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Electrochemical preparation of poly(2,5-dimethoxy-1,4-phenylene)

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SUMMARY

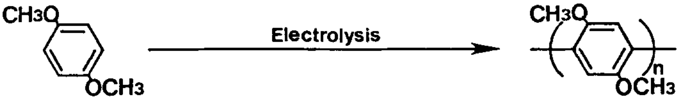
p-Dimethoxybenzene was electro-oxidatively polymerized to give poly(2,5-dimethoxy-1,4-phenylene) with high yield. 1,4-Structure of polyphenylene was confirmed by ^{13}C-NMR and IR spectrum. The polymer was deposited on electrode, and electrolysis solvent affected the polymer yield and morphology of the polymer. In a strongly basic solvent the polymerization was inhibited, which suggests that cation radical of p-dimethoxybenzene is an active species of this polymerization.

INTRODUCTION

It is well known that benzene is oxidatively polymerized to polyphenylene with Lewis acid such as aluminium chloride and an oxidizing agent such as copper(II) chloride(1-4). p-Dimethoxybenzene is similarly polymerized with the catalyst although this polymerization is carried out under reduced pressure to prevent from demethylation of the methoxy group(5).

This polymerization also proceeds by anodic oxidation to yield an insolble polyphenylene powder deposited on electrode(6-9). However the electrolysis condition is very hard: hydrofluoric acid is used as an electrolyte, which brings about following problems for the electro-polymerization of benzene. (i) Structure of the formed polyphenylene is not a linear or 1,4 phenylene structure but a mixed structure of 1,2- , 1,3- and 1,4-phenylene bond containing a crosslinking bond. (ii) Current efficiency of the electrolysis is very low to obtain the polymer. (iii) Solvent for the electrolysis is restricted to uncommon ones such as sulfur dioxide. (iv) The polyphenylene is deposited as a brittle powder which is insoluble in any solvents.

Benzene derivatives substituted with two electron-donor groups are expected to be oxidized relatively lower oxidation potential and polymerized to linear polyphenylene derivatives. Recently the authors found that p-dimethoxybenzene is efficiently electro-oxidatively polymerized to give poly(2,5-dimethoxy-1,4-phenylene) without both crosslinking reaction and demethylation from the methoxy group. This paper describes the electro-oxidative polymerization of p-dimethoxybenzene and structure of the formed polymer.



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EXPERIMENTAL

p-Dimethoxybenzene was purified by recrystallization from methanol-water. Tetraethyl- and tetrabutylammonium perchlorate as a supporting electrolyte was used after recrystallization and drying in vacuo for 1 day at 80°C. Dichloromethane and acetonitrile were distilled twice befor the electrolysis.

The apparatus for the preparative electrolysis was reported previously(10). One pair of platinum plate (2 x 5 cm) was set in the cell with 1 cm spacing as the working and auxiliary electrode. Reference electrode was Ag/AgCl. p-Dimethoxybenzene (8 mmol) and the ammonium perchlorate (16 mmol) was dissolved in the solvent (80 ml) under nitrogen atmosphere. The electrolysis was carried out with controlled potential at 1.5 V supplied by a potentiostat (Nikko Keisoku NPGS-301). Electrycity was measured by a digital coulomb meter (Nikko Keisoku NDCM-1).

After the electrolysis, the deposited polymer on the electrode was taken off, washed with methanol and aqueous ammonia, extracted with refluxed methanol to remove the ammonium salt, and dried in vacuo for 1 day at 80°C.

Poly(2,5-dimethoxy-1,4-phenylene): Anal. Calcd. for $C_8H_8O_2$: C,70.59; H,5.88%. Found: C,69.8; H,5.98%. IR(KBr): ν_{C-H}= 2940, 2830 cm^{-1}, ν_{COC}= 1210 , 1180 cm^{-1}, $\nu_{C=C}$= 1600 cm^{-1}, δ_{C-H}= 860 cm^{-1}, ^{13}C-NMR: δ(methoxy carbon) = 57 ppm, δ(tertiary carbon) = 114 ppm, δ (quaterary carbon) = 127, 151 ppm. mass spectrum: m/e = 409, 546, 682, 818, 954

Cyclic voltammometry was carried out in a two compartment cell. Platinum disk (0.126 cm^2), platinum wire and Ag/AgCl were used a working, an auxiliary and a reference electrode, respectively. Potential was controlled by a dual potentiogalvanostat (Nikko Keisoku DPG-3) and a function generator (Nikko Keisoku NFG-3), and was sweeped at 100 mv/sec.

