part 1, p 488. (b) *Electroactive Polymer Electrochemistry—Methods and Applications*; Lyons, M. E. G., Ed.; Plenum Press: New York, 1996; Part 2, p 332. (c) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vols. 1–2, p 1417.

(2) (a) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13, p 191. (b) Inzelt, G. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1994; Vol. 18, p 89. (c) Andrieux, C. P.; Savéant, J.-M. In *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; John Wiley & Sons: New York, 1992; Vol. 22, p 207. (d) Oyama, N.; Ohshaka, T. In *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; John Wiley & Sons: New York, 1992; Vol. 22, p 333. (e) Martin, C. R.; Van Dyke, L. S. In *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; John Wiley & Sons: New York, 1992; Vol. 22, p 403.

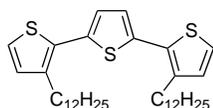
(3) (a) Hillman, A. R. In *Electrochemical Science and Technology of Polymers*; Linford, R. G., Ed.; Elsevier Applied Science: London, 1987; Vol. 1, p 103. (b) *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman & Hall: London, 1993; p 353.

(4) (a) MacDiarmid, A. G.; Heeger, A. J. *Synth. Met.* **1979/80**, *1*, 101. (b) Shacklette, L. W.; Chance, R. R.; Ivory, D. M.; Miller, G. G.; Baughman, R. H. *Synth. Met.* **1979/80**, *1*, 307. (c) Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1979**, 535.

(5) Bredas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309.

(6) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

(7) Reynolds, J. R.; Pomerantz, M. In *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1991; Vol. 2, p 187.



**Figure 1.** Structural formula of the starting monomer 3,3'-didodecyl-2,2':5',2''-terthiophene.

in the chain.<sup>8</sup> Moreover, the symmetrical pattern of substitution in 33''DDTT may allow a better packaging of the polymeric chains with improvement of the inter-chain electrical transport. In this work we report a scanning electrochemical microscopy (SECM)<sup>9</sup> study of electron transfer at a poly(33''DDTT) modified electrode with a redox system in the electrolytic solution.<sup>10</sup> Conditions inhibiting the electrochemistry at the underlying metallic substrate were employed with the aim of fully characterizing only the electrochemical response of poly33''DDTT. This was possible because SECM allowed the observation of the strong passivating effects of electrodeposited poly(33''DDTT) when it was in the neutral insulating state.

Correlations between the relevant properties of the polymer (thickness, potential, and conductivity) and the rate constant  $k_{\text{eff}}$  of the electrochemical reaction between the polymer and tip-generated mediator have been investigated. Particularly intriguing is the observed direct relationship between  $k_{\text{eff}}$  and the conductance of the film under specific experimental conditions, leading to a new possible approach to the determination of the conductivity of a CP by means of a microscopic technique. In fact, a previous paper on SECM characterization of polypyrrole<sup>11</sup> showed the feasibility of this technique in the study of the transition between the insulating and conductive states of the CPs, but the authors reported observations on conductivity only in a qualitative fashion. Moreover, the use of scanning tunneling microscopy to evaluate conductivity of CPs<sup>12</sup> gives only a rough estimate of this property because of the experimental difficulties arising from the continuous changes of the tip-film contact area and possible distortions of the penetrating tip. We show that SECM determination of rate constants can be exploited as a noninvasive approach to the in situ evaluation of the fundamental properties of CPs.

## Experimental Section

**Chemicals.** Methyl viologen dichloride hydrate (MVCl<sub>2</sub>·2H<sub>2</sub>O), KPF<sub>6</sub>, KClO<sub>4</sub>, AgNO<sub>3</sub>, tetrabutylammonium perchlorate (TBAP), tetrabutylammonium hexafluorophosphate ((TBA)-

(8) Andreani, F.; Salatelli E.; Lanzi, M. *Polymer* **1996**, *37*, 661.

(9) Bard, A. J.; Fan, F.-R. F.; Kwak, J.; Lev, O. *Anal. Chem.* **1989**, *61*, 132.

(10) (a) Grass, P.; Gibson, T.; Bergel, A.; Comtat, M. *J. Electroanal. Chem.* **1997**, *437*, 125. (b) Bobacka, J.; Grzeszczuk, M.; Ivaska, A. *J. Electroanal. Chem.* **1997**, *427*, 63. (c) Levi, M. D.; Algsatova, N. M.; Ovsyannikova, E. V.; Vorotyntsev, M. A. *J. Electroanal. Chem.* **1993**, *351*, 271. (d) Deslouis, C.; Musiani, M. M.; Tribollet, B. *J. Phys. Chem.* **1996**, *100*, 8994. (e) Kazarinov, V. E.; Levi, M. D.; Skundin, A. M.; Vorotyntsev, M. A. *J. Electroanal. Chem.* **1989**, *271*, 193. (f) Diaz, A. F.; Kanazawa, K. K. *J. Chem. Soc., Chem. Commun.* **1979**, 635. (g) Evans, G. P. In *Advances in Electrochemical Science and Engineering*; Gerischer, H., Tobias, C. W., Eds.; VCH: Weinheim, Germany, 1990; Vol. 1, p 1.

(11) Kwak, J.; Lee, C.; Bard, A. J. *J. Electrochem. Soc.* **1990**, *137*, 1481.

(12) Yang, H.; Fan, F.-R. F.; Yau, S.-L.; Bard, A. J. *J. Electrochem. Soc.* **1992**, *139*, 2182.

