

Letter

A New Method for Preparing Metallic Luster of 3-Methoxythiophene Polymers

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Abstract: A green metallic luster and a red metallic luster were observed from the film obtained by multi-step potentiostatic polymerization of 3-methoxythiophene. Compared to previously proposed electrochemical preparation methods, the polymerization time was shortened and the resulting film had a metallic luster of different colors. The transmission electrochromism of many conductive polymers is due to changes in the electronic state within the polymer chain, but the electrochromism of metallic luster is assumed to be due to changes in the electronic states within the polymer chains and the higher-order structure of polymer chains.

Key words: Conductive Polymers, Metallic Luster, 3-Methoxythiophene, Multi-step Potentiostatic Polymerization

Research by Hoshino et al. at Chiba University has reported that a gold metallic luster can be obtained from 3-methoxythiophene polymers.¹⁾ In their reports, it was stated that in polymer preparation by electrochemical polymerization, cyclic scanning of the applied potential at a slow sweep rate of 10 mV/sec is required for the formation of the polymer film with high reflectance.²⁾ They explained the reason for this as follows: a long reduction time was necessary for the lamella formation of the formed polymer. In this method, a thick film is required to suppress light transmission through the polymer film, but the sweep speed is slow, which results in a long preparation time. Furthermore, since the applied potential is constantly changing, the polymers being polymerized are a mixture of different qualities, and therefore homogeneous polymers are necessary to obtain a high reflectance. To solve these problems, a method called multi-step potentiostatic (MS-PS) polymerization was proposed, in which a constant potential is alternately applied to oxidize the monomer and reduce the resulting polymer. In this method, a homogeneous polymer can be obtained at a constant applied potential, and reduction of the polymer can be performed only at the optimum applied potential. Furthermore, this method will enable the film thickness to be changed by the repeat cycle number of the potential application, and the reflectance and reflected color to be changed by setting different applied potentials and application times for each cycle.

In order to obtain 3-methoxythiophene polymer (PMOT) on the electrode, the polymerization solution was prepared by dissolving 3-methoxythiophene (0.1 M, from Tokyo Chemical Industry Co., Ltd.), lithium perchlorate (0.1 M, Kishida Chemical Co., Ltd.), and sodium dodecyl sulfate (0.1 M, SDS, FUJIFILM Wako Pure Chemical Corporation) in a mixed solvent of ultrapure water and butanol (96:4).³⁾ SDS is used to enhance the lamellar formation and crystallinity of the resulting polymer. ITO transparent conductive

film immobilized glass (Geomatec), silver chloride wire, and platinum wire were used as the working electrode, reference electrode, and counter electrode, respectively. Potential 1 for monomer oxidation was applied at +1.4 V for 15 seconds, and then potential 2 for polymer reduction was applied at -1 V for 15 seconds. The application of these two potentials was counted as one cycle, and polymerization of 10 cycles were performed as typical conditions for obtaining a PMOT film with the required film thickness. A potentiostat Biologic SP-50e was used for electrochemical measurements, and a spectrophotometer Ocean Photonics Flame with OP-TF/RF-GONIO-MN was used for measuring reflected light.

Fig. 1 shows the time course of the applied potential and response current during MS-PS polymerization from the first cycle to the seventh cycle. Both the oxidation current and the reduction current increase with the number of cycles. This indicates that the amount

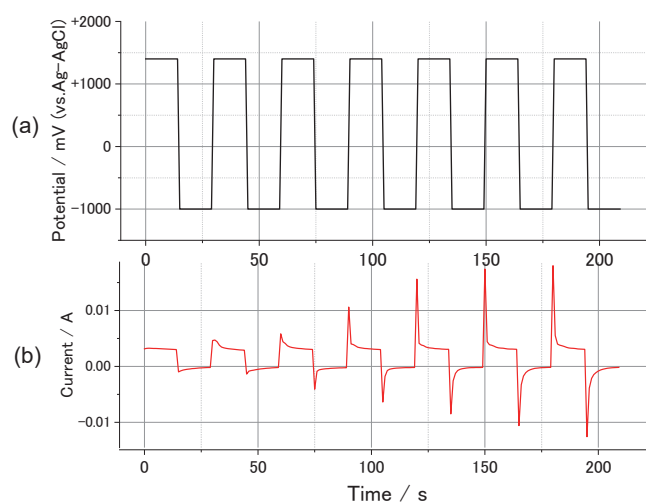


Fig.1 Time dependence of applied potential (a) and reaction current (b) during MS-PS polymerization of 3-methoxythiophene.

