

Preparation and oxidative polymerization of 2-fluoro-6-(3-methyl-2-butenyl)phenol

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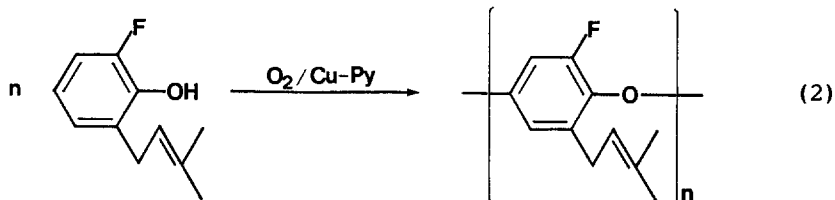
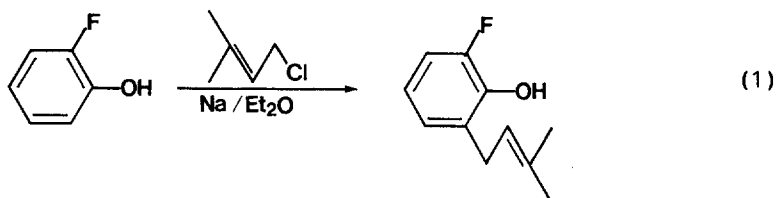
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SUMMARY

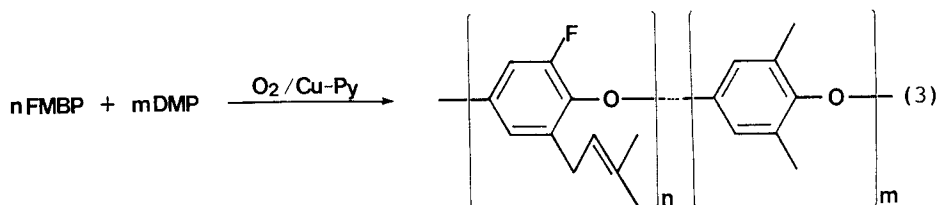
2-Fluoro-6-(3-methyl-2-butenyl)phenol(FMBP) is prepared by the reaction of 2-fluorophenol with 1-chloro-3-methyl-2-butene in the presence of metallic sodium. FMBP is oxidatively polymerized with a copper-pyridine catalyst to yield poly[oxy-2-fluoro-6-(3-methyl-2-butenyl)-1,4-phenylene]. FMBP is also copolymerized with 2,6-dimethylphenol(DMP). The copolymerizability of FMBP is discussed.

INTRODUCTION

2,6-Disubstituted phenols are oxidatively polymerized to yield poly(oxy-2,6-disubstituted phenylene)s with a copper-amine complex as catalyst in the presence of oxygen at room temperature¹⁻³). We have reported this polymerization for phenols bearing bulky substituents to give new poly(oxy phenylene) derivatives⁴⁻⁷). This paper describes preparation and oxidative polymerization of 2-fluoro-6-(3-methyl-2-butenyl)phenol(FMBP) which has the fluorine as an electron-attractive group and the 3-methyl-2-butenyl group as a bulky and an electron-donative group.



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The polymerization of FMBP and the copolymerization of FMBP with 2,6-dimethylphenol(DMP) are carried out with a copper-pyridine catalyst. The polymerization mechanism is discussed kinetically and spectroscopically.

EXPERIMENTAL

MATERIALS: FMBP was prepared as follows. To an ethereal solution (80 ml) of 2-fluorophenol (0.1 mol, 11.2 g), metallic sodium (0.15 mol, 3.45 g) was added and vigorously stirred for 2 h. To this mixture, 1-chloro-3-methyl-2-butene (0.1 mol, 10.5 g) was added dropwisely. The reaction mixture was diluted with water, neutralized, and extracted with ether. The ether extract was then dried and distilled under reduced pressure to yield 11.9 g (66 %) of FMBP. bp 72-73°C /0.8 mmHg.

¹H-NMR(CCl₄, TMS standard); δ(ppm)= 1.85 (s, 3H, -CH₃), 1.84 (s, 3H, -CH₃), 3.35 (d, J=7 Hz, 2H, -CH₂-), 5.06 (s, 1H, -OH), 5.30 (t, 1H, =CH-), 6.60-7.05 (m, 3H, Ar-H).

IR(ν_{cm}⁻¹); 3400, 1630, 1480, 1270, 1220, 840, 778, 740.

