Electrochemical Polymerization and Depolymerization of 2,5-Dimercapto-1,3,4-thiadiazole. QCM and Spectroscopic Analysis

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Electrochemical oxidation of a dimercaptan, 2,5-dimercapto-1,3,4-thiadiazole (DMcT), to a polydisulfide (DMcT polymer) and electrochemical reduction of the polydisulfide at a carbon electrode and an indium−tin oxide electrode have been studied in 0.1 M LiClO₄−acetonitrile by means of an in situ electrochemical quartz crystal microbalance and in situ spectroelectrochemistry, respectively. It is observed that the polymerization potential is more positive than the dimerization potential. Both the potentials at which DMcT dimer and DMcT polymer are formed are made more negative by the presence of a base. The potential at which the DMcT polymer is reductively depolymerized is also shifted in the negative direction in the presence of a base. The experiments also show that the DMcT polymer reacts with DMcT monomer under open-circuit conditions. This results in dissolution of the polymer in the presence of the monomer. The results also suggest that the product of the redox reaction is the DMcT dimer. Base is shown to hinder this reaction.

Introduction

The dimercaptan, 2,5-dimercapto-1,3,4-thiadiazole (DMcT, Figure 1), has been studied as a cathode-active material for lithium secondary batteries.[1−6] We have developed high-energy-density composite cathodes by coupling DMcT with the conducting polymer, polyaniline.[4−6] It is believed that DMcT is polymerized upon oxidation and that the resulting polymer is depolymerized upon reduction (Figure 1). However, these processes are not yet well understood. In particular, differentiation between dimerization and polymerization has been difficult. Although electrochemical polymerization and depolymerization of DMcT at a gold electrode have been studied with the aid of an electrochemical quartz crystal microbalance (EQCM),[7,8] it is hard to observe reproducible and well-defined behavior at gold, due probably to interaction between gold and DMcT including formation of an adsorbed monolayer and dissolution of gold.

In the present work, we have used a carbon-coated quartz crystal to observe reproducible polymerization and depolymerization processes by an in situ EQCM technique. A transparent indium−tin oxide (ITO) electrode is also used to observe dimerization, polymerization, and depolymerization by means of in situ UV−visible spectroelectrochemistry. Additionally, effects of base and acid on those processes are studied because electrochemistry of DMcT is known to depend strongly on basicity and acidity of the solution.[7−14]

Experimental Section

Materials. DMcT (98%) and LiClO₄ (99.99%) were purchased from Aldrich. HPLC-grade acetonitrile was stored over 3 Å molecular sieves. DMcT polymer was synthesized by oxidizing DMcT in methanol (0.15 M) with equimolar iodine at room temperature. The resulting polymer was thoroughly washed with water, methanol, and acetonitrile. Quartz crystal plates (5 MHz, 25 mm diameter, from Valpey-Fisher) were modified with (3-mercaptopropyl)trimethoxysilane by a method described by Goss *et al.*[15] Gold films (6.2 mm diameter, 200 nm thick) were deposited on both sides of the quartz plate by evaporation. To obtain a carbon-coated quartz crystal, a 2-µL aliquot of aqueous carbon paint (T-602, Nippon Kokuen, Japan, diluted 10-fold with water) was spread on one of the gold electrodes and then baked at 100 °C for 60 min. The carbon-coated quartz oscillator was baked again at 100 °C for 30 min just before use.

EQCM Measurements. The carbon-coated electrode of the crystal was in contact with the electrolyte solution (0.1 M LiClO₄−acetonitrile, 20 mL) and used as a working electrode. Nitrogen gas was flushed through the solution for at least 10 min before experiments. The quartz crystal was connected to a feedback oscillator (built in-house), and the oscillation frequency was measured with a frequency counter (Philips PM-6654). The working electrode was connected also to the ground and to a Wenking style potentiostat (built in-house). Reference and counter electrodes were a Ag/AgCl/NaCl(saturated) and platinum wire, respectively. The potential of the working electrode was scanned between +1.5 and −1.5 V vs Ag/AgCl at 10 mV/s, starting from −0.4 V in the positive direction (unless otherwise noted).

Spectroelectrochemical Measurements. A thin-layer cell was constructed from an ITO-coated glass plate, a normal glass plate, and a Teflon spacer (0.1 mm thick). The electrolyte solution (0.1 M LiClO₄−acetonitrile) containing 2 mM DMcT was introduced to the cell by capillarity from a dish, in which reference and counter electrodes were set.[16] Nitrogen gas was flushed through the solution for about 15 min before experiments. The ITO working electrode (6.4 cm²) was connected to a potentiostat (PS-07, Toho Giken, Japan). Reference and counter electrodes were a Ag/Ag⁺ separated by a Vycor glass, of which the potential was +0.22 V vs Ag/AgCl, and a platinum wire, respectively. The potential of the working electrode was scanned at 1 mV/s, starting from a rest potential in the positive direction. UV−visible spectra were obtained by using a U-Best-55 spectrophotometer (JASCO, Japan). The scan rate of the wavelength was 1000 nm/min (500−300 nm).