PF<sub>6</sub>), propylene carbonate, and benzonitrile, from Aldrich (Milwaukee, WI), and acetonitrile, from J. T. Baker (Phillipsburg, NJ), were used as received. The redox mediator MV-(PF<sub>6</sub>)<sub>2</sub> was precipitated in water from saturated solutions of KPF<sub>6</sub> and MVCl<sub>2</sub>·2H<sub>2</sub>O. The resulting precipitate was filtered and dried under vacuum for 16 h at 150 °C. The monomer 33''DDTT was synthesized by the method of Andreani et al.<sup>8</sup> All aqueous solutions were prepared with deionized water (Milli-Q, Millipore Corp.).

**Electrodes and Electrochemical Cells.** A Pt wire (25 μm diameter; Goodfellow, Cambridge, U.K.) was used to construct a tip microelectrode for the SECM measurements. The procedure of tip preparation has been described previously.<sup>13</sup> The substrate electrode for the electropolymerization of 33''DDTT was a 1 mm diameter Pt wire (Aldrich,) heat-sealed in a glass capillary. The tip electrode and substrate were always polished with 0.05 μm alumina (Buehler, Lake Bluff, IL) before use. In the electropolymerization of 33''DDTT and the SECM characterization, 0.01 M Ag/AgNO<sub>3</sub> in acetonitrile<sup>14</sup> and Ag/AgCl were used as reference electrodes, respectively. A saturated solution of KClO<sub>4</sub> in propylene carbonate bridged the Ag/AgCl reference electrode with the solution of propylene carbonate used in the SECM experiments. Pt wires (1 mm diameter) were used as counter electrodes. The electrochemical cell for SECM experiments was a 5 mL Teflon cylinder with a hole in the bottom for the insertion of the substrate electrode.

**Preparation of Poly 33''DDTT.** The electrochemical synthesis of poly(33''DDTT) was accomplished with a three electrode cell configuration. The deposition of poly(33''DDTT) was carried out in acetonitrile/benzonitrile (volume ratio, 4/1) containing 0.1 M TBAP and 0.2–2 mM 33''DDTT. The solution was bubbled with N<sub>2</sub> before the polymer synthesis. The poly(33''DDTT) was electrodeposited in the potentiodynamic mode with the substrate potential cycled over the range 0 ≤ E ≤ 0.9 vs Ag/AgNO<sub>3</sub> at 100 mV s<sup>-1</sup>. Cyclic voltammetry during poly(33''DDTT) synthesis was carried out with a PAR Model 173 potentiostat (Princeton Applied Research, Princeton, NJ) driven by a PAR 175 universal programmer. At the end of the deposition, the polymer films were held at E = 0 V for 1 h to produce completely reduced neutral systems. After the synthesis, the polymer film was rinsed with acetonitrile and dried under vacuum for 3 h at room temperature. The uniform coverage of the Pt substrate with polymer was checked with an Olympus BH-2 optical microscope. Scanning electron microscopy (Cambridge 100) showed a rough surface of poly(33''DDTT) with no appearance of fibrous structures. Before SECM characterization, poly(33''DDTT) covered substrates were stored in an inert atmosphere drybox. The thickness of the polymer film was determined with an alpha-step 200 profilometer (Tencor Instruments, Mountain View, CA) when the film was deposited on an ITO substrate (Delta Technologies, Stillwater, NY).

**In Situ Conductance Measurements of Poly(33''DDTT).** The conductance of poly(33''DDTT) was measured during the polymer growth by means of a double-band electrode according to the method described by Kankare and Kupila.<sup>15</sup> The double-band electrode was constructed following the procedure of Schiavon et al.<sup>16</sup> with a 3.5 μm insulating spacer.

**SECM Apparatus and Procedure.** The experimental setup for SECM measurements has been described previously.<sup>17</sup> Potentiostatic experiments and cyclic voltammetry of the polymer-covered substrate were carried out with a mediator when the tip was close to the substrate to study the electron transfer at the poly(33''DDTT) film. Tip positioning was

(13) Bard, A. J.; Fan, F.-R. F.; Mirkin, M. V. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1994; Vol. 18, p 243.

(14) Pleskov, V. A. *Zh. Fiz. Khim.* **1948**, *22*, 351.

(15) Kankare, J.; Kupila, E.-L. *J. Electroanal. Chem.* **1992**, *322*, 167.

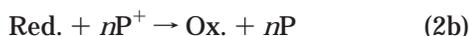
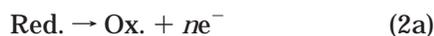
(16) Schiavon, G.; Sitran, S.; Zotti, G. *Synth. Met.* **1989**, *32*, 209.

(17) Wipf, D. O.; Bard, A. J. *J. Electrochem. Soc.* **1991**, *138*, 489.

accomplished with the polymeric film in the conductive state ( $E_{\text{sub}} = 0.9 \text{ V vs Ag/AgCl}$ ). Slow rate approach curves ( $0.05 \mu\text{m s}^{-1}$ ) allowed the determination of  $d = 0$ , taken when the tip current increased abruptly with no appreciable deformation of the polymeric film. In every measurement, the tip potential was held constant at a value where the redox mediator reduction was diffusion-controlled. The electrolyte was propylene carbonate with  $0.05 \text{ M (TBA)PF}_6$  and  $0.2\text{--}50 \text{ mM MV}(\text{PF}_6)_2$ . Both 33''DDTT and poly(33''DDTT) are insoluble in propylene carbonate. The solutions of  $\text{MV}(\text{PF}_6)_2$  in propylene carbonate were bubbled with  $\text{N}_2$  before SECM measurements, and a flow of  $\text{N}_2$  was maintained over the solution during the experiments. A Model 660 electrochemical workstation (CH Instruments, Memphis, TN) was employed for the tip characterization in the absence of the polymeric substrate.

