Electrochemical dissolution of polythiophene films

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Abstract

Polythiophenes, which are electrically conducting polymers, are generally insoluble except for 3-substituted derivatives with long alkane chains. The electrochemical oxidation of poly(3-methylthiophene) in solution without the monomer caused dissolution of the film at potentials similar to the polymerization potentials until the film was removed completely from the electrode. This is due to oxidative degradation. The kinetics of the dissolution was examined by time-variations of film thickness as well as of the mass by means of EQCM. Dissolved species, which were estimated from UV-, FTIR-spectroscopy and GC–MS, were monomer derivatives with a thiophene ring. When the solution included the monomer of which concentrations were o

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1. Introduction

Conducting polymers coated on electrodes [1,2] show intriguing electrochemical features such as electronic conduction [3–11], ionic conduction [12–16], ion exchange ability [17–21], ion-selectivity [22,23], accumulation of charge [24,25], voltage-controlled-chronic change [26–28], propagation of conducting zones [29–34] and voltage-dependent molecular recognition [35–38]. These features, however, have not been well applied industrially to electrochemically-controlled materials, partly because of not only fragility but also poor processability [39,40]. This drawback can be overcome with techniques of co-polymerization [41], blending [42], hybrid formation [43,44] and surfactant-assisted polymerization [45]. Unfortunately, conducting polymers do not generally show affinity for foreign soft polymers to make polymer alloys.

The other strategy of enhancing the processability is to introduce a functional group to a monomer or a backbone such that a conducting polymer may swell or be dissolved in solvent. For example, polythiophene films substituted with poly(o-toluidine), poly(o-methoxyani

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tion arises as to whether the amount of film is increased by polymerization or decreased by degradation. We pay attention here to the dissolution rate as well as dissolved species rather than the degradation, and report the dissolution of poly(3-methylthiophene) films in nitrobenzene when a potential similar to that for the polymerization is applied to the films for a long time.

2. Experiment

2.1. Chemicals

All the chemicals were of analytical grade. Nitrobenzene (NB) was purified by distillation and then was kept over active alumina of 300 mesh for 1 day. Acetonitrile (AN) was treated with molecular sieves. 3-Methylthiophene (3MT) and tetra-n-butylammonium tetrafluoroborate (TBATFB) were used as received.

2.2. Electrochemistry

For the electrochemical measurements, a standard three-electrode cell was used. The working electrode (WE) for measurements of film thickness was a Pt wire 0.1 mm in diameter. The WE for voltammetry was a Pt disk 1.6 mm in diameter. The counter electrode (CE) was a Pt coil, and the reference electrode was Ag | 0.01 M AgNO3 in AN. The potential was controlled with a HECS-318C potentiostat (Huso Electrochemical System). In contrast, a two-compartment cell separated with a glass filter was used for bulk electrolysis. The CE was wrapped in a molecular porous membrane, Spectra/Por (Funakoshi Co.), in order to suppress mixing of the solutions in the two compartments.

The EQCM instrument was an HQ-101B (Hokuto Denko). The WE was the Au-coated AT-cut 5 MHz quartz crystal, of which the active area was 1.44 cm2.

2.3. Polymerization

Polythiophene was synthesized electrochemically by applying potentials of more than 1.5 V in NB containing 0.1 M TBATFB and 0.1 M 3MT (monomer) at room temperature. Then the polymer film was rinsed well with NB before electrochemical measurements.

2.4. Spectroscopy

GC–MS spectra were obtained by a system of MS-HP5972A and GC-HP5890. Samples were injected directly into the GC, and substances with a retention time between 5 and 13 min was transferred to the MS. The FTIR instrument was a Protege 360 (Nicolet).

3. Results and discussion

Poly(3MT) is generally insoluble in organic solvents or is not even suspended in any solvent by ultrasonic treatment. When a potential of 1.8 V was applied to the poly(3MT)-coated electrode in the NB solution without 3MT, we observed a dark blue flow from the electrode toward the bulk, as is seen in Fig. 1. The area of the polymer film was larger than the electrode area because of the propagation of conducting zones [29–34]. The edge of the film deviated largely from a circle. The flow became dense with the electrolysis time. The flow faded away gradually. Finally, the film was removed completely from the electrode. Therefore, the poly(3MT) film was dissolved in the solution by the electrochemical oxidation. In other words, the species formed by the degradation are soluble. The flow far from the electrode was bent downward (Fig. 1). In order to investigate the direction of flow, we tilted the cell. Then the flow was not directed to gravity. When we returned the cell to its original position, the flow was always directed to the CE. Thus, the flow is influenced by the electric field, indicating that the flow has positive charge. A product in the degradation has also positive charge [56,57].