of polymer deposited on the electrode increases with the number of cycles. About 2 μm thickness of the PMOT film was obtained by 10 cycles of MS-PS polymerization. In Hoshino et al.'s method, a PMOT film with a thickness of about 2 μm was obtained by 21 times applied potential cycling between -0.5 V and +1.3 V at a scanning speed of 10 mV/s. In this case, it takes 7560 seconds to complete 21 cycles. In contrast, our MS-PS polymerization required 300 seconds for 10 cycles. By changing to MS-PS polymerization, the polymerization time was shortened to about 1/20.

Fig. 2 shows the color tone of the PMOT film obtained by 10 cycles of MS-PS polymerization in the oxidized and reduced states. A metallic luster of green was observed in the reduced state and that of red in the oxidized state. A black base was used during the observation, which prevented white light from passing through the PMOT film and reflecting off the base, so the color tone observed here can be said to be a reflected color. Metallic luster for PMOT was successfully obtained by MS-PS polymerization.

Fig. 3 shows the transmission and reflection spectra of a PMOT film (film thickness 1.5 microns) obtained by 7 cycles of MS-PS polymerization. In the transmission spectrum of the PMOT in the reduced state, a strong absorption band due to π - π^* transition is observed around the wavelength of 500 nm. This indicates that green light is being absorbed in the PMOT film. In the reflection spectrum of the PMOT in the reduced state, a reflection maximum is observed at the wavelength of 570 nm (specular reflectance is about 8%). Because the reflection band is broad, this reflected light also contains light with wavelengths around 500 nm. On the other hand, light components in the visible region with wavelengths longer than 500 nm were absorbed (doping-induced transitions) and reflected by the oxidized PMOT film. It is known that transmitted color consists of the sum of all light except that absorbed from white light. These PMOT films contain light that would otherwise be absorbed in the reflected light, indicating that the green (or red) color of the PMOT film is not a transmitted color. The transmittance spectrum of PMOT obtained by MS-PS polymerization is very similar to that of polythiophene derivatives obtained by conventional electrochemical polymerization.⁴⁾ The difference is that the PMOT film obtained from conventional method has no reflection or only a very weak reflection. This suggests that the electronic state of the polymer chains of PMOT obtained by the conventional method (with-

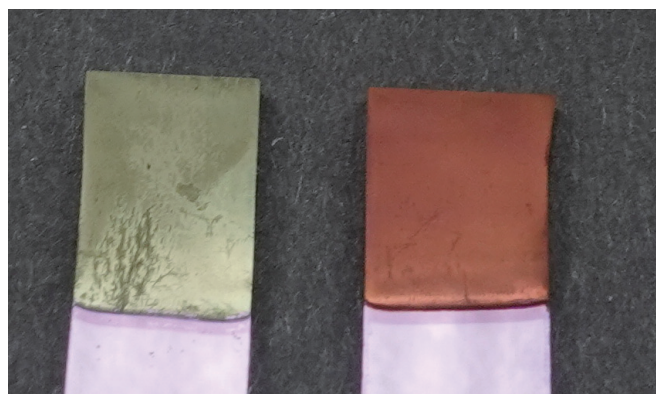


Fig.2 Photographs of the obtained PMOT film (film thickness: 2 μm) in the reduced state (left) and the oxidative state (right) .

out SDS and low speed potential scanning) and PMOT obtained by this MS-PS polymerization is the same, but the latter has a metallic reflection which is assumed to be due to the high density of polymer chains aggregated by lamellar formation. Unlike the electrochemical polymerization by Hoshino et al., a green metallic luster was obtained from PMOT film by our method. In the reflection spectrum of the former (golden one) , reflection begins at wavelengths longer than 500 nm, while in the latter (green one) , reflection begins at approximately 450 nm. This difference in color tone between gold and green requires further detailed investigation, but we believe it is related to the fact that the homogeneous PMOT obtained by MS-PS polymerization is able to reflect light of shorter wavelengths.

