Preparation and Time-Resolved in Situ Reflection Spectra of Bilayer Electrodes with Polythiophene Outer Layers

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Bilayer electrodes, Pt/poly-**1**/polythiophene [**1**: tris(4-vinyl-4′-methyl-2,2′-bipyridine)ruthenium(II) perchlorate], where polythiophene is derived from poly(3-methylthiophene) [poly(3-methyl-2,5-thienylene), abbreviated as PMeT] and poly(2,2′-bithiophene) [poly(2,2′-dithienyl-5,5′-ene), abbreviated as PBT], have been prepared. Electropolymerizations of MeT and BT at Pt/poly-**1** occur at the platinum electrode surface, followed by phase separation of the polymer components which results in the bilayer structure. Significant imbalance, observed between charge densities involved in the cathodic and anodic waves of the cyclic voltammogram for Pt/poly-**1**/PBT, is explained as being due to the positive charge leakage from the PBT layer to the platinum substrate through the 2+/3+ redox level of the intervening poly-**1** during the potential sweep in the negative direction. This charge leakage is ascribed to the consequence of the closely located oxidation potential of PBT to that of the 2+/3+ of poly-**1** ($E^{\circ\prime}=+0.875$ V vs. Ag/Ag^+). Time-resolved in situ reflection spectra taken at Pt/poly-**1**/PMeT immersed in electrolytic solutions give evidence for the mediated redox reactions of PMeT by the poly-**1** layer. The spectral changes strongly suggest the transient occurrence of polarons during the doping process.

Electrically conducting polyheterocycles, e.g., polypyrrole [poly(2,5-pyrrolylene), hereafter abbreviated as PP] and polythiophene [poly(2,5-thienylene), hereafter abbreviated as PT] have attracted increasing interest in the past decade. One of the reasons for this stems from their important situation as examples for nondegenerate ground-state systems. It has been shown that bipolarons are evolved in those polymer chains upon electrochemical dopings (oxidations) as the most stable charged states (Fig. 1).[1-3] Polarons have also been detected in PP.[4,5] Although there has been some controversy,[2] Kaneto et al. and Hattori et al. first obtained the spectroscopic evidence for polarons in very dilutely doped PTs.[6-8] Basically consistent results were subsequently reported for poly(3-methylthiophene) [poly(3-methyl-2,5-thienylene), hereafter abbreviated as PMeT].[9] Thus, the studies of the electrochemically induced changes in PP and PT have provided understanding of the charged states in PP and PT.

It has been recognized that several tens of minutes are required to achieve quasi equilibria in PP[4] and PT[2,8] upon charge injections. The relaxations possibly involve manifold processes in the polymer chains, which apparently has confined the former studies basically to static conditions, except for a transient ESR study of PP.[5] Another aspect of the preceding studies is that they have been based exclusively on the configuration in which the positive and negative charge injections (i.e., doping-undoping reactions) into the conducting polymers are performed at the conducting substrates, simply as a consequence of the electropolymerization of conducting polymers at metallic or semiconducting substrates. In this configuration, the electronic states of the conducting polymers are totally governed by the Fermi level of the substrates, even in the course of relaxations within them. This becomes disadvantageous for studying the relaxation processes taking place in conducting polymers upon charge injections.

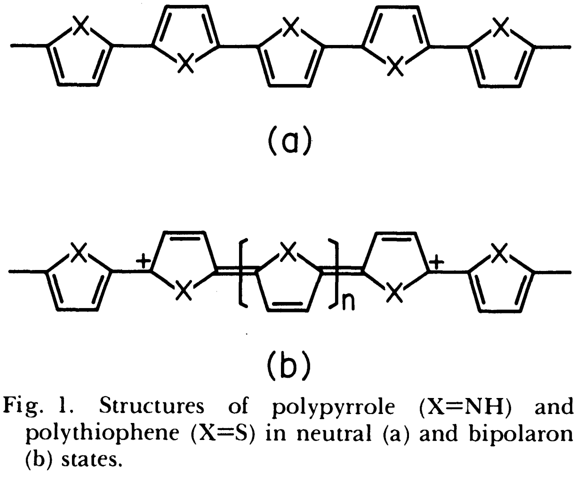

Fig. 1. Structures of polypyrrole (X=NH) and polythiophene (X=S) in neutral (a) and bipolaron (b) states.

In the above context, it would be interesting to realize a configuration in which charge injections into the bulk of conducting polymers are performed via discrete electronic levels of the adjacent layer which is electrochemically active but electrically insulating. In a previous communication,[10] we reported on the first example of PP deposited on the electrically insulating film, poly[tris(4-vinyl-4′-methyl-2,2′-bipyridine)ruthenium(II) perchlorate] (hereafter abbreviated as poly-**1**), to give a bilayer electrode, Pt/poly-**1**/PP. Deposition of PP at the Pt/poly-**1** electrode is initiated at the platinum electrode. The PP film growth occurs within the existing poly-**1** layer and proceeds further outside it. Phase separation of the both polymer components, poly-**1** and PP, is subsequently caused by repeated electrochemical potential sweeps in 0.1 M† TBAP (tetrabutylammonium perchlorate)-acetonitrile, and the above