DMP was purified by recrystallization from hexane. Cuprous chloride was prepared by reduction of cupric chloride. Pyridine was distilled after being dried over potassium hydroxide.

PREPARATIVE POLYMERIZATION: Cuprous chloride(0.25 mmol, 25 mg) was dissolved in pyridine(63 mmol, 5 ml) in a sealed flask and benzene(30 ml) was added. This solution was stirred under oxygen atmosphere to oxidize Cu(I)-ion to Cu(II) and to obtain active copper-pyridine complex catalyst solution. FMBP(2.5 mmol, 0.45 g) was added to the catalytic solution under oxygen atmosphere and the mixture was stirred for 1 day. Then, the reaction mixture was slowly poured to 500 ml of methanol containing 10 % of hydrochloric acid with stirring, and the obtained polymer was washed with methanol and dried in vacuo. The structure of the reperfired polymer was determined by IR, NMR spectrum and elemental analysis.

¹H-NMR of the polymer(CDCl₃, TMS standard); δ(ppm)= 1.80, 1.82 (6H, -CH₃), 3.30 (2H, -CH₂-), 5.20 (1H, =CH-), 6.55-6.75 (2H, Ar-H).

MEASUREMENTS: The polymerization rate to be followed by the oxygen uptake accompanying the oxidative polymerization. Visible absorption spectrum of the reaction mixture was measured under nitrogen atmosphere. The viscosity of the benzene solution of the polymers was measured at 25°C.

RESULTS and DISCUSSION

We have reported that 3-methyl-2-butenyl group is easily introduced to the 6-position of o-cresol in the presence of metallic alkaline in non-polar solvents. FMBP was successfully prepared in this paper by the reaction of 2-fluorophenol and 1-chloro-3-methyl-2-buten in the presence of metallic sodium.

FMBP was polymerized by the copper-pyridine catalyst under oxygen atmosphere as it has been for DMP, to yield poly[oxy-2-fluoro-6-(3-methyl-2-butenyl)-1,4-phenylene] as a brown powder. The polymer showed IR absorption at 990 and 1180 cm^{-1} , assigned to an ether bond, and the absorption at 3400 cm^{-1} corresponding to the hydroxyl group has almost disappeared. The $^1\text{H-NMR}$ spectra were in complete agreement with those of FMBP (see Experimental section).

Fig.1 Polymerization curves of FMBP and DMP in the benzene solution O: FMBP, \circ : FMBP/DMP = 0.5, \bullet : DMP at 30 $^{\circ}\text{C}$ under oxygen atmosphere [Cu] = 0.01 mol/l, Pyridine 20 vol% in benzene

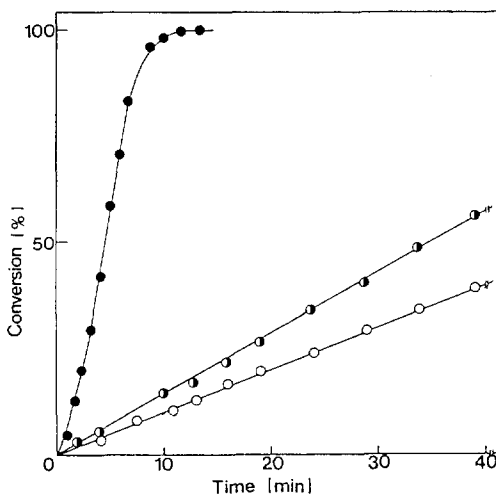
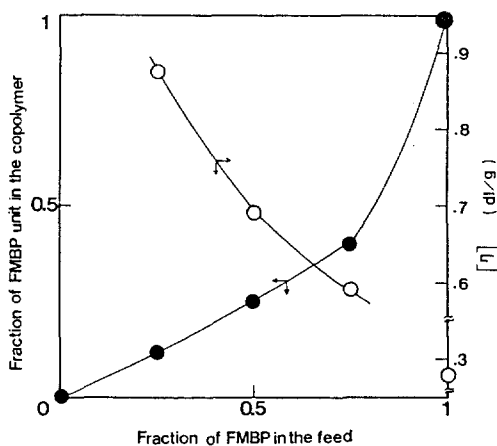


Fig.2 Effect of the feed fraction of FMBP on the composition and the intrinsic viscosity of the copolymers



Oxygen-uptake curve of the polymerization of FMBP is shown in Fig. 1. The rate of the FMBP polymerization is much smaller than that of the DMP

polymerization.

