234 © *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***62***, *234—238 (1989)* [Vol. 62, No. 1

Effective Doping of Polymer Anion during Chemical Polymerization of Pyrrole Using $Fe(OH)_3$ Oxidant

Akira OHTANI[†] and Takeo SHIMIDZU*
Division of Molecular Engineering, Graduate School of Engineering, Kyoto University,
Sakyo-ku, Kyoto 606
[†]Central Research Laboratory, Nitto Electric Industrial Co., Ltd.,
Ibaraki, Osaka 567

(Received May 16, 1988)

Polypyrroles were prepared by the chemical polymerization of pyrrole using various combinations of Fe^{3+} oxidants and electrolytes. The morphology and yield of the resulting polymers were affected by the property of the electrolyte anion in the oxidative solution. The size of the particles of the resulting polymers was decreased by using a high-molecular-weight polymer anion as the electrolyte anion. Both the polymer anion and Cl^- were incorporated as a dopant into the polypyrrole matrix during the chemical polymerization of pyrrole, using an aqueous solution containing both $FeCl_3$ and the polymer anion. On the contrary, the polymer anion was effectively incorporated as a dopant into the polypyrrole matrix during the chemical polymerization of pyrrole, using an aqueous solution containing both $Fe(OH)_3$ and the polymer acid. A novel type of chemical preparation of the polypyrrole-polymer anion composite using the $Fe(OH)_3$ oxidant and the polymer acid was developed.

Conducting polypyrrole (PPy)[1–6] has applications in such equipment as electronic devices,[7,8] electrochromic displays,[9–11] polymer batteries,[12–15] polymer modified electrodes,[16] and functional membranes.[17–20] An electrochemical polymerization, a chemical polymerization, and a photo-electrochemical polymerization of pyrrole easily provided conducting PPy. Moreover, many hydridization procedures of PPy have been developed so as to improve the properties of PPy.[21–40] In electrochemical polymerization, dopant anions are freely chosen, since they act as supporting electrolytes. Many kinds of PPy-functional anion composites have been prepared.[21–23, 32, 33] The functional anions to be doped were such as electrochromic molecules, photosensitive molecules, nucleic acids, amino acids, tenside anion, and polymer anions. In the chemical polymerization of pyrrole in a solution containing both an oxidant and a functional anion, an anion of oxidant, e.g. Cl^- of $FeCl_3$, is easily incorporated as a dopant into the PPy matrix, though the doping of the functional anion is not efficient. However, chemical polymerization is a useful method for preparing of large amount of conducting polymers, since it is performed without electrodes.[41–45] In this study, $Fe(OH)_3$ was chosen as an oxidant; and discussions are presented concerning the effective doping of the polymer anion into the PPy matrix during the chemical polymerization of pyrrole in H_2O containing the $Fe(OH)_3$ oxidant and the polymer acid.

Experimental

Materials. Pyrrole (Aldrich Chemical) was distilled and stored under a N_2 atmosphere. $FeCl_3\cdot 6H_2O$ (Wako Chemical), $Fe_2(SO_4)_3$ (Wako Chemical), sodium 1-propanesulfonate (PSNa) (Nakarai Chemical), and 1-propanesulfonic acid (PSH) (Kodak) were used without further purification. $Fe(OH)_3$ was prepared by adding a $FeCl_3$ aqueous solution to a NaOH aqueous solution; then, the precipitate of $Fe(OH)_3$ was filtered to remove Na^+ and Cl^-. Sodium polyethylenesulfonate (PESNNa) was prepared by the polymerization of sodium ethylenesulfonate (Tokyo Kasei), using a combination of potassium peroxodisulfate (Wako Chemical) and sodium hydrogensulfite (Wako Chemical) as a redox-initiator in H_2O. The degree of polymerization was controlled by varying the polymerization time. Polyethylenesulfonic acid (PESNH) and polystyrenesulfonic acid (PSSH) were obtained by an ion-exchange treatment of PESNNa and sodium polystyrenesulfonate (Toyo Soda) through ion-exchange column (DOWEX 50W-12; Dow Chemical), respectively.