RESULTS AND DISCUSSION

Characterization of the polymer

IR spectrum of the electro-oxidatively prepared polymer was in complete agreement with that of poly(2,5-dimethoxy-1,4-phenylene). Characteristic absorption at 860cm^{-1} attributed to 1,2,4,5-substituted benzene indicates a linear or 1,4-conjugated polyphenylene structure.

Table 1 Chemical shifts of poly(2,5-dimethoxy-1,4-phenylene)

	Chemical Shift (ppm)			
	C_1	C_2	C_3	C_a
Found	151	114	127	57
Calcd.	151.5	114.4	127.1	-

Calcd. equation

$C_1 = 128.5 + (OCH_3)_s + (Ph)_o + (Ph)_m + (OCH_3)_p$

$C_2 = 128.5 + (OCH_3)_o + (Ph)_o + (Ph)_m + (OCH_3)_m$

$C_3 = 128.5 + (OCH_3)_o + (Ph)_s + (Ph)_p + (OCH_3)_m$

$(OCH_3)_s$ means chemical shift of methoxy group-substituted carbon. $(Ph)_p$ means chemical shift of para position carbon at benzene substituted with phenyl group.

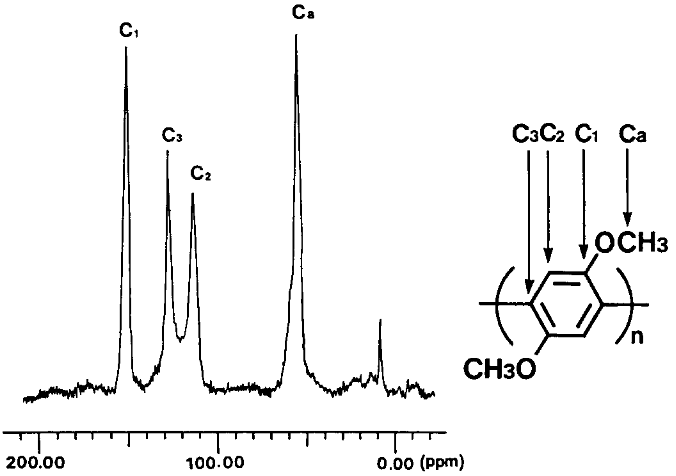

Fig. 1 Solid^{13}C-NMR spectrum of the electro-oxidatively polymerized polymer

Fig. 1 shows solid ^{13}C-NMR spectrum of the polymer. The chemical shifts in Tab. 1 completly agreed with the calculated ones. The structure of poly(2,5-dimethyl-1,4-phenylene) was confirmed. Peaks of mass spectrum m/e(see Exp. part.) are corresponding to the ionic fragment derived from trimer, tetramer, pentamer, hexamer, and heptamer, respectively. Residues were remained on probe of mass spectrometer after operation , which suggestes that the polymer contains a fraction of more than eight degree of polymerization.

Electrochemistry of p-dimethoxybenzene oxidation

Oxidation peak potential of benzene derivatives in acetnitrile is listed in Tab. 2. The oxidation peak potential of p-dimethoxybenzene was 1.4 V, while for benzene was 2.8 V(11); p-dimethoxybenzene is easily oxidized in comparison with benzene and other derivatives.

Fig. 2 shows cyclic voltammograms of p-dimethoxybenzene in acetnitrile and dichloromethane. The oxidation potential and the i-v curve are different for the oxidation in each solvent, which suggests that diffusion rate, electron-transfer rate or chemical reaction rate is dependent on the electrolysis solvent used.

Table 2 Oxidative peak potential of benzene derivatives

Benzene derivative	Oxidative peak potential (V) vs Ag/AgCl
benzene	2.8
p-dimethoxybenzene	1.4
p-diethoxybenzene	1.4
methoxybenzene	1.9
1-tert-butyl-4-methoxybenzene	>2.0
p-di-tert-butylbenzene	>2.0

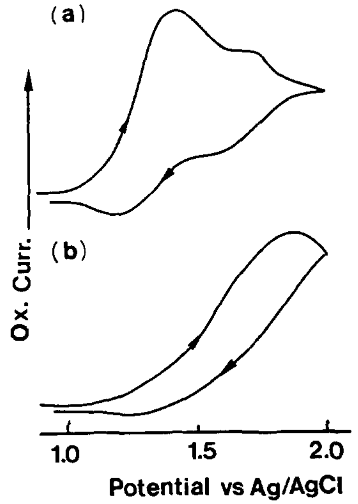

Fig. 2

Cyclic voltammograms of p-dimethoxybenzene in acetnitrile (a) and in dichloromethane (b)