Polymerization of 2,5-Dimercapto-1,3,4-thiadiazole

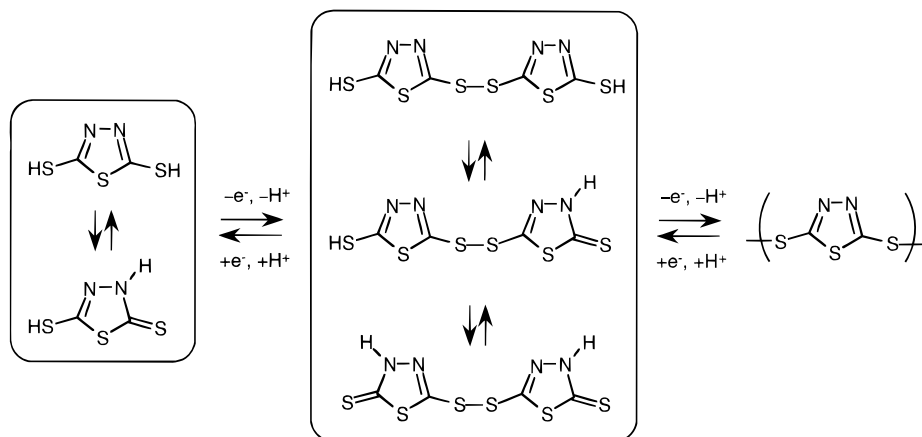*J. Phys. Chem. B, Vol. 101, No. 38, 1997* **7557**

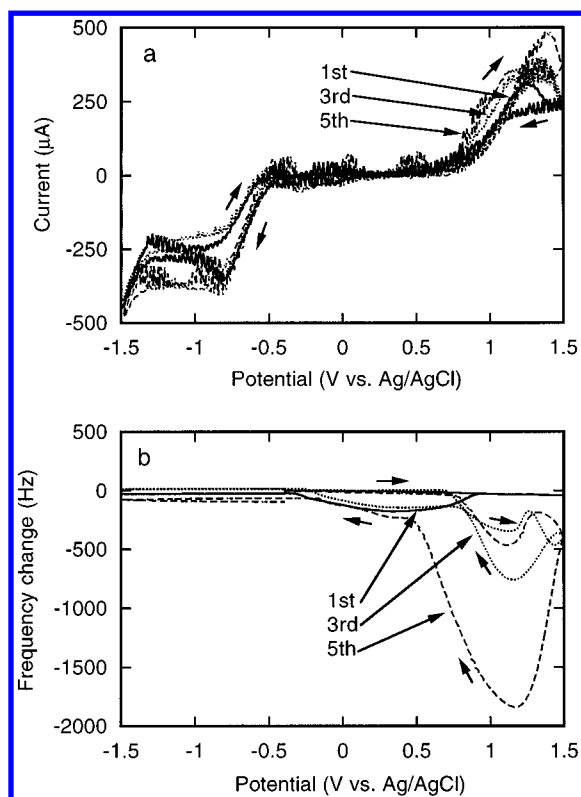**Figure 1.** Proposed redox reactions of DMcT. Tautomerization is also shown.

Figure 2. Typical EQCM results obtained at a gold electrode in 0.1 M LiClO$_4$−acetonitrile containing 10 mM DMcT. Scan rate is 10 mV/s. (a) Cyclic voltammograms and (b) frequency change−potential curves.

A normal optical cell (2 cm thick) was used for in situ observation of light scattering (at 500 nm) by DMcT polymer deposited on the ITO surface (1.2 cm^2). The potential was cycled between +1.5 and −1.5 V vs Ag/AgCl at 10 mV/s, starting from a rest potential in the positive direction.

Results and Discussion

EQCM Results at a Gold Electrode. Prior to examination of DMcT electrochemistry at a carbon electrode, it was examined at a gold electrode for comparison. EQCM experiments were performed in 0.1 M LiClO$_4$−acetonitrile containing 10 mM DMcT using a quartz crystal oscillator with gold electrodes. Under these conditions the behavior of the resonance frequency was not reproducible. Figure 2 shows typical EQCM behavior. In the first potential cycle in the positive direction, only a slight frequency decrease was observed at a potential positive of +0.6 V vs Ag/AgCl, while a significant anodic

current was observed. The anodic current must be due to the oxidation of DMcT. Among the oxidized DMcTs (*i.e.*, DMcT polymer and oligomers), the most soluble one is the DMcT dimer. The solubility of the DMcT dimer in 0.1 M LiClO$_4$−acetonitrile is 2−3 mM at least. Under the conditions of the present experiment, the maximum concentration of DMcT dimer at the electrode surface is less than 5 mM, on the assumption that the diffusion coefficient of DMcT dimer equals that of DMcT monomer. Thus, some DMcT dimer might precipitate, though most of the produced DMcT dimer was dissolved since the frequency decrease was small. After the potential scan was reversed at +1.5 V (*i.e.*, in the negative potential scan), however, a significant frequency decrease started at around +1.0 V. Since a frequency decrease means a mass increase, it should reflect deposition of electrochemically oxidized DMcT.

After a few cycles, the mass gains increased steadily, even showing deposition during the positive scan. This suggests that a small amount of the deposited DMcT polymer may stay on the gold surface even after the negative scan to −1.5 V, with this material serving as nucleation centers for further deposition of the polymer at the gold surface. During experiments involving repeated cycling, the frequency steadily decreased after each cycle, indicating that the material was building up on the surface. It has been previously demonstrated by means of cyclic voltammetry that the DMcT polymerization is facilitated by the deposited DMcT polymer at a glassy carbon electrode.[17] The irreversible frequency changes observed in the present case were in the range +10 to −100 Hz, which indicates that −3 × 10^{-9} to 3 × 10^{-8} mol/cm^2 (monomer unit-based) of DMcT polymer deposited in each cycle. Similar behavior was also observed at a carbon electrode (see below). This has also been verified by means of Raman spectroscopy.[18] However, the amount of the polymer deposited irreversibly in each cycle was 9 × 10^{-9} to 1.3 × 10^{-7} mol/cm^2 for the carbon electrode; the irreversible deposition on a gold surface is more difficult than that on a carbon surface. The poor reproducibility at gold electrodes may be caused by such effects. Additionally, DMcT may facilitate electrochemical dissolution of gold and DMcT may form an adsorbed monolayer on the gold surface. Actually, the dissolution of gold was observed in the presence of DMcT occasionally. These factors might also be responsible for the poor reproducibility.