Preparation of PPy. Reaction of Pyrrole with $FeCl_3$ and $Fe_2(SO_4)_3$ Aqueous Solutions: Pyrrole (0.187 ml) was added to a 10 ml $FeCl_3$ aqueous solution (0.54 mol dm^{-3}) or in 10 ml $Fe_2(SO_4)_3$ aqueous solution (0.27 mol dm^{-3}); the solution instantly acquired a black color as the PPy precipitate was formed. After 2 hours at room temperature, the mixture was filtered and the precipitate was washed with distilled water. After a final rinse with acetone, the black powder was dried in vacuo.

Reaction of Pyrrole with $FeCl_3$ Aqueous Solution Containing Polymer Anion: Pyrrole (0.187 ml) was added in 10 ml $FeCl_3$ aqueous solution (0.54 mol dm^{-3}) containing 1.62 mol dm^{-3} PESNNa; the solution instantly acquired a black color as the PPy precipitate was formed. After 2 hours at room temperature, the mixture was filtered and the precipitate was washed with distilled water. After a final rinse with acetone, the black powder was dried in vacuo.

Reaction of Pyrrole with $Fe(OH)_3$: An acid (PSH, PESNH, or PSSH) (0.0162 mol) was added to 10 ml of H_2O containing pyrrole (0.0027 mol) and suspended $Fe(OH)_3$ (0.0054 mol); the solution instantly acquired a black color. After 2 hours at room temperature, the mixture was filtered and the precipitate was washed with distilled water (in the case that the precipitate was obtained). On the contrary, when a precipitate was not obtained, the mixture was centrifuged at 3000 rpm; then, the supernatant was disposed of. The remaining mixture was filtered and the precipitate was washed with distilled water. After a final rinse with acetone, the black powder was dried in vacuo.

Measurements. The conductivity was measured by using a standard van der Pauw method. The PPy powder was molded into a disk by pressing. Scanning and transmission electron microscopic (SEM and TEM) observations were carried out with a Hitachi S-450 and a Hitachi H-800, respectively. The preparation of ultrathin sections of the resulting polymers used for TEM observations was carried out by cutting the PPy powder dispersed PET film, which was embedded in epoxy resin (Polysciences), with an ultra microtome (Sorvall, MT-6000). An elementary analysis of Fe atoms in the PPy matrix was carried out with an X-ray Microanalyzer attachment (Hitachi H-8010).

Results and Discussion

Table 1 shows the conditions of the chemical polymerization of pyrrole using various Fe^{3+} oxidants and electrolytes, as well as the characteristics of the resulting polymers. Pyrrole was polymerized by $FeCl_3$ and $Fe_2(SO_4)_3$ aqueous solutions containing no other electrolyte. The resulting polymers (PPy/Cl^- and PPy/SO_4^{2-}) were precipitated, and black powders were obtained by filtration. On the contrary, pyrrole was not polymerized by $Fe(OH)_3$ suspended H_2O containing no electrolyte. Upon adding an electrolyte, PSNa or PESNNa, into the $Fe(OH)_3$ suspended H_2O, pyrrole was not polymerized either. It was considered that $Fe(OH)_3$ cannot oxidize pyrrole. Upon adding an acid, PSH, PESNH, or PSSH, into the $Fe(OH)_3$ suspended H_2O, $Fe(OH)_3$ was dissolved and pyrrole was polymerized. When PSH and low-molecular-weight PESNH (η_{inh}=0.05) were used as an electrolyte, the resulting polymers (PPy/PS^- and PPy/$PESN^-$(1)) were precipitated. In contrast, when high-molecular-weight PESNH (η_{inh}=0.19 and 0.24) and PSSH (η_{inh}=0.77) were used as an electrolyte, the resulting polymers (PPy/$PESN^-$(2), PPy/$PESN^-$(3), and PPy/PSS^-) were suspended. On the other hand, the resulting polymer (PPy/mix.) prepared by $FeCl_3$ aqueous solution containing PESNNa (η_{inh}=0.19) was precipitated. PPy/PS^-, PPy/mix., and PPy/$PESN^-$(1) were easily obtained by filtration. On the contrary, PPy/$PESN^-$(2) and PPy/$PESN^-$(3) were obtained by a combination of centrifugation (3000 rpm) and filtration. Particles of these polymers did not precipitate perfectly. The PPy/PSS^- did not precipitate upon centrifugation (3000 rpm). These results indicate that the size of the particles of the resulting polymer depended on the property of the electrolyte anion.

