CHEMISTRY LETTERS, pp. 539-542, 1987.

Electrochemical Synthesis of Poly(p-phenylene vinylene) Films

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Electroreduction of α,α,α',α'-tetrabromo-p-xylene at an indium tin oxide (ITO), platinum, copper or nickel electrode in ethereal solution afforded a thick and uniform poly(p-phenylene vinylene) film in the undoped state. Addition of $Cr(CO)_6$ or $Mo(CO)_6$ accelerated the film growth at the ITO electrode.

Electrically conducting organic polymers have received considerable recent attention because of their fundamental interests and the diversity for application in electronic devices.1) Synthetic methods govern their π-conjugated chain length and consequently their qualities such as conductivity and film-forming abilities. Electrochemical oxidation methods have been preferably used for the preparation of high-quality films of π-conjugated organic polymers, e.g. polypyrrole,2) polythiophene,3,4) polyfuran,5) polyselenophene,6) polyphenylene,7,8) and their derivatives. Contrary to those examples of electrooxidation, electroreduction has scarecely been utilized for the synthesis of the conducting polymers.

We report here the first electroreductive synthesis of thick and uniform films of π-conjugated organic polymer, poly(p-phenylene vinylene) (PPV) in the undoped state, from α,α,α',α'-tetrabromo-p-xylene (**1**). PPV has previously been prepared by several methods using chemical reactions,9-11) and recently, Murase et al. have obtained a high-quality film by thermal decomposition of a poly(p-phenylene ethylene) sulfonium salt.12) Its electrical and optical properties have been reported by Yoshino et al.13) Although the conductivity of the doped film obtained in this study is only modest,14) this electrochemical synthetic methodology is simple and convenient. Electrochemical conditions to afford thick and uniform films and their characteristics in the undoped state are described in this paper.

A typical procedure of the PPV film preparation is as follows. Constant potential electrolysis at -3.0 V vs. Ag/Ag^+ in 10 cm^3 of THF solution containing 0.05 M of **1** and 0.1 M of $n\text{-}Bu_4NBF_4$ at an ITO electrode (area: 2.5 cm^2) afforded ca. 0.7 mA of nearly constant cathodic current. After 6 h of the electrolysis and holding the potential at 0 V vs. Ag/Ag^+ for 20 min in order to make the film

Table 1. Conditions a) and results of electrochemical preparation of PPV films

Run	Electrode	Solvent	Electrolyte b)	Mediator c)	Cathodic Charge/C cm^{-2}	Film weight mg cm^{-2}
1	ITO	MeCN	n-Bu$_4$NClO$_4$	-	2.15	0.23
2	ITO	DME	n-Bu$_4$NClO$_4$	-	10.85	1.21
3	ITO	THF	n-Bu$_4$NClO$_4$	-	8.23	1.49
4	ITO	THF	n-Bu$_4$NBr	-	2.58	0.58
5	ITO	THF	n-Bu$_4$NI	-	2.14	0.44
6	ITO	THF	n-Bu$_4$NBF$_4$	-	6.17	1.26
7	ITO	THF	n-Bu$_4$NBF$_4$	Fe(CO)$_5$	11.75	1.68 d)
8	ITO	THF	n-Bu$_4$NBF$_4$	Co$_2$(CO)$_8$	3.87	0.41 d)
9	ITO	THF	n-Bu$_4$NBF$_4$	Cr(CO)$_6$	9.51	1.61
10	ITO	THF	n-Bu$_4$NBF$_4$	Mo(CO)$_6$	7.98	1.36
11	ITO	THF	n-Bu$_4$NBF$_4$	(C$_6$H$_6$)Cr(CO)$_3$	2.77	0.82
12	GC	THF	n-Bu$_4$NBF$_4$	-	0.11	e)
13	Pt	THF	n-Bu$_4$NBF$_4$	-	17.28 f)	1.31
14	Cu	THF	n-Bu$_4$NBF$_4$	-	20.06	1.84
15	Ni	THF	n-Bu$_4$NBF$_4$	-	14.49	1.40

a) Constant potential electrolysis at -3.0 V vs. Ag/Ag$^+$ in a 47 mM solution of **1** for 6 h. b) 100 mol m^{3}. c) 10 mol m^{3}. d) A mottled dark brown film was obtained. e) Current density decreased to <10 μA within 10 min and the film was not separated. f) Electrolysis for 10 h.

neutral, a thick (30 μm) and flexible yellow film (3.1 mg) was obtained. The film could be easily separated from the electrode by immersing that in THF for a short time.

Dependency of growth rates and qualities of the film on the electrolysis conditions was examined and the results are shown in Table 1. Ethereal solvents such as THF or 1,2-dimethoxyethane (DME), tetraalkylammonium salts of tetrafluoroborate or perchlorate as the supporting electrolyte, and ITO, platinum, nickel or copper as the electrode material were the best combinations for the formation of thick and uniform films. The film growth rate increased in the following order of electrode materials, glassy carbon (GC) < ITO < Pt < Ni < Cu, and this tendency seems to be related to the capacity for oxidative-addition of organic halides.15) Effects of transition-metal complexes on the electrolysis were also investigated. Cromium and molybdenum carbonyl complexes, Cr(CO)$_6$ and Mo(CO)$_6$, had acceleration effects on the film growth rate at the ITO electrode as represented in Table 1.