A frequency increase, which should reflect dissolution or depolymerization of the DMcT polymer, was seen during the negative scan at a potential of +1.1 V, even though an anodic current still flowed (Figure 2, 3rd and 5th cycles). These results are similar to those reported previously, in which a large frequency increase was observed while only a small cathodic current flowed.[7,8] In our experiments, no electrochemical
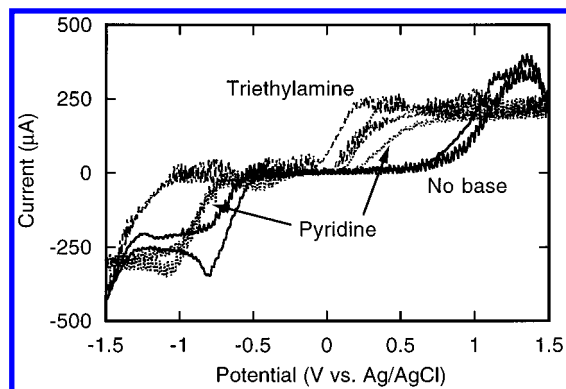
Figure 3. Cyclic voltammograms obtained at a gold electrode in 0.1 M LiClO$_4$−acetonitrile containing 10 mM DMcT. Those obtained in the presence of 20 mM pyridine or 20 mM triethylamine are also shown. Scan rate is 10 mV/s.

reaction seemed to be necessary for the apparent dissolution or depolymerization, suggesting a reaction with solution-phase species. This is discussed in further detail in the last section.

At potentials of about −0.5 V, cathodic currents are observed with no accompanying frequency change. These may be ascribed to the reduction of DMcT to DMcT$^-$ and $^1/_2$H$_2$,[14] since those cathodic currents were observed even if the potential was scanned between 0 and −1.5 V, during which no anodic current was observed.

EQCM Results at a Gold Electrode: Effects of Bases. The addition of pyridine or triethylamine (10, 20, and 40 mM) modified the cyclic voltammetry (Figure 3) and suppressed the frequency changes. The oxidation potential of DMcT was shifted from +0.6 V to +0.1 V in the presence of 20 mM pyridine or 10 mM triethylamine, and to −0.1 V in the presence of 20 mM triethylamine. These negative shifts have already been reported elsewhere.[7−14] The pK_a values of DMcT are −1.4[19] to 2.1[14] and 7.5.[14,19] On the other hand, the pK_a values of pyridinium ion and triethylammonium ion are 5.3 and 11.0, respectively.[20] Therefore, one of the two −SH groups of most DMcT molecules may be deprotonated in the presence of ≥10 mM pyridine or ∼10 mM triethylamine (note that the DMcT concentration is 10 mM), although there is some uncertainty because those pK_a values are not for acetonitrile solutions. Here we refer to the anion as DMcT$^-$. In the presence of ≥20 mM triethylamine, the two −SH groups of most DMcT molecules should be deprotonated (DMcT^{2-}). That is, we assume that DMcT, DMcT$^-$, and DMcT^{2-} are oxidized at potentials of +0.6, +0.1, and −0.1 V, respectively, from Figure 3.

During a positive scan, the frequency slightly decreased at a potential of +0.5 V vs Ag/AgCl in the presence of pyridine or triethylamine. The frequency decrease at +1.5 V was less than 50 Hz. This suppression of the frequency change suggests that the polymerization of DMcT or precipitation of DMcT polymer was inhibited in the presence of base. However, the anodic current was not suppressed, meaning that dimerization was not inhibited. As described below, the addition of a base did not interfere with the deposition of the polymer at a carbon electrode. This difference may be explained in terms of an adsorbed monolayer of DMcT, which may form on the gold surface. Since the monolayer should be negatively charged in the presence of a base, further oxidation of the electrochemically generated, negatively charged dimer or oligomer (*i.e.*, polymerization) may be suppressed at such a surface. Thus, we speculate that the formation of insoluble polymer is not efficient at the gold surface.

Reduction currents were observed during negative scans even in the presence of a base, where only a small amount of DMcT
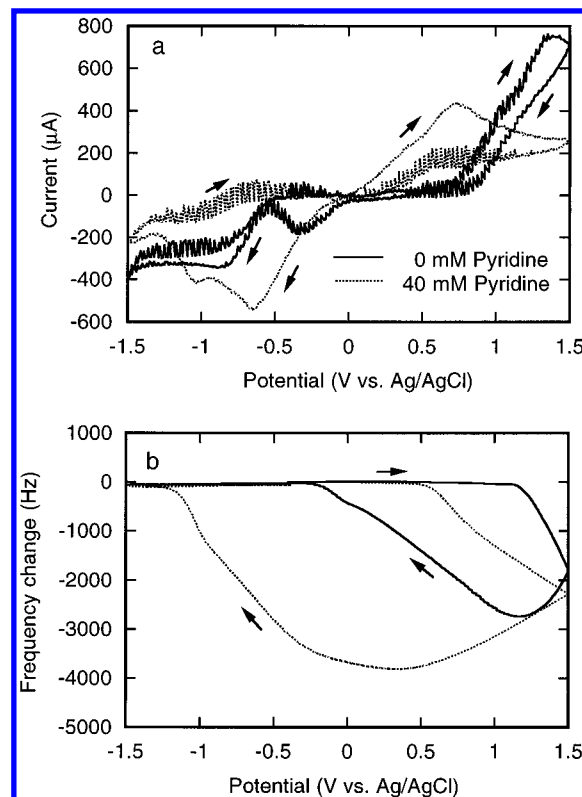
Figure 4. EQCM results obtained at a carbon electrode in 0.1 M LiClO$_4$−acetonitrile containing 10 mM DMcT. Those obtained in the presence of 40 mM pyridine are also shown. Scan rate is 10 mV/s. (a) Cyclic voltammograms and (b) frequency change−potential curves.