Table 2 shows elementary analysis and conductivity data of the resulting polymers. These PPy had as high conductivity (ca. 10^0 S cm^{-1}) as PPy prepared by electrochemical polymerization in H_2O.[37] The Cl/N and the S/N ratios allowed us to estimate the ratio of incorporated anions to the pyrrole moiety (*f*). As for the polymer anion, the present *f*-value does not necessarily indicate the doping ratio, since the existence of

Table 1. Conditions and Proceedings of Polymerization

Oxidant	Electrolyte[a]	Viscosity/η_{inh}[b]	Resulting polymer	Abbreviation
$FeCl_3$	None	—	Precipitated	PPy/Cl^-
$Fe_2(SO_4)_3$	None	—	Precipitated	PPy/SO_4^{2-}
$Fe(OH)_3$	None	—	Not polymerized	—
$Fe(OH)_3$	PSNa	—	Not polymerized	—
$Fe(OH)_3$	PSH	—	Precipitated	PPy/PS^-
$Fe(OH)_3$	PESNNa	0.19	Not polymerized	—
$FeCl_3$	PESNNa	0.19	Precipitated	PPy/mix.
$Fe(OH)_3$	PESNH	0.05	Precipitated	PPy/$PESN^-$ (1)
$Fe(OH)_3$	PESNH	0.19	Suspended	PPy/$PESN^-$ (2)
$Fe(OH)_3$	PESNH	0.24	Suspended	PPy/$PESN^-$ (3)
$Fe(OH)_3$	PSSH	0.77	Suspended	PPy/PSS^-

a) PSNa; sodium 1-propanesulfonate, PSH; 1-propanesulfonic acid PESNNa; sodium polyethylenesulfonate, PESNH; polyethylenesulfonic acid PSSH; polystyrenesulfonic acid. b) Logarithmic viscosity number of polyelectrolyte at 0.5 g dl^{-1}.

Table 2. Elemental Analysis and Conductivity of the Resulting Polymers

PPy	Elemental analysis/wt%					Mole ratio		*f*[a]	Conductivity
	H	C	N	S	Cl	Cl/N	S/N		S cm^{-1}
PPy/Cl^-	3.55	57.80	16.78	0	8.53	0.201	0	0.201	1.70
PPy/SO_4^{2-}	3.53	55.97	15.82	4.00	0	0	0.111	0.222[b]	2.80
PPy/mix.	3.83	54.26	14.66	4.95	1.34	0.036	0.147	0.183	0.73
PPy/$PESN^-$ (1)	4.12	44.19	10.92	9.53	0	0	0.381	0.381	2.70
PPy/$PESN^-$ (2)	4.16	46.12	11.28	9.25	0	0	0.359	0.359	1.20
PPy/$PESN^-$ (3)	3.93	43.22	10.79	9.33	0	0	0.378	0.378	0.18

a) f = Cl/N + S/N. b) f = S/N × 2.

