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Oxidative polymerization of phenols having trimethylsilyl groups

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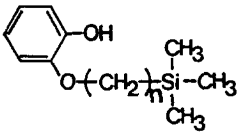
SUMMARY

Phenols 2-substituted with trimethylsilyl groups (1, 2 and 3) were oxidatively polymerized with 2,6-dimethylphenol (4) in the presence of a copper-pyridine catalyst to yield the corresponding poly(phenyleneoxide) copolymers. The polymerization mechanism was studied kinetically and spectroscopically.

INTRODUCTION

2,6-Dimethylphenol(4) is oxidatively polymerized in the presence of a copper-pyridine complex at room temperature to yield poly(2,6-dimethyl-1,4-phenyleneoxide), while 2,6-disubstituted phenols with bulky groups and 2-substituted phenols are only oxidized to 2,2',6,6'-tetrasubstituted biphenoquinone and complicated oxidation products with low molecular weight[1,2]. But the latter phenols are able to be copolymerized with 4 to yield the corresponding poly(phenyleneoxide) copolymers with relatively high molecular weight[3,4].

The oxidative polymerization of phenols with substituents bearing silane groups has not been reported so far. The present paper describes the oxidative polymerization of 2-trimethylsilylpropyloxy phenol(1), 2-trimethylsilylmethoxy phenol(2), and 2-trimethylsilyloxy phenol(3). The polymerization mechanism is discussed.



n=3 1
1 2
0 3

EXPERIMENTAL

Materials; 1-3 were gifted from Mitsubish Chemical Industry Co.. 4 and CuCl were purified as in the previous paper[2].

Preparative Polymerization; 49.5 mg of CuCl(0.5 mmol) was dissolved in 10 ml of pyridine (0.125 mmol) in a sealed flask equipped with an oxygen inlet tube, dropping bottle, and magnetic stirrer, and 50 ml of benzene was added. This solution was stirred under oxygen to oxidize Cu(I)-ion to Cu(II) and to obtain deep-green colored copper-pyridine catalytic solution. 1 and 4 (total amount of 5 mmol) was added to the catalytic solution under oxygen atmosphere and the mixture was stirred for 2 h at room temperature. Then, the reaction mixture was slowly poured to 500 ml of methanol containing a small amount of hydrochloric acid with stirring, and the obtained polymer was washed with methanol and dried in vacuo. The structure and the composition of the copolymer were determined by NMR spectrum. The viscosity of the benzene solution of the polymer was measured at 25 °C.

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^{1}H-NMR of the 1/4 copolymer($CDCl_3$); δ(ppm)= 0.00 (9H $-Si(CH_3)_3$), 0.6(2H $-CH_2Si$), 1.8 (2H $-CH_2-$), 2.1 (6H $-(CH_3)_2$), 3.6(2H $-OCH_2$), 6.5-7.5(5H Ar-H).

Referential signals for 1; δ(ppm)= 0.00 (9H $-Si(CH_3)_3$), 0.59 (2H $-CH_2Si$), 1.78 (2H $-CH_2-$), 3.5 (2H $-OCH_2$), 5.75 (1H -OH), 6.7-7.0 (4H Ar-H).

^{1}H-NMR of the 2/4 copolymer($CDCl_3$); δ(ppm)= 0.00 (9H $-Si(CH_3)_3$), 3.6 (2H $-OCH_2$), 6.6-7.1(5H Ar-H).

Referential signals for 2; δ(ppm)= 0.00 (9H $-Si(CH_3)_3$), 3.5(2H $-OCH_2$), 5.8 (1H -OH), 6.7-7.0 (4H Ar-H).

Measurement of the polymerization rate; The polymerization rate was followed by the oxygen uptake as the oxidation of Cu(I) was very fast under the polymerization conditions. The oxygen uptake was measured with a Warburg apparatus.

Spectroscopic measurement; Visible absorption spectrum of the reaction mixture was measured under nitrogen atmosphere.

Oxidation potential measurement; Oxidative peak potential of the phenols vs Ag/AgCl was measured in methanol with sodium hydroxide as a supporting electrolyte by cyclic voltammogram.

RESULTS and DISCUSSION

The polymerization curves of 1 with 4 are shown in Fig.1. The polymerization rate and the final conversion decrease with the feed amount of 1 to 4. The homopolymerization of 1 did not proceed at room temperature and at 60 °C. The intrinsic viscosity of the polymer solutions and the fraction of 1 unit in the copolymers are presented in Fig. 2. Although the 1 fraction in the resulting copolymer increases with increasing the fraction of 1 in the feed, the fraction was saturated at ca. 0.5. Probably the sterically bulky 1 is inhibited to be homopolymerized, only giving the 1:1 copolymer with 4 even under the feed fraction [1]/[4] > 0.5. The same relationship between the feed fraction, the copolymer fraction and the intrinsic viscosity was observed for the copolymerization of 2 or 3 with 4, as shown in Fig.3.