polymer was deposited (Figure 3). This supports our speculation that this current can be ascribed to the reduction of DMcT. The potential for this reaction shifted in the negative direction in the presence of pyridine, as expected.[14]

EQCM Results at a Carbon Electrode. Similar experiments were performed using a QCM with a carbon paint-coated working electrode in a 0.1 M LiClO$_4$−acetonitrile solution containing 10 mM DMcT (Figure 4). The reproducibility was much better than for the experiments with the gold electrode; almost the same behavior was seen in each potential cycle. Also, independently prepared carbon-coated quartz crystals provided similar results. A slight decrease of the resonance frequency and a small anodic current were seen at a potential positive of +0.5 V vs Ag/AgCl. Although significant oxidation current flowed after the potential passed +0.7 V, the frequency decrease was still smaller than 100 Hz at potentials less positive than +1.2 V, presumably because most of the anodic current is producing the soluble DMcT dimer. At a potential more positive than +1.2 V, a significant frequency decrease was observed; DMcT polymer was formed and precipitated on the electrode surface. The equivalent mass of the deposited species is calculated from the frequency decrease and the passed charge to be 50−55 g/(mol electron). Since the formula weight of the monomer unit of DMcT polymer is 148 g/mol and the polymerization is a two-electron reaction, the polymerization/deposition efficiency is about 70%. The low efficiency may be due to the transport of soluble dimer away from the solution−electrode interfacial region.

During the potential scan in the negative direction, the frequency increased at potentials negative of +1.2 V, even though a cathodic current did not flow until a potential of 0.0 V. Thus, the apparent dissolution or depolymerization of the deposited DMcT polymer proceeded without consumption of electrons similarly to the case of the gold electrode, once again

Polymerization of 2,5-Dimercapto-1,3,4-thiadiazole

J. Phys. Chem. B, Vol. 101, No. 38, 1997 **7559**

suggesting reaction of the polymer with a solution-phase species. The reduction peak observed at -0.3 V must correspond to electrochemical reduction of DMcT polymer. Cathodic current continued to flow even after the frequency had almost reverted to the initial value (-0.3 to -0.5 V). This may be because the polymer and oligomers that had detached from the electrode surface were still reduced electrochemically. The reduction current observed at a potential more negative than -0.6 V was not accompanied by any frequency change. It can be ascribed to the reduction of DMcT, as described above.
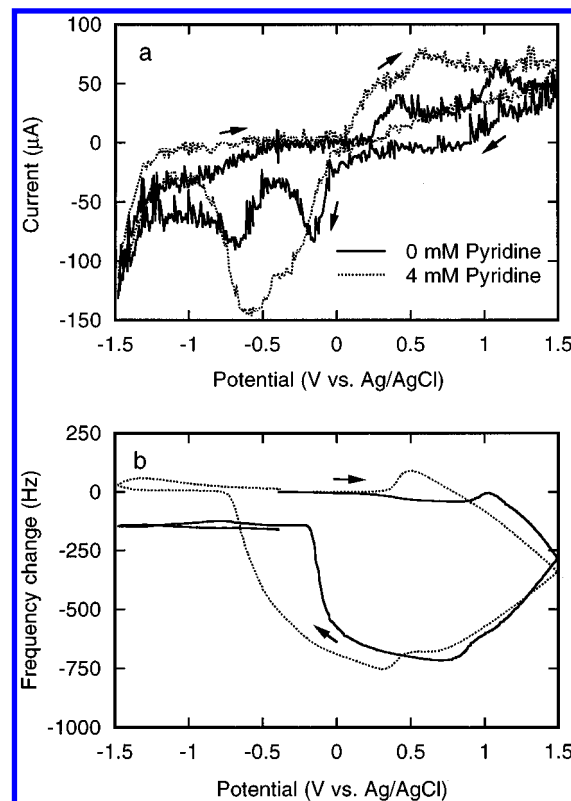
EQCM Results at a Carbon Electrode: **Effects of Bases.** The electrochemical behavior of DMcT (10 mM) in the presence of pyridine (10, 20, and 40 mM) was also examined (Figure 4 shows the 40 mM case). As described above, one of the two $-$SH groups of most DMcT molecules should be deprotonated under these conditions, producing DMcT$^-$. A significant oxidation current accompanied by a slight frequency decrease was seen at potentials positive of 0.0 V vs Ag/AgCl. Most of the electrochemical reaction occurring at this potential is probably oxidation of DMcT to the soluble DMcT dimer. This conclusion basically agrees with previous speculations.[7,8,14] In the presence of pyridine, DMcT polymer was found to deposit at potentials positive of $+0.5$ V. Thus, the addition of pyridine makes both the dimerization potential and the polymerization less positive than in the absence of base. Also, the addition of pyridine suppressed the apparent open-circuit dissolution or depolymerization (this is discussed in the last section). Thus, currents for reduction of the DMcT polymer are larger at higher pyridine concentrations, presumably because more of the polymer remains on the surface due to slower loss from these solution-phase processes. In addition, the reduction potential of the DMcT polymer is shifted in the negative direction upon addition of pyridine.