the undoped sulfonate moiety in the PPy matrix was observed (as mentioned below). PPy/PESN$^-$ had a higher f-value than PPy/Cl$^-$ and PPy/SO$_4^{2-}$. As for PPy/mix., because of the existence of Cl and S atoms in the PPy matrix, both Cl$^-$ and PESN$^-$ seemed to be incorporated as a dopant into the PPy matrix. Interestingly, the f-value of PESN$^-$ was 4-times larger than that of Cl$^-$, in spite of the same concentration of the two anions in the oxidative solution. A similar behavior was observed for the PPy prepared by electrochemical polymerization in H_2O containing both the polymer anion and ClO_4^- as an electrolyte anion.[46] This result indicates that the polymer anion was easily incorporated, compared with the small anion, owing to a multi-negative charge. However, doping by only the polymer anion was not expected when $FeCl_3$ was used as an oxidant. When $Fe(OH)_3$ was used as an oxidant, on the contrary, effective doping by the polymer anion seemed to be achieved, since only S atoms existed in the PPy matrix. Because the $Fe(OH)_3$ oxidant and PESN$^-$ gave the PESN-Fe and H_2O, the polymer anion was the only anionic species in the oxidative solution. Therefore, the polymer anion could be incorporated as a dopant into the PPy matrix.

Table 3 shows the molecular weight (MW) per residue of the resulting polymer and yield. The MW per residue was calculated by using the f-value, the MW of pyrrole moiety, and the MW of anion:

$$\text{MW per residue} = (\text{MW of pyrrole moiety}) + (\text{MW per one anion moiety}) \times f. \quad (1)$$

Assuming that the f-value corresponds to the real doping ratio, the theoretical yield was calculated in terms of the moles of the oxidant used, the f-value, and the MW per residue. $(2+f)$ electrons were consumed

Table 3. Molecular Weight per Residue of the Resulting Polymer and Yield

PPy	MW per residue	Theoretical yield/g	Experimental yield/g	Yield/%
PPy/Cl$^-$	72.2	0.177	0.180	102
PPy/SO$_4^{2-}$	75.8	0.184	0.180	98
PPy/mix.	82.3	0.203	0.208	102
PPy/PESN$^-$ (1)	106.9	0.241	0.233	97
PPy/PESN$^-$ (2)	103.9	0.238	0.176	74
PPy/PESN$^-$ (3)	106.0	0.241	0.158	66