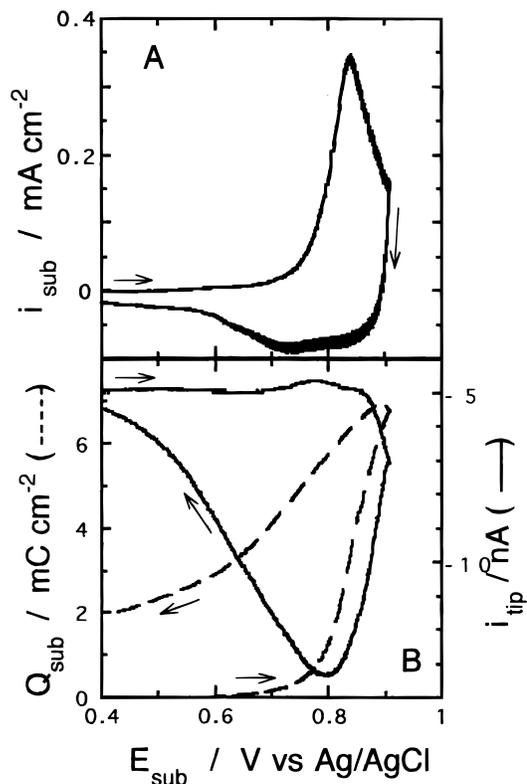
## Results and Discussion

**SECM Analysis of Poly(33''DDTT) in Different Stages of Oxidation.** The charge transfer between a PME with the polymer in the conductive state and a redox species, Red., in the bathing solution can occur by direct reaction at the conductive material (electrochemical path; eq 2a) or by a chemical reaction (eq 2b).<sup>18</sup>



Where process 2a takes place depends on the chemical nature of the polymeric film and the redox couple. In some cases, polymeric films may act as porous membranes<sup>19,20</sup> with resulting electron transfer (ET) (eq 2a) at the underlying metal. On the other hand, ET can be localized at the polymer/solution interface with the CP behaving as a conductive electrode material.<sup>21,22</sup> Equation 2b represents a catalytic electron-transfer reaction between the CP and the redox couple and can be regarded as a bimolecular reaction.<sup>18</sup> In this case as well, we should distinguish between a surface and a bulk electron exchange, depending on the penetration depth of the redox species inside the polymer film.

The cyclic voltammogram of poly(33''DDTT) with the tip close to the polymer-covered substrate ( $d < 10 \mu\text{m}$ ) is shown in Figure 2A. A slow scan rate ( $5 \text{ mV s}^{-1}$ ) was used for the cyclic voltammograms, and under these conditions, the tip current ( $i_{\text{tip}}$ ) values were comparable to those measured under steady-state conditions with  $E_{\text{sub}}$  constant. The tip current (Figure 2B) is due to the electrochemical reaction  $\text{MV}^{2+} + 1\text{e}^- \rightarrow \text{MV}^+$ , with the tip potential  $E_{\text{tip}}$  biased at  $-0.55 \text{ V vs Ag/AgCl}$  and the tip process under diffusion control. The variation of  $i_{\text{tip}}$  corresponds to the  $\text{MV}^{2+}$  concentration change in the solution trapped between tip and polymer substrate during substrate cyclic voltammetry. In this way the substrate product,  $\text{MV}^{2+}$ , is reduced at the tip in a thin-layer cell configuration. The most important feature in the voltammogram in Figure 2 is the cathodic rise of  $i_{\text{tip}}$  following the anodic current peak of the substrate ( $E_{\text{sub}} = 0.84 \text{ V vs Ag/AgCl}$ ). The substrate current is



**Figure 2.** (A) Cyclic voltammogram of poly(33''DDTT) (scan rate,  $5 \text{ mV s}^{-1}$ ). (B) Tip current,  $i_{\text{tip}}$ , and substrate exchanged charge,  $Q_{\text{sub}}$ . Tip potential,  $E_{\text{tip}} = -0.55 \text{ V vs Ag/AgCl}$  in  $0.05 \text{ M TBAPPF}_6$  in propylene carbonate. Tip-polymer,  $d < 10 \mu\text{m}$ ; tip radius,  $a = 12.5 \mu\text{m}$ ;  $[\text{MV}] = 50 \text{ mM}$ ; and polymer deposition charge,  $0.3 \text{ C cm}^{-2}$ .