The polymerization products were brown powders. Their IR spectrum shows that the absorption at 3400 cm^{-1}, corresponding to the hydroxyl

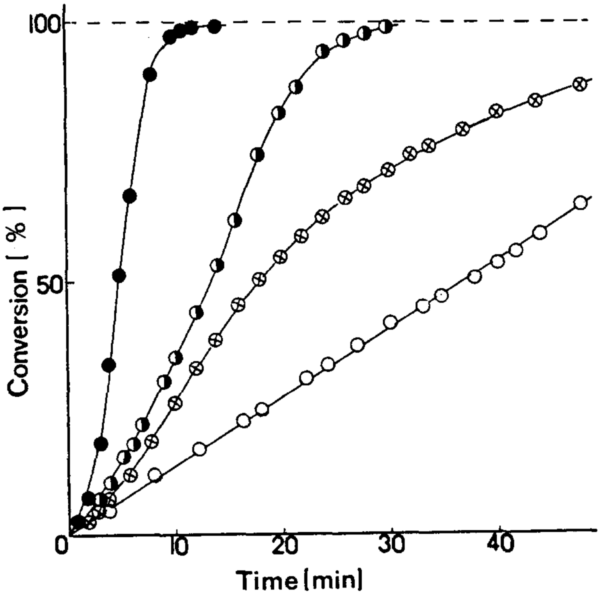


Fig.1 Polymerization curves of 4 with 1 in benzene at 30 °C under O_2 atmosphere
Feed monomer ratio (1/4);
●: 0, ◑: 0.25, ⊗: 1, ○: 4,
[Cu]=0.01 mol/l, in 20vol%-pyridine-benzene solution

Fig.2 Effect of the feed fraction of 1 on the copolymer fraction and the intrinsic viscosity

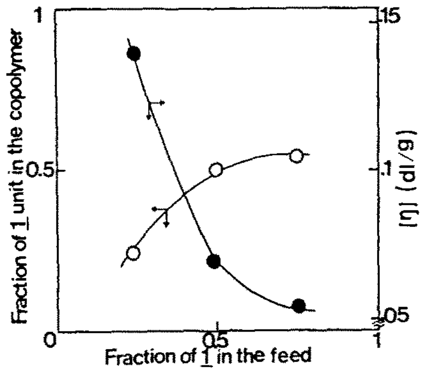
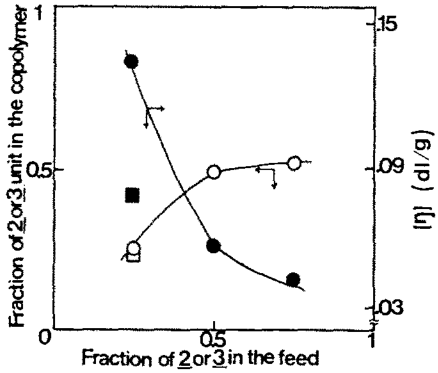


Fig.3 Efeect of the feed fraction of 2 and 3 on the copolymer fraction and the intrinsic viscosity



group, has almost disappeared, and new absorptions assigned to an ether bond were observed at 990 and 1180 cm^{-1}. The ^{1}H-NMR spectra were in complete agreement with those of 1-4 (see Experimental Part).

The authors previously reported that the polymerization of 4 in the presence of a copper-pyridine complex catalyst proceeds via Michaelis-Menten mechanism and following kinetic constants are estimated: the intermediate formation constant of phenol and the catalyst, K (the reciprocal of the Miachaelis constant), and the reaction-rate constant, k.

$$\text{PHENOL} + \text{Cu(II)} \xrightleftharpoons{K} \text{Phenol-Cu} \xrightarrow{k} \text{Phenol Radical} + \text{Cu(I)} \quad (1)$$

The initial polymerization rates for 1/4 were plotted with the feed phenol concentrations; their reciprocals (Lineweaver-Burk plot) show linear relationships as in Fig. 4. This indicates that a kinetic treatment based on the Michaelis-Menten mechanism is also adequate for the 1/4 copolymerization. K and k values calculated from the slope and intercepts of the straight lines are summarized in Table 1.

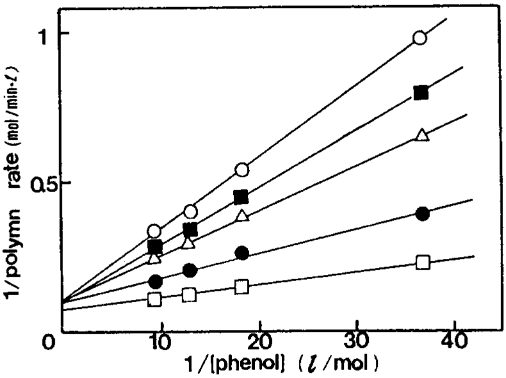


Fig.4 Lineweaver-Burk plots for the copolymerization ○; 4, ■; 1/4= 0.25, △; 1/4= 1, ●; 1/4= 4, □; 1, [Cu]= 1 mmol/l, in benzene solution at 30 °C under O_2 atmosphere

K increases with the feed 1 fraction, which suggests that 1 coordinates to the copper catalyst more easily than 4 does. Oxidation peak potentials of 1-4 are listed in Table 2. Although 1-3 have bulky substituting groups, their oxidation peak potentials are lower than that of 4. Thus it is considered that 1 forms the copper intermediate complex with larger formation constant.

