CHEMISTRY LETTERS, pp. 415-418, 1993. © 1993 The Chemical Society of Japan

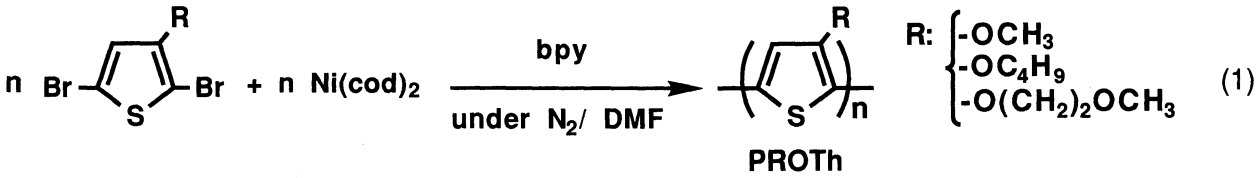
Preparation of Poly(3-alkoxythiophene-2,5-diyl)s by Organometallic Process and Doping-Undoping Behaviors of the Polymers

Yuichi MIYAZAKI, Takaki KANBARA, Kohtaro OSAKADA, and Takakazu YAMAMOTO*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

Poly(thiophene-2,5-diyl) derivatives having alkoxy substituents at 3-positions are synthesized by dehalogenation polycondensation of the corresponding 2,5-dibromothiophene derivatives with zero-valent nickel complex. The obtained polymers show not only usual p-type doping and undoping behaviors but also unique n-type doping and undoping behaviors due to the stabilization of n-doped state by interaction between dopant cation and ethereal oxygen.

Poly(thiophene-2,5-diyl)s with π-conjugated systems along the polymer chain have been widely investigated as typical electrically conducting polymers. In particular, 3-substituted poly(thiophene-2,5-diyl) derivatives[1,2] have attracted strong attention in view of not only their processability but also their interesting properties caused by the introduction of the substituents. Recently, such polymers with 3-alkoxy substituent, e.g., poly(3-methoxythiophene-2,5-diyl) (PMeOTh), were prepared by electropolymerization,[2] and it was reported that p-doped state of the polymers had higher stability than that of poly(thiophene-2,5-diyl) and poly(3-alkylthiophene-2,5-diyl)s due to electron donating property of alkoxy groups. However, NMR spectra of PMeOTh suggest the presence of several types of bonding (e.g. 2,5- and 2,4- bonding) between the monomer units in the electrochemically polymerized PMeOTh,[2d,e] and further investigations of poly(3-alkoxythiophene-2,5-diyl)s (PROTh) prepared by other methods are desired to reveal the doping behavior of the polymer. Furthermore, in contrast to the p-doping of the polymers, much less attention has been paid on n-doping behavior of poly(3-alkoxythiophene-2,5-diyl)s.

We now report preparation of PROTh's by the following dehalogenation polycondensation using zero-valent nickel complexes[3] and p- and n-doping behavior of the polymers. The polymerization method affords the p-conjugated polymers with well-defined linkage between the monomer units in high yields.



(1)

Three 2,5-dibromo-3-alkoxythiophenes were prepared by the reported method.[4] Stirring the monomer (1.6 mmol) with a mixture of bis(1,5-cyclooctadiene)nickel (Ni(cod)2, 2.0 mmol), 1,5-cyclooctadiene (1.6 mmol), and 2,2'-bipyridine (bpy, 2.0 mmol) in *N*,*N*-dimethylformamide (13 cm^3) for 48 h at about 30 °C

afforded the polymers as blue black precipitates. Work up of the polymers, involving removal of nickel compounds with ethylenediaminetetraacetic acid, was carried out in a manner similar to that previously reported.[3] Results of the polymerization and analytical data of the polymers are summarized in Table 1.

Table 1. Preparation of poly(3-alkoxythiophene-2,5-diyl) derivatives[a]

		Yield / %	C / %	H / %	S / %	Halogen / %
Poly(3-methoxythiophene-2,5-diyl)	(PMeOTh)	76	53.31	3.35	27.25	0
			(53.57)	(3.57)	(28.57)	(-)
Poly(3-butoxythiophene-2,5-diyl)	(PBuOTh)	71	60.23	6.06	20.07	0
			(62.34)	(6.49)	(20.78)	(-)
Poly(3-(2-methoxyethoxy)thiophene-2,5-diyl)	(PMeOEOTh)	85	54.59	5.18	19.50	0
			(53.85)	(5.13)	(20.51)	(-)

a) The numbers in round brackets are calculated values.