associated with the switching reaction  $\text{poly(33''DDTT)} + x\text{PF}_6^- \rightarrow (\text{poly(33''DDTT)}^{x+})(\text{PF}_6^-)_x + x\text{e}^-$ . The steady tip current in the potential range  $0 \leq E_{\text{sub}} \leq 0.7 \text{ V vs Ag/AgCl}$  is due to redox mediator diffusion from the edges. The  $i_{\text{tip}}$  cathodic increase peaks at approximately  $0.8 \text{ V vs Ag/AgCl}$  due to the production of  $\text{MV}^{2+}$  at the PME following the change of poly(33''DDTT) into the conducting state. Therefore, monitoring  $i_{\text{tip}}$  during substrate cyclic voltammetry reveals that the doping process and charge transfer between the PME and the redox couple do not occur simultaneously when  $[\text{MV}] = 50 \text{ mM}$ . We can argue that ET does not involve the underlying metal in the time scale of the experiment as confirmed by completely negative feedback of the tip approach curve<sup>13</sup> when poly(33''DDTT) is insulating (as discussed below). In this sense, insulating poly(33''DDTT) behaves like a passivating film that is not permeable to the redox species in solution. As a consequence, ET must be localized at the polymer/solution interface<sup>22</sup> with  $\text{MV}^+$  not permeating inside the conductive poly(33''DDTT) film. The  $i_{\text{tip}}$  changes shown in Figure 2B are not consistent with  $\text{MV}^{2+/+}$  exchange inside the poly(33''DDTT). If ionic aggregates including MV cations were the actual species exchanged by the poly(33''DDTT), then the  $i_{\text{tip}}$  should vary closely with  $Q_{\text{sub}}$  in the anodic scan of the cyclic voltammetry as well.

The substrate cyclic voltammetry with  $[\text{MV}] = 0.2 \text{ mM}$  (Figure 3A) gives a different tip response (Figure 3B) than the tip response with  $[\text{MV}] = 50 \text{ mM}$  (Figure 2B). In fact, the onset of the polymer oxidation (at  $\sim 0.75 \text{ V vs Ag/AgCl}$ ) is accompanied by a small  $i_{\text{tip}}$

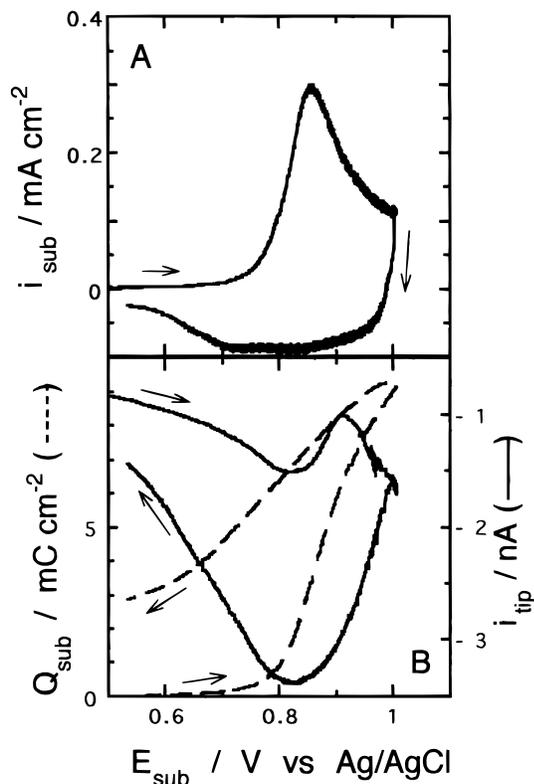
(18) Doblhofer, K. *J. Electroanal. Chem.* **1992**, *331*, 1015.

(19) Bull, R. A.; Fan, F.-R. F.; Bard, A. J. *J. Electrochem. Soc.* **1982**, *129*, 1009.

(20) Pearce, P. J.; Bard, A. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *112*, 97.

(21) Doblhofer, K.; Zhong, C. *Synth. Met.* **1991**, *41–43*, 2865.

(22) Arca, M.; Mirkin, M. V.; Bard, A. J. *J. Phys. Chem.* **1995**, *99*, 5040.

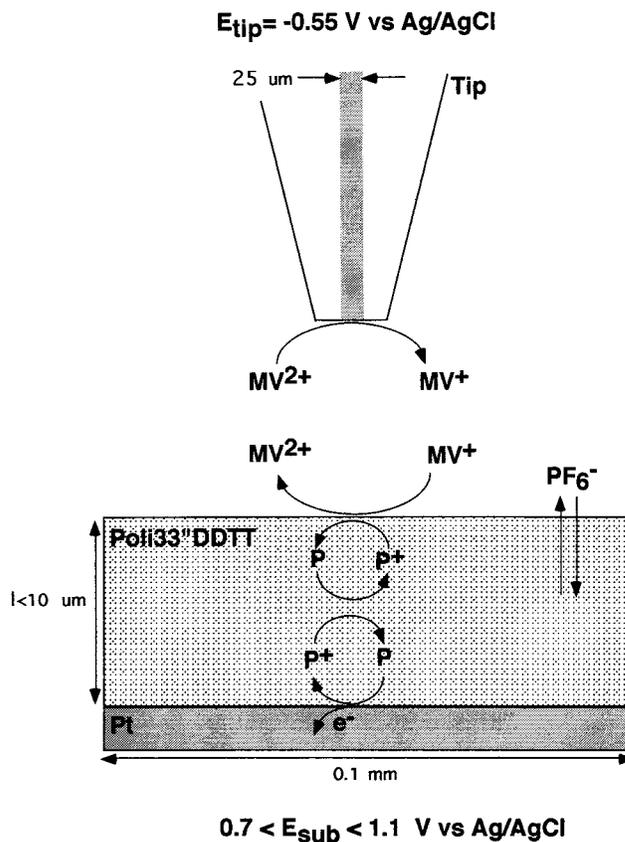


**Figure 3.** (A) Cyclic voltammogram of poly(33''DDTT) (scan rate, 5 mV s<sup>-1</sup>). (B) As in Figure 2B with [MV] = 0.2 mM.

