The Oxidative Polymerization of 2-Methyl-6-(3,7-dimethyl-2,6-octadienyl)phenol

Sang-Heon Hyun, Hiroyuki Nishide, Eishun Tsuchida,* and Shigetoshi Yamada†
Department of Polymer Chemistry, Waseda University, Tokyo 160
†Junior College of Technology, Shizuoka University, Hamamatsu 432

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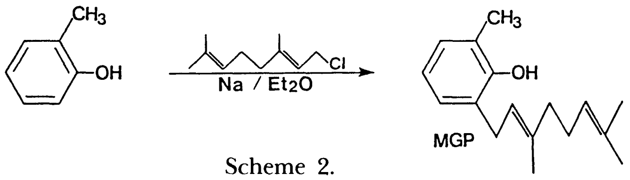
2-Methyl-6-(3,7-dimethyl-2,6-octadienyl)phenol (MGP) was prepared by the reaction of *o*-cresol and 1-chloro-3,7-dimethyl-2,6-octadiene in the presence of sodium. This MGP was then oxidatively polymerized with a copper-pyridine catalyst to yield poly[oxy[3-methyl-5-(3,7-dimethyl-2,6-octadienyl)-1,4-phenylene]]. The MGP and 2,6-dimethylphenol (DMP) copolymerized with a similar reactivity to form copolymer. The properties of the polymers were also studied.

The oxidative polymerization of 2,6-disubstituted phenols with a copper-pyridine complex as a catalyst produces poly[oxy(3,5-disubstituted phenylene)] under an oxygen atmosphere at room temperature.1—3) Phenolic derivatives bearing isoprenoid substituents exist in nature. They are also interesting as monomers of the oxidative polymerization because they provide poly(oxyphenylene) with bulky and rigid isoprenoid groups. For example, poly[oxy(3,5-dimethyl-1,4-phenylene)] is known to show a high permselectivity of oxygen in preference to nitrogen in spite of its low permeability. Thus, it is interesting to study the effect of the bulky isoprenoid group of poly(oxyphenylene) on its gas permeability.

The present authors have previously reported the preparation of 2,6-diprenylphenol and 2-methyl-6-butenylphenol and their oxidative polymerization,4,5) and preliminarily reported the preparation of 2-methyl-6-(3,7-dimethyl-2,6-octadienyl) phenol (2-methyl-6-geranylphenol, MGP).6) The present paper will describe the preparation and oxidative polymerization of MGP and the copolymerization of MGP with 2,6-dimethylphenol (DMP). The reactivity of the 3,7-dimethyl-2,6-octadienyl group in the copolymer and the polymerization mechanism will also be reported.

Experimental

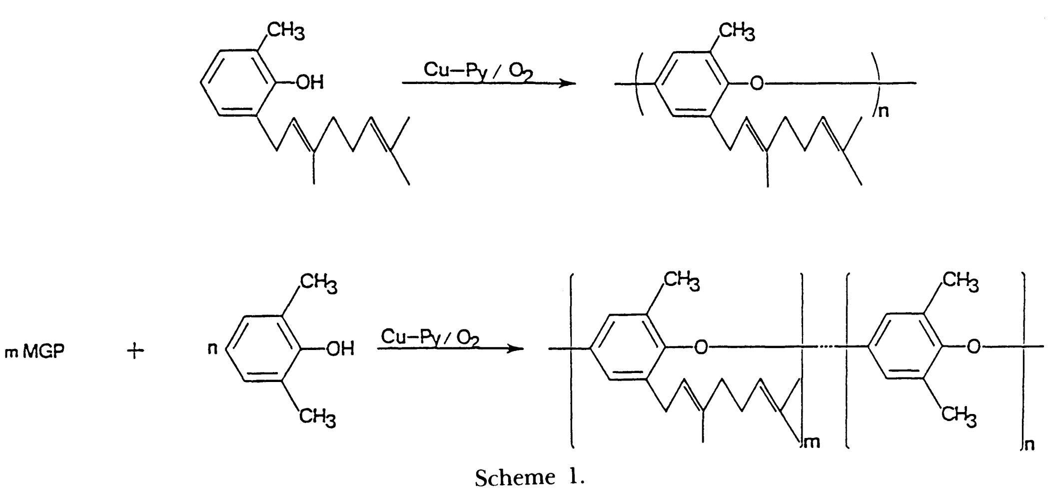
Materials: MGP was prepared as follows; *o*-cresol (1.08 g, 0.01 mol) was dissolved in dry diethyl ether (15 ml), and then metallic sodium (0.3 g, 0.013 g, atom) was added at room temperature. After 0.5 h, 1-chloro-3,7-dimethyl-2,6-octadiene (1.73 g, 0.01 mol) was slowly stirred into the mixture, and the mixture was refluxed for 1.5 h. After a usual work-up, a light yellow oil (2.68 g) was distilled i.vac.; bp 111—113 °C/0.2 mmHg (1 mmHg=133.322 Pa); yield, 71% (1.72 g). ^{1}H NMR of MGP (CCl$_4$, TMS standard): δ=1.60, 1.66 (s, 6H, =C(CH$_3$)$_2$), 1.72 (s, 3H, =(CH$_3$)-), 2.05 (m, 4H, -CH$_2$CH$_2$-), 2.19 (s, 3H, Ar-CH$_3$), 4.42 (d, *J*=7 Hz, 2H, O-CH$_2$-), 5.0 (m, 1H, -CH=C), 5.42 (t, 1H, -CH=) and 6.53—7.0 (m, 4H, Ar-H).



