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The Preparation of Poly(3-methoxy-2,5-thiophenediyl) with Iron(III) Chloride and Its Properties

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Soluble and conductive poly(3-methoxy-2,5-thiophenediyl) was obtained by the chemical oxidation of 3-methoxythiophene with iron(III) chloride. The resulting polymer was found to be in a doped state, since it contained 0.1—0.2 counterions ($FeCl_4^-$ and Cl^-) per monomeric unit. This means that the oxidation is a convenient method for preparing conductive polymers in one step. We also obtained a poly-MOT solution and film in a state doped to a great extent, showing no π-π^* transition band and a high stability in air. An undoped polymer film was prepared by the electrochemical reduction of the doped film. The undoped film had a π-π^* transition band at 2.3 eV, indicating that the effective conjugation length of the polymer could be assumed to be the same as that of the poly(3-methoxythiophene) prepared electrochemically.

Electrochemical polymerization has been found to be an advantageous method for preparing conductive polyheterocycles, such as polythiophene[1)] and polypyrrole,[2)] since it permits polymers to be obtained on the surface of an electrode as films. In electrochemical polymerization, film thickness is proportional to the amount of charge flowed. However, film conductivity has been found to decrease extremely when the thickness becomes great.[3)] Heterocyclic conductive polymers can be prepared not only by the electrochemical means, but also by the chemical method using transition metal salts.[4)] By this method, the polymers are obtained as powdery products, but the amounts of polymers obtained increase in proportion to the feed of the starting materials.

We have previously prepared poly(3-methoxythiophene)(poly-MOT) electrochemically and found it to be soluble in organic solvents.[5)] The doped state of poly-MOT was stable in air. In this paper, we wish to report on the preparation of poly-MOT with iron (III) chloride and its properties. The polymer obtained is soluble in organic solvents and in a doped state, as in the case of the electrochemically prepared one. This is a convenient method for preparing conductive polymers in one step.

Experimental

Materials. MOT[6)] was prepared as reported previously. It was then distilled in vacuo: bp 62 °C (30 mmHg; 1 mmHg≈133.322 Pa) (lit,[6)] bp 80—82 °C (65 mmHg)). Iron(III) chloride was used without any further purification. Chloroform was washed five times with about half its volume of water, dried with anhydrous calcium chloride, and distilled over calcium hydride under argon; bp 62 °C. Methanol was distilled and dried with Zeolite; bp 65—66 °C. Benzene was dried with anhydrous calcium chloride and distilled over calcium hydride; bp 80.0—80.5 °C. Nitromethane and acetonitrile were purified as reported previously.[3)]

Polymerization. The typical polymerization procedures were as follows. In a three-necked flask equipped with a stirrer, a condenser, and an argon inlet, chloroform and iron(III) chloride were placed. Prior to polymerization, argon was bubbled, and bubbling was continued up to the end of the polymerization. The resulting yellowish green suspension was stirred at 30 °C, and MOT was added. A rapid color change into dark red took place. When benzene was used as the solvent, the brown suspension was changed into a dark red one by the addition of MOT. After stirring for 2 h, the reaction mixture was poured into methanol to remove the unreacted iron(III) chloride and iron(II) chloride. The precipitate was collected on a filter, washed with methanol, and dried in vacuo.

Reprecipitated poly-MOT was obtained by adding 100 ml of benzene to a solution of 0.1 g of poly-MOT in 20 ml of dimethyl sulfoxide (DMSO).

An undoped polymer was prepared by the electrochemical reduction of the doped film cast on an indium-tin oxide glass (ITO).

A cast film was obtained from a solution of 20 mg of the polymer in 4 ml of DMSO. About 20 mg of the solution was cast on ITO (1 cm×1 cm=1 cm^2) and dried in vacuo at 120 °C for 1 h.