cathodic peak not found in the experiment with [MV] = 50 mM. Both  $i_{tip}$  cathodic peaks in Figure 3B are centered at the same value of substrate potential ( $E_{sub} = 0.82$  V vs Ag/AgCl). This implies that the chemical reaction eq 2b does not give a significant contribution to the  $i_{tip}$  changes. In fact, the substrate charge (Figure 3B, dotted line) increases continuously, whereas  $i_{tip}$  (Figure 3B, solid line) decreases in the range  $0.85 < E_{sub} < 0.92$  V vs Ag/AgCl during the anodic scan of the cyclic voltammetry. In other words, the bimolecular reaction depicted in eq 2b should give an  $i_{tip}$  proportional to the polymer exchanged charge. The defined value of  $E_{sub}$  at which  $i_{tip}$  shows its minimum corresponds to an intermediate oxidation state of the poly(33''DDTT) between the polaronic and bipolaronic regimes.<sup>23</sup> Therefore, ET becomes faster when poly(33''DDTT) is partially oxidized with approximately 50% of the charge corresponding to the fully oxidized state.<sup>24</sup> Moreover,  $E_{sub}$  influences the ET rate between poly(33''DDTT) and MV<sup>+/2+</sup> because of the changes in polymer conductivity with  $E_{sub}$ . A comparison of  $i_{tip}$  at different redox mediator concentrations (Figures 2B and 3B, dotted lines) suggests that high concentrations of mediator species slow the ET as deduced from the  $i_{tip}$  peak disappearance at the onset of polymer oxidation when [MV] = 50 mM.

In the following discussion, the effects of substrate potential, mediator concentration, and polymer thickness will be analyzed within the framework of SECM theory to investigate how these factors can influence the ET in the system under examination.

**SECM Approach Curves with Poly(33''DDTT).** The electric current across the PME/solution interface in an SECM experiment<sup>13</sup> when the polymer becomes



**Figure 4.** Schematic view of the processes involved in an SECM experiment with the poly(33''DDTT) substrate and MV<sup>2+/+</sup> redox mediator.

electronically conductive is affected by four factors: mediator diffusion between the tip and polymer surface, ET at the polymer/liquid interface, charge transport across the polymeric film, and ET between the underlying metal and the polymeric film (Figure 4). Similar to the treatment of the ET across a liquid/liquid interface,<sup>25</sup> one can treat the rates of a number of processes that occur in a serial fashion as a summation of kinetic parameters, represented as currents. Thus, we can express the total current across a conductive polymer/liquid interface  $i_p$  as the sum of several contributions:<sup>2c</sup>

$$\frac{1}{i_p} = \frac{1}{i_T} + \frac{1}{i_{ET}} + \frac{1}{i_{pol}} + \frac{1}{i'_{ET}} \quad (3)$$

where  $i_T$ ,  $i_{ET}$ ,  $i_{pol}$ , and  $i'_{ET}$  represent respectively the tip current due to the diffusion of the redox mediator, the current due to the ET at the conductive polymer/liquid interface, the current due to the charge transport across the polymeric film, and the current for ET at the polymer/metal interface. Because ET is fast at the underlying metal/conductive polymer interface,  $i'_{ET}$  is not rate determining in the overall process. Moreover, it is convenient to define a term  $i_{ET,mod}$  in such a way that eq 3 can be rewritten in the form

(23) Zotti, G.; Schiavon, G. *Synth. Met.* **1989**, *31*, 347.  
 (24) Chung, T. C.; Kaufman, J. H.; Heeger, A. J. Wudl, F. *Phys. Rev. B: Condens. Matter* **1984**, *22*, 317.  
 (25) (a) Wei, C.; Bard, A. J.; Mirkin, M. V. *J. Phys. Chem.* **1995**, *99*, 16033. (b) Tsionsky, M.; Bard, A. J.; Mirkin, M. V. *J. Am. Chem. Soc.* **1997**, *119*, 10785.

$$\frac{1}{i_p} = \frac{1}{i_T^c} + \frac{1}{i_{ET_{mod}}} \quad (4)$$

where

$$\frac{1}{i_{ET_{mod}}} = \frac{1}{i_{ET}^c} + \frac{1}{i_{pol}} \quad (5)$$

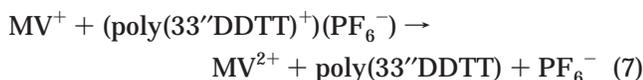
Equation 4 shows two contributions for the ET in electronically conductive polymers characterized with SECM. The first contribution is associated with the diffusion-controlled redox mediator generation and the second with the ET across the polymer film. Depending on the initial experimental conditions, e.g., concentration of the redox mediator in solution, thickness of the film, and morphology of the film, we can find two different regimes with diffusive or polymeric charge-transfer control. Diffusive control is obtained for very thin polymeric films or for low concentrations of redox mediator. On the other hand, thicker films and a high concentration of redox couple will lead to charge-transfer control.

In the present case, the ET at the polymer/electrolyte interface depends primarily on the conductivity of the film. Parameters affecting polymer conductivity must be taken into account to determine their influence on the charge-transfer properties of poly(33''DDTT) with the SECM technique. This technique allows the accurate determination of heterogeneous rate constants  $k_{eff}$  because of the high sensitivity of feedback current to the rate of heterogeneous reactions.<sup>26</sup> From the SECM feedback current–distance curves, it is possible to extract a first-order effective heterogeneous constant with the equation<sup>25,27</sup>

$$i_T^k = i_S^k \left( 1 - \frac{i_T^{ins}}{i_T^c} \right) + i_T^{ins} \quad (6)$$

when the ion transfer from oxidized polymer to solution is not rate determining.