Table 1 Kinetic parameters for the oxidative polymerization of 4 with 1

Phenols	K (l/mol)	k (min^{-1})	k_e (min^{-1})
4	1.95	0.040	1.10
1/4(0.25)	2.95	0.016	0.78
1/4(1)	4.41	0.011	0.54
1/4(4)	7.52	0.009	0.22
1	12.4	0.005	0.14

Table 2 Oxidation peak potentials of phenols

Phenols	Potential(V)
4	1.6
1	0.55
2	0.55
3	0.33

On the other hand, the rate constant k decreases with the feed $\underline{1}$ fraction. The k value was also estimated spectroscopically as follows. The deep-green color of the catalyst solution is based on the Cu(II) complex. After the addition of the phenol to the catalyst solution, the color changed to brown one, which is corresponding to the Cu(I) complex formation or the electron transfer from the phenol to the Cu(II) catalyst. The visible absorption spectra are shown in Fig. 5. The measurement on the decrease in absorption at 745 nm under oxygen-free atmosphere provides the rate constant (electron transfer step: k_e). The k_e values given also in Table 1 decreases with the $\underline{1}$ feed fraction, which agrees with the result for k. This behavior is consistent with the overall polymerization as has been shown in Fig.1. The k or k_e step is the rate-determining in this polymerization.

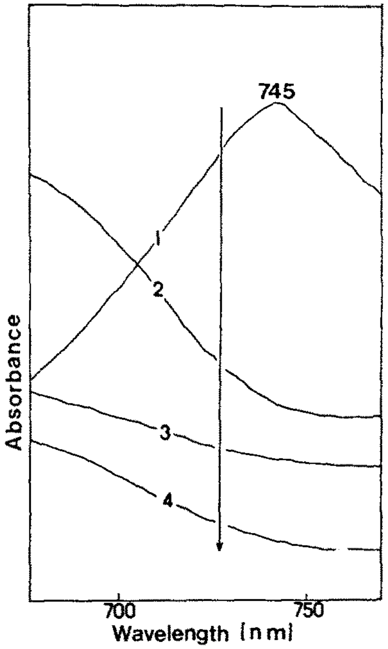
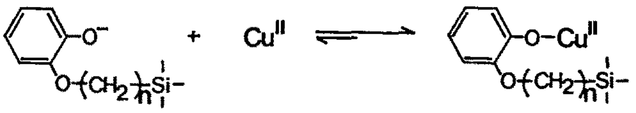
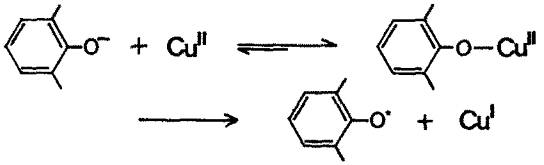


Fig.5 The visible spectral change of the reaction system with time [CuCl]=5 mmol/l, [$\underline{1}$]/[$\underline{4}$]=0.25, in pyridine
1: without phenol, 2: 1 min, 3: 2 min, 4: 5 min after mixing.

From the results mentioned above, the copolymerization mechanism is considered as shown below. First $\underline{1}$ coordinates to the copper catalyst predominantly (Eq. 2). Although the complex formation of $\underline{4}$ with the catalyst is restricted, $\underline{4}$ is more efficiently activated to the phenoxy



(2)



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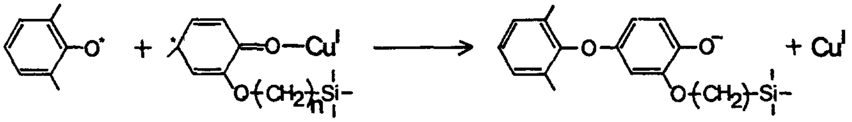

(4)

$$\mathrm{Cu^{I}} \xrightarrow{\mathrm{O_2}} \mathrm{Cu^{II}} \qquad (5)$$

radical due to its larger k or k_e value (Eq. 3). The activated 4 couples with the 1 intermediate complex, forming the dimer (Eq. 4). The repeated reaction brings about the copolymer.

ACKNOWLEDGEMENT

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REFERENCES

1) A. S. Hay, Adv. Polymer Sci., 4, 496(1967)

2) E. Tsuchida, H. Nishide, T. Nishiyama, Makromol. Chem., 176, 1349(1975)

3) A. S. Hay, R. F. Clark, Macromolecules, 3, 533(1970)

4) H. Nishide, T. Minakata, E. Tsuchida, S. Yamada, Makromol. Chem., 183, 1889(1982)

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