Electrochemical Doping. A cast film on ITO was used as a working electrode. The counter electrode was a platinum plate or wire. A reference electrode consisting of Ag/Ag^+ was connected to the cell by means of a salt bridge. Acetonitrile was used as the solvent, and $NaClO_4$ (0.1 mol l^{-1}) as the electrolyte. The electrochemical data were obtained using a Hokuto Denko HA-501 potentiostat/galvanostat and an HB-104 function generator.

Measurements. The electrical conductivity was measured on pressed pellets by Van der Pauw's four probe method. Fourier transform IR and VIS-near IR spectra were recorded on a Perkin-Elmer Model 1720 spectrometer and a Hitachi U-3400 spectrometer respectively. The spectral change and cyclic voltammograms were measured according to the method described in a previous paper.[5)]

Results and Discussion

Polymerization. The results of the polymerization of MOT are summarized in Table 1. Among the four kinds of solvents shown in Table 1, iron(III) chloride is soluble in nitromethane and methanol, while it is almost insoluble in benzene and chloroform. Considering the color change described in the Experimental section, iron(III) chloride is slightly soluble in benzene and chloroform, and polymerization should

Table 1. Preparation of Poly-MOT with Iron(III) Chloride a)

Exp. No.	Solvent	$FeCl_3$	Temp	Yield b)	Conductivity
		mol l^{-1}	°C	mg	S cm^{-1}
1	PhH	0.4	30	58.8	2.8×10^{-4}
2	$MeNO_2$	0.2	30	48.8	8.2×10^{-4}
3	$CHCl_3$	0.2	30	54.5	9.3×10^{-3}
4	MeOH	0.4	30	—	—
5	$CHCl_3$	0.2	−30	8.0	4.2×10^{-4}
6	$CHCl_3$	0.2	0	50.1	1.7×10^{-3}
7	$CHCl_3$	0.2	45	84.7 c)	1.3×10^{-2}
8	$CHCl_3$	0.2	60	109.5 c)	3.1

a) The concentration of MOT was 0.1 mol l^{-1}. b) The feed of MOT was 100 mg. c) Partly soluble in DMSO. Elemental analyses of poly-MOT obtained in Exp. No. 3: Before reprecipitation: C, 39.94; H, 2.82; S, 20.54; Fe, 5.76; Cl, 17.06. After reprecipitation: C, 44.21; H, 3.49; S, 20.61; Fe, 4.40; Cl, 10.97.

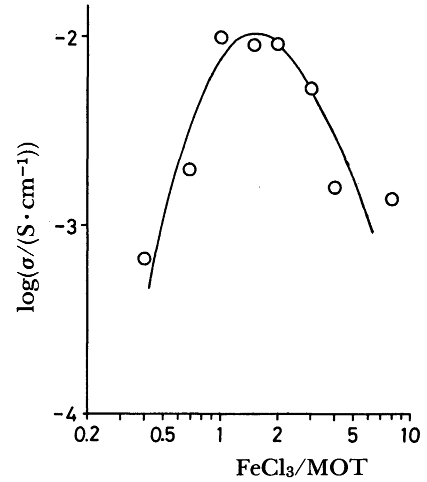

Fig. 1. Effect of the molar ratio of iron(III) chloride to MOT on conductivity of poly-MOT.

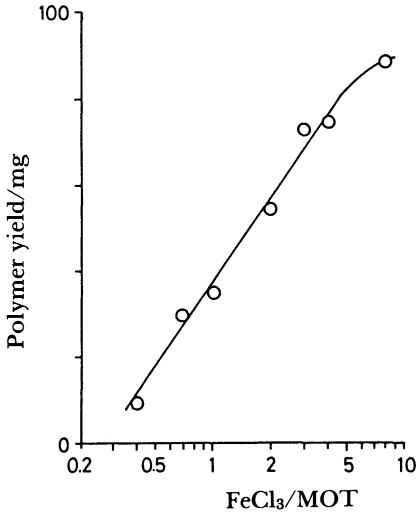

Fig. 2. Effect of the molar ratio of iron(III) chloride to MOT on polymer yield.