As shown in Table 1, the desired polymers are obtained in good yield. IR spectra of the polymers (*vide infra*) show strong absorption peaks at about 1180 cm^{-1} (C-O-C antisymmetric stretching) and 1080 cm^{-1} (C-O-C symmetric stretching).

PMeOTh thus prepared has considerably lower solubility than the electrochemically prepared PMeOTh presumably due to highly regular structure or higher molecular weight. The obtained polymers are partially soluble in *N*-methylpyrrolidone (NMP), dimethyl sulfoxide and chloroform. In the case of PMeOTh, about half of the polymer is soluble in NMP, and gel permeation chromatograms indicate that the soluble PMeOTh has a number-average molecular weight of 1800 and a weight-average molecular weight of 3000 (*vs.* polystyrene), respectively.

The UV-vis absorption spectra of the polymers in NMP show λ_{max} at 576 nm (PMeOTh), 548 nm (PBuOTh), and 578 nm (PMeOEOTh), respectively. These peak positions are at longer wavelength compared with those of poly(3-alkylthiophene-2,5-diyl)s,[3] and as for PMeOTh the absorption peak appears at considerably longer wavelength than that (λ_{max}=470-490 nm[2]) of the electropolymerized PMeOTh.

The ^{1}H-NMR spectrum of soluble part of PMeOTh in $CDCl_3$ shows two signals assigned to the methoxy protons (3.8 ppm and 4.0 ppm) and four signals assigned to the aromatic protons (6.83 ppm, 6.87 ppm, 6.92 ppm, and 7.02 ppm). Two methoxy proton signals at 3.8 ppm and 4.0 ppm are assigned to head-to-head (HH) and head-to-tail (HT) conjunctions, respectively, from analogy with the ^{1}H-NMR chemical shifts of poly(3-alkylthiophene-2,5-diyl)s.[5] Four aromatic proton signals are also assigned to the four possible different triads of thiophene rings.[6]

The obtained polymers themselves are insulators. However, on p-doping with iodine (exposure to vapor of iodine at room temperature for 48 h), the electrical conductivity (σ) of each polymer increases to 1.8×10^{0} S cm^{-1}, 2.1×10^{-2} S cm^{-1}, and 2.1×10^{-1} S cm^{-1} for PMeOTh, PBuOTh, and PMeOEOTh, respectively, as measured with pressed pellets using a two-probe method. The iodine-doped polymers can be reversibly undoped by treatment with hydrazine.

Figure 1 shows cyclic voltammograms (CV) of PMeOTh film in (a) 0.1M-Bu_4NClO_4/ CH_3CN and (b) 0.1M-$LiClO_4$/ CH_3CN. PMeOTh film was prepared by casting the NMP solution of PMeOTh on ITO-glass plate and evaporation of the solvent under vacuum. In Fig. 1(a), the p-type doping and undoping peaks are observed at -0.20 V (peak iii) *vs.* Ag/Ag^+ and -0.55 V (peak iv), respectively. The polymer film is stable during repeated scanning, showing essentially the same CV. These potentials are in agreement with those of PMeOTh

prepared by the electropolymerization.[2b] The p-type redox potentials of the PMeOTh film are more negative than those of poly(3-alkylthiophene-2,5-diyl)s,[3] indicating that PMeOTh is oxidized (p-doped) more easily than poly(3-alkylthiophene-2,5-diyl)s due to the electron donating alkoxy substituent.

On the other hand, sweeping to -2.10 V gives a new unreported n-doping peak at -2.02 V(peak v) with shoulder (< -2.06 V) and corresponding n-undoping peaks at two positions at -2.04 V(peak i) and -0.52 V(peak ii). These unique redox behavior in CV has good reproducibility during repeated scanning. The appearance of two n-undoping peaks coupled with the n-doping peak at about -2.0 V suggests the presence of two types of n-doped states or the presence of cations in two different environments corresponding to the two types of n-doped states; the n-undoping peak i is considered to be due to usual simple type undoping, while the peak ii is considered to be due to undoping involving removal of cations having strong interaction with the ethereal oxygen. When a Li salt is used as the electrolyte, the cation (Li^+) seems to have stronger interaction with the ethereal oxygen to give only one n-undoping peak at a high voltage overlapped with the p-doping peak (Fig. 1b).