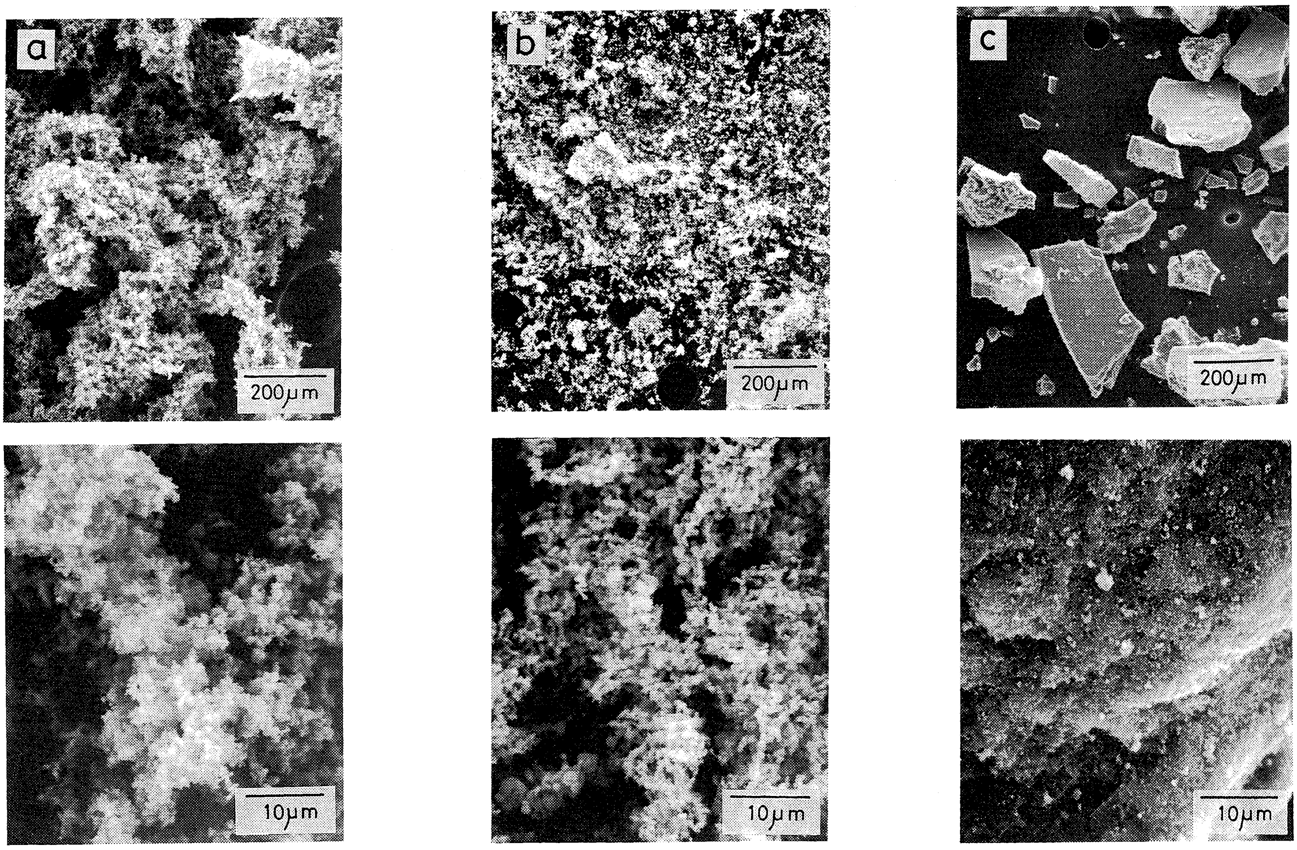

Fig. 1. Typical SEM photographs of the resulting polymers. Accelerating voltage was 15 kV. (a) PPy/SO$_4^{2-}$, (b) PPy/PESN$^-$(1), (c) PPy/PESN$^-$(3).

during the oxidative polymerization of one pyrrole. Thus,

$$(\text{mole of oxidant used})/(\text{mole of pyrrole consumed}) = [2(x-1)+(fx)]/x;$$

$$\text{if } x \text{ is large,} \qquad \simeq 2+f.$$

Here, x denotes the degree of polymerization. Accordingly,

$$\text{Theoretical yield} = [(\text{mole of oxidant used})/(2+f)] \times (\text{MW per residue}). \qquad (2)$$

The yields for PPy/Cl$^-$, PPy/SO$_4^{2-}$, PPy/mix., and PPy/PESN$^-$(1), which were precipitated, were ca. 100%. The yields for PPy/PESN$^-$(2) and PPy/PESN$^-$(3), which were suspended, were low.

Figures 1(a)—(c) show typical SEM photographs for the resulting polymers. The morphology of the resulting polymers was affected by the size of the dopant. Powders of PPy with a small-size anion and PPy with a low-molecular-weight polymer anion have clusters of globules with void spaces between, as shown in Fig. 1(a) and (b). On the other hand, powders of PPy with a high-molecular-weight polymer anion were curds composed of very small particles, as shown in Fig. 1(c). Figures 2(a)—(d) show typical TEM photographs of the resulting polymers. The size of particles estimated by TEM photographs were 2800—4000 Å, 2000—2800 Å, 800—1200 Å, and 200—400 Å for PPy/Cl$^-$, PPy/mix., PPy/PESN$^-$(2), and PPy/PSS$^-$, respectively. The higher molecular-weight of the polymer anion seems to give a smaller size of PPy particle. PPy/mix. showed an intermediate property between PPy/Cl$^-$ and PPy/PESN$^-$(2). These photograph observations indicates that the polymer anion, which has a multi-negative charge, acted as an inhibitor for the growth of PPy particles. The existence of a small amount of Fe atom was observed in the PPy matrix in the X-ray microanalysis measurement. The present Fe atom was considered to be a counter cation of sulfonic acid of the polymer anion, since it was removed from the PPy matrix by washing