This latter statement excludes the occurrence of the chemical reaction



with removal of doping anions from the oxidized polymer film, because under potentiostatic conditions the content of oxidized sites in the polymer is fixed. In eq 6,  $i_T^k$ ,  $i_T^{ins}$ , and  $i_T^c$  are the normalized tip currents for substrate finite kinetics, insulating substrate (i.e., no mediator production occurs at the substrate), and diffusion-controlled regeneration of the redox mediator. The normalized tip currents are usually expressed as functions of the normalized tip–substrate distance  $L = d/a$ , where  $d$  is the distance between the tip and the substrate and  $a$  is the radius of the disk-shaped microelectrode.  $i_S^k$  represents the substrate current under

kinetic control and can be expressed by the analytical approximation

$$i_S^k = \frac{0.78377}{L(1 + (1/\Lambda))} + \frac{0.68 + 0.3315 \exp(-(1.0672/L))}{1 + F(L, \Lambda)} \quad (8)$$

where  $\Lambda = k_{eff}d/D_0$ ,  $k_{eff}$  is the apparent heterogeneous rate constant, and  $D_0$  is the diffusion coefficient of the oxidized species,  $MV^{2+}$ , in the electrolyte. From steady-state cyclic voltammetry of the tip ( $a = 12.5 \mu\text{m}$ ), we obtained  $D_R = 2.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  for  $MV^+$  in propylene carbonate at room temperature using the relation  $i_{T, \infty} = 4nFD_0C_0a$ .<sup>9</sup> The term  $F(L, \Lambda)$  is given by the function

$$F(L, \Lambda) = \frac{11 + 7.3\Lambda}{\Lambda/(110 - 40L)} \quad (9)$$

For  $i_T^c$  and  $i_T^{ins}$  the analytical approximations are respectively

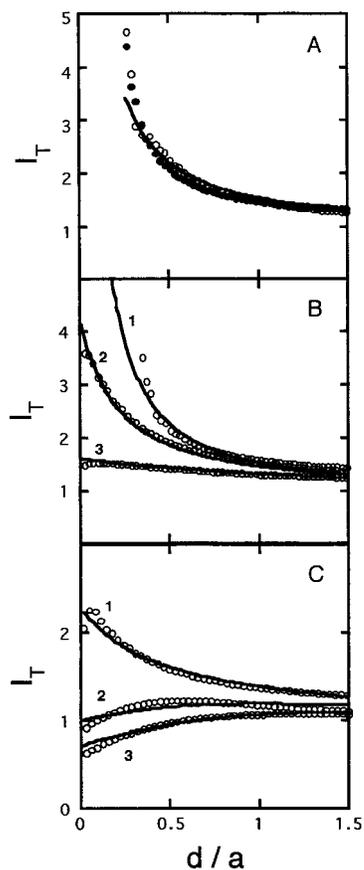
$$i_T^c = \frac{0.78377}{L} + 0.3315 \exp\left(-\frac{1.6072}{L}\right) + 0.68 \quad (10)$$

$$i_T^{ins} = 1 \left[ 0.15 + \frac{1.5358}{L} + 0.58 \exp\left(-\frac{1.14}{L}\right) + 0.0908 \exp\left(\frac{L - 6.3}{1.017L}\right) \right] \quad (11)$$

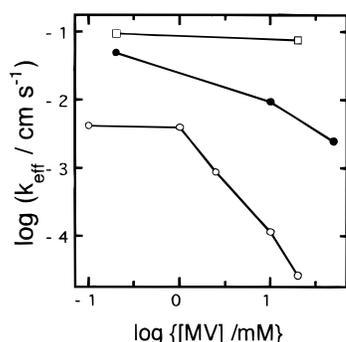
Possible  $MV^+$  oxidation by conducting poly(33''DDTT) from the tip–polymer cavity may cause a decrease of  $i_T$  and the consequent lowering of  $k_{eff}$  calculated by eqs 6 and 8–11. This phenomenon could start to be significant at very low approach rates ( $< 0.01 \mu\text{m s}^{-1}$ ); this is not the case for our experimental time scale. Figure 5 shows the evolution of SECM approach curves when the thickness of the deposited polymer film and the redox mediator concentration in solution varied ( $E_{pol} = 0.9 \text{ V vs Ag/AgCl}$ , where the polymer is in the conductive state at this potential value). The control of polymer film thicknesses was obtained from the measurements of net deposition charges during cyclic voltammetry of 33''DDTT solutions. To obtain a uniform coverage of the Pt substrate, the lower limit of deposited charge was  $0.1 \text{ C cm}^{-2}$ . On the other hand, large amounts of deposited charge could produce polymer films with considerable lateral growth outside the Pt substrate area, leading to a nonlinear relationship between deposited charge and film thickness. We found  $0.6 \text{ C cm}^{-2}$  to be the upper limit for the deposited charge density. Profilometry on dry poly(33''DDTT) films gave a polymer density equal to  $0.002 \text{ cm}^3 \text{ C}^{-1}$ . Using eq 6 and the data in Figure 5, we obtained the trend of heterogeneous rate constant vs MV concentration at three different poly(33''DDTT) thicknesses (Figure 6). For very thin films ( $t \leq 2 \mu\text{m}$  or  $Q_{dep} \leq 0.1 \text{ C cm}^{-2}$ ), the SECM response is under diffusive control, and  $k_{eff}$  is independent of the redox mediator concentration [MV]. This is equivalent to saying that the PME behaves like a metal electrode. An increase of poly(33''DDTT) thickness ( $t \geq 4 \mu\text{m}$  or  $Q_{dep} \geq 0.2 \text{ C cm}^{-2}$ ) brings about a dependence of  $k_{eff}$  on [MV], and the effect of polymer film resistance can be observed. Under these conditions the formation of redox mediator at the substrate is prevented by charge transfer across the polymer. Therefore the SECM response can be considered under

(26) Hubbard, A. T.; Anson, F. C. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1970; Vol. 4, p 129.

