Polymer Bulletin 19, 533–538 (1988)

Polymer Bulletin

Electro-oxidative polymerization of p-dialkoxybenzenes and its mechanism

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SUMMARY

p-Dimethoxybenzene is anodically oxidative polymerized to poly(2,5-dimethoxy-1,4-phenylene). p-Diethoxybenzene and p-dipropoxybenzene are also polymerized because the alkoxy groups reduce oxidation peak potentials of the benzene derivatives. This electro-oxidative polymerization is studied with the preparative electrolysis and cyclic voltammetry. The polymerization contains an electrophilic reaction of cation radical of the benzene and proceeds through a stepwise or chain propagation according to the supplied potential.

INTRODUCTION

Since Kovacic prepared polyphenylene through the oxidation of benzene with aluminum chloride and cupric chloride(1), many preparative studies of polyphenylene derivatives have been reported(2-7). The polymerization of benzene also proceeds by anodic oxidation(8-13). But the electrolysis condition of this polymerization was very hard: the supplied oxidation potential of benzene is higher in comparison with those of common organic solvents, which brings about complexity of the electro-polymerization of benzene.

Recently the authors found that p-dimethoxybenzene easily electro-oxidatively polymerized at lower potential to give poly(2,5-dimethoxy-1,4-phenylene) without crosslinking and side reactions(14). The polymerization mechanism is expected to be clearly analyzed for p-dimethoxybenzene. This paper describes the electro-oxidative polymerization of p-dialkoxybenzenes and its mechanism.

EXPERIMENTAL

p-Dimethoxy, p-diethoxy and p-propoxybenzene were purified by recrystallization from methanol-water(1/1). Tetraethyl- and tetrabutylammonium perchlorate were used as a supporting electrolyte after recrystallization from ethanol-water(1/2) and drying in vacuo for 1 day at 80^{o}C. All solvents were distilled before the electrolysis.

One pair of platinum plate (2 x 5 cm) was set in the sell with 1 cm spacing as the working and the auxiliary electrode. Reference electrode was Ag/AgCl. The design of the electrolysis cell was previously reported(15,16). The solution (80 ml) of p-dialkoxybenzene (0.1 mol/l) and the ammonium perchlorate (0.2 mol/l) was kept at 20^{o}C under nitrogen

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atmosphere in the cell. The preparative electrolysis was carried out with controlled potential at 1.5 V supplied by a potentiogarvanostat (Nikko Keisoku NPGS-301) without stirring. Electricity was measured by a digital coulomb meter (Nikko Keisoku NDCM-1). After the electrolysis, the adhered products were removed from the working electrode, washed by alkaline methanol, and dried in vacuo for 1 day at 80°C.

Cyclic voltammetry was carried out in the 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 p-dimethoxybenzene was 1 mmol/l. The potential was controlled by a dual potentiogalvanostat (Nikko Keisoku DPG-3) and a function generater (Nikko Keisoku NFG-3).

The polymer was ascribed to poly(alkoxy-1,4-phenylene) by IR, ^{13}C-NMR, mass spectroscopy and elemental analysis.

Poly(2,5-dimethoxy-1,4-phenylene): Anal. Calcd. for ($C_8H_8O_2$);C 70.6, H 5.88, Found C 69.8, H 5.92. Solid ^{13}C-NMR (ppm): 57($-OCH_3$), 114(secondary carbon), 151(tertiary carbon), 127(quaternary carbon). IR(KBr, cm^{-1}) : ν_{C-H} = 2830, 2940; $\nu_{C=C}$=1600; ν_{C-O-C}= 1210, 1180; δ tetrasubstituted C-H = 860. Mass spectrum (m/e) 409, 546, 682, 818, 953

Poly(2,5-diethoxy-1,4-phenylene): IR(KBr, cm^{-1}) ν_{C-H}=2870, 2925, 2975; $\nu_{C=C}$=1600, 1490, 1470; ν_{C-O-C}=1200; δ_{C-H}=865.

Poly(2,5-dipropoxy-1,4-phenylene): IR(KBr, cm^{-1}) ν_{C-H}=2850, 2920, 2945; $\nu_{C=C}$=1600, 1460, 1480; ν_{C-O-C}=1200; δ_{C-H}=860.