Infrared absorption spectra of the films prepared at an ITO electrode in 0.1 M n-Bu$_4$NBF$_4$-THF without and with Mo(CO)$_6$ and at a copper electrode are shown in Fig. 1. They are almost consistent with the spectrum of the PPV prepared from the sulfonium salt by Murase et al.12) An extra absorption band is observed at 1700 cm^{-1} assignable to ν(C=O) in the spectra of the films prepared at ITO (Fig.

1A, B) but not in the film prepared at copper (Fig. 1C). This suggests the participation of the oxygen in the oxide electrode material into the electropolymerization reaction. Addition of $Mo(CO)_6$ led to decrease of the absorption at 620 cm^{-1} due to ν(C-Br) (Fig. 1B). Elemental analyses of these films also showed the decrease of Br contents indicative of longer conjugated chains by the addition of the molybdenum complex during the electrolysis.16) The spectrum and analysis of the film formed at the copper electrode also indicated weaker ν(C-Br) absorption (Fig. 1C) and lower Br contents16) than that prepared at the ITO electrode (Fig. 1A).

The elemental analysis data16) indicate that the average degrees of polymerization, n, are 3, 11, 7.5 for the films prepared at ITO without and with $Mo(CO)_6$ and at copper, respectively, provided that the polymers consist of structures with a single formula, $Br_2CH{+}C_6H_4\text{-}CH{=}CH{+}_nC_6H_4CHBr_2$. These numbers seem small because the polymer films are quite insoluble in organic solvents such as DMF, chloroform, acetone or benzene. We suppose at present that the polymers are mixtures of completely and incompletely reduced structures, $+C_6H_4CH{=}CH+_n$ and $+C_6H_4CHBrCHBr+_n$. Contamination of the films with impurities such as electrolyte is also suggested by the shortage in the sum of C, H and Br contents of the films from 100%.16)

Conductivities of the PPV films were measured by the two-probe techniques. Figure 2 displays the temperature dependence of the conductivity for the film formed at an ITO electrode in 0.1 M $n\text{-}Bu_4NBF_4$-THF. The activation energy was 0.56 eV, calculated from the slope of the line in the figure. This is similar to the value, 0.52 eV, reported by Yoshino et al.13) for the undoped state of the

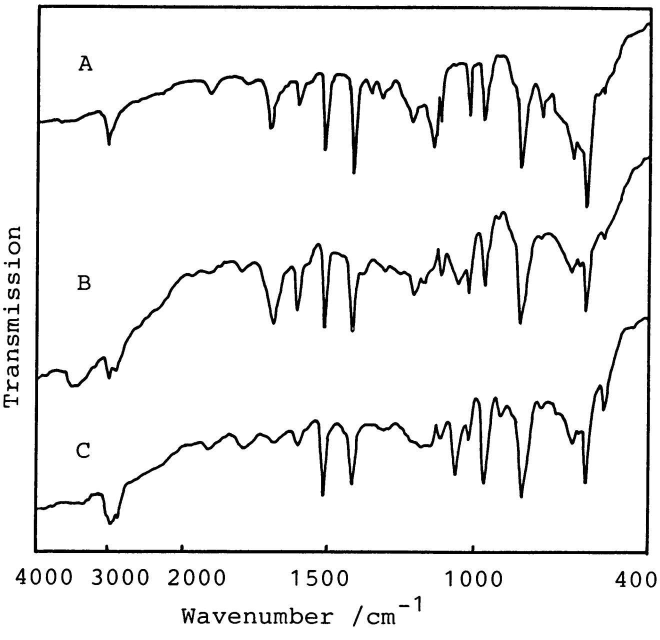

Fig. 1. Infrared absorption spectra of PPV prepared at ITO in $n\text{-}Bu_4NBF_4$-THF (A) without and (B) with $Mo(CO)_6$, and (C) at copper.

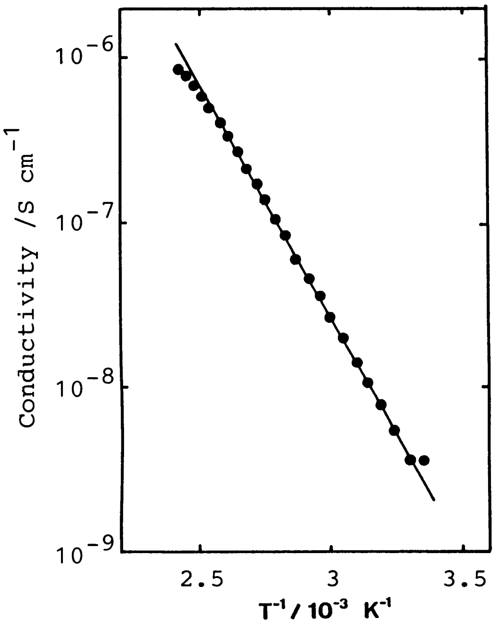

Fig. 2. Temperature dependence of electrical conductivity of undoped PPV prepared at ITO in $n\text{-}Bu_4NBF_4$-THF.

film prepared by the Murase's method.[12] However, the conductivity of the film prepared in this study is 6×10^{-9} S cm^{-1} at room temperature and higher as much as four orders than that of the above film. At this stage, it seems most likely that this higher conductivity is due to the effects of structural units other than phenylene vinylene and/or those of impurities as mentioned above.

Preliminaly results for the study on doping properties of the PPV films are as follows. The PPV prepared at ITO could be doped with vapor of iodine and fuming sulfuric acid, and the respective conductivities were 2×10^{-6} and 5×10^{-2} S cm^{-1} at room temperature. It is noteworthy that the conductivities increase in contact with moisture.

We thank Professor Katsumi Yoshino, Osaka University, for informative comment and discussion.

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(Received December 22, 1986)