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† 1 M=1 mol dm^{-3}.

bilayer structure is eventually obtained. In this bilayer electrode, oxidation (doping) and reduction (undoping) reactions of the PP layer are mediated by the 2+/1+ and 2+/3+ redox levels of the $[Ru(bpy)_3]^{2+}$ centers (bpy: 2,2′-bipyridine moiety) in the inner layer. Recently,[11] we preliminarily reported on the successful applications of this procedure to PMeT and poly(2,2′-bithiophene) [poly(2,2′-dithienyl-5,5′-ene), hereafter abbreviated as PBT] in preparations of the bilayer electrodes, Pt/poly-**1**/PMeT and Pt/poly-**1**/PBT. Figure 2 depicts the energy diagram for the Pt/poly-**1**/PMeT bilayer electrode. The locations of the conduction and valence bands are estimated based on optical (band gap energy: 2.1 eV)[6] and electrochemical data,[11] and are consistent to the reported values.[12] The redox potentials of poly-**1** are determined according to the published data.[10,13] The reductive and oxidative charge transfers to the PMeT layer are performed through the electrochemical mediation by 2+/1+ and 2+/3+ redox levels of poly-**1**, respectively. Mid-gap states are evolved upon oxidation of PMeT. In these bilayer systems, it has been found that the quasi equilibria in PMeT and PBT are established within anomalously short periods of time upon electrochemical charge injections. This remarkable feature enabled us to detect transiently occurring polarons in PMeT in the course of achieving equilibria.[14] The above electrochemical procedures might be an important step towards the establishment of molecular technolgy to construct microstructures involving conducting polymers,[15] in view of the generally untractable nature of conducting polymers. This paper describes the preparations, electrochemistry and time-resolved in situ reflection spectra of the bilayer electrodes of PMeT and PBT.

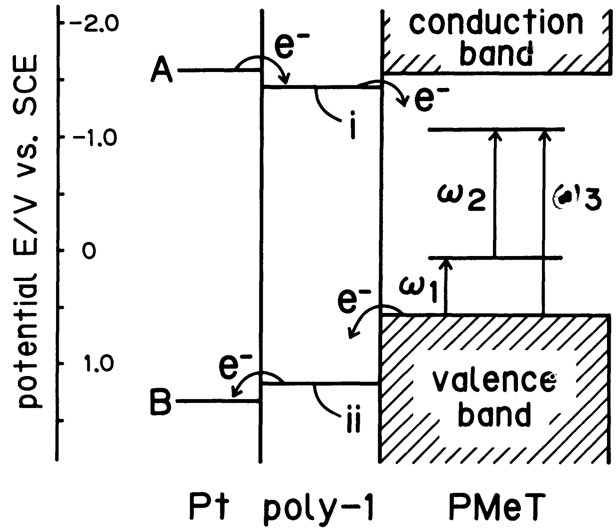


Fig. 2. Energy diagram for the Pt/poly-**1**/PMeT bilayer electrode. i and ii denote 2+/1+ and 2+/3+ redox levels of poly-**1**, respectively. ω_1, ω_2, and ω_3 are the possible optical transitions involving the mid-gap states of PMeT. PMeT: poly(3-methylthiophene). For poly-**1** see text.

Experimental

Materials. The monomer precursor of poly-**1**, tris(4-vinyl-4′-methyl-2,2′-bipyridine)ruthenium(II) perchlorate (**1**), was synthesized according to a modified method of the reported procedures.[16] Pt/poly-**1** electrodes were prepared using the reported method.[10,13] Commercially obtained TBAP was purified by thermal recrystallization from an EtOH–H_2O 2 : 3 mixed solvent and was dried in vacuo at 80 °C for 32 h. Commercial acetonitrile was refluxed over P_2O_5 and distilled before use.

Electrochemical Experiments. Platinum disks (4 mm diameter) embedded in glass, and evaporated films of plati-

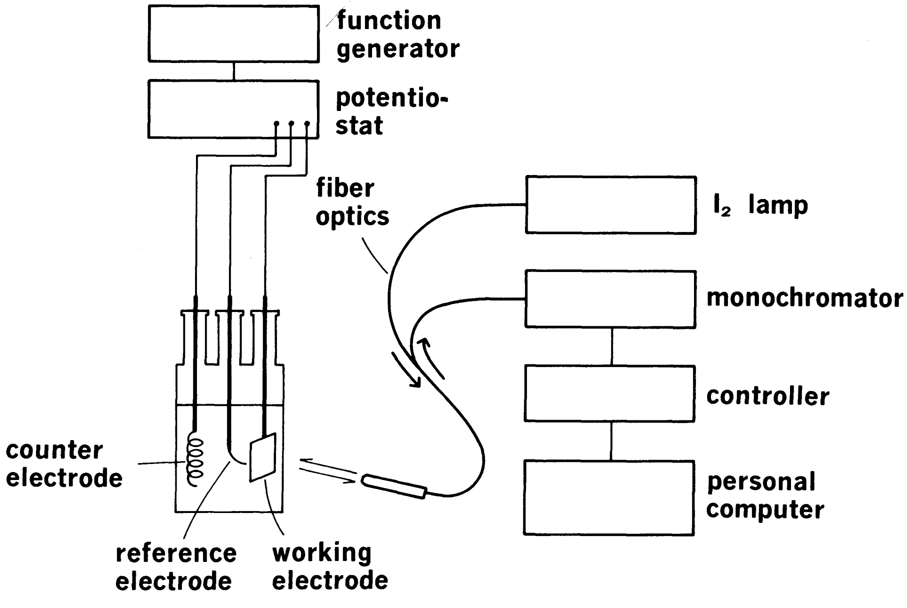


Fig. 3. Schematic representation of the experimental setup for time-resolved in situ reflection spectroscopy during the electrochemical reactions.