(27) Tsionsky, M.; Bard, A. J.; Mirkin, M. V. *J. Phys. Chem.* **1996**, *100*, 17881.



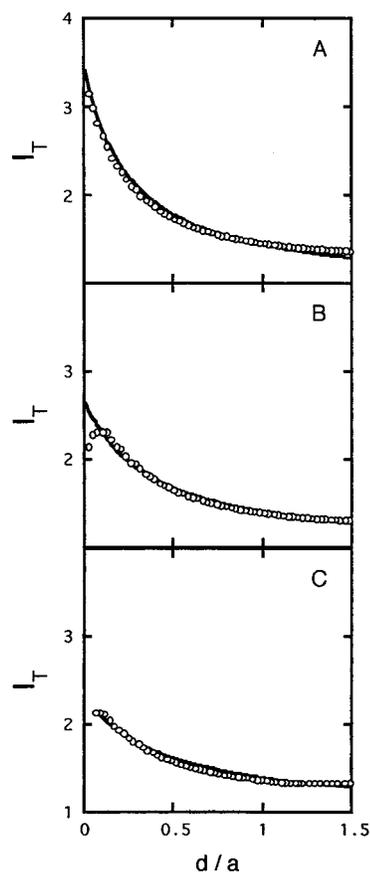
**Figure 5.** SECM tip ( $a = 12.5 \mu\text{m}$ ) approach curves with  $MV^{2+}$  redox mediator on poly(33''DDTT).  $E_{tip} = -0.55$  V vs Ag/AgCl and  $E_{sub} = 0.9$  V vs Ag/AgCl. Circles are experimental points, and lines are theoretical fits from eqs 6 and 8. (A)  $[MV] = (\circ)$  0.2 mM;  $Q_{dep} = 0.1$  C cm<sup>-2</sup>. (B)  $[MV] = (1)$  0.2, (2) 10, and (3) 50 mM;  $Q_{dep} = 0.1$  C cm<sup>-2</sup>. (C)  $[MV] = (1)$  0.1, (2) 2.5, and (3) 10 mM.



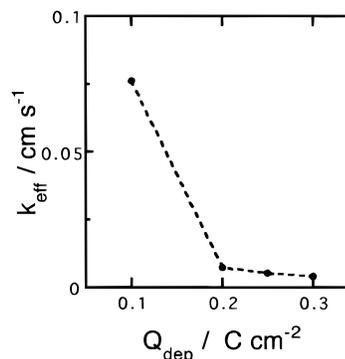
**Figure 6.** Plot of  $k_{eff}$  vs  $\log [MV]$  at different polymer thicknesses. Values of  $k_{eff}$  were calculated from the approach curves in Figure 5. Poly(33''DDTT) deposition charge was (□) 0.1, (●) 0.25, and (○) 0.5 C cm<sup>-2</sup>. The approach curves at  $[MV] = 1$  and 20 mM when  $Q_{dep} = 0.5$  C cm<sup>-2</sup> are not shown in Figure 5C.

charge-transfer control. There are several mechanisms of charge transfer in electronically conductive polymers, ranging from intrachain to interfiber electron hopping,<sup>28</sup> and SECM provides a useful tool for determining the controlling factor of such processes.

Figure 7 shows the effect of poly(33''DDTT) thickness on the SECM response when  $[MV] = 20$  mM and  $E_{pol} = 0.9$  V vs Ag/AgCl. Higher feedback is associated with the thinner film, and a high concentration of redox mediator maintains finite substrate kinetics, even if  $Q_{dep}$



**Figure 7.** SECM tip approach curves with  $a = 12.5 \mu\text{m}$  on poly(33''DDTT) with different thicknesses.  $E_{tip} = -0.55$  V vs Ag/AgCl,  $E_{sub} = 0.9$  V vs Ag/AgCl, and  $[MV] = 20$  mM. poly(33''DDTT) deposition charge was (A) 0.2, (B) 0.25, and (C) 0.3 C cm<sup>-2</sup>. (○) Experimental points; (—) theoretical fit from eqs 6 and 8.

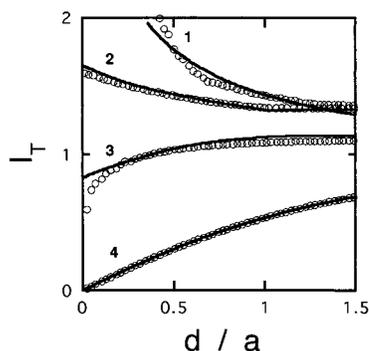


**Figure 8.** Variation of  $k_{eff}$  with poly(33''DDTT) film thickness. The  $k_{eff}$  values were determined from the approach curves in Figures 3A (at  $[MV] = 20$  mM) and 7 using eqs 6 and 8–11.