Similar n-type doping-undoping behaviors with large potential difference between the n-doping peak and n-undoping peak were previously reported for poly(3-(3,6-dioxaheptyl) thiophene) (PDHT) having alkyl substituent with chelating 1,4-diethereal oxygens in the side chain.[7] PMeOEOTh has the 1,4-diethereal oxygens similar to those of PDHT, and CV of PMeOEOTh in 0.1 M Bu_4NClO_4/ CH_3CN (Fig. 2) also shows a large difference between the n-doping potential (< -2.3 V) and n-undoping potential (-0.3 V), suggesting the presence of the strong interaction between the dopant cation and the ethereal oxygens.

The supposed strong interaction between the dopant cation and ethereal oxygens in PMeOTh might

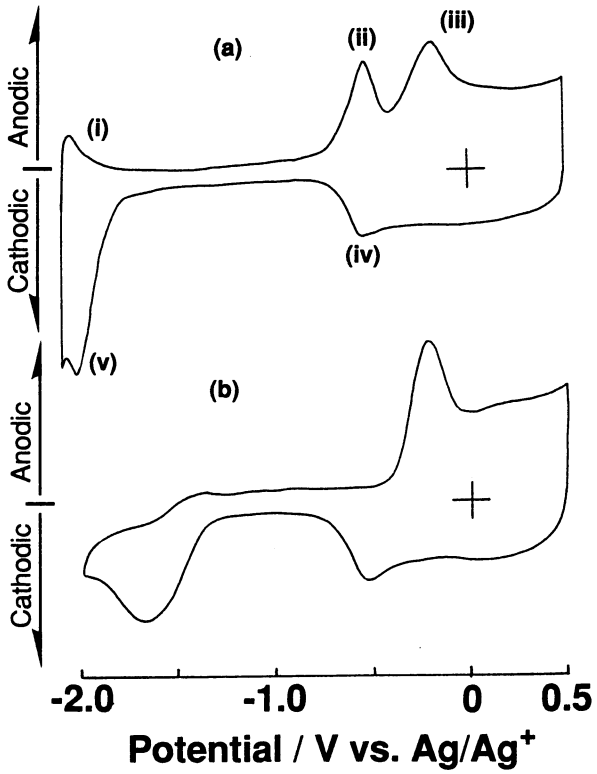


Fig. 1. Cyclic voltammograms of PMeOTh cast on ITO electrode. (a) In 0.1M-Bu_4NClO_4/ CH_3CN, and (b) in 0.1M-$LiClO_4$/ CH_3CN. At 10 mV s^{-1} at room temperature.

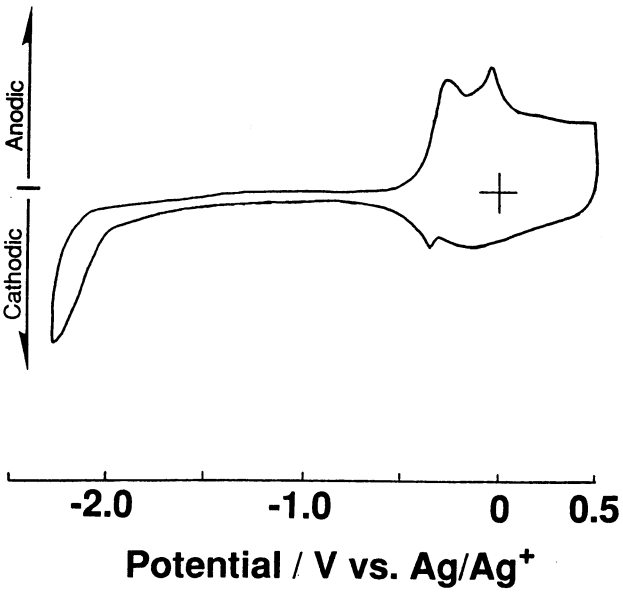


Fig. 2. Cyclic voltammograms of PMeOEOTh in 0.1M-Bu_4NClO_4/ CH_3CN. At 10 mV s^{-1} at room temperature.

result not only from interchain interaction of the cation with MeO oxygens in different PMeOTh molecules but also from the presence of chelating diethereal unit, which is formed in the head-to-head unit of PMeOTh.

Chemical n-doping/undoping were also examined. Treatment of the polymers with sodium naphthalide in tetrahydrofuran gave Na-doped polymers which were able to be undoped by treatment with methanol. The σ values of Na-doped polymers are in a range of 10^{-2}-10^{-3} S cm^{-1}. Figure 3 shows the IR spectra of PMeOTh and PMeOEOTh at non-doped, Na-doped, and undoped states. In Fig. 3, the absorption peaks at 1200-1000 cm^{-1} assigned to C-O-C stretching vibration are weakened at the Na doping, and this IR spectral change strongly indicates that cations are coordinated by the ethereal oxygens in the n-doped state.