Scheme 2.

The DMP was a commercial one which was purified by recrystallization from hexane. the copper(I) chloride was prepared by the reduction of copper(II) chloride. The pyridine was purified by distillation after having been dried over KOH.

Preparative Polymerization. The polymerization of MGP was carried out in a benzene solution with the copper-pyridine complex as follows: CuCl (25 mg, 0.25 mmol) was dissolved in pyridine (5 ml) in a sealed flask equipped with an oxygen inlet tube, a dropping bottle, and a magnetic stirrer, and then 30 ml of benzene was added. This solution was vigorously stirred under an oxygen atmosphere to oxidize



Scheme 1.

the Cu(I) ion to Cu(II) and to obtain deep-green colored copper-pyridine complex catalytic solution. A benzene solution (15 ml) of MGP (1.22 g, 5 mmol) was then added to this catalytic solution, after which the mixture was stirred for 1 h at room temperature. The reaction mixture was then stirred into 500 ml of methanol containing a small amount of hydrochloric acid; the viscous, light brown polymer thus obtained was washed with methanol and dried i. vac. Yield, 94%.

The structure of the polymer was confirmed by NMR, IR, and elemental analysis. ^{1}H NMR of the polymer ($CDCl_3$, TMS standard): δ=1.57, 1.69 (9H, $-CH_3$), 1.94 (4H, $-CH_2CH_2-$), 2.0 (3H, $-CH_3$), 3.12 (2H, $-CH_2-$), 5.08 (2H, -CH), and 6.34—6.63 (2H, Ar-H). The intrinsic viscosity of the toluene solution of the polymer was measured at 25 °C. The content of double bonds in the polymer was determined by the method of Wijs by adding an excess of ICl to the polymer solution in the dark and by titrating the excess with $Na_2S_2O_3$. It was ascertained by the titration that no replacement reaction of the phenol ring occurred.

The copolymerization of MGP and DMP was carried out in the same way. The light yellow powder thus precipitated was filtered, washed with methanol, and dried i. vac. Yield, 91%. H NMR ($CDCl_3$, TMS standard): δ=1.59, 1.70 (9H, $-CH_3$), 1.95 (4H, $-CH_2CH_2-$), 2.1 (9H, $-CH_3$), 3.12 (2H, $-CH_2-$), 5.08 (2H, -CH=) and 6.45 (4H, Ar-H). The fraction of the MGP residue in the copolymer was determined by means of the NMR spectra.

Measurement of the Polymerization Rate. The polymerization rate was followed by means of 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. The visible absorption spectrum of the mixture of the copper-pyridine complex and phenol was measured in a pyridine solution at room temperature under an oxygen-free atmosphere.

Oxidative-Peak-Potential Measurement. The oxidative peak potential of the phenols vs. Ag/AgCl was measured by means of a cyclic voltammogram in methanol, with potassium hydroxide as the supporting electrolyte.

Addition of Bromine. One gram of the copolymer was dissolved in 50 ml of CCl_4, and then 0.2 g of bromine was stirred, drop by drop, into the solution in the dark. After 1 h, the reaction mixture was poured into methanol, and the precipitate was filtered and dried i. vac. The amount of bromine introduced to the copolymer was determined by the Volhard method.

Permeation Measurement. A membrane of the MGP copolymer was prepared by casting a chloroform solution of the copolymer on a Gore-tex film and dried i. vac. at room temperature over a two-day period before measurement. The oxygen and nitrogen permeation coefficients were measured with a low-vacuum permeation apparatus (Rika Seiki Inc. Model K-315 N-031) and were calculated from the slopes of the steady-state straight lines of the permeation curves.

Results and Discussion

The oxygen-uptake curve of the polymerization of the MGP catