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Electrochemically Oxidative Polymerization of 1,2,3,4,-Tetrahydronaphthalene

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Synopsis. Electrochemical oxidation of 1,2,3,4-tetrahydronaphthalene (**1**) at higher anode potential than 3.0 V and high concentration of **1** gave a polymer of **1**. The polymer deposited on an anode was slightly soluble in organic solvents and the polymer separated from the solution had number average molecular weight up to 1500.

Dehydro coupling reactions of aromatic hydrocarbons have been widely studied for the purpose of syntheses of the conducting and heat-resistant polymer. Polymerization of benzene and other aromatic compounds has been studied by Kovacic and Jones using $AlCl_3$-$CuCl_2$ as catalyst.[1] Dehydro coupling of 1,2,3,4-tetrahydronaphthalene (**1**) was studied to give a polymer having 5—11 units.[2] Electrochemically oxidative polymerization of benzene[3] and naphthalene[4] has been reported. Electrochemically oxidative polymerization of **1** seems to have not been reported. In this report it will be reported that electrochemical oxidation of **1** at higher anode potential than that expected from the oxidation potential of **1** and under high concentration of **1** gives the polymer of **1**.

Experimental

Apparatus and Cell. A gas tight one-compartment 100 ml cell equipped with platinum plate anode and cathode was used for electrochemically oxidative polymerization of **1**. Potential of anode vs. Ag/Ag$^+$ ($AgNO_3$ in DMSO) reference electrode was controlled using Hokuto HAB 151. Temperature of a cell was controlled using a pair stirrer, which stirs a magnetic bar in an electrolysis cell and at the same time can stir water outside the electrolysis cell. Molecular weight of the polymer was measured by means of gel-permeation chromatography (GPC) using THF as a solvent and was calibrated to those of standard polystyrene.

General Procedure. Propylene carbonate (PC) used as a solvent was purified by the method of Jasinski and Kirkland.[5] Electrolysis of the mixture of 55 ml of PC and 15 ml of **1**[6] containing 0.1 M of n-Bu_4NClO_4 (1 M=1 mol dm^{-3}) was carried out about 20 h under nitrogen bubbling and magnetic stirring at 60° or 25 °C. After electrochemical reaction polymer obtained was separated by following procedure. A brownish black polymer deposited on anode was separated and was washed with fresh methanol repeatedly and dried (hereafter called polymer-1). Total reaction solution was poured into 280 ml of fresh methanol to give a brownish black polymer. The polymer was washed with methanol repeatedly and dried (hereafter called polymer-2).

Results and Discussion

The experimental conditions and yields of polymers are shown in Table 1. Elemental analyses and molecular weight of the polymer are shown in Table 2. Infrared absorption spectra of the polymers are shown in Fig. 1. ^{1}H NMR spectra of the polymers showed absorptions of aromatic and olefinic protons at 6.4—8.5 ppm. These spectra showed absorptions of methylene protons at 1.5—2.2, 2.4—3.2 ppm, intensities of which were weaker than those of starting **1**, and weak absorptions of methine protons at 3.2—4.2 ppm. Since solubility of the polymers was insufficient for the measurement of ^{13}C NMR, ^{13}C NMR measurement did not give so much information.

Figure 1 indicates that these polymers contain vinyl ether linkages and OH groups. Considering the fact

Table 2. Elemental Analyses and Molecular Weight of the Polymers Shown in Table 1

Polymer	Elemental analyses			Molecular weight		
	C	H	Cl	M_n[a]	M_w[b]	M_w/M_n
Run 2 Polymer-1	82.40	4.83	0		—[c]	
Run 2 Polymer-2	83.10	6.03	0	1154	3140	2.72
Run 3 Polymer-1	85.71	5.00	0		—[c]	
Run 3 Polymer-2	88.71	6.07	0	1051	3223	3.07
Run 4 Polymer-1	81.06	4.28	3.88		—[c]	
Run 4 Polymer-2	84.57	5.57	0	1502	4392	2.92
Run 5 Polymer-1	81.17	4.35	2.01		—[c]	
Run 5 Polymer-2	83.72	5.97	2.38	1268	6608	5.21

a) M_n: number average molecular weight. b) M_w: weight average molecular weight. c) Molecular weight of polymer-1 could not be determined because of its low solubility.

Table 1. Yields of the Polymer Formed by Electrochemically Oxidative Polymerization of 1,2,3,4-Tetrahydronaphthalene

Run	Anode potential	Temperature	Quantity of electricity/C	Amount of polymer/g	
	V vs. Ag/Ag$^+$	°C		Polymer-1[a]	Polymer-2[a]
1	1.8	60	140	0	0
2	2.8	60	740	0.03	0.03
3	3.5	25	2410	0.12	0.17
4	3.5	60	3610	0.27	0.14
5	3.8	60	5970	0.34	0.19

a) See Experimental.