num (280 nm thick; active area: 4 mm diameter) on glass substrates (Corning # 7059, 1.2 mm thick) were used as the working substrates. The surfaces of the platinum disks were polished using 1 μm diamond paste. A platinum wire (1 mm diameter) was used as the counter electrode. An Ag/Ag$^+$ quasi reference electrode was used which showed 290 mV vs. SCE (saturated calomel electrode) in 0.1 M TBAP-acetonitrile. Potentials indicated in the following are all vs. Ag/Ag$^+$ unless otherwise noted. Preparations and electrochemical measurements were performed by immersing electrodes in electrolytic solutions in one compartment cells. All of the electrochemical experiments were carried out under Argon-purged conditions. The preparations of Pt/poly-**1**/PMeT and Pt/poly-**1**/PBT electrodes have been outlined in a previous communication.[11] Electrochemical polymerizations of MeT and BT were carried out by both potential sweeps and galvanostatic anodizations. Typically, the galvanostatic polymerizations of MeT and BT were performed at a current density of 275 μA cm^{-2} at Pt/poly-**1** electrodes immersed in anhydrous acetonitrile containing 120 mM monomers and 0.1 M TBAP.

In situ reflection spectra at electrode surfaces were measured with a normally incident light beam led by fiber optics using an MCPD-100 Multi-Channel Photo Detector (Ohtsuka Denshi Co.), as shown in Fig. 3. Each spectrum is based on the accumulated signal obtained by eight repeated wavelength sweeps with a gate time of 12 ms each.

Results and Discussion

Preparations of Pt/Poly-1/PMeT and Pt/Poly-1/PBT. The cyclic voltammograms (CVs) monitored during the electropolymerizations of MeT and BT at Pt/poly-**1** electrodes by potential sweeps are depicted in Fig. 4. The expansion of the waveforms at every cyclic sweep, as indicated by the arrows in Fig. 4(a), is a result of the deposition and the film growth of PMeT at the electrode. When the positive sweeps were limited to potentials lower than +1.1 V, the expansion of the CV waves was not observed and only the redox waves for poly-**1** were repeatedly observed. This means that the electropolymerization of MeT occurs at potentials higher than +1.1 V. This is consistent with the fact that the applied potential upon galvanostatic electropolymerization of MeT (Fig. 5) reached a steady value of +1.17 V. The fact that MeT has a substantially higher oxidation potential than that of 2+/3+ of poly-**1** ($E^{\circ\prime}=+0.875$ V) rules out the possibility of the mediated oxidation of MeT by poly-**1**. The observed potential for MeT oxidation during the galvanostatic anodization is initially lower than the ultimately achieved steady value, +1.17 V. This is understood as being due to the initially predominant oxidation of the poly-**1** layer. The subsequently occurring peak in the V vs. *t* curve would be representing a crossover from poly-**1** oxidation to MeT oxidation. These observations indicate that the electropolymerization of MeT occurs at the surface of the platinum substrate as a result of the permeation of the monomer molecules through the poly-**1** layer. In fact, the PMeT-as-deposited Pt/poly-**1** electrode showed the CV waves for