occur in a solution of iron(III) chloride. In Exps. Nos. 1—3, a black powdery product was obtained. The highest conductivity was obtained when chloroform was used as the solvent. In the case of methanol, no polymer was obtained as a precipitate from the solution nor by adding benzene or chloroform to the solution. In Exps. Nos. 3 and 5—8, the conductivity of the pressed pellet and polymer yield increased with the increase in the polymerization temperature. However, the polymer obtained above 45 °C was partly soluble in DMSO, although that obtained below 30 °C was soluble in DMSO. Figure 1 shows the effect of the molar ratio of iron(III) chloride to MOT on the conductivity of poly-MOT when MOT was polymerized at 30 °C in chloroform. The conductivity was highest when the ratio was in the range of 1—2. Figure 2 shows the effect of the ratio on the polymer yield when polymerization was done at 30 °C in chloroform. The yield increased with the increase in the ratio.

The above results show that a conductive and soluble product is obtained in a high yield when MOT is polymerized at 30 °C in chloroform with a molar ratio of 2. Thereafter, the polymerization was carried out under these conditions except otherwise mentioned. Elemental analyses showed the resulting poly-MOT to contain 0.16 and 0.11 counterions ($FeCl_4^-$ and Cl^-) per monomeric unit respectively, judging from the ratios of iron to sulfur and of chlorine to iron. However, reprecipitated poly-MOT contained 0.12 counterions ($FeCl_4^-$), indicating that reprecitipation brought about the removal of Cl^-. As to a polythiophene and its derivatives prepared by this method, they have been obtained in the undoped state. The reaction of thiophene with iron(III) perchlorate gave an insulating polymer.7) Using iron(III) chloride, soluble polythiophene derivatives were prepared from alkylthiophene monomers ($n \geqq 4$), but the polymers were in an undoped state.8) Only a small number of papers on a one-step synthesis of doped polythiophenes have been published. Inoue et al. reported that the reaction of 2,2′-bithiophene with copper(II) perchlorate yielded doped polythiophene in one step.9) 2,2′-Bithiophene was polymerized more easily than thiophene, since the oxidation potentials of the former and the latter were 1.26 and 1.65 V vs. SCE respectively.10) MOT was also polymerized easily because of its low oxidation potential.11) The oxidation potential of polythiophene was lower by 0.55 V than that of the thiophene monomer. Therefore, the polymerization of thiophene should be followed by the oxidation of polythiophene in view of the thermodynamic data, but in fact polythiophene was obtained in an undoped state. We have to consider, therefore, that the reaction was not simply controlled thermodynamically.

IR Spectra. Figure 3 shows the Fourier transform IR spectra of doped and undoped poly-MOT. Both

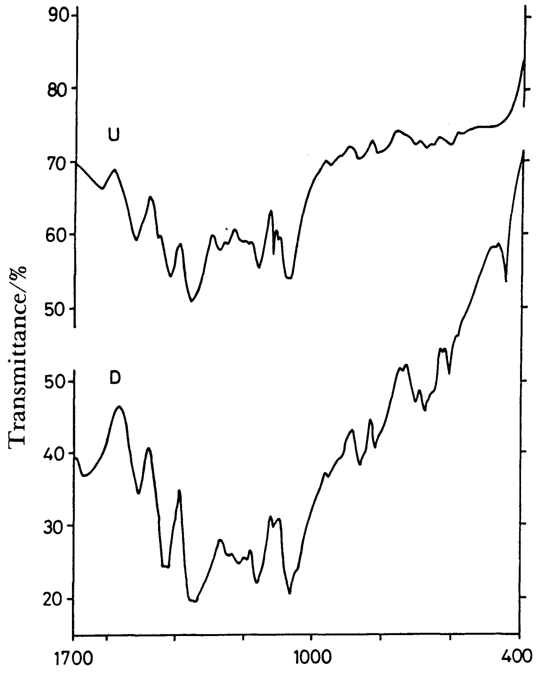

Fig. 3. IR spectra of poly-MOT.
U: an undoped polymer, D: a $FeCl_4^-$ doped polymer.

