

Electrosynthesis of Conducting Poly(*p*-phenylene)

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SYNOPSIS

The polymerization of benzene was studied in bulk and in nitrobenzene using $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ as a supporting electrolyte at platinum electrodes to obtain poly(*p*-phenylene). The polymers were formed as a black thready mass on the anode and their yields were restricted to the area of the anode in the electrochemical cell. The yields of the polymers formed in the bulk and in nitrobenzene were almost equal, although electrical resistances of the polymers obtained from the bulk were relatively lower. Cyclic voltammetry measurements suggest that the polymerization of benzene took place from the species generated anodically *in situ*. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The electrically conducting polymers have recently become an active research field. Interest in such polymers is due to their potential technological applications such as in batteries, photoelectrochemical solar cells, electrochromic display devices, as well as nonclassical electrical and optical uses.¹ Poly(*p*-phenylene) represents one of the most widely studied conducting polymers.^{2,3} Several techniques for the synthesis of conducting polymers are available such as stepwise synthesis routes, polycondensation, oxidative coupling, the metal-catalyzed polymerization method, and the electrochemical method. The electrochemical polymerization leads directly to polymers with high electrical conductivity. The literature contains few reports on the anodic polymerization of benzene to poly(*p*-phenylene).^{4,5} The electrochemical polymerization of benzene at In–Sn oxide-coated conducting glass plate/Ni plate electrodes with $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ in nitrobenzene was briefly reported by Japanese workers.⁶ In this article, we describe the polymerization of benzene with $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ under constant current electrolysis conditions as well as under potentiodynamic controls. The polymerization was carried out both in bulk and in a diluent.

EXPERIMENTAL

Materials

Benzene and nitrobenzene were purified by fractional distillation and middle fractions were collected. $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ was used without further purification.

Polymerization

Under constant current electrolysis, polymerization was carried out in a simple one-compartment glass cell that could accommodate two platinum electrodes of the area $2.5 \times 1.7 \text{ cm}^2$. The cell was charged with known amounts of monomer, solvent, and supporting electrolyte and the resulting solution was saturated with N_2 gas to purge oxygen. Then, the cell was thermostated at 30°C and subjected to electrolysis at 40 mA. The electrolysis was terminated at a known time and the anode that was heavily covered with a black polymer mass was taken out. When the polymer film became dry, the resistance of the polymer film was measured on the platinum substrate at ambient temperature with a high vacuum tube voltmeter and then the deposited polymers were removed with a sharp razor and weighed.

Cyclic Voltammograms

Cyclic voltammograms were recorded with CV-27 BAS (Bio Analytical System, U.S.A.) cyclic voltam-

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metry system equipped with BAS X-Y recorder. All electrical measurements were performed in a single-compartment three-electrode cell under a N_2 atmosphere. The working electrode was a platinum microelectrode, the counter electrode was a platinum wire, and the reference electrode was a saturated calomel electrode that was isolated from the cell by a salt bridge.

RESULTS AND DISCUSSION

The polymerization of benzene was investigated in bulk and in nitrobenzene using $BF_3O(C_2H_5)_2$ as a supporting electrolyte to obtain poly(*p*-phenylene). Polymers were formed as a black thready mass on the anode. The polymerization did not take place if the benzene solution was not subjected to electrolysis. The polymer formation occurred only on the surface of the anode in the electrochemical cell and not in the body of the solution. The yield and the electrical resistance of the resulting polymers that were formed in the bulk and in nitrobenzene are summarized in Table I, which shows that polymer yields in bulk and in diluent are almost equal although electrical resistances of the polymers are relatively lower in the bulk. The thickness of the polymer films increases with the increase of polymerization time and therefore the electrical resistance of the polymer decreased with the increase of electrolysis time. When the temperature of polymerization was varied from 0 to 50°C, some variation in the yield and electrical resistance of the resulting polymers were observed, as shown in Table II. The decrease in polymer yield with the increase of temperature is attributed to the increase in the termination process with the rise of reaction temperature.