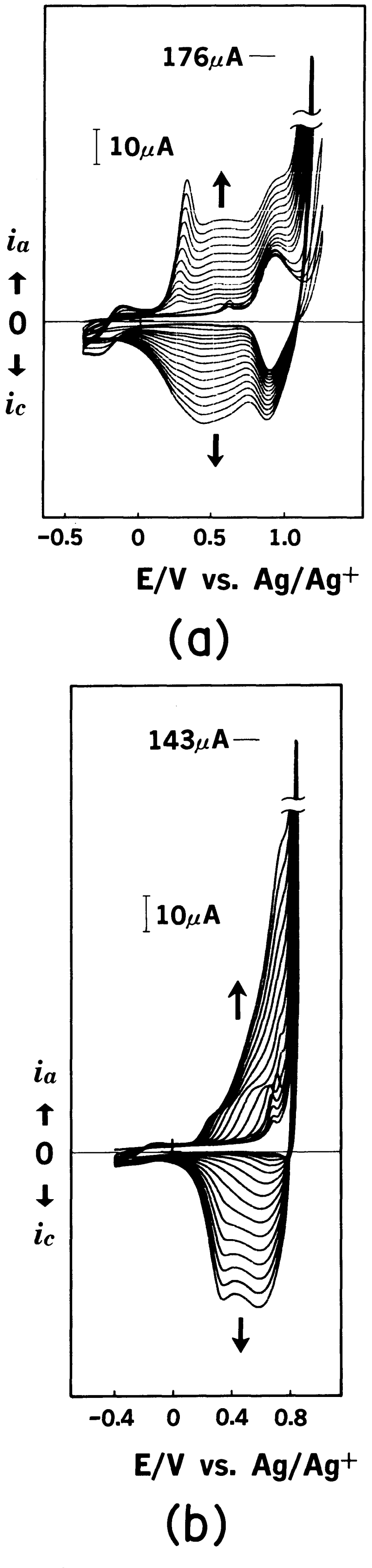


Fig. 4. Cyclic voltammograms monitored on electropolymerizations of 3-methylthiophene (a) and 2,2′-bithiophene (b) at Pt/poly-**1** electrodes immersed in 0.1 M tetrabutylammonium perchlorate–acetonitrile including 30 mM 3-methylthiophene (a) and 2,2′-bithiophene (b), respectively. The employed coverages of poly-**1** layers for (a) and (b) are 1.85×10^{-9} and 3.60×10^{-9} mol cm^{-2}, respectively. Sweep rate: 0.1 V s^{-1}. For poly-**1** see text.

PMeT and 2+/3+ of poly-**1** independently, essentially as a superimposition of the CV waves for both origins in 0.1 M TBAP-acetonitrile, which means that PMeT was electrochemically accessed directly from the platinum substrate. On the other hand, in the negative potential region, where PMeT is electrochemically inert, the 2+/1+ waves of poly-**1** are totally absent except for a spiky current peak centered at −1.33 V, indicating that PMeT present at the platinum electrode surface is blocking the reduction of the $[\mathrm{Ru(bpy)_3}]^{2+}$ centers. The subsequent cyclic potential sweeps between the 2+/1+ and 2+/3+ potentials of poly-**1** caused the CV changes (depicted in Fig. 1 of Ref. 11) as follows; 1) anodic peak shifts of PMeT in the positive direction followed by peak growths as a prewave of the 2+/3+ wave of poly-**1**, 2) gradual loss of the cathodic wave of PMeT, 3) growths of the spiky peak at −1.33 V with a slight shift at every cycle in the negative direction, 4) evolution of the 2+/1+ waves of poly-**1** in the negative potential region. These concurrent changes eventually lead to the final waveform as shown in Fig. 6(a). In Fig. 6(a), the large spiky current peaks (i and iii) are observed only for virgin scans in negative and positive directions after allowing the spiky current peaks of the opposite signs, respectively. When potential sweeps are repeated in the same direction, the second sweeps produce small waves only (ii and iv), which reproduce the CV waves for Pt/poly-**1** before the deposition of PMeT, except for a residual small peak in iv. The CV waves in Fig. 6(a) represent the mediated redox reactions of PMeT by poly-**1**, and are essentially consistent with the electrochemistry of bilayer electrodes.[10,13,17–19]

The electropolymerization of BT at Pt/poly-**1** by potential cyclings occurs at potentials near $E^{\circ\prime}$ of poly-**1** as evidenced by the onsets of large current peaks (Fig. 4(b)). The galvanostatic electropolymerization of BT proceeds at potentials lower than +0.83 V (Fig. 5) which is slightly lower than the $E^{\circ\prime}$ of poly-**1**. This means that oxidation of BT (and hence the deposition of PBT) can be mediated by the poly-**1** layer, which should directly lead to the bilayer structure. However, for both modes of BT oxidations (i.e., by potential cyclings and by galvanostatic anodization) the occurrence of PBT at the platinum substrates was evidenced by the fact that the initial potential sweeps of the PBT-as-deposited electrodes in 0.1 M TBAP-acetonitrile showed the CV waves for PBT that was electrochemically accessed directly from the platinum substrates, in the same way as for the PMeT-deposited poly-**1** electrode described above. These observations, however, do not exclude the possibility that the anodization of BT is partly mediated by $[\mathrm{Ru(bpy)_3}]^{2+}$ centers in poly-**1**. The bilayer electrode, Pt/poly-**1**/PBT, was subsequently brought by repeated potential sweeps in 0.1 M

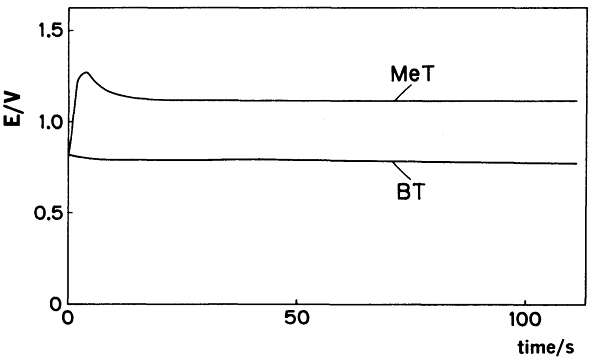


Fig. 5. Potential vs. *t* curves monitored on galvanostatic polymerizations of 3-methylthiophene (MeT) and 2,2′-bithiophene (BT) at Pt/poly-**1** electrodes immersed in 0.1 M tetrabutylammonium perchlorate-acetonitrile including 120 mM MeT (a) and 120 mM BT (b). Current densities are 275 $\mu\mathrm{A\,cm^{-2}}$ for both runs. The employed coverages of poly-**1** layers for (a) and (b) are 1.98×10^{-9} and 2.90×10^{-9} $\mathrm{mol\,cm^{-2}}$, respectively. For poly-**1** see text.