Poly(methylphenylene): IR(KBr, cm^{-1}) ν_{C-H}=2850, 2925; $\nu_{C=C}$=1600, 1460; ν_{C-O-C}=1180; δ_{C-H}=830.

RESULTS AND DISCUSSION

Preparative electrolysis

We reported in the previous paper(14) that poly(2,5-dimethoxy-1,4-phenylene) is deposited on anode by the electrolysis of p-dimethoxybenzene in dichloromethane, nitromethane, acetonitrile and propylenecarbonate, but is not produced in strong basic solvents and that this polymerization proceeds by a cation species.

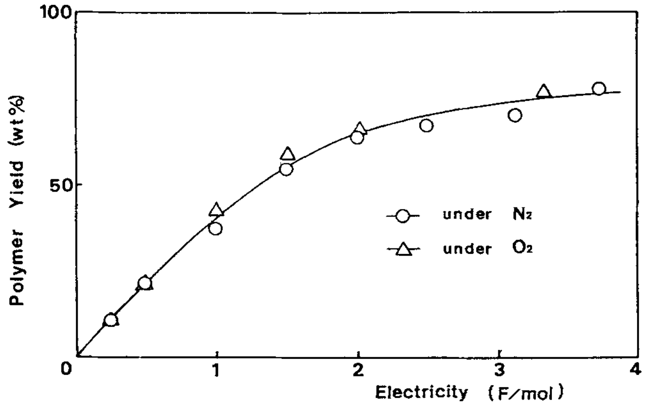


Fig. 1
Electro-oxidative polymerization of p-dimethoxybenzene under oxygen and nitrogen.

Fig. 1 shows the electro-polymerization curve of p-dimethoxybenzene in acetonitrile. Oxygen does not affect the polymerization rate. This indicates that the polymerization dose not proceed through a radical propagation or radical coupling(18,19) but a cationic propagation.

Electrode reaction of p-dimethoxybenzene

Cyclic voltammograms of p-dimethoxybenzene in acetonitrile are shown in Fig. 2. The oxidation peaks appear at 1.4 and 1.7 V. The first peak is corresponding to the oxidation of p-dimethoxybenzene to produce the cation radical with one-electron oxidation. The broaden second peak is attributed to the oxidation of the first oxidation product. The increase of the current near 2.0 V is corresponding to two-electron oxidation of the benzene. The later has been reported by the study using rotating disk voltammetry(14). The cation radical produced by the first oxidation is reduced at 1.3 V and the reduction peak increased with potential sweep rate, which means that following chemical reaction, i.e. the polymerization occurs slowly.

The second reduction peak appears at 0.1 V in Fig. 2, which agrees with the reduction wave (0.1 V) of $HClO_4$. This means that proton exists in the mixture during the electrolysis. These results indicate that p-dimethoxybenzene is oxidized to its cation radical and is polymerized accompanying with the proton elimination.

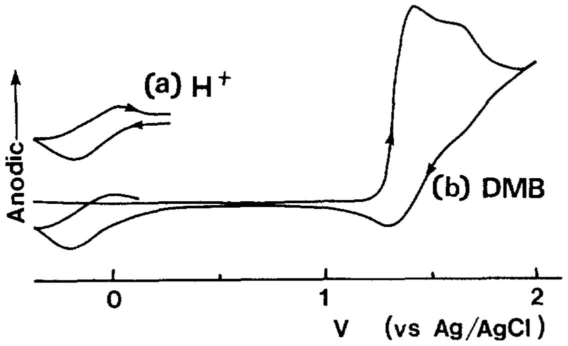
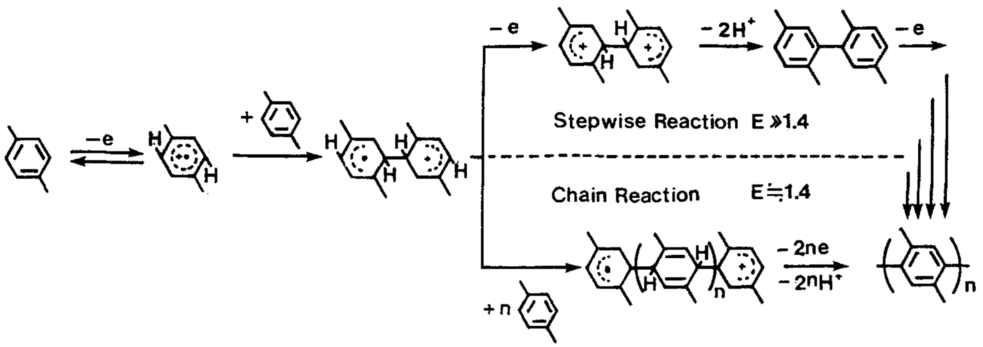


