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Preparation of Poly(*p*-phenylene) by Electrooxidative Polymerization in Acidic Media

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The electro-oxidative polymerization of benzene in the presence of strong acids yields poly(*p*-phenylene) efficiently. A strong protonic acid such as trifluoromethanesulfonic acid or Lewis acid such as an aluminum trichloride forms a complex with benzene and reduces the oxidation potential of benzene to 1.7 V, which brings about the high current efficiency. The acids act both as an electrolyte and as a catalyst in this polymerization of benzene.

There is much interest in the electrochemical preparation of aromatic conjugated polymers such as polypyrrole[1,2] polythiophene,[3,4] polyaniline,[5] poly(oxyphenylene),[6,7] poly(thiophenylene),[8] and polyazulene.[9] These polymers exhibit significant electrical conductivity and are potentially useful materials.[10,11] However, benzene is not polymerized under the same electrolytic conditions, and even under a large given potential.

Some attempts to electrooxidatively polymerize benzene to poly(*p*-phenylene) (PPP) have been reported: the electrochemical oxidation of benzene in liquid SO_2,[12] with HF,[13] with $AlCl_3$,[14] with $LiAsF_6$ and $CuCl_2$,[15] and with BF_4^-.[16] However, their yield and current efficiency were extremely low and the electrooxidative polymerization of benzene has not been studied quantitatively. We previously reported[17] that *p*-dimethoxybenzene with a lower oxidation potential is efficiently polymerized to poly(2,5-dimethoxy-1,4-phenylene) and that its polymerization proceeds via a cationic mechanism and is suppressed by basic additives. We recently found and preliminarily reported[18] that the electrooxidative polymerization of benzene is the presence of trifluoromethanesulfonic acid (FSA) gave PPP in high yield. This paper describes the efficient preparation of PPP by the electrooxidative polymerization of benzene in the presence of strong acids as well as the mechanism of this polymerization.

Experimental

Materials. Benzene was purified by distillation twice after contaminated thiophene was removed. Tetraethylammonium tosylate and other supporting electrolytes were recrystallized from ethanol–water and dried in vacuo for 1 d at 80 °C. All solvents were distilled before the electrolysis. Lewis acids, protonic acids and 9-phenylanthracene were guaranteed reagents and were used without further purification.

Electrolysis. One pair of platinum plate (2×5 cm) was set in the Cell[19] with 1 cm spacing as a working and an auxiliary electrode. The reference electrode was Ag/AgCl. The benzene solution (75 ml) of acid was kept at 20 °C under a nitrogen atmosphere in the cell. The preparative electrolysis was carried out under a controlled current with a potentiogarvanostat (Nikko Keisoku NPGS-301) without stirring. The electricity was measured by a digital coulomb meter (Nikko Keisoku NDCM-1). After the electrolysis, the adhered product was de-doped by supplying a cathodic potential at −0.1 V, and then removed from the working electrode. The product was washed with alkaline methanol and dried in vacuo for 1 d at 80 °C.

The current efficiency of the electrolysis was calculated as follows. One mole of benzene was quantitatively polymerized to PPP by two-electron oxidation. The current efficiency (%) was calculated by dividing the polymer yield by the theoretical value. Theoretical yield=$(Q/2nF)\times 100$ (n: molar number, F: 96484 (c), Q: electricity (c))

Spectroscopies on the Polymer. The polymer was characterized by IR (Jasco IR-810) and Solid ^{13}C NMR (JEOL FX-100). Poly(*p*-phenylene): Solid ^{13}C NMR (ppm): 130 (broaden); IR (KBr, cm^{-1}): ν_{C-H}=3020, $\nu_{C=C}$=1600, 1480, δ_{C-H}=1000, 805.

Cyclic Voltammetry (CV). Cyclic voltammetry was carried out in a two-compartment cell. Platinum disk (0.126 cm^2), platinum wire and Ag/AgCl were used as a working, an auxiliary and a reference electrode, respectively. The concentration of benzene was 1 mmol l^{-1}. The potential was controlled with a dual potentiogarvanostat (Nikko Keisoku DPG-3) and a function generater (Nikko Keisoku NFG-3). The scanning rate of the potential was 100 mV s^{-1}. The *i–E* curve was recorded with a X-Y recorder.