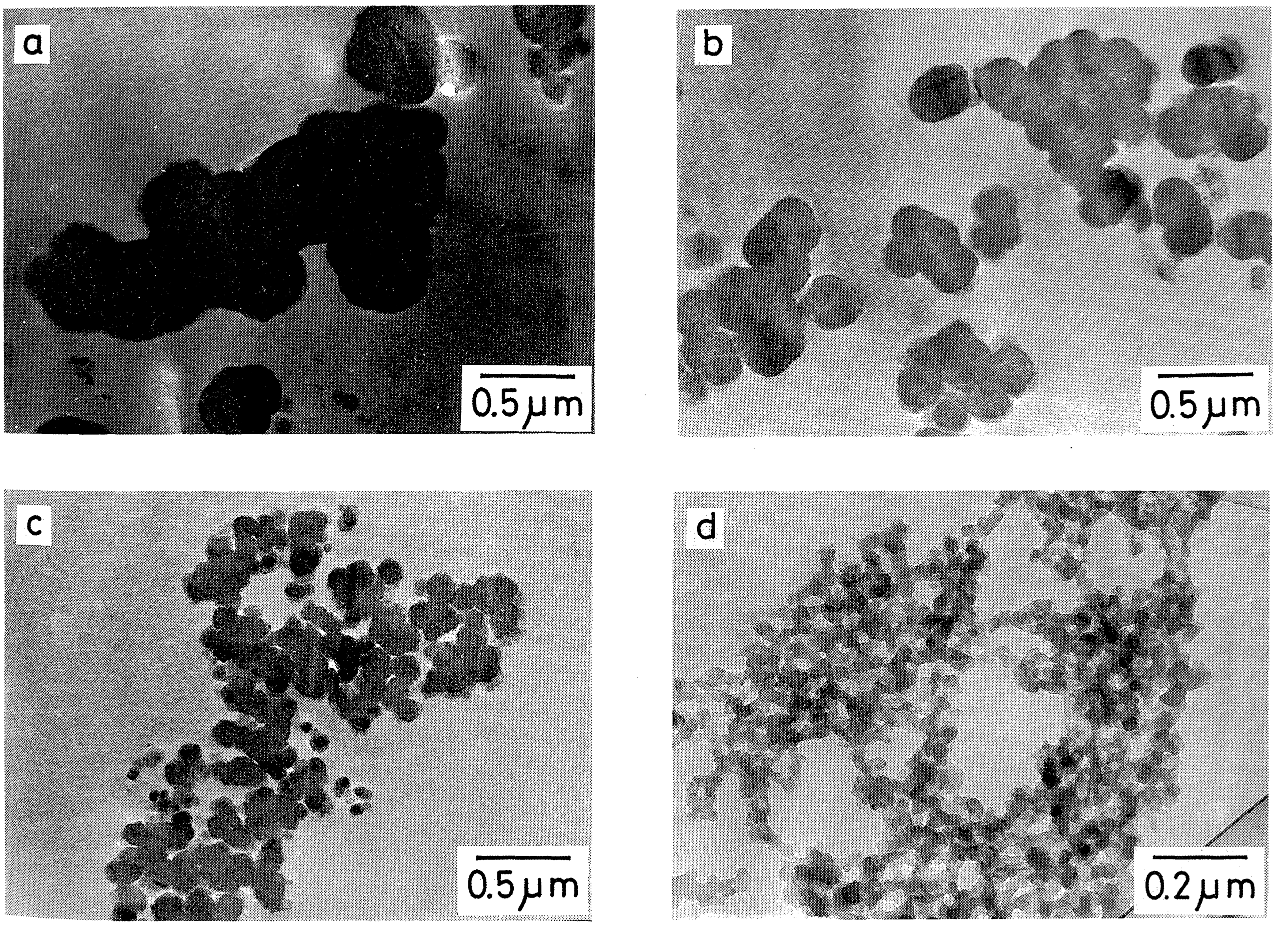

Fig. 2. Typical TEM photographs of the resulting polymers. Accelerating voltage was 100 kV. Ultrathin section of (a) PPy/Cl$^-$, (b) PPy/mix., and (c) PPy/PESN$^-$(2), and dispersion of (d) PPy/PSS$^-$.

using an HCl aqueous solution. Moreover, PPy/PESN$^-$ had a higher doping ratio than PPy/Cl$^-$ and PPy/SO$_4^{2-}$, as mentioned above. Thus, it was considered that there are a considerable amount of undoped polymer anions in the PPy matrix. It is speculated that during the chemical polymerization of pyrrole, the partly incorporated polymer anion into PPy has a considerable amount of free, undoped sulfonic acid, so that PPy was prevented from aggregation, owing to the high charge density of the remaining undoped sulfonic acid. Low yields of PPy/PESN$^-$(2) and PPy/PESN$^-$(3) could be explained by the unrecovered smaller particle of PPy. It was concluded that the Fe(OH)$_3$ oxidant has a capability to effectively dope the acid and that the morphology of the resulting polymers can be controlled by the property of the electrolyte anion.

The present method, using an Fe(OH)$_3$ oxidant and an acidic solution, is considered to be one of the effective hybridization procedures in conducting polymer syntheses.

We thank Mr. Hajime Tsuchiya, Nitto Technical Information Center, for his TEM observations.

References

1) A. F. Diaz, K. K. Kanazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, **1979**, 635.