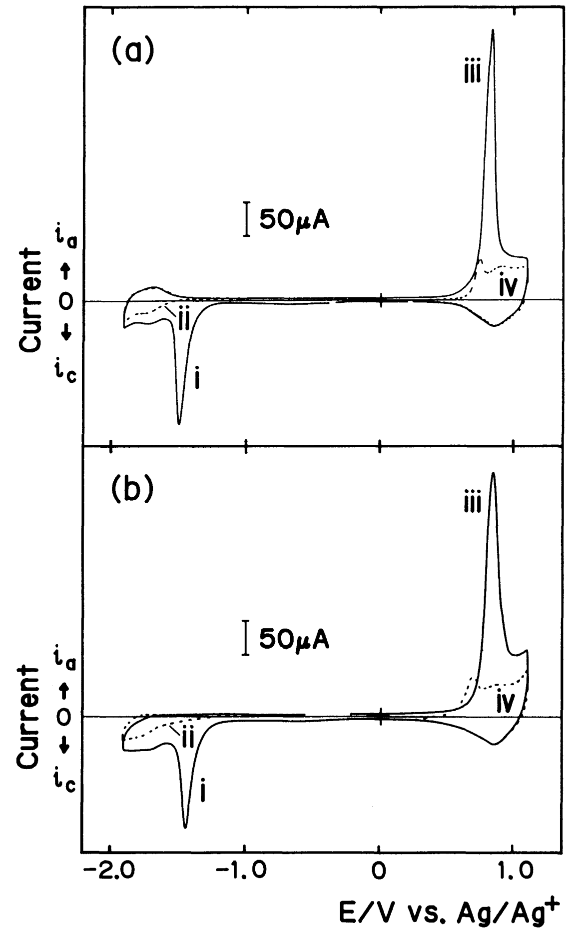
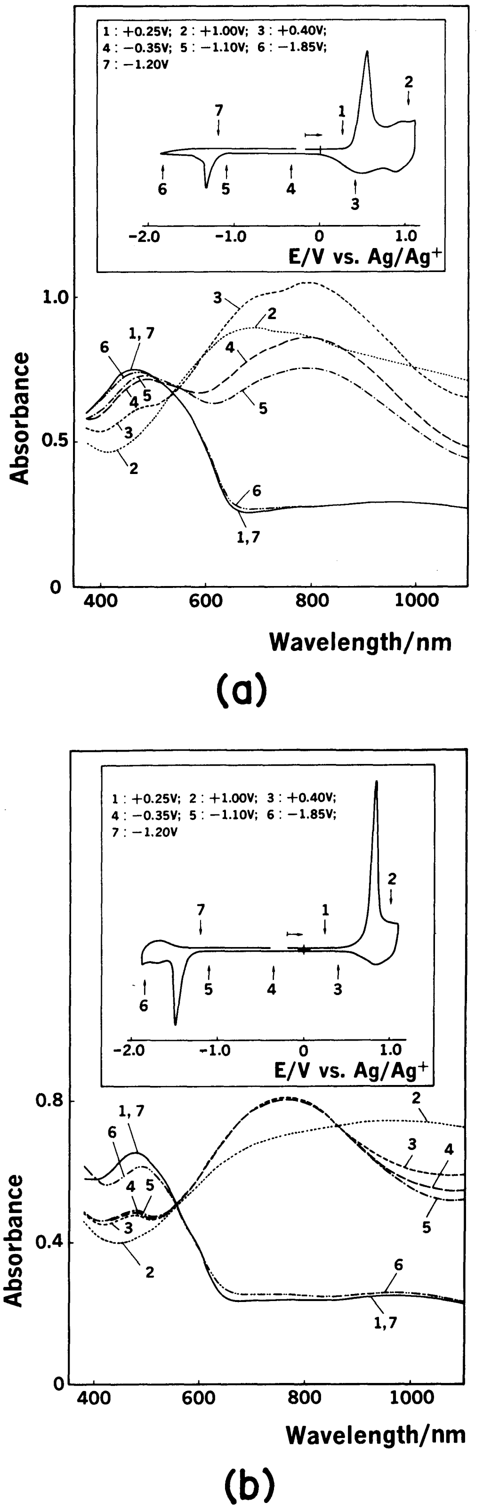


Fig. 6. Cyclic voltammograms for Pt/poly-**1**/poly(3-methylthiophene) (a) and Pt/poly-**1**/poly(2,2′-bithiophene) (b) bilayer electrodes in 0.1 M tetrabutylammonium perchlorate-acetonitrile. Coverages of the inner layer are 2.62×10^{-9} (a) and 2.58×10^{-9} (b) $\mathrm{mol\,cm^{-2}}$, respectively. Outer layers were deposited by galvanostatic polymerizations at current densities of 275 $\mu\mathrm{A\,cm^{-2}}$ and charge densities passed during the depositions of 32.4 $\mathrm{mC\,cm^{-2}}$ for both (a) and (b). For poly-**1** see text.