Effects of triethylamine were also examined. In the presence of 10 mM triethylamine, conditions under which most of the DMcT molecules (10 mM) exist as DMcT$^-$, the behavior was similar to that in the presence of pyridine; an anodic current with a slight frequency decrease was seen at a potential more positive than 0.0 V, a significant frequency decrease started at potentials positive of $+0.5$ V, and the reduction peak current for the electrochemical depolymerization was seen at around -0.8 V. In the presence of ≥ 20 mM triethylamine, an oxidation current started to flow at -0.2 V, and a significant frequency decrease started at potentials positive of $+0.4$ V. Thus, the dimerization and polymerization potentials were negatively shifted. However, oxidation of triethylamine or its impurity interfered with the polymerization reaction of DMcT. Owing to this effect, electrochemical reduction of the polymer was not clearly observed.

EQCM Results at a Carbon Electrode: **Effects of an Acid.** Cyclic voltammetry was conducted in a 0.1 M LiClO$_4-$acetonitrile solution containing 10 mM DMcT and 10 mM methanesulfonic acid to examine the effect of an acid on the electrochemistry of DMcT. The slight frequency decrease at potentials below $+1.0$ V vs Ag/AgCl was not observed in this case. The small frequency decrease and anodic current previously observed at this potential were attributed to trace amounts of DMcT$^-$. In the presence of acid this response is not observed, because the acid maintains the DMcT$^-$ concentration at negligibly low levels. The addition of methanesulfonic acid made no other significant difference except a large cathodic current accompanied by a large frequency decrease at potentials negative of -0.2 V. We believe these effects are due to proton reduction and the consequent evolution of hydrogen gas.

Figure 5. EQCM results obtained at a carbon electrode in 0.1 M LiClO$_4-$acetonitrile containing 1 mM DMcT. Those obtained in the presence of 4 mM pyridine are also shown. Scan rate is 10 mV/s. (a) Cyclic voltammograms and (b) frequency change$-$potential curves.

**EQCM Results at a Carbon Electrode**: **Effects of Water.** The addition of water ($10-160$ mM) to the 10 mM DMcT solution led to only small differences. The anodic current and frequency decrease in the range 0 to $+0.9$ V vs Ag/AgCl (in the positive potential scan) were larger. This may be explained in terms of DMcT deprotonation promoted by water; DMcT$^-$ is oxidized to its dimer or even to polymer in that potential region. However, after the potential passed $+0.9$ V, the frequency increased to the initial value once and then decreased significantly again at ca. $+1.1$ V. This behavior may be due to oxidation of water; the protons generated by oxidation of water may facilitate the depolymerization of DMcT polymer, or oxygen bubbles may dislodge the polymer. Since we did not observe dissolution of chemically polymerized DMcT in the presence of 10 mM methanesulfonic acid (see the preceding section), the former does not seem plausible.

EQCM Results at a Carbon Electrode: **Diluted DMcT Solutions.** Decreasing the DMcT concentration produced a qualitative change in the responses (Figure 5). First, the anodic current observed between 0 and $+0.7$ V vs Ag/AgCl was not negligible compared to the current at $+0.7$ to $+1.5$ V even in the absence of a base. As mentioned above, this current can be ascribed to oxidation of deprotonated DMcT (DMcT$^-$), which is produced by deprotonation of DMcT by a basic impurity in the supporting electrolyte. At lower concentrations, this effect is more pronounced because the relative concentration of this impurity is higher compared to the DMcT concentration. One also observes the frequency decrease (mass gain) that corresponds to deposition of the polymer produced during this oxidation. The irreversible deposition of DMcT polymer in each cycle for the 1 mM DMcT solution was 5×10^{-8} to 8×10^{-8} mol/cm^2 (monomer unit-based), which is close to the value for the 10 mM solution (9×10^{-9} to 1.3×10^{-7} mol/cm^2 as described above). Second, the apparent open-circuit dissolution
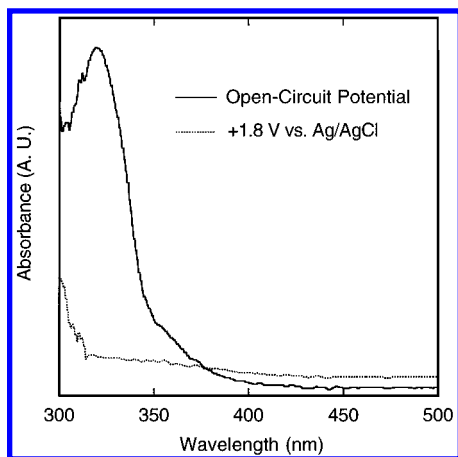
Figure 6. UV−visible spectra of 0.1 M LiClO₄−acetonitrile containing 2 mM DMcT in the thin-layer spectroelectrochemical cell (ca. 0.1 mm thick) with an ITO electrode before electrochemical treatments (open circuit) and at +1.8 V vs Ag/AgCl (after potential scan from the open-circuit potential at 1 mV/s).

or depolymerization of DMcT polymer was slower. Third, the reduction peak current at −0.2 V was large, and it was accompanied by a large frequency increase (mass loss). This should be a consequence of a reduction in the rate of the open-circuit dissolution or depolymerization process; most of the electropolymerized DMcT remained on the electrode during the negative scan. At a DMcT concentration of 10 mM, most of the DMcT polymer was lost by the open-circuit process before the potential reached 0 V, at which the polymer can be electrochemically depolymerized, as described above. Since DMcT seems to facilitate the open-circuit dissolution or depolymerization process, it may be a reaction of DMcT polymer with DMcT monomer.