2) K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt, and G. B. Street, *J. Chem. Soc., Chem. Commun.*, **1979**, 854.

3) A. F. Diaz and J. I. Castillo, *J. Chem. Soc., Chem. Commun.*, **1980**, 397.

4) A. F. Diaz, J. I. Castillo, J. A. Logan, and W.-Y. Lee, *J. Electroanal. Chem.*, **129**, 115 (1981).

5) A. F. Diaz, A. Martinez, K. K. Kanazawa, and M. Salmon, *J. Electroanal. Chem.*, **130**, 181 (1981).

6) A. F. Diaz, J. I. Castillo, K. K. Kanazawa, J. A. Logan, M. Salmon, and O. Fajardo, *J. Electroanal. Chem.*, **133**, 233 (1981).

7) H. S. White, G. P. Kittlesen, and M. S. Wrighton, *J. Am. Chem. Soc.*, **106**, 5375 (1984).

8) G. P. Kittlesen, H. S. White, and M. S. Wrighton, *J. Am. Chem. Soc.*, **106**, 7389 (1984).

9) F. Garnier, G. Tourillon, M. Gazard, and J. C. Dubois, *J. Electroanal. Chem.*, **148**, 299 (1983).

10) R. Bjorklund, S. Andersson, S. Allenmark, and I. Lundström., *Mol. Cryst. Liq. Cryst.*, **121**, 263 (1985).

11) S. Kuwabata, H. Yoneyama, and H. Tamura, *Bull. Chem. Soc. Jpn.*, **57**, 2247 (1984).

12) K. Kaneto and K. Yoshino, *Kino Zairyo*, **4**, 8 (1984).

13) A. Mohammadi, O. Inganas, and I. Lundström, *J. Electrochem. Soc.*, **133**, 947 (1986).

14) N. Mermilliod, J. Tanguy, and F. Petiot, *J. Electrochem. Soc.*, **133**, 1073 (1986).

15) T. Osaka, K. Naoi, H. Sasaki, and S. Ogano, *J. Electrochem. Soc.*, **134**, 285 (1987).