TBAP-acetonitrile, accompanying CV changes in the same way as for PMeT-deposited poly-**1** electrodes. The above electrochemical scheme in preparing bilayer electrodes — i) permeation of monomeric precursors of the outer layer through the first layer, ii) electropolymerization of the monomer at the surface of the substrate, iii) repeated potential sweeps in 'innocent' electrolytic solutions — is basically the same as that employed for the preparation of the bilayer electrodes with PP as the outer layer,[10] suggesting the extensive applicability of this scheme to other material systems. The above scheme, i—iii), contrasts with other processes employed in obtaining bilayer electrodes,[13,17—19] where the outer layer is deposited directly at the surface of the first layer, i.e., by mediated electropolymerizations of the monomer precursors by the first layer, or droplet evaporation of polymer solutions of the outer layer at the surface of the first layer. In step iii) phase separation occurs between poly-**1** and PMeT or PBT. This phase separation is consistently understood with that of the PP-based bilayer electrode and will be discussed in a separate paper.

Significant imbalance was found to exist between involved charges for anodic (>+0.60 V) and cathodic (<−1.25 V) peaks in the CVs of Pt/poly-**1**/PBT (Fig. 6(b)). The amount of charge involved in the cathodic peak is only 60—70% that of the anodic counterpart. Although precise quantitative arguments regarding the amount of charges are not possible due to the complexities arising from background currents and capacitive components of PBT, such an apparently large imbalance in charges has not been observed for Pt/poly-**1**/PP.[10] It was found from Q (charge densities) vs. V plot that the amount of the negative and positive charges were balanced by adding an amount of cathodic charges collected during the sweeps in the negative direction in the potential region more negative than +0.25 V. This can be reasonably explained by assuming a leakage of positive charges of the outer layer to the platinum substrate through the poly-**1** layer during the sweep in the negative direction. The significant overlapping of the distributions of the electrochemical density of states for PBT oxidation and 2+/3+ oxidation of poly-**1** is likely due to the nearness of their oxidation potentials each other (PBT: E_{pa}=+1.00 V vs. SSCE,[20] 2+/3+ of poly-**1**: $E^{\circ\prime}$=+0.875 V vs. Ag/Ag$^+$). Actually, substantial optical changes have been detected corresponding to the reduction of the PBT layer, when the applied potential is fixed at 0 V for 20 s after oxidizing the PBT layer by sweeping the potential of the platinum substrate, 0 V → +1.15 V → 0 V,[21] which is indicative of a positive charge leakage from PBT layer to the platinum substrate. Similar leakage behavior has also been observed, though less significantly, for PMeT. In contrast, the corresponding negative charge leakage has not been detected for both PBT and PMeT. This is also consistent with the above explanation. The charge leakage in a polymeric Fe(II) complex bilayer electrode has been similarly explained by Denisevich et al.[17] and Leidner et al.[19]



(a)

(b)

Fig. 7. In situ reflection spectra at Pt/poly-**1**/poly(3-methylthiophene) immersed in 0.1 M tetrabutylammonium perchlorate-acetonitrile during potential sweeps (scan rate: 50 mV s^{-1}, inset), before (a) and after (b) the repeated potential sweeps causing phase separation. The employed coverage of poly-**1** is 2.70×10^{-9} mol cm^{-2}. PMeT was deposited by passing 31.7 mC cm^{-2}. For poly-**1** see text.

Time-Resolved in Situ Reflection Spectra of Pt/Poly-1/PMeT and Pt/Poly-1/PBT. In situ reflection spectra of Pt/poly-**1**/PMeT during the potential sweeps at 50 mV s^{-1} before and after the phase separation are shown in Figs. 7(a) and (b), respectively. Each spectrum is taken within ca. 100 ms. During this period, the potential is swept ca. 5 mV. The absorption band centered at ca. 480 nm in **1** of Fig. 7(a) has been ascribed to the interband transition of PMeT.[2,6] Optical switching occurs on the potential sweep across the sharp oxidation peak of PMeT (**1**→**2**), i.e., loss of the interband absorption and the evolution of bands for 560 nm$<\lambda$. However, the sweep **2**→**5** is seen to regenerate the interband absorption with paralleled decrease of the absorption for 560 nm$<\lambda$. The subsequent sweep **5**→**6** nearly completes the backward changes. These optical changes imply that a major portion of the PMeT layer is electrochemically accessible directly from the platinum substrate, and that only a small portion of PMeT is electrochemically mediated by poly-**1** before the phase separation. These features are consistent with the concurrent CV (inset).