The effects of pyridine and triethylamine (1, 2, and 4 mM) were also examined (Figure 5 shows the case of 4 mM pyridine). Negative shifts of the depolymerization potential as well as the dimerization and polymerization potentials were obvious in both the pyridine and triethylamine cases. As can be seen in Figure 5, these bases (pyridine and triethylamine) suppressed the irreversible deposition, though this was not clear at 10 mM DMcT. This may be explained in terms of solubility of the DMcT oligomers and/or polymer. That is, the pyridinium and triethylammonium salts of them may be more soluble than the lithium salts. An additional possibility is electrostatic repulsion between the negatively charged electrode surface and the anionic end groups of the DMcT polymer and oligomers.

Spectroelectrochemical Results at an ITO Electrode. In situ UV−visible spectroelectrochemical measurements were performed by using the thin-layer cell (ca. 0.1 mm thick) with a transparent ITO electrode. The potential was cycled at 1 mV/s. Figure 6 shows the spectrum obtained for 0.1 M LiClO₄−acetonitrile containing 2 mM DMcT at a rest potential before the potential cycling and that obtained at +1.8 V vs Ag/AgCl. The peak at 320 nm is ascribed to DMcT monomer.[12] After the potential scan was started from the open-circuit potential (0.0 V in this case) in the positive direction, a gradual decrease in the absorbance at 320 nm and an increase in the anodic current were observed (Figure 7a,b). Those changes were accelerated above +0.8 V. The decrease in the absorbance should be due to the consumption of DMcT monomer which is responsible for the absorption at 320 nm. Figure 7b also depicts changes in the absorbance at 330 nm, at which DMcT dimer has an absorbance peak. On the basis of the difference in the curves for the absorbance at 320 nm and that at 330 nm, we
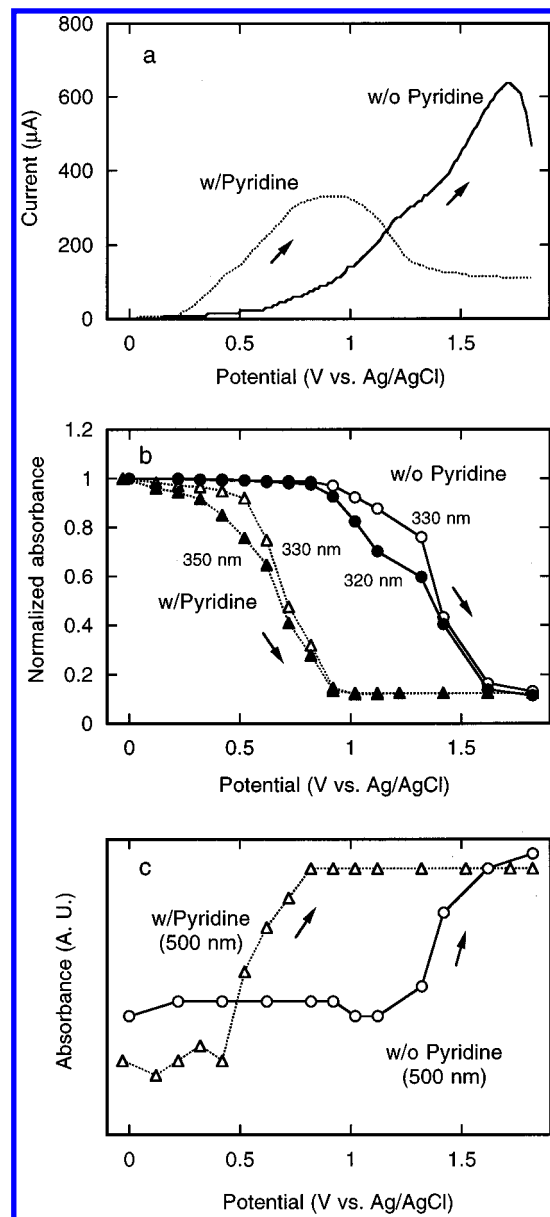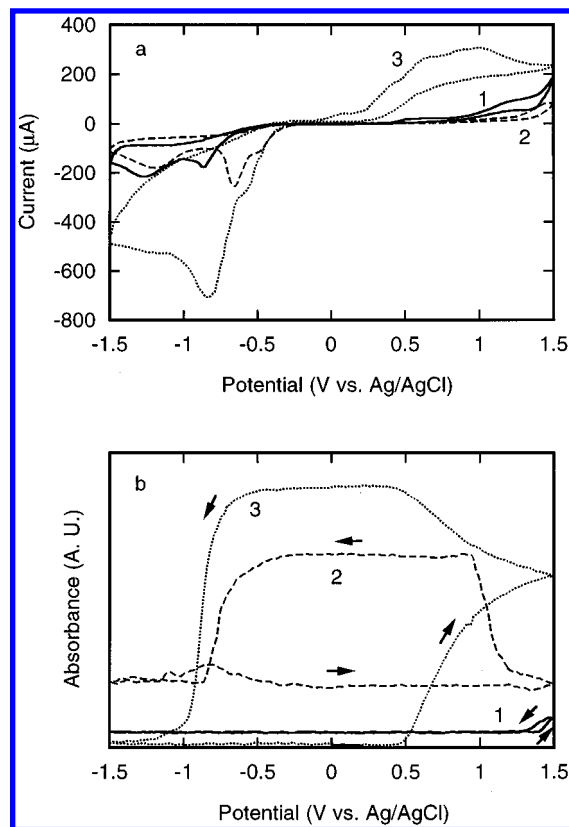

Figure 7. Changes in the anodic current (a), normalized absorbance at 320, 350, and 330 nm (b), and absorbance at 500 nm (c) during potential scan in 0.1 M LiClO₄−acetonitrile containing 2 mM DMcT at 1 mV/s. The thin-layer cell with an ITO electrode is used. Those obtained in the presence of 4 mM pyridine are also shown.

presume that the dimer is preferably generated by the DMcT oxidation at more negative potentials than +1.3 V.