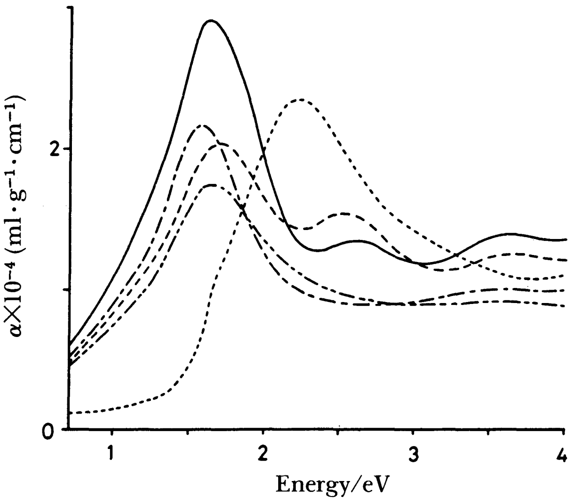

Fig. 4. VIS-near IR spectra of poly-MOT in DMSO. ———: Just after preparation, ----: After 4 days in air, — — —: Just after preparation (reprecipitated), —-—-: After 4 days in air (reprecipitated), ------: an undoped polymer solution (reprecipitated).

polymers had two peaks, at 820 and 1260 cm^{-1}, assigned to the C-H deformation vibration of the 2,3,5-trisubstituted thiophene ring[12] and the C-O-C stretching vibration of the methoxyl group respectively. Neither had a peak at 795 cm^{-1} assignable to the C-H deformation vibration of the 2,5-disubstituted thiophene ring. Therefore, the structure of poly-MOT was consistent with that of poly(3-methoxy-2,5-thiophenediyl). In the 3000—3100 cm^{-1} frequency range,[12] no peak could be observed. We have previously reported the IR spectra of doped and undoped poly-MOT prepared electrochemically.[5] There was no difference between the spectra of the two undoped poly-MOT. As to the spectra of the two doped poly-MOT, some differences were observed; electrochemically prepared poly-MOT had two bands at 560 and 845 cm^{-1}, possibly due to the supporting electrolyte (Bu_4NPF_6), since the electrolyte had these peaks. The peaks at 445, 610, 870, and 1425—1440 cm^{-1} were observed only in the present poly-MOT.

VIS-Near IR Spectra. As has been mentioned above, poly-MOT was soluble in DMSO. Other polar solvents, such as 1-methyl-2-pyrrolidinone (NMP) and propylene carbonate (PC), were found to dissolve poly-MOT. Figure 4 shows the VIS-near IR spectra of poly-MOT in DMSO. The solid line had three absorption bands, at 1.6, 2.6, and 3.6 eV. The absorbance at 3.6 eV decreased in a broken line, suggesting that the band at 3.6 eV was not due to a π-π^* transition, since the doped state of poly-MOT should gradually change to the undoped state in air.[5] On the contrary, the band at 2.6 eV was considered to be due to a π-π^* transition, judging from the increase in the absorbance at 2.6 eV of the broken line.

To confirm the above estimation, the reprecipitation of poly-MOT was carried out. The spectra of reprecipitated poly-MOT are presented in the same figure. The spectrum of an undoped poly-MOT solution had only one band, at 2.2 eV, assigned to a π-π^* transition. The spectrum of a doped poly-MOT solution had two bands, at 1.6 and 3.6 eV. No band was observed around 2.2 eV, indicating that the reprecipitation brought about the removal of the poly-MOT containing undoped sites.