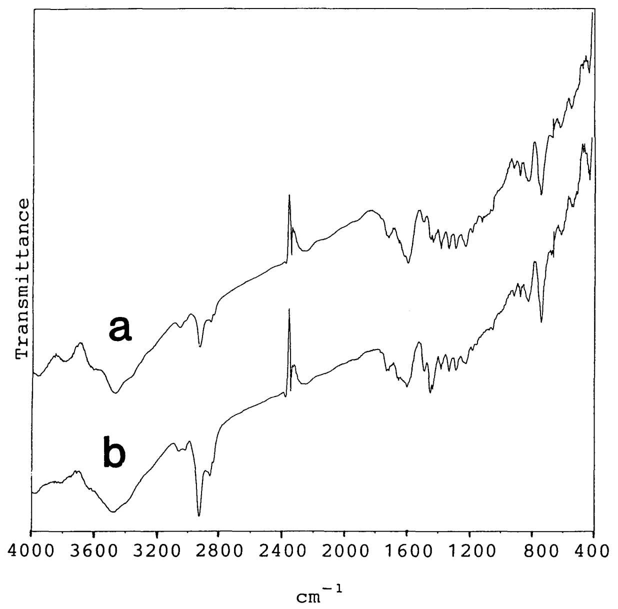

Fig. 1. IR spectra of the polymers obtained by the electrochemically oxidative polymerization of **1** at 60 °C. a: Polymer-1 obtained in Run 4 (see Table 1); b: Polymer-2 obtained in Run 4.

that sum of elemental analyses of the polymers are less than 100%, it can be concluded that these polymers contain oxygen atom. It has been reported that the polymer of benzene obtained by electrochemical oxidation also contained oxygen atom.[3a,b] Although there is a possibility that some portion of molecules of **1** is combined through vinyl ether linkages, the fact that IR absorptions of OH group are intense (see Fig. 1) suggests that the vinyl ether linkages probably are attributed to phenolic OH groups. Weak IR absorption at 1730 cm^{-1} in Fig. 1 is presumably attributed to small amount of carbonyl groups. Weaker intensities (vide ante) of ^{1}H NMR absorption of methylene protons of polymer compared to starting **1** indicate that oxidation of methylene groups of **1** takes place. One sort of oxidation would results in formation of the carbonyl group. Other sort of oxidation would result in formation of C=C double bonds (vide ante). Oxygen atom in vinyl ether, OH groups, and carbonyl groups are presumably come from perchlorate anion since electrolysis is conducted in complete dry nitrogen atmosphere, which is dried by passing through anhydrous $CaSO_4$ and silica gel column.

Table 2 indicates that the polymers obtained at 3.5 or 3.8 V and at 60 °C contain chlorine atom. It has been reported that the polymers of benzene[3a,e,f,j] or naphthalene[4a,c] contained halogen atom. In those cases it was considered that the polymers were doped by electrolytes used during electrolysis. In the present study the polymer containing chlorine atom would be formed by doping by perchlorate anion.

In the polymer each molecule of **1** presumably is combined by C–C linkage between two phenyl groups. Figure 1 shows CH bending bands at 746 and 829 cm^{-1}. These absorptions presumably correspond to reported values of 755 and 830 cm^{-1} of poly(1,4-naphthylene).[4c,7] Although ring deformation signals are not so obvious, it is probable that the polymers obtained in this report have similar structure to poly(1,4-naphthylene) rather than poly(2,6-naphthylene) which has CH bending bands at 860, 800, and 700 cm^{-1}.[4a] Similar structure to poly(1,4-naphthylene) means that each molecule of **1** is combined at 5,8 position.

Half-wave oxidation potential of benzene has been reported to be 2.08 V vs. Ag/Ag$^+$ in acetonitrile[8] or 2.4 V vs. SCE in acetonitrile.[9] Electrochemical polymerization of benzene has been reported to be carried out in this potential range[3] or lower than this range.[3i,j] Half-wave oxidation potential of **1** has been reported to be 1.57 V vs. Ag/Ag$^+$ in acetonitrile.[8] In the present study cyclic voltammetry of **1** was carried out and it was found that oxidation potential of **1** is 1.6 V vs. Ag/Ag$^+$ in PC. Table 1 indicates that considerably higher anode potential than 1.6 V is needed for formation of the polymer. Considering the fact that high concentration of **1** is necessary for formation of the polymer,[6] it is supposed that radical cation of **1** has lower polymerization ability than the radical cation of benzene. It is interesting that solvent has a considerable effect on electrochemical polymerization of **1**. Although **1** was electrochemically polymerized in PC, electrochemical oxidation of **1** in dimethylformamide did not give a polymer.

The number average molecular weight (M_n) of soluble part of the polymer of **1** (polymer-2) is up to 1500. Polymer-1 is slightly soluble and GPC chart of soluble portion of polymer-1 showed broad molecular weight distribution and higher molecular weight part of the GPC chart reached to more than 10000. Therefore, M_n of polymer-1 would be much higher than those of polymer-2.

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6) When electrochemical oxidation of a mixture of 6 ml of **1** and 64 ml of PC was carried out at 3.8 V and at 60 °C for 20 h, only 0.07 g of polymer-2 was obtained and polymer-1 was not obtained. Because of low yield analysis of the polymer, which was obtained at this low concentration of starting **1**, was not carried out.

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