The degradation is obviously a drawback in applications to electrochemical switching devices. However, it can be used for geometrical processing of a film, if the dissolution can be controlled by approaching the film with a potentiostated foreign electrode. When we put a potentiostated Pt wire into contact with the poly(3MT) film, that had been polymerized on a gold electrode, all the film was dissolved immediately. This is probably because the Pt wire comes into electrical contact with the substrate (gold) electrode. In order to avoid the electrical contact, we shielded the tip of the Pt wire with

![Fig. 1](image-url)
epoxy resin, and brought it into contact with the film, as illustrated in Fig. 2A. The Pt tip was scanned spatially at the open-circuit potential of the film on a gold electrode. A clear trace of the scanned tip was observed on the film when the tip was potentiostated at 2.0 V, as is shown in Fig. 2B (the scan direction was from the left to the right). In contrast, no trace or no flaw was found when the tip was at open-circuit potential. Therefore, geometrical processing can be made readily by tracing a potentiostated foreign electrode on the film.

A quantitative measure of the dissolution is the time-variation of the thickness of the film. We synthesized the poly(3MP) at a Pt wire electrode (0.1 mm in diameter) in the NB solution including the monomer, and transferred it to the solution without the monomer. After applying positive potentials to the electrode at a given period, we rinsed the electrode with NB and measured the diameter of the film with a microscope. Since the surface of the cylindrical film was not smooth, 50 diameters were obtained and averaged. The typical standard deviation for the diameter was 10% of the average value. The film was oxidized again for another given period and its thickness was measured. This process was repeated. The diameters decreased with the time at potentials of more than 1.4 V. The amount of poly(3MT) left on the electrode should be proportional to \( r(t)^2 - r_o^2 \), where \( r(t) \) is the radius of the film-coated cylindrical electrode at an electrolysis time, \( t \), and \( r_o \) is the radius of the uncoated Pt electrode. Initial amounts of the film varied from film to film although the polymerization was made potentiostatically. Thus, we normalized the amount of the film left on the electrode as \( s = [r(t)^2 - r_o^2]/[r(0)^2 - r_o^2] \). Variations of \( s \) were plotted against \( t \) for several applied potentials in Fig. 3. The values of \( s \) decreased gradually for 10 min after the potential application, and then decreased linearly with the time. The variation became small for a long time period. The slopes of the lines became steeper with an increase in the potential, suggesting more rapid dissolution of the film at more positive potentials.

EQCM was used for evaluating accurately the weight of the dissolved film. Even mechanical oscillation by the quartz might dissolve the film, like stimulated dissolution by ultrasonication. We confirmed that the frequency of the EQCM did not change during 30 min without potential application. When potentials of more than 1.4 V were applied to the film, the mass (the frequency) of the film increased (decreased), as is shown in Fig. 4, probably because of insertion and immobilization of cations and/or solvent into the film. The insertion always occurs at the oxidation of conducting polymers. In the present case, the film was initially in the oxidized state, and hence further oxidation might not occur. The increase in the mass suggests the presence of multi-cationic states. The frequency remained constant for the first 10 s, and then increased with the time. The rate of the frequency change decreased for a long electrolysis time and at high potentials, probably because the film was removed completely from the electrode.

In contrast, chronoamperometric currents obtained simultaneously for the EQCM measurement decreased rapidly for 50 s and then became almost constant, as is shown in Fig. 5. The plateau of the current suggests a constant oxidation rate or constant dissolution rate of the film. Logarithmic values of the constant currents are plotted against potentials, showing a straight line. In order to estimate a contribution of charge transfer

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Fig. 2. Illustration of: (A) the electrochemical dissolution of the external electrode; and (B) the resulting photograph.

Fig. 3. Time-variations of the dimensionless amount of poly(3MT) left on the electrode after application of potentials of: (a) 1.5; (b) 1.8; (c) 1.9; and (d) 2.0 V. The amounts were evaluated from measurements of diameters through a microscope. The films were synthesized by applying 2.4 V to the Pt wire electrode (0.1 mm diameter) for 6 min.
kinetics to the whole reaction rate, we applied the Tafel equation to the line. Then we obtained the transfer coefficient as 0.05 or 0.025 for one- and two-electron transfer reactions, respectively. These small values indicate that the oxidation is controlled mainly by a chemical process, rather than by a conventional charge transfer process. Of interest is the absence of the frequency change (Fig. 4) for the initial period although the initial dissolution was confirmed visually by a loss of the dark blue flow from the electrode. In other words, the initial oxidation does not contribute directly to the dissolution.

The difference in the frequency might be converted into change in mass through Sauerbrey’s equation if the film were rigid. Unfortunately, the film is so thick (50 μm) that the viscoelasticity may relax the frequency change. We assume that a given fraction, $p$, of the mass is responsible for the frequency change. Let $m$ be the net mass change, then the mass calculated through Sauerbrey’s equation is expressed by $pm$. Combination of $m$ with the electricity, $q$, estimated by the current allows us to evaluate the molar mass of dissolved species through $W_M = ml(q/nF)$, where $n$ is the number of electrons for the oxidation. Since both $m$ and $q$ are a function of $t$, $W_M$ should vary also with the time. Fig. 6 shows the variation of $pmF/q$ or $pnW_M$ with $t$ for three values of the potential. The initial values of $pnW_M$ are almost zero because of the absence of dissolution. The values of $pnW_M$ increased with time, and some reached a peak.