In the case of the poly-MOT prepared electrochemically, the spectrum of a doped polymer solution had a small π-π^* transition band at 2.3 eV in addition to the two bands at 1.0 and 1.5 eV,[5] suggesting that a slight undoping occurred in this case. These three characteristic bands were also observed in a doped poly-MOT film cast on ITO. On the other hand, the spectrum of the present poly-MOT film had only one band, at 1.6 eV, and no band was exhibited around 2.2 eV (Fig. 5). Thus, we obtained a poly-MOT solution and film in a state doped to a great extent. These results indicate that the doped state of the present poly-MOT was more stable in air than that of the electrochemical one.

As for the two bands at 1.6 and 3.6 eV shown in Fig. 4, further discussion will be given below.

The change in the VIS-near IR spectra during the doping of the film of poly-MOT is shown in Fig. 5. Cast films on the ITO anode were electrochemically doped at different voltages, and in situ spectra were recorded. At −0.7 V, the film had two bands, at 2.3 and 3.4 eV. The doping level became higher as the applied voltage was increased. At 0.3 V, a band at 1.9 eV was observed. When the voltage decreased to −0.7

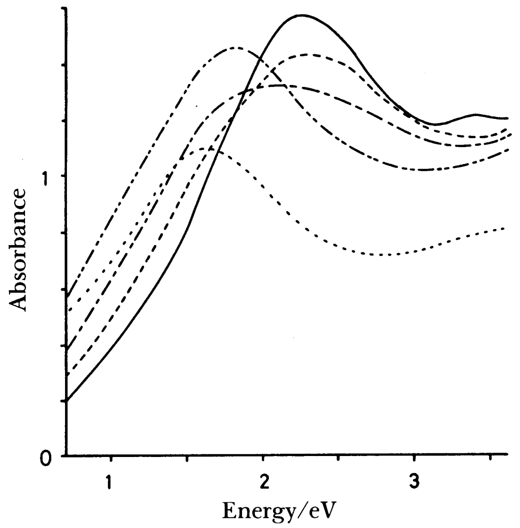

Fig. 5. VIS-near IR spectrum of reprecipitated poly-MOT film cast on ITO (------) and spectral change during electrochemical doping of poly-MOT. Electrolyte: NaClO$_4$ (0.1 mol l^{-1}). Applied voltage: ——: −0.7V; ----: −0.3V; — — —: −0.1V; —·-—: 0.3V.

V again, the film had only one band, at 2.3 eV, and the band at 3.4 eV disappeared completely. These results indicate that the band at 2.3 eV is to be assigned to a π–π^* transition, while the band at 3.4 eV might be caused by a contamination. The low-molecular-weight part of poly-MOT should be more soluble than the other part. Moreover, the solubility of undoped poly-MOT was higher than that of doped poly-MOT. Accordingly, at the lower applied voltage, acetonitrile might dissolve the low-molecular-weight part. The band at 1.9 eV observed in the doped film could be attributed to Würster-type radical cations produced by the oxidation of poly-MOT, as has been discussed in the previously reported paper.5)

Concerning the change in the VIS-near IR spectra of the reprecipitated poly-MOT film, as a whole it was the same as that presented in Fig. 5, including that the band at 3.4 eV, observed initially at −0.7 V, disappeared on the second sweep. The undoped film had a band at 2.3 eV, and the doped one, one at 1.55 eV. The effective conjugation length of the undoped poly-MOT was assumed to be the same as that of the poly-MOT prepared electrochemically, since the latter showed a π–π^* transition band at 2.3 eV.5)