Fig. 2
Cyclic voltammogroms of p-dimethoxybenzene(b) and perchloric acid(a) in acetonitrile.

Polymerization mechanism

From the results mentioned above and in the previous paper(14), the following polymerization mechanism is described (Scheme 1). The cation radical is produced by the oxidation of p-dimethoxybenzene with one electron oxidation. It is allowed to react with phenyl ring and to yield the cation radical of hydrodimer(I). From the results in the cyclic voltammetry, the second oxidation peak appeared after the first oxidation is ascribed to the oxidation of the hydoro-type intermediate, (I) or (II), which is produced by an electrophilic reaction of the cation radical with p-dimethoxybenzene.

Two routes for the propagation are considered: a stepwise and a chain reaction, to which the supplied potential is responsible because the following chemical reaction proceeds slowly in comparison with the oxidation on the electrode. When the potential is supplied higher than the oxidation peak potential of (I), the formed (I) is immediately oxidized to dication and produces biphenyl with deprotonation. Biphenyl is rapidly oxidized and the propagation reaction occurs since the oxidation potentials of the oligomers are lower than that of monomer. When the potential is supplied between the oxidation potential of monomer and the (I) cation radical, the cation radical electrophilically reacts with p-dimethoxybenzene as a chain reaction to produce hydoropolymer(II), which propagates to the extent where the hydoropolymer is oxidized by the supplied potential to rearomatize to polyphenylene accompanying with deprotonation.



(Scheme 1)

Table 1 Electro-oxidative polymerization of alkoxybenzenes

Benzene derivatives Substituents	Oxidation peak Potential (Ag/AgCl)	Electrolysis Electricity (F/mol)	 Yield (wt%)	Cat. Polymn.[a)] Yield (wt%)
1,4-dimethoxy	1.4	2.8	70	32
1,3-dimethoxy	1.5	0.3[b)]	4	43
1,4-diethoxy	1.4	2.8	56	23
1,4-dipropoxy	1.3	2.8	81	25
methoxy	1.9	0.3[b)]	9	0
1-methoxy-4-chloro	1.9	3.8	0	0
1,4-diacetoxy	1.2	2.8	0	0

a) Oxidative cationic Polymerization with $CuCl_2$ and $AlCl_3$
b) passivation

Electro-oxidative polymerization of alkoxybenzene

p-Dialkoxybenzenes were easily electro-oxidized to give the correspondingly polyphenylenes as p-dimethoxybenzene was(Table 1). In acetonitrile electrolysis of methoxybenzene and 1,3-dimethoxybenzene were suppressed due to passivation of the electrode, which causes the formation of crosslinking or nonlinear conjugated polymers.

Other benzenes derivatives such as benzene and p-dichlorobenzene were not electro-oxidatively polymerized to polyphenylenes under the same conditions. Electron donative alkoxy groups reduce the oxidation peak potential of benzene (Table 2). The reduced oxidation peak potential allows the cation to react electrophillicaly with the alkoxybenzene.

Table 2 Oxidation peak potential of benzene derivatives in acetonitrile

 R_1	R_2	Oxidation Peak Potential (Ag/AgCl)
-H	-H	2.8
-H	$-CH_3$	2.3
-H	$-OCH_3$	1.9
-Cl	-Cl	2.8
$-CH_3$	$-CH_3$	2.1
$-C_2H_5$	$-C_2H_5$	2.1
$-C(CH_3)_3$	$-C(CH_3)_3$	2.2
$-OCH_3$	$-OCH_3$	1.4
$-OCH_3$	-Cl	1.9
$-OCH_3$	$-C(CH_3)_3$	1.9

ACKNOWLEDGMENT

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

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Accepted March 15, 1988 C