The copolymerization of FMBP with DMP proceeds as shown in Fig. 1. The fraction of the FMBP unit in the copolymers and the intrinsic viscosity of the copolymers are given in Fig. 2. FMBP is incorporated to the copolymer with about half reactivity of DMP, but the molecular weight of the copolymer is much decreased with the feed fraction of FMBP. This polymerizability of FMBP is hardly affected by the polymerization temperature as shown in Fig. 3.

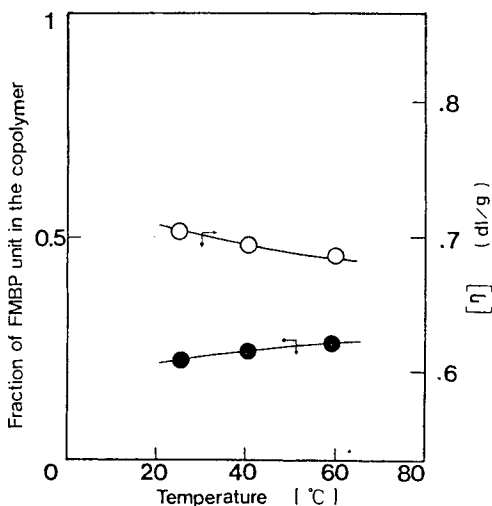


Fig.3 Effect of the reaction temperature on the composition and the intrinsic viscosity of the copolymers

The polymerization process of phenols with a copper-pyridine catalyst can be described by following four steps²⁾; (1) coordination step of phenol to the catalyst, (2) electron-transfer step from the coordinated phenol to the catalyst copper(II), (3) dissociation step of the activated phenol from the catalyst, and (4) reoxidation step of catalyst. That is, this



polymerization proceeds via a mechanism similar to that of Michaelis-Menten type reaction. The plots for the reciprocals of the polymerization rates in a steady state and of the feed phenol concentrations (Lineweaver-Burk plot) show linear relationships, as shown in Fig. 4, supporting this mechanism.

Kinetic constants, the intermediate formation constant of the phenol and the copper catalyst, K (the reciprocal of the Michaelis constant), and the reaction-rate constant, k , are calculated from the slopes and intercepts of the straight lines (Table 1). The K and k values of FMBP are smaller than those of DMP because the bulky 6-substituted 3-methyl-2-butenyl group hinders the coordination of FMBP to the copper catalyst and because the 2-substituted electron-attractive fluorine retards the activation step.

The reactivity of FMBP was also studied spectroscopically. The deep-green color of the catalyst solution which is based on the Cu(II) complex

turned brown by the addition of the phenol, which corresponds to the Cu(I)

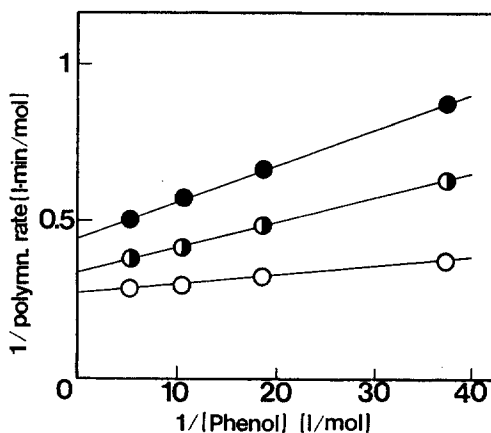


Fig.4 Lineweaver-Burk plots for the polymerization O: DMP, ◐: DMP-FMBP (feed fraction 0.5), ◑: FMBP, [Cu]= 1 mmol/l, in benzene solution at 30°C under oxygen atmosphere

Table 1. Kinetic parameters for the polymerization of FMBP and DMP

Feed Monomer Fraction of FMBP	K (l/mol)	k (min ⁻¹)	k _e (min ⁻¹)
0	4.1	0.39	1.62
0.5	3.7	0.19	-
1	2.9	0.11	0.63

complex formation or the electron transfer from the phenol. The rate constant (electron transfer step: k_e) is calculated from the straight line of the logarithm of the decrease in the d-d absorption at 745 nm under an oxygen-free atmosphere for the time (Table 2). The k_e value of FMBP is smaller than that of DMP, which agrees with the result for k. The 2-fluoro substituent reduces the reactivity and the polymerizability of FMBP to about the half of those of DMP.

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