A PMOT film with metallic luster was obtained by MS-PS polymerization. This PMOT film reflected green light in the reduced state and red light in the oxidized state. It is believed that the application of a constant potential for the reduction of MS-PS polymerization promoted the formation of lamellae. The change in color tone of the metallic luster between the oxidized and reduced states

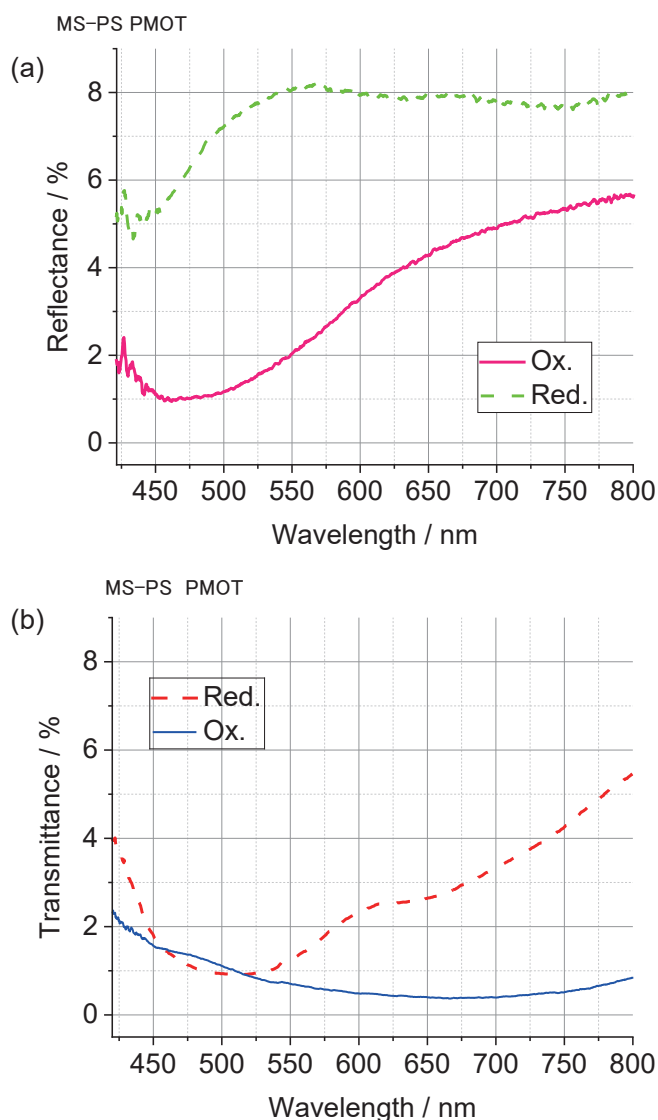


Fig.3 Reflectance (a) and transmittance (b) spectra of the PMOT film (film thickness: 1.5 μm) .

is thought to result from the difference in both the chemical structure in the polymer chains and the higher-order structure of the polymer chains. We will continue to study this new electrochromism in the future.

References

- 1) R. Tagawa, H. Masu, T. Itoh and K. Hoshino, *RSC Adv.*, **4**, 24053 (2014).
- 2) T. Tokuda and K. Hoshino, *Polymer Journal*, **48**, 1141 (2016).
- 3) M. Fall, J. J. Aaron, N. Sakmeche, M. M. Dieng, M. Jouini, S. Aciyach, J. C. Lacroix and P. C. Lacaze, *Synth. Met.*, **93**, 175 (1998).
- 4) E. C. Rios, A. V. Rosario, A. F. Nogueira and L. Micaroni, *Solar Energy Materials and Solar Cells*, **94**, 1338 (2010).