16) A. F. Diaz, *Chem. Scripta*, **17**, 145 (1981).

17) P. Burgmayer and R. W. Murray, *J. Am. Chem. Soc.*, **104**, 6139 (1982).

18) P. Burgmayer and R. W. Murray, *J. Phys. Chem.*, **88**, 2515 (1984).

19) B. Zinger and L. L. Miller, *J. Am. Chem. Soc.*, **106**, 6861 (1984).

20) H. Shinohara, M. Aizawa, and H. Shirakawa, *Chem. Lett.*, **1985**, 179.

21) R. A. Bull, F.-R. Fan, and A. J. Bard, *J. Electrochem. Soc.*, **130**, 1636 (1983).

22) R. Noufi, *J. Electrochem. Soc.*, **130**, 2126 (1983).

23) K. Okabayashi, O. Ikeda, and H. Tamura, *J. Chem. Soc., Chem. Commun.*, **1983**, 684.

24) R. B. Bjorklund and I. Lundström, *J. Electron. Mater.*, **13**, 211 (1984).

25) O. Niwa and T. Tamamura, *J. Chem. Soc., Chem. Commun.*, **1984**, 817.

26) S. E. Lindsey and G. B. Street, *Synth. Metals*, **10**, 67 (1984).

27) M-A. de Paoli, R. J. Waltman, A. F. Diaz, and J. Bargon, *J. Chem. Soc., Chem. Commun.*, **1984**, 1015.

28) N. Bates, M. Cross, R. Lines, and D. Walton, *J. Chem. Soc., Chem. Commun.*, **1985**, 871.

29) T. Ojio and S. Miyata, *Polym. J.*, **18**, 95 (1986).

30) F.-R. F. Fan and A. J. Bard, *J. Electrochem. Soc.*, **133**, 301 (1986).

31) H. Yoneyama, T. Hirai, S. Kuwabata, and O. Ikeda, *Chem. Lett.*, **1986**, 1243.

32) T. Iyoda, A. Ohtani, T. Shimidzu, and K. Honda, *Chem. Lett.*, **1986**, 687.

33) T. Iyoda, A. Ohtani, T. Shimidzu, and K. Honda, *Synth. Metals*, **18**, 725 (1987).

34) T. Shimidzu, A. Ohtani, T. Iyoda, and K. Honda, *J. Chem. Soc., Chem. Commun.*, **1986**, 1414.

35) T. Shimidzu, A. Ohtani, T. Iyoda, and K. Honda, *J. Chem. Soc., Chem. Commun.*, **1986**, 1415.

36) T. Shimidzu, A. Ohtani, T. Iyoda, and K. Honda, *J. Chem. Soc., Chem. Commun.*, **1987**, 327.

37) T. Shimidzu, A. Ohtani, T. Iyoda, and K. Honda, *J. Electroanal. Chem.*, **224**, 123 (1987).

38) T. Shimidzu, A. Ohtani, and K. Honda, *J. Electroanal. Chem.*, **251**, 323 (1988).

39) T. Shimidzu, A. Ohtani, and K. Honda, *Bull. Chem. Soc. Jpn.*, **61**, 2885 (1988).

40) T. Shimidzu, A. Ohtani, M. Aiba, and K. Honda, *J. Chem. Soc., Faraday Trans. 1*, in press.

41) M. Salmon, K. K. Kanazawa, A. F. Diaz, and M. Krounbi, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 187 (1982).

42) K. Yoshino, S. Hayashi, and R. Sugimoto, *Jpn. J. Appl. Phys. Part 2*, **23**, L899 (1984).

43) V. Bocchi and G. P. Cardini, *J. Chem. Soc., Chem. Commun.*, **1986**, 148.

44) R. E. Myers, *J. Electron. Mater.*, **15**, 61 (1986).

45) T. H. Chao and J. March, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 743 (1988).

46) K. Hyodo and M. Nozaki, *Electrochim. Acta*, **33**, 165 (1988).