Table I Yields and Electrical Resistances of Poly(*p*-phenylene) Prepared from Benzene^a

Time (h)	Yield (mg)		Electrical Resistance 10^{-4} (ohm-cm)	
	Bulk	Nitrobenzene	Bulk	Nitrobenzene
1	30	26	2.5	150
2	55	50	2.0	50
3	75	80	1.5	5
4	110	130	0.5	1

^a In bulk and in nitrobenzene containing $BF_3O(C_2H_5)_2$ (1.3 mol/L) at different electrolysis times. Constant current, 40 mA; concentration of benzene in nitrobenzene, 0.3 mol/L; volume of the reaction mixture, 11 mL at 30°C.

Table II Yields and Electrical Resistances of Poly(*p*-phenylene) Prepared from Benzene (0.3 mol/L)^a

Temperature (°C)	Yield (mg)	Electrical Resistance 10^{-4} (ohm-cm)
0	72	40
30	50	50
50	45	55

^a In nitrobenzene containing $BF_3O(C_2H_5)_2$ (1.3 mol/L) at different temperatures. Constant current, 40 mA; electrolysis time, 2 h; volume of the reaction mixture, 11 mL.

Consequently, some oligomers might have been formed that did not deposit as insoluble polymers on the anode. During electrolysis, the electrolyzing solution turned brown-black from light yellow. On filtration, no polymers were isolated. The decrease in the electrical resistance with the decrease of temperature is due to the increase of the thickness of the deposited polymer films. The extreme insolubility of the polymer precluded molecular weight determination by the usual methods. The infrared spectrum shows vibrational bands at 1195, 800, 720, 650, and 545 cm^{-1} , indicating benzene rings linked in the *para* position. Ohsawa et al.⁶ obtained analogous results.

The polymers synthesized under our experimental conditions are amorphous and less conducting as compared to those prepared by the Japanese group.⁶ These differences must be due to the differences in the preparing conditions of the polymers. The Japanese group applied a constant voltage (20 mV) and In-Sn oxide-coated conducting glass plate/Ni plate electrodes, whereas we used a constant current of 40 mA and platinum electrodes. There were also differences in the concentrations of benzene (monomer) and $BF_3O(C_2H_5)_2$ (electrolyte).

Cyclic Voltammograms

The polymerization of benzene was also carried out under potentiodynamic and potentiostatic conditions using the CV-27 BAS cyclic voltammetry system. The solution of $BF_3O(C_2H_5)_2$ in benzene did not show a CV wave, although potentials were scanned from +3.5 to -3.5 V. However, in the solution of $BF_3O(C_2H_5)_2$ in nitrobenzene, well-defined redox peak currents were recorded at +1.1 and +0.6 V vs. SCE, as shown in Figure 1. The redox peak currents gradually decreased with the number of potential scans. At the different scan rates, the redox