The absorbance all across the visible region increased above +1.2 V (Figure 7c shows changes in the absorbance at 500 nm). This change, which is shown in Figure 6, should be caused by scattering of the incident light by the DMcT polymer deposited on the electrode surface. This suggests that the polymerization proceeds at potentials positive of +1.2 V. The fact that scattering is observed reveals that the deposit has roughness features comparable to the wavelength of the light.

The anodic charge passed during the electrolysis of DMcT (0.0 to +1.8 V) was 360 mC. Since charge needed for complete oxidation of DMcT in the thin-layer part of the cell to its polymer (two-electron reaction) is 25 mC, the DMcT oxidation primarily occurs at the lower edge of the ITO electrode, at which DMcT is facilely supplied from the underneath dish. Owing to the depletion of DMcT in the thin layer and a consequent supply of DMcT from the dish, it is difficult to study the reduction process with this experimental system.

Figure 8. Changes in the anodic current (a) and absorbance at 500 nm (b) during potential cycling in 0.1 M LiClO$_4$−acetonitrile containing 1 mM DMcT (1), 0.5 mM DMcT dimer (2), or 1 mM DMcT + 2 mM pyridine (3) at 10 mV/s. The normal cell (2 cm thick) with an ITO electrode is used.

The light scattering by DMcT polymer deposited on the ITO surface was monitored at 500 nm during cyclic voltammetry (10 mV/s) in the normal optical cell (2 cm thick), in which mass transfer processes are not as complicated as in the thin-layer experiment. Figure 8 depicts the results for a 1 mM DMcT solution (curve 1). In this case, the deposition of polymer was observed at a more positive potential than +1.4 V. The deposited polymer vanished at +1.3 V on the return scan, where anodic current still flowed. Thus, the smooth diffusion seems to facilitate the apparent open-circuit dissolution or depolymerization. This supports our speculation that this is a reaction of DMcT polymer with DMcT monomer. Incidentally, the irreversible deposition was not observed.

We also used 0.5 mM DMcT dimer instead of 1 mM DMcT monomer (Figure 8, curve 2). Residual polymer, which may be suspended in the solution, is presumably responsible for the relatively high background absorbance. The absorbance at 500 nm increased above +1.3 V (Figure 8b). The increase was accelerated from +1.2 V in the negative scan, and it continued until the potential reached +0.9 V. Residual monomer in the solution may have retarded the polymerization in the initial region, and the polymerization may have been facilitated after the monomer was depleted in the diffusion layer, since the reaction between the polymer and the monomer may result in the polymer dissolution. The depolymerization was seen at potentials negative of −0.3 V, where the cathodic current was seen. That is, the apparent open-circuit dissolution or depolymerization does not occur in the dimer solution. In the dimer solution, the open-circuit potential of the ITO electrode (+80 mV) was more positive than that in the monomer solution (0 mV). This is in line with our speculation that the dimerization potential of DMcT is more negative than the polymerization potential.

TABLE 1: Time Needed for the Apparent Dissolution of DMcT Polymer[a] in DMcT Solutions[b]

[DMcT] (mM)	[pyridine] (mM)	time (min)
0	0	unchanged[c]
1	0	21
2	0	4.3
5	0	1.2
10	0	0.5
1	2	>60
2	4	25
5	10	2.8
10	20	1.7

[a] Deposited on an ITO electrode by electrochemical oxidation of DMcT at +1.8 V vs Ag/AgCl for 3 min. Observed by absorbance at 500 nm. [b] 0.1 M LiClO$_4$−acetonitrile containing DMcT and pyridine. [c] The absorbance at 500 nm was unchanged at least for 20 min.

Spectroelectrochemical Results at an ITO Electrode: Effects of Bases. As for the experiment using the thin-layer cell (2 mM DMcT), the addition of 4 mM pyridine made the apparent dimerization and polymerization potential more negative (0.0 and +0.5 V vs Ag/AgCl, respectively) (Figure 7). It was revealed from the changes in the absorbance at 350 nm, which features DMcT$^-$,[12] and that at 330 nm that the primary product of the electrochemical oxidation of DMcT is DMcT dimer at potentials more negative than +0.5 V (Figure 7b).

As for the experiment using the normal cell (2 cm thick) for a 1 mM DMcT solution containing 2 mM pyridine, the apparent open-circuit dissolution−depolymerization was negligible (Figure 8, curve 3). Thus, it is obvious that the apparent dissolution−depolymerization is decelerated by pyridine, as described above. The open-circuit potential was more negative than that in the absence of pyridine by ca. 30 mV.

Reaction of DMcT Polymer with DMcT Monomer. We used chemically synthesized DMcT polymer to study the open-circuit dissolution or depolymerization process. The polymer was immersed in (1) 0.1 M LiClO$_4$−acetonitrile and (2) 0.1 M LiClO$_4$−acetonitrile containing 10 mM DMcT and (3) 0.1 M LiClO$_4$−acetonitrile containing 10 mM methanesulfonic acid under air. DMcT polymer apparently dissolved in solution 2 within 1 min, whereas no dissolution was observed for solutions 1 and 3. This indicates that DMcT caused the apparent dissolution or depolymerization of DMcT polymer and that protons liberated from DMcT by its polymerization are not responsible for that.