Cyclic Voltammetry. Figure 6 shows the cyclic voltammograms of cast films of poly-MOT with NaClO$_4$. On the sweep ranging from −0.7 V to 0.2 V, an anodic shoulder was observed at −0.2 V and a cathodic shoulder at −0.5 V, as is shown by the solid line. The film was blue above the oxidation potential and red-purple below the reduction potential. On another sweep ranging from −1.0 V to 0.2 V, the anodic shoulder could be observed more clearly than before, as is shown by the broken line. However, in this case, the anodic and cathodic currents decreased gradually when the sweep was carried out repeatedly, suggesting that poly-MOT deteriorates at applied voltages lower than −0.7 V. Electrochemically prepared poly-MOT presented an anodic peak and a cathodic peak quite clearly at −0.20—−0.18 V and at −0.50—−0.48 V respectively. The present polymer had the anodic and cathodic shoulders in the same regions, but no clear peak was observed. The same results were found in the cyclic voltammograms of the cast films of reprecipitated poly-MOT. The ambiguity of the oxidation and reduction peaks should be mainly explainable by the finding that the background current was about 10 times as high as that in poly-MOT prepared electrochemically.5)

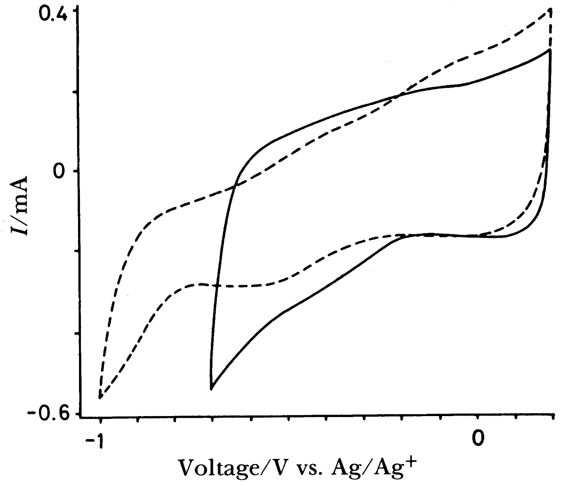

Fig. 6. Cyclic voltammograms of poly-MOT. In every case, current was calculated under the conditions that 1 mg of the polymer was deposited on ITO (1×1=1 cm^2). Electrolyte: NaClO$_4$ (0.1 mol l^{-1}). Sweep rate: 2 mV s^{-1}.

References

1) V. L. Afanas'ev, I. B. Naznrova, and M. L. Khidekel, *Izv. Akad. Nauk SSSR. Ser. Khim.*, **1980**, 1687. K. Kaneto, K. Yoshino, and Y. Inuishi, *Jpn. J. Appl. Phys.*, **21**, L567 (1982).

2) A. F. Diaz and K. K. Kanazawa, *J. Chem. Soc., Chem. Commun.*, **1982**, 635.

3) S. Tanaka, M. Sato, and K. Kaeriyama, *Makromol. Chem.*, **185**, 1295 (1984).

4) a) T. H. Chao and J. March, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 743 (1988). b) S. Rapi, V. Bocchi, and G. P. Gardini, *Synth. Met.*, **24**, 217 (1988).

5) S. Tanaka, M. Sato, and K. Kaeriyama, *Synth. Met.*, **25**, 277 (1988).

6) S. Gronowitz, *Ark. Kemi*, **12**, 239 (1958).

7) N. M. -Thevenin and G. Bidan, *Mol. Cryst. Liq. Cryst.*, **118**, 227 (1985).

8) R. Sugimoto, S. Takeda, H. B. Gu, and K. Yoshino, *Chem. Express*, **1**, 635 (1986).

9) M. B. Inoue, E. F. Velazquez, and M. Inoue, *Synth. Met.*, **24**, 223 (1988).

10) G. Tourillon and F. Garnier, *J. Electroanal. Chem.*, **161**, 51 (1984).

11) R. L. Blankespoor and L. L. Miller, *J. Chem. Soc., Chem. Commun.*, **1985**, 90.

12) M. Akiyama, *J. Mol. Spectrosc.*, **43**, 226 (1972). T. Yamamoto, K. Sanechika, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **56**, 1497 (1983). G. Tourillon and F. Garnier, *J. Phys. Chem.*, **87**, 2289 (1983). S. Hotta, T. Hosaka, M. Soga, and W. Shimotsuma, *Synth. Met.*, **9**, 87 (1984).