Electrical Conductivity Measurement. After the electrolysis, PPP adhering to the anode was peeled off and washed with dry hexane. The d.c. conductivity of the PPP tablet was measured using a two-point probe method. The as-grown PPP was doped with the anions used as electrolytes and exhibited an electrical conductivity as high as 10^{-3}—10^{-4} S cm^{-1}. The doping was confirmed by the IR spectrum and fluorescence X-ray.

Results and Discussion

IR and ^{13}C NMR spectroscopic data of the de-doped sample are given in Experimental. The PPP shows the absorption band at 805 cm^{-1}, which is ascribed to a C–H out-of-plane deformation vibration of 1,4-disubstitued benzene and no strong absorptions at 840 cm^{-1} and 860 cm^{-1}, which are ascribed to trisubstituted and tetrasubstituted benzene, respectively. This IR absorption spectrum agrees with that reported for chemically prepared PPP[20,21] and indicates that the main structure of the polymer is poly(*p*-phenylene) without crosslinking. A weak absorption of C–H out-of-plane vibration of monosubstituted phenyl rings appeared at 760 cm^{-1} in the IR spectrum. The ratio of the transmittance at the C–H out-of-plane vibration of di-substituted to that of monosubstituted one suggests that the degree of polymerization of PPP is over 7.

Table 1 shows the current efficiency for the electrooxidative polymerization of benzene in the presence of acids. The polymerization proceeds efficiently with a strong acid like FSA and a Lewis acid such as aluminum trichloride, but does not with a weak acid such as acetic acid. FSA which is one of the strongest protonic acids yields PPP with the highest current efficiency.

In the absence of acids, the electropolymerization does not sufficiently proceed with tetraethylammonium tosylate (TEATs), perchlorate, chloride or hydrogensulfate as an electrolyte. These results indicate that the polymerization of benzene is associated with the acidity of the electrolytic mixture and is retarded by the supporting electrolyte in the absence of acid.

Table 2 shows that this electropolymerization is suppressed by a strongly basic solvent such as propylene carbonate and *N*,*N*-dimethylformamide. The current efficiency was not influenced by oxygen bubbling through the electrolytic mixture, which often deactivates a radical species. These results support the idea that this polymerization proceeds via a cationic mechanism.

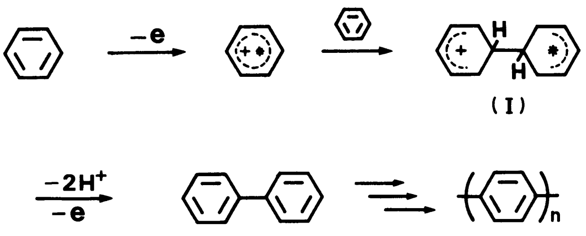
Table 1. Electrooxidative Polymerization[a] of Benzene in the Presence of Acids under Controlled Current

Acid	Current density	Current efficiency
	mA cm^{-2}	%
CF_3SO_3H	10	63
CF_3COOH	5	8
H_2SO_4	5	6
CCl_3COOH	5	0
CH_3COOH	5	0
HNO_3[b]	5	0
HCl[c]	5	0
$AlCl_3$	17.5	54
$BF_3\cdot O(C_2H_5)_2$	17.5	58
$SbCl_5$	17.5	16
$FeCl_3$	17.5	10
$SnCl_4$	17.5	20
HF[13]	12.0	>1
None[d]	17.5	0
CF_3SO_3H/TEATs[e]	10	64
CF_3COOH/TEATs[e]	5	0
$AlCl_3$/TEATs[e]	17.5	54

a) Starting solutions composed: [Benzene]=1.4 mol l^{-1}, [Acid]=2.0 mol l^{-1} Electricity: 0.6 F mol l^{-1}, Solvent: Nitromethane. Polymerization in the presence of Lewis acid carried out in addition of small amount of water (1 ml) due to increase of the solution conductivity. b) 12 mol l^{-1} concd HNO_3. c) 12 mol l^{-1} concd HCl. d) The electrolyte was used as tetraethylammonium tosylate, perchlorate, chloride, or hydrogensulfate (0.2 mol l^{-1}). e) TEATs: Tetraethylammonium tosylate (0.2 mol l^{-1}).