To study this process further, we also conducted spectroelectrochemical measurements. DMcT polymer was deposited on an ITO electrode (1.2 cm^2) at +1.8 V vs Ag/AgCl in 0.1 M LiClO$_4$−acetonitrile containing 2 mM DMcT for 3 min, and then the electrode was transferred to 0.1 M LiClO$_4$−acetonitrile containing 0−10 mM DMcT and 0−20 mM pyridine (Table 1). The electrochemically synthesized DMcT polymer was also apparently dissolved or depolymerized in the presence of DMcT. This process was faster at a higher DMcT concentration, whereas pyridine retarded it. In a 1 mM DMcT dimer solution, only a partial dissolution (ca. 20%), which may be due to residual DMcT monomer, was observed. Those results are in line with those for the above-mentioned EQCM and spectroelectrochemical experiments.

A plausible explanation for those observations is a reaction between the polymer and monomer to give DMcT dimer, which is soluble in acetonitrile (Figure 9). On the basis of the QCM and spectroelectrochemical results, we can assume that the redox potential for the monomer−dimer couple is more negative than that for the dimer−polymer couple. If this is the case, the above-mentioned "proportionation" reaction is possible from the
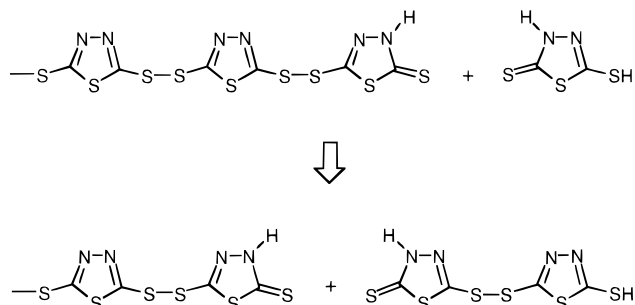
Figure 9. Proposed mechanism for the reaction of DMcT polymer with DMcT monomer yielding DMcT dimer.
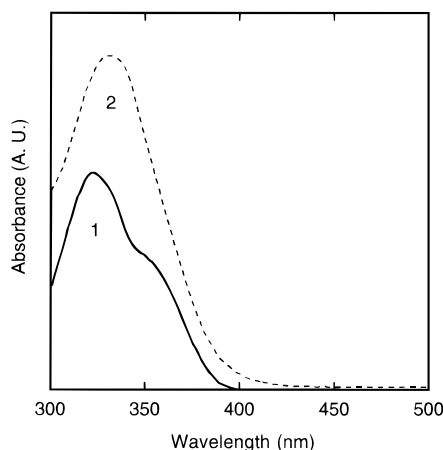
Figure 10. UV−visible spectra of 0.1 M LiClO$_4$−acetonitrile containing 0.2 mM DMcT before (curve 1) and 2 h after (curve 2) the addition of the chemically polymerized DMcT.

thermodynamic point of view. In the presence of a sufficient concentration of pyridine or triethylamine, the reaction between the polymer and monomer was slow, as mentioned above. This may be because DMcT dimer is less soluble in the presence of a base, as we observed. An additional possibility is that the redox potentials of the monomer−dimer couple and the dimer−polymer couple are close in the presence of a base. Also, the negatively charged end groups of the DMcT polymer and monomer may repel each other so that this reaction is slow.

To prove the formation of DMcT dimer, we measured changes in the DMcT spectrum in the presence of DMcT polymer. Figure 10 shows the spectra of ca. 0.2 mM DMcT in 0.1 M LiClO$_4$−acetonitrile before and 2 h after the addition of chemically polymerized DMcT (under argon). The spectrum obtained after the addition of the polymer indicates that most of the DMcT monomer has been transformed into DMcT dimer, because the absorbance peak at 330 nm features the DMcT dimer. The peak height at 330 nm 2 h after the addition of the polymer (almost the same height as that obtained 15 min after the addition) was about 1.5-fold higher than that at 320 nm before the addition. This strongly supports our scheme shown in Figure 9 because the extinction coefficient of DMcT dimer (chemically synthesized in our laboratory) is about 1.6-fold larger than that of DMcT monomer at 320 nm; one DMcT molecule was transformed into one DMcT dimer, by the reaction with DMcT polymer. Incidentally, no significant change was seen for control experiments. These results now support the assumption that the polymerization potential of DMcT is more positive than the dimerization potential, otherwise the "proportionation" reaction cannot proceed thermodynamically.

Likewise, we added the polymer to 0.1 M LiClO$_4$−acetonitrile containing 0.1 mM DMcT dimer. However, no appreciable change in the spectrum was observed for several hours. Thus,

the reaction of DMcT dimer and the polymer to yield the trimer does not proceed or proceeds very slowly. The redox potential of the dimer−trimer couple may be very close to that of the trimer−polymer couple.

This reaction thus leads to depolymerization and loss of the integrity of the film. Therefore, as to the composite cathode consisting of DMcT and polyaniline, in which polyaniline works as a molecular current collector,[4−6] the effect may raise the accessibility of the oxidized DMcT to polyaniline, resulting in larger capacity, better reversibility, and larger current capability.

Conclusions

Electrochemical reactions of DMcT in 0.1 M LiClO$_4$−acetonitrile were examined at carbon and ITO electrodes. The polymerization potential of DMcT is more positive than its dimerization potential. Although this has been previously speculated, it is verified in this study by means of in situ EQCM and spectroelectrochemistry. When base is present, it can deprotonate the DMcT, causing both the polymerization and the dimerization to occur at less positive potentials. A significant finding of this study is that the DMcT monomer in solution appears to reduce the polymeric film in an open-circuit redox process, resulting in a type of chemical etching. Base interferes with this reaction.

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