Preparative electrolysis of p-dimethoxybenzene

The electro-oxidative polymerization of p-dimethoxybenzene was carried out in various solvens (Table 3). The polymerization proceeded continuously to form the polymer on electrode without passivation. The polymer was obtained as an amorphous film on the electrode and was partially solble in conc. sulfuric acid. In acetnitrile the polymer yield is relatively high. The yield is higher than that with $CuCl_2$-$AlCl_3$ catalyst. The electropolymerization did not proceede in the solvents with strong basicity or with high donor nomber such as N,N-dimethylformamide and dimethylsulfoxide. This indicates that cation radical of demethoxybenzene is an active spieces of this polymerization and basic solvent nucleophillically reacts the cation radical and prohibits the polymerization.

Table 3 Electro-oxidative polymerization of p-dimethoxybenzene in various solvents

Solvent	Solvent Donor Number	Polymer 1) Yield (wt%)
CH_2Cl_2	--	40
CH_3NO_2	2.7	63
CH_3CN	14.7	84
PC	15.1	51
THF	20.0	0
DMF	26.6	0
DMSO	29.6	0
$C_6H_5NO_2$ 2)	4.4	32

1) Electricity 2.5 F/mol, 2) Oxidative, cationic polymerization ($CuCl_2$-$AlCl_3$)

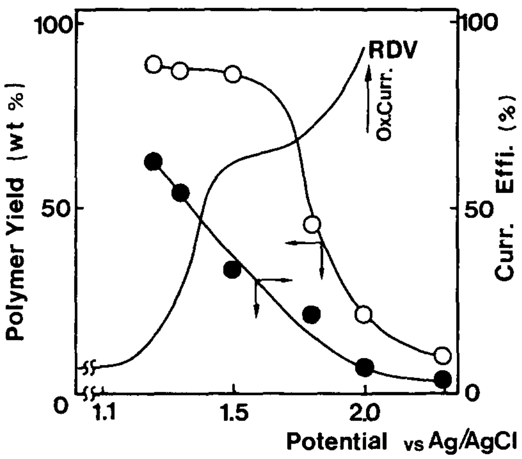

Fig. 3

Relationship between the supplied potentialand the polymer yield (○), and the current efficiency (●). Rotating disk voltammogram of p-dimethoxybenzene in acetonitrile (-)

For the electro-oxidative polymerization of p-dimethoxybenzene in acetnitrile, the polymer yield was affected by the given potential as shown in Fig. 3. The polymer yield decreased above 1.6 V, which suggestes that the second step oxidation wave of p-dimethoxybenzene in rotating disk voltammogram is corresponding to formation of p-dimethoxybenzene dication with high reactivity and is not related to the polymerization. Only the first oxidation, that is the formation of cation radical, is related to the polymerization. It was concluded that p-dimethoxybenzene is oxidized with one-electron transfer to its cation radical and polymerized cationically to polydimethoxyphenylene.

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REFERENCE

1) P. Kovacic and A. Kyriakis, J. Am. Chem. Soc., 85, 452(1963)
2) K. Mukai, T. Tshirogi, N. Kuramoto and K. Kawamura, J. Polymer Sci. Polymer Chem Ed., 23, 1259(1985)
3) E. B. Mano and L. A. Alves, J. Polymer Sci. A-1, 10, 655(1972)
4) S. A. Milosevich, K. Saichek, L. Hinchey, W. B. Engrand and P. Kovacic, J. Am. Chem. Soc., 105, 1088(1983)
5) M. Delamar, P. C. lacaze, J. Y. Dumousseau and J. E. Dubois, Electrochimica Acta., 27, 1, 61(1982)
6) I. Rubinstein, J. Polymer Sci. Polymer Chem. Ed., 21, 3035(1983)
7) I. Rubinstein, J. Electrochem. Soc., 130, 1506(1983)
8) M. Satoh, M. Tabata, K. Kaneto and K. Yoshino, J. Electroanal. Chem., 195, 203(1985)

9) A. V. Ragimov, S. I. Sadykh-Zode, T. Sh. Zakirov and A. A. Berlin, Polym. Sci. USSR, 5, 1632(1973)
10) E. Tsuchida, H. Nishide and T. Maekawa, ACS Symp. Ser., 282, 175(1985)
11) T. Osa, A. Yildiz and T. Kuwana, J. Am. Chem. Soc., 91 3994(1969)
12) V. Cutmann , "Co-ordination Chemistry in Nonaqueous solutions", Spring-Verlage(1968)

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