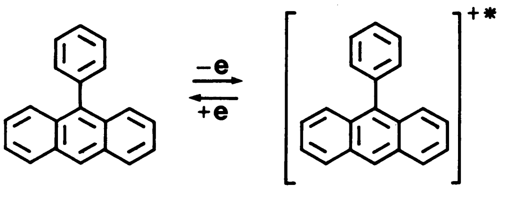
At a lower concentration, the polymerization is retarded probably because a reaction between benzene and an activated benzene does not easily occur. Then the current efficiency increases with the benzene concentration and becomes saturated at a concentration of 1.5 mol l^{-1}.

The above-mentioned results suggest a mechanism of this electropolymerization as given in Scheme 1. Benzene is one-electron oxidized to its cation radical. The cation radical electrophilically reacts with benzene to form a hydrodimer (**I**). It is oxidized to biphenyl accompanied by a proton elimination. The biphenyl is repeatedly oxidized to PPP.



Scheme 1.

The cationic mechanism of the polymerization is consistent with the results that the polymerization is affected by a coexisting electrolyte anion and is suppressed by the basic solvent. This was further studied by UV spectroscopy and cyclic voltammetry. Since the cation radical of benzene is not stable and rapidly reacts with benzene, the effect of electrolyte species was studied by using a stable cation radical of 9-phenylanthracene[22] (9-PA) as a model for the benzene cation radical (Eq. 1). During the electrolysis



(1)

Table 2. Solvent Effect on Current Efficiency of the Electropolymerization of Benzene in the Presence of CF_3SO_3H

Solvent	Solvent donor number	Current efficiency
		%
CH_2Cl_2	—	79
CH_3NO_2	2.7	64
$C_6H_5NO_2$	4.4	56
CH_3CN	14.1	0
PC[a]	15.1	0
DMF[b]	26.6	0

a) Propylene carbonate. b) *N*,*N*-Dimethylformamide.

of 9-PA in the presence of trifluoroacetic acid or tin tetrachloride, the electrolytic solution was colored dark bluish (λ_{max}=722, 642, 569 nm), indicating the formation of the 9-PA cation radical. Immediately after a small amount addition of TEATs or DMF, the absorption of 9-PA cation radical disappeared. This suggests that the electrolyte anions and basic solvents nucleophilically react with the 9-PA cation radical.

Figure 1 shows a cyclic voltammograms of 9-PA in an acidic medium. The 9-PA cation radical is produced by a one-electron oxidation at 1.1 V, which is corresponds to the redox potential of 9-PA. The cathodic peak current coincided with the anodic one: I_{pc}/I_{pa}=1.0, which indicates that the 9-PA cation radical is stable in the acidic mixture. However, the anodic peak potential of 9-PA shifted anodically and the reduction peak of 9-PA cation radical was not observed in the presence of a small amount of such basic species as TEATs or DMF. These facts also support the observation that the 9-PA cation radical is not able to exist stable in the presence of a basic species. That is, the cation radical as an active species for the polymerization of benzene is strongly influenced by a supporting electrolyte and the acidity of the electrolytic mixture.

PPP was not given upon the addition of TEATs in a weakly acidic medium. However, in the presence of a strong acid such as FSA or $AlCl_3$, the polymerization yields PPP efficiently, even with the coexistence of an electrolyte such as TEATs and is not entirely retarded. The effect of a strong acid such as FSA and $AlCl_3$, in this polymerization process is remarkable in comparison with that of weak acids. This suggests a specific role of a strong acid in this polymerization process.

Figure 2 shows cyclic voltammograms of benzene in nitromethane. The virgin oxidation of benzene is initiated at 1.7 V and the oxidation peak potential (2.3 V) shifts toward less anodic potential in the presence of FSA, compared with a voltammogram in the absence of one (E_{pa}=2.8 V). Benzene was also oxidized above 1.7 V in the presence of $AlCl_3$. Upon the addition of benzene to strong acid solutions, the mixtures turned light brown (λ_{max}=380 nm) from colorless. Benzene is electropolymerized in the presence of these acids at a lower potential in comparison with that in the absence of ones. In the presence of a weak acid such as trifluoroacetic acid, the oxidation potential did not shift cathodically: The voltammogram was the same as in the absence of a weak acid, and the mixture remained colorless. The remarkable decrease in the oxidation potential of benzene in the presence of the strong acids can be explained as follows: Benzene forms a complex[23]