Since it is not reasonable to presume that $n$ and $W_M$ increase from zero with time, it is the time-variation of $p$ that is responsible for the increase in $pnW_M$. The thinner the film becomes, the smaller is the value of $p$, according to the definition of $p$. In other words, the increase in $pnW_M$ represents a process of thinning the film.

The maximum values of $pnW_M$ were almost independent of the oxidation potential, as is shown in Fig. 7. They range from 30 to 80 g mol$^{-1}$ with a large scatter. The scatter was ascribed to non-uniform dissolution of the film, according to visual observation of the film surface. At the maximum, the film is so thin that $p$ may be regarded as unity or Sauerbrey’s equation may be valid. If $n = 1/3$ for the oxidation from the doping state to the degraded state [57], values of $W_M$ are in the range of the molar mass of the monomer ($W_M = 98$) or a dimer.

The dissolved species were identified with FTIR, UV and GC–MS. The phenyl group in NB blocked transmittance of optical beams through 3MT and poly(3MT). Thus, we used AN as a solvent. We confirmed that the behavior of the dissolution in NB was similar to that in AN. The dissolved species were collected by the oxidation at a Pt plate electrode in the monomer-free AN solution in the two-compartment cell. As a FTIR sample, the solution of the dissolved species was coated on an ATR prism (KRS-5). FTIR spectra were obtained within a short time, e.g. at the highest scan rate in a narrow wave domain in order to minimize evaporation of the dissolved species. As a criterion of the short time, we chose conditions under which components of 3MT could be detected in 1 mM concentrations.
Although the solution before the oxidation of the film did not include thiophene components (Fig. 8(b)), the spectra after the oxidation had bands at 853 cm\(^{-1}\) for NB from the polymerization, 711 cm\(^{-1}\) for the thiophene ring, and 681 cm\(^{-1}\) for \(\delta_{S-C}\) (Fig. 8(a)). Therefore, the oxidation released thiophene rings from the film. These bands are different from those in spectra of the degraded films \[57\] because they are for the dissolved species.

UV–vis spectra are shown in Fig. 9. The AN solution into which the film was inserted for a few hours without electrolysis showed no absorption band. The AN solution after the oxidation of the film showed a band (curve (a)) at 312 nm, which is red-shifted from the \(\pi-\pi^*\) band (curve (b)) of 1 mM 3MT + 0.1 M TBATFB + AN (274 nm). Oligomers of thiophenes have been demonstrated to exhibit a red-shifted band, for which the wavelength has a linear relation with the inverse of the number of rings \[66–68\]. The band at 312 nm may be for thiophene derivatives with a conjugation higher than that of 3MT.

GC–MS spectra were noisy, suggesting the presence of many kinds of decomposed species. The predominant band was at 45 g mol\(^{-1}\). This species can be assigned certainly to the cleavage product [HCS\(^+\)], in which isotopic molar ratios of S were identical with the intensities of the spectra. [HCS\(^+\)] is a prime scission product of the thiophene ring. Three possible species that include the thiophene ring can be deduced, as shown in Fig. 10(A–C). The intensity for species (A) was larger than the other two. There was a band, which could be assigned to (D). If poly(3MT) is decomposed at the bonds shown as dotted lines in Fig. 10(E), species (A), (B) and (D) can be produced.

A question that needs to be addressed is whether the oxidation in a 3MT solution brings about the polymerization or the dissolution. Two extremes can be considered: only the dissolution occurs in the absence of the monomer, whereas the polymerization should be predominant over the dissolution at high concentrations of the monomer. We measured voltammograms at 0.01 V s\(^{-1}\) in the various concentrations of 3MT, \(c\), in 0.1 M TBATFB + NB. Fig. 11 (curve (a)) shows the dependence of the currents at 2.0 V on the concentrations at the poly(3MT)-coated electrode, as a concave curve. Possible reasons for the deviation from the proportionality are: (i) a non-linear order in the polymerization kinetics; and (ii) a larger contribution of the dissolution at lower concentrations. In order to see the validity of reason (i), currents were measured at the bare Pt electrode (curve (b)). They were 1/5 smaller than those in curve (a) because the electrode for curve (a) was coated with a thick porous poly(3MT) film. The variation of \(c > 6\) mM still shows a concave curve, supporting reason (i). No polymerization occurred for \(c < 6\) mM. Thus, the difference in the currents for \(c > 6\) mM contributes mainly to the dissolution. It is obvious that the polymerization and the dissolution occur concomitantly for \(c > 6\) mM.
4. Conclusions

Poly(3MT) films are dissolved up to disappearance in terms of the electrochemical oxidation at more than 1.5 V in NB or AN without 3MT. The dissolution begins a few minutes after the potential application. Geometrical processing can be provided by tracing a potentiostated foreign electrode around the film, as is shown in Fig. 2. This occurs concomitantly with the polymerization when \( c > 6 \) mM. The main dissolved species are derivatives with a thiophene ring, according to the spectroscopic data.

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