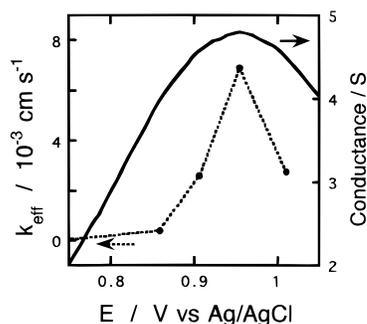
$= 0.2$  C cm<sup>-2</sup>. The dependence of the poly(33''DDTT) electrochemical response on film thickness (Figure 8) can be ascribed to control by interchain electron hopping without involvement of associated co-ion motion.<sup>29</sup> In fact, such coupled movement should be independent of thickness because of its confinement to the polymeric superficial layers in contact with solution. An increase

(28) (a) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. B* **1980**, *22*, 2209. (b) Roth, S.; Bleier, H.; Pukacki, W. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 223.

(29) Albery, W. J.; Mount, A. R. *J. Electroanal. Chem.* **1991**, *305*, 3.



**Figure 9.** SECM tip approach curves with  $a = 12.5 \mu\text{m}$  on poly(33''DDTT) ( $Q_{\text{dep}} = 0.25 \text{ C cm}^{-2}$ ) at different potential values with  $[\text{MV}] = 50 \text{ mM}$ .  $E =$  (1) 0.95, (2) 1, (3) 0.85, and (4) 0.5 V vs Ag/AgCl. (○) Experimental points; (—) theoretical fit from eqs 6 and 8.



**Figure 10.** Plot of  $k_{\text{eff}}$  (···●···) and conductance  $G$  (—) with substrate potential.  $k_{\text{eff}}$  values were calculated from the approach curves in Figures 3B (at  $E = 0.9 \text{ V}$  vs Ag/AgCl) and 9.

in film thickness leads to a leveling of  $k_{\text{eff}}$  for the onset of the lateral contribution to the SECM response. Moreover, one must also consider the loss of effectiveness in the thickness control with deposited charge due to significant morphological and electrical changes that occur during advanced polymeric film growth.

A matter of crucial importance is the variation of polymer properties with the applied potential.<sup>30</sup> The SECM response of poly(33''DDTT) at different potentials (Figure 9) changes dramatically, ranging from a situation in which the system is completely insulating with pure negative feedback (Figure 9, curve 4) when  $E_{\text{pol}} = 0.5 \text{ V}$  vs Ag/AgCl to a highly conductive form (Figure 9, curve 1) with pure positive feedback when  $E_{\text{pol}} = 0.95 \text{ V}$  vs Ag/AgCl. The intermediate states (Figure 9, curves 2 and 3) can be ascribed to a poly(33''DDTT) with semiconductive properties. Note that the curve of  $k_{\text{eff}}$  vs  $E$  (Figure 10) passes through a maximum for  $E = 0.95 \text{ V}$  and decreases at a higher potential value. In this sense SECM verifies a well-defined situation in which the ratio  $O/R$  (where  $O$  and  $R$  are the concentra-

tion of oxidized and reduced sites in the film, respectively) reaches an optimum value for charge transport. The drop of  $k_{\text{eff}}$  when  $E_{\text{sub}} > 0.95 \text{ V}$  thus corresponds to a situation where an increase in the number of charge carriers in the polymer also brings about a decrease of the electrical mobility with a resulting reduction of the conductance,  $G$ . The trends of  $G$  and  $k_{\text{eff}}$  (Figure 10) provide evidence of a correlation between these properties. The  $G$  increase shows a potential threshold somewhat lower than  $k_{\text{eff}}$ . Such a difference can be ascribed to a short circuit of the double-band electrode when the polymer is not yet homogeneously doped at the imposed potential.

## Conclusions

The electrochemical response of a poly(33''DDTT) modified electrode has been characterized by SECM. By monitoring the tip current during the electrochemical switching of the polymer from an electronically insulating to an electronically conductive state, a delay between the doping process and the subsequent electron transfer with the redox mediator in solution was detected when high concentrations of redox mediator were employed. For the case of a low mediator concentration, the SECM response identified a well-defined value of substrate potential where the electron transfer between poly(33''DDTT) and the redox mediator  $\text{MV}^{+/2+}$  had the highest rate. Such results showed a metallic behavior of conducting poly(33''DDTT) modified electrodes in terms of electrode kinetics. SECM approach measurements were conducted with different thicknesses and potentials of the polymeric substrate. The proper choice of experimental conditions allowed the distinction between two regimes of electron-transfer control. Thick films ( $Q_{\text{dep}} \geq 0.2 \text{ C cm}^{-2}$ ) and high concentrations of redox mediator ( $[\text{MV}^{2+}] \geq 10 \text{ mM}$ ) gave finite kinetics of electron transfer at the polymer/solution interface. On the other hand thinner films and more dilute solutions showed diffusive control of the electron transfer. In the latter case the determination of  $k_{\text{eff}}$  was unaffected by the thickness of the polymer. Finally, an important correlation between rate constant  $k_{\text{eff}}$  and polymer conductance was found from the trend of  $k_{\text{eff}}$  vs  $E_{\text{sub}}$  with thick films.

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(30) (a) Kalaji, M.; Peter, L. M.; Abrantes, L. M.; Mesquita, J. C. *J. Electroanal. Chem.* **1989**, *274*, 289. (b) LaCroix, J. C.; Diaz, A. F. *J. Electrochem. Soc.* **1988**, *135*, 1457.