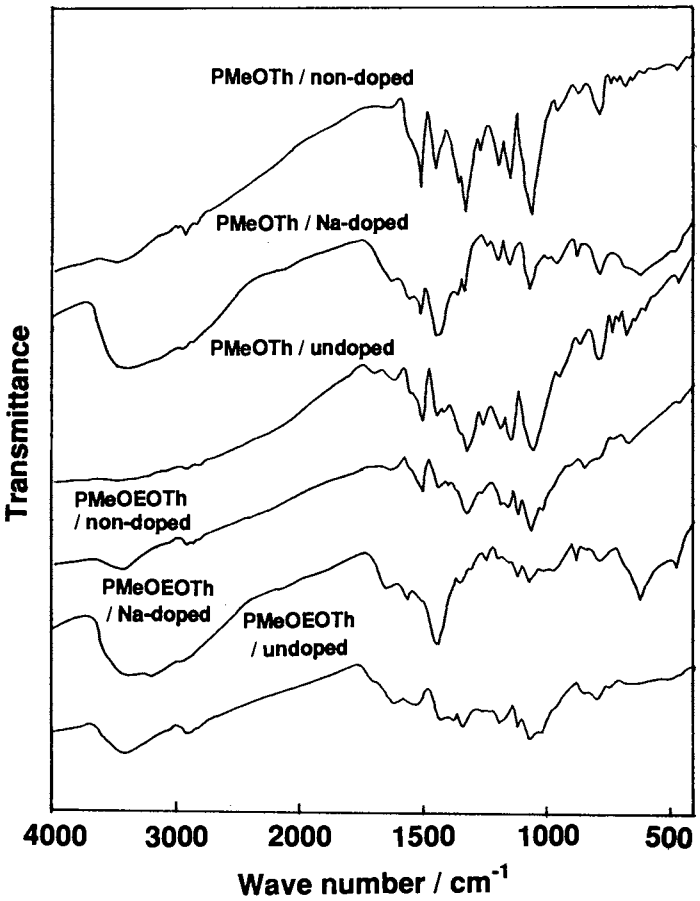


Fig. 3. IR spectral change of PMeOTh and PMeOEOTh on Na-doping and undoping.

References

1) T. Yamamoto and K. Sanechika, *Chem. Ind.(London)*, **1982**, 301; T. Yamamoto, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **56**, 1497 and 1503 (1983); R. S. Elsenbaumer, K. Y. Jen, and R. Oboodi, *Synth. Met.*, **15**, 169 (1986); K. Yoshino, S. Nakajima, and R. Sugimoto, *Jpn. J. Appl. Phys.*, **26**, L1038 (1987); M. Sato, S. Tanaka, and K. Kaeriyama, *J. Chem. Soc., Chem. Commun.*, **1986**, 873.

2) a) A. -C. Chang, R. L. Blankespoor, and L. L. Miller, *J. Electroanal. Chem.*, **236**, 239 (1987); b) S. Tanaka, M. Sato, and K. Kaeriyama, *Synth. Met.*, **25**, 277 (1988); c) K. Kaeriyama, S. Tanaka, M. Sato, and K. Hamada, *ibid.*, **28**, C611 (1989); d) T. Yamamoto, A. Kashiwazaki, and K. Sanechika, *Denki Kagaku*, **56**, 898 (1988); e) T. Yamamoto, A, Kashiwazaki, and K. Kato, *Makromol. Chem.*, **190**, 1649 (1989).

3) T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z. -H. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki, and K. Kubota, *Macromolecules*, **25**, 1214 (1992).

4) K. Kaeriyama, S. Tanaka, A. Yamauchi, and Z. Matsuzaki, *Jpn. Kokai Tokkyo Koho* Jp 02229186 (1990).

5) R. M. S. Major, K. Hinkelmann, H. Eckert, and F. Wudl, *Macromolecules*, **23**, 1268 (1990).

6) W. A. Goedel, N. S. Somanathan, V. Enkelmann, and G. Wegner, *Makromol. Chem.*, **193**, 1195 (1992).

7) J. Roncali, R. Garreau, D. Delabouglise, F. Garnier, and M. Lemaire, *J. Chem. Soc., Chem. Commun.*, **1989**, 679.

(Received November 27, 1992)