On the other hand, from the spectra of Fig. 7(b) it is evident that reversible optical switchings occur when the potential is swept across the sharp anodic and cathodic CV waves i.e., **1**→**2** and **5**→**6**. This means that the spectra of Fig. 7(b) give further evidence for the mediated electrochemical doping and undoping reactions of PMeT. The forward (doping) optical change (**1**→**2**) consists of the disappearance of the absorption band for interband transition and the evolution of bands for 560 nm$<\lambda$. Small backward increase in absorption below 560 nm is observed for **2**→**3**, while the absorption also increases for 560 nm$<\lambda<$870 nm. During the sweep **3**→**5**, absorption below 560 nm changes only slightly, while the absorption intensity decreases for 870 nm$<\lambda$. Throughout these changes, the isosbestic point is maintained, which is indicative of quasi-equilibria established in the present system in the time scale of the CV sweep (50 mV s^{-1}); this is surprising, since much longer durations of time have been required for the achievement of the quasi-equilibria in PTs deposited at metallic or other conducting substrates.[2,8]

It should be noted that the essentially consistent optical changes were observed with various modes of positive charge injections, i.e., linear sweep, or potential step with and without subsequent open-circuiting. Figure 8 shows the reflection spectra at Pt/poly-**1**/PMeT taken as follows: Positive charges were first injected by stepping the applied potential of the platinum substrate from 0 to +0.90 V. After the potential was held at +0.90 V for 1 s, the electrode was then opencircuited. The optical change **1**→**2** is due to the doping (oxidation) reaction upon the positive potential step, and the subsequent changes **2**→**3**—**6** occurred during 70 s after the open-circuiting. The observed spectral changes are similar to those for **1**→**2**→**3** in Fig. 7(b), where the backward increase of the absorption in the interband region is observed here again together with the 'unparalleled' forward increase for 560 nm$<\lambda<$870 nm. The optical spectra of a Pt/poly-**1** electrode were measured upon the electrochemical cycle to assess the electrochromic contribution of the inner layer to the observed changes in Figs. 7 and 8, since the potential cycling involves the redox reactions of the inner layer. Figure 9 shows the reflection spectra at Pt/poly-**1** obtained upon potential sweeps. The absorption band centered at 465 nm in Fig. 9(a) is due to the MLCT (metal-to-ligand charge transfer) which is lost upon the positive sweep causing the reaction,

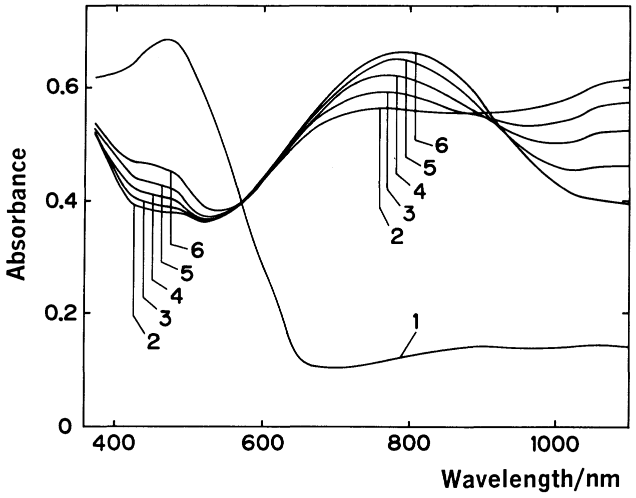


Fig. 8. In situ reflection spectra at a Pt/poly-**1**/poly(3-methylthiophene) bilayer electrode immersed in 0.1 M tetrabutylammonium perchlorate–acetonitrile. Potential was first stepped from 0 V (initial neutral state, spectrum **1**) to +0.90 V vs. Ag/Ag^+. After the potential was held there for 1 s, the electrode was open-circuited. Spectra, 2—6, were taken 1, 5, 13, 33, and 73 s after the open-circuiting, respectively. The coverage of poly-**1** is 2.60×10^{-9} mol cm^{-2}. 27.0 mC cm^{-2} was passed for deposition of PMeT. For poly-**1** see text.

$$[Ru(bpy)_3]^{2+} \xrightarrow{-e^-} [Ru(bpy)_3]^{3+}. \quad (1)$$

The spectral changes indicate that at least for 560 nm$<\lambda$, the absorption change caused by the inner layer upon the doping (positive) sweep is negligible, while the Reaction 1 can contribute to the spectral changes in the interband region of PMeT. Therefore, the spectral changes for $\lambda<$560 nm in Figs. 7(b) and 8 are the results of i) the Reaction 1, ii) the doping reaction of PMeT driven by $[Ru(bpy)_3]^{3+}$, and iii) the reactions between charged states in PMeT.

Well-defined band maxima centered at 670—680 nm and near 1000 nm are often observed in spectrum **2** in Fig. 7(b) among a number of tested electrodes. The transient occurrence of the bands is also seen in difference spectra upon positive charge injections by a potential step.[14] These characteristic changes are