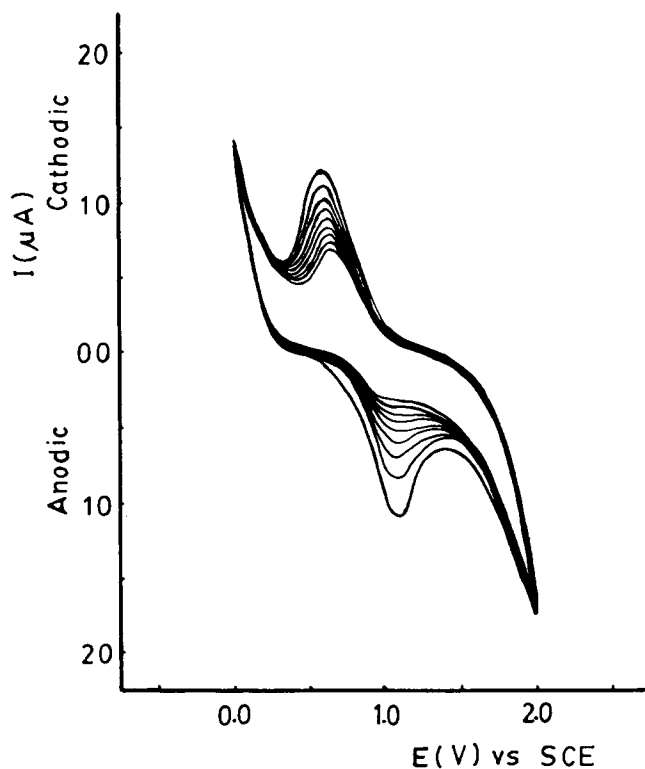


Figure 1 Multisweep cyclic voltammograms of the solution of $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ (0.19 mol/L) in nitrobenzene at 75 mV/s. The redox peak currents decrease with the number of scans.

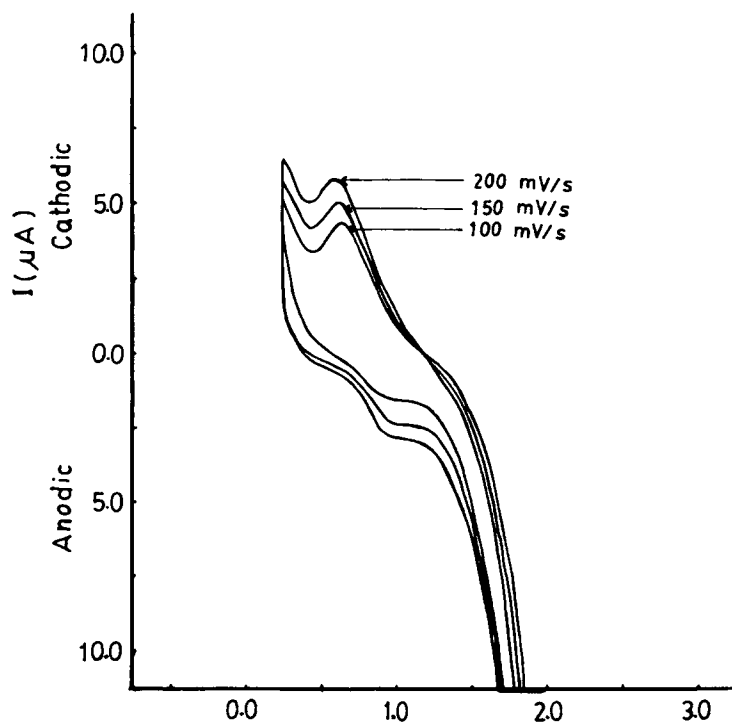
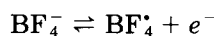


Figure 2 Cyclic voltammograms of the solution of $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ (0.19 mol/L) in nitrobenzene at different scan rates as depicted in the curves at 30°C.

peak currents increased, as depicted in Figure 2. When benzene was added to the solution of $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ in nitrobenzene, the same cyclic voltammograms shown in Figure 1 were obtained.

Boronfluoride etherate, $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$, may exist in diethyl ether as a polar molecule,⁷ $(\text{C}_2\text{H}_5)_3\text{O}^+$, BF_4^- , which furnishes the conducting medium. The anion goes plausibly under the following electrochemical reaction:



The voltammograms shown in Figure 1 could be due to this redox reaction.

The possibility of initiation by direct anodic oxidation of benzene at the anode was ruled out because no CV wave appeared for benzene. Therefore, it seems that the polymerization was initiated either by the BF_4^{\bullet} radical or other reactive species that might have been generated electrochemically *in situ*.

In conclusion, our study reveals two new facts in relation to the previous work by the Japanese group. First, benzene with $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ (1.3 mol/L) without any diluent furnishes a good conducting medium (40 mA at 100 V) and polymerizes electrochemically in the bulk. Second, the cyclic voltam-

metry results suggest that the polymerization occurs via species generated anodically *in situ*.

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