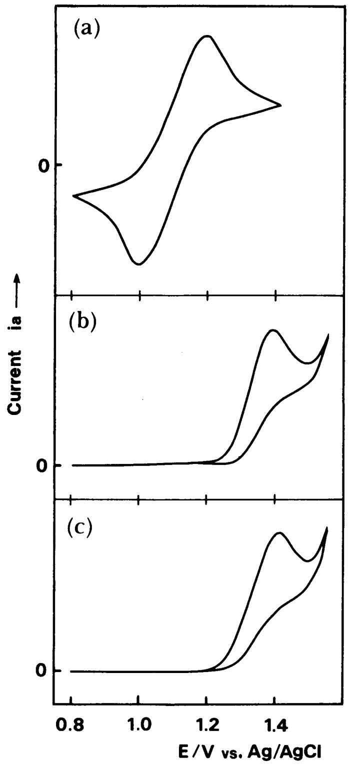


Fig. 1. Cyclic voltammograms of 9-phenylanthracene in the presence of CF_3COOH (a), tetraethylammonium tosylate (b), and DMF (c). Sweep rate: 0.1 V s^{-1}.

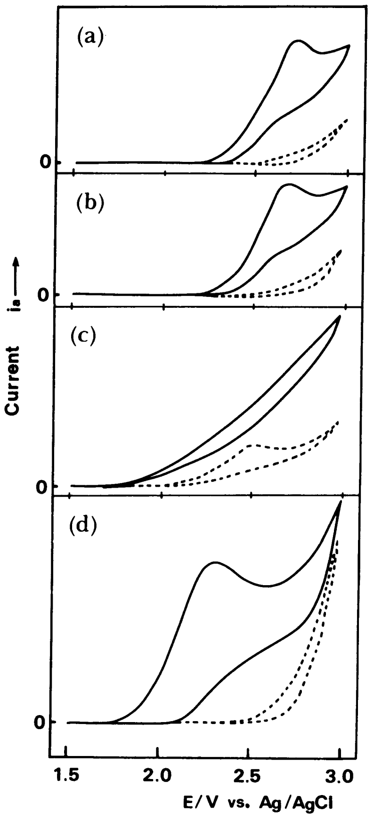


Fig. 2. Cyclic voltammograms of benzene in CH_3NO_2–TBAP (a) containing CF_3COOH (b), $AlCl_3$ (c), CF_3SO_3H (d). Dotted lines are background i–E curves in the same medium. Sweep rate: 0.1 V s^{-1}.

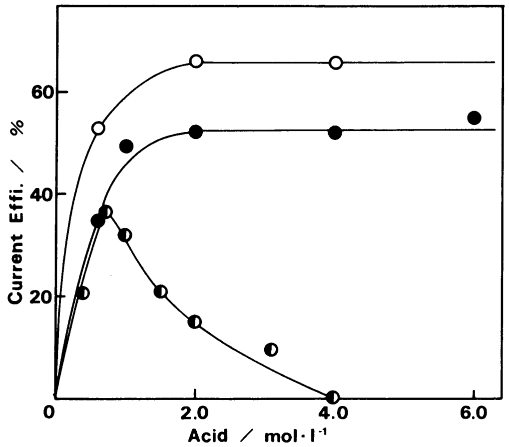


Fig. 3. Effect of the added amount of $AlCl_3$ (●), $SbCl_5$ (◐), and CF_3SO_3H (○) on the current efficiency of benzene-polymerization. [benzene] 2.0 mol l^{-1}, [tetrabutylammonium tosylate] 0.2 mol l^{-1} in nitromethane, at 17.5 mA cm^{-2}.

with a strong acid and Lewis acid such as FSA and $AlCl_3$, and the resonance stabilization of the benzene ring is reduced. That is, the oxidation potential slightly shifts toward less anodic potential in the presence of these strong acids, which corresponds to the current efficiency in the polymerization.

Figure 3 shows the effect of the concentration of FSA or $AlCl_3$. The current efficiency becomes saturated upon an equimolar addition of the acid: an equimolar addition of acid is required for a high current efficiency in PPP formation, which corresponds to the formation of a complex with an acid.

The roles of the acid for this electropolymerization of benzene are summarized as follows. The acid suppresses a nucleophilic reaction of the cation radical produced by a one-electron oxidation of benzene with basic species. The strong acid, such as FSA or $AlCl_3$, forms a cationic complex with benzene, which promotes an electrophilic attack of the cation radical to benzene and increases the polymerization efficiency. These strong acids also act as an electrolyte in this electrooxidative polymerization of benzene.

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