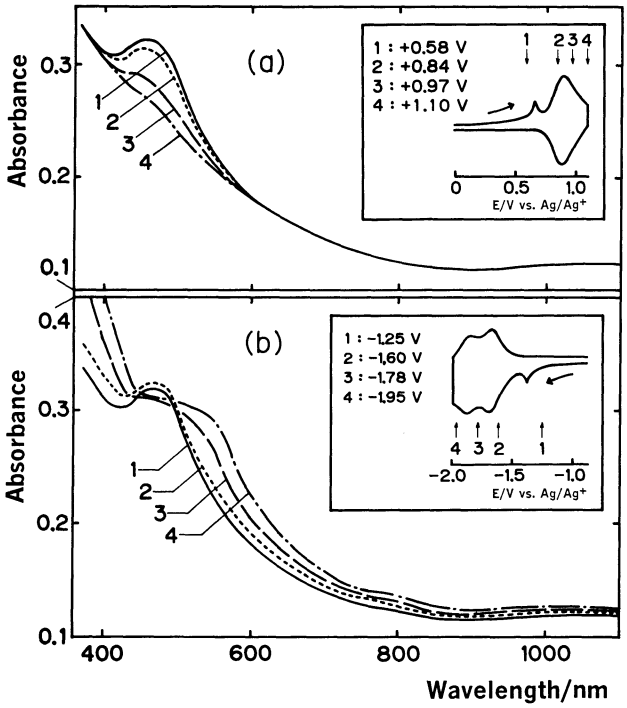


Fig. 9. In situ reflection spectra at Pt/poly-**1** (coverage: 2.90×10^{-9} mol cm^{-2}), immersed in 0.1 M tetrabutylammonium perchlorate-acetonitrile, taken during the potential sweeps (inset). For poly-**1** see text.

strikingly consistent with those reported by Kaneto et al. on very dilutely doped PT under static conditions[8] where the former two bands and the latter band are assigned to polaronic (ω_2 in Fig. 2) and bipolaronic (ω_3 in Fig. 2) transitions, respectively. Harbeke et al.[9] also reported on the similar spectral changes for PMeT at very low doping levels in equilibria, while they did not detect a band corresponding to the band at 670 nm in the present study. Hence, we conclude that the spectral changes of **2**→**3** in Fig. 7(b) and **2**→**3** of Fig. 8 are understood as follows; the polaron states are initially predominant upon doping, but are subsequently transformed to bipolarons due to the self-quenching reaction,

$$P^+ + P^+ \longrightarrow BP^{2+} \qquad (2)$$

where P^+ and BP^{2+} represent a polaron and a bipolaron, respectively. Although further experiments are needed to find the origin of the band centered at 670—680 nm, which is higher in energy than the bipolaronic transition, we assume that the band is due to the excitonic transitions which become prominent in the presence of polarons, as a result of strong interactions between excitons and polarons.

In a separate run, backward spectral changes are observed for $\lambda<560$ nm similar to Figs. 7(b) and 8 described above, even when the PMeT in the bilayer configuration is doped by applying a pulse potential, 0 V→ +0.90 V for 1 s →0 V vs. Ag/Ag$^+$.[22] The backward spectral relaxations subsequently take place in the time scale similar to Fig. 8. In this mode of potential application, the residual $[Ru(bpy)_3]^{3+}$ centers in the inner layer, after the mediated doping Reaction 3,

$$[Ru(bpy)_3]^{3+} + PMeT^{\circ} \longrightarrow [Ru(bpy)_3]^{2+} + P^+ \qquad (3)$$

where PMeT° denotes a neutral portion in a PMeT chain, are reduced back to the 2+ state at the electrode. Hence, the contribution of $[Ru(bpy)_3]^{3+}$ to the spectral changes for $\lambda<560$ nm is substantially negligible. This means that the mediated doping Reaction 3 is rapid compared to the Reaction 2, and that the backward spectral changes in $\lambda<560$ nm in Fig. 8 should be attributed principally to the Reaction 2. We assume that the backward increase in absorption for $\lambda<560$ nm in Fig. 8, and possibly in Fig. 7(b), is due to the increase in the neutral portion in the PMeT chains as a result of the Reaction 2 and the subsequent reduction of the bipolaron size. The latter effect would occur in the last stage of a series of relaxation processes upon charge injections.

Most of the spectral studies on PTs reported so far have been performed under static conditions based on relatively thick films ($\approx\mu$m). In contrast, the spectral changes for 560 nm$<\lambda$ of Figs. 7(b) and 8 represent dynamic processes in the course of achieving equilibrium within the PMeT layer. This scheme is enabled by the configuration in which a relatively thinner PMeT layer (<100 nm) is isolated from the substrate by the intervention of an electrically insulating but electrochemically active inner layer. Without the intervening layer, i.e., for Pt/PMeT electrodes, no isosbestic behavior was observed even at very low sweep rates (<5 mV s^{-1}) with similar PMeT thickness (<100 nm). Detection of the transient P^+ at Pt/PMeT was not successful with varying doping conditions because the spectral changes under the dynamic conditions were ambiguous and much less systematic, probably reflecting the manifold relaxation processes occurring within the PMeT layer. The charge injections via discrete electronic levels into the conducting polymers would generate charged states which are energetically more confined. These charged states should be able to relax more rapidly through less diversified relaxation pathways, giving rise to the isosbestic behavior in Fig. 7(b). This characteristic feature has allowed the detection of the transiently occurring polarons. Studies of electrochemically induced changes in conducting polymers based on the structure of the present study, i.e., substrate/electrochemically active film/conducting polymer film, would yield further insight into the charged states of the conducting polymers.

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22) Doping at lower potentials produces quasi-equilibrated spectral changes as shown in Fig. 2 of Ref. 14.