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# Electrochemical Preparation of Poly(p-phenylene) Using Trifluoromethane Sulfonic Acid as a Catalytic Electrolyte

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Electro-oxidative polymerization of benzene in the presence of trifluoromethane sulfonic acid yields poly(p-phenylene) efficiently; The acid forms a protonated complex of benzene and cathodically shifts its oxidation potential.

Much effort has been expended in electrochemically preparing aromatic conjugated polymers such as polypyrrole[1)] and polythiophene.[2)] But benzene is not polymerized under the same electrolytic conditions and even under large supplied potential (see the lowest line in Table 1). Some attempts to electro-oxidatively polymerize benzene to poly(p-phenylene)(PPP) have been reported: electrochemical oxidation of benzene in liquid sulfur dioxide,[3)] with HF,[4)] with $AlCl_3$,[5)] with $LiAsF_6$ and $CuCl_2$,[6)] and with $BF_4^-$.[7)] However their yield and current efficiency were extremely low (see also Table 1). We previously reported[8)] that p-dimethoxybenzene with lower oxidation potential is efficiently polymerized to poly(2,5-dimethoxy-1,4-phenylene) and that its polymerization proceeds via cationic mechanism and is suppressed by basic additives. In this communication we report that benzene is electro-oxidatively polymerized to PPP with high current efficiency in the presence of a strong acid such as trifluoromethane sulfonic acid.

Electrochemical polymerization was carried out under nitrogen atmosphere in one compartment cell equipped with platinum electrodes. A Reference electrode was Ag/AgCl. The results are listed in Table 1. Benzene is very efficiently polymerized in the presence of trifluoromethane sulfonic acid as a supporting electrolyte. The given potential of 1.7 V to polymerize benzene in the presence of trifluoromethane sulfonic acid is much lower than the potentials in the presence of

Table 1. Electro-oxidative polymerization[a) of benzene in the presence of acids

| Acid | Potential V vs. Ag/AgCl | Current efficiency/% |
|---|---|---|
| $CF_3SO_3H$ | 1.7 | 31 |
| $H_2SO_4$ | 3.0 | 3 |
| $CF_3COOH$ | 5.0 | 0.5 |
| $CCl_3COOH$ | 5.0 | 0 |
| $CH_3COOH$ | 5.0 | 0 |
| HF[4) | -[b) | <1.0 |
| $AlCl_3$[5) | -[b) | 0.9 |
| TBAP | 5.0 | 0 |

a) Solvent: nitromethane 80 $cm^3$, benzene: 5 $cm^3$ acid: 10 $cm^3$, platinum electrode (2 x 5 $cm^2$).
b) Controlled current electrolysis: current density 12 $mA\cdot cm^{-2}$.

other acidic additives.

One notices also in Table 1 for the polymerization that the current efficiency increases and the given potential decreases with acidity of the additive. The formed polymer on the electrode is identified as PPP by IR and $^{13}$C-NMR after washing with alkaline methanol. IR: 700, 760, 800, 1000, 1380, and 1480 $cm^{-1}$. $^{13}$C-NMR: 130 ppm (broaden). The as-grown PPP was doped with trifluoromethane sulfonium ion and exhibited an electrical conductivity as high as $5 \times 10^{-4}$ $S\cdot cm^{-1}$.

By addition of benzene (5 $cm^3$) to a trifluoromethane sulfonic acid solution (10 $cm^3$ in nitromethane 80 $cm^3$) at 20 °C, the mixture turns light brown ( $\lambda_{max}$= 380 nm) from colorless. This suggests the formation of a protonated complex of benzene.[9) In cyclic voltammograms of benzene (Figs. 1, 2), the virgin oxidation of benzene initiates at 1.7 V and oxidation peak potential (2.3 V) shifts toward less anodic potential in the presence of trifluoromethane sulfonic acid, comparing with the voltammogram in the absence of one ($E_{pa}$ = 2.8 V). This means remarkable decrease in the oxidation potential of benzene probably because benzene is protonated and resonance stabilization of benzene ring is reduced. On the other

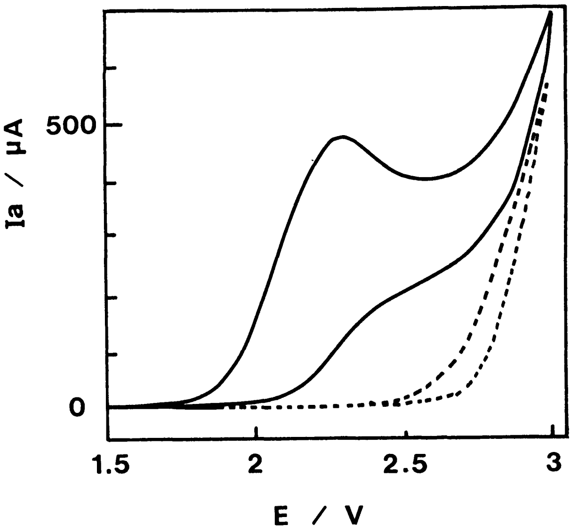

Fig. 1. Cyclicvoltammograms with platium electrode: benzene (10 mM) + $CF_3SO_3H$ (1 M) + tetrabutylammoniumperchlorate (TBAP) (—), $CF_3SO_3H$ (1 M) + TBAP (--) in nitromethane.

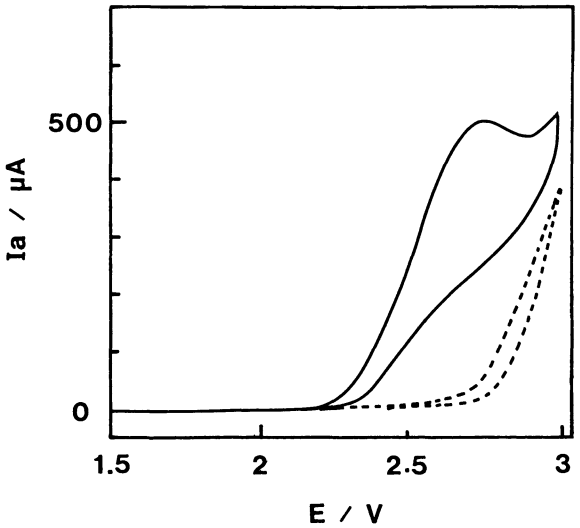

Fig. 2. Cyclicvoltammograms with platinum electrode: benzene (10 mM) + TBAP or benzene (10 mM) + TBAP+ $CF_3COOH$ (1 M) (—), $CF_3COOH$ (1 M) + TBAP (--) in nitromethane.

hand, the oxidation potential slightly shifts toward less anodic in the presence of trifluoromethane sulfonic acid, which corresponds to the current efficiency in the polymerization. These results indicates that the polymerization of benzene is associated with acidity of the electrolytic mixture. This effect of the protonic acid could be observed also by using other strong acids. But only trifluoromethane sulfonic acid was effective in this study, because strong acids such as HF are not homogeneously miscible with benzene and because trifluoromethane sulfonic acid is one of the strongest protonic acids. Trifluoromethane sulfonic acid acts both as an electrolyte and as a catalyst in this electro-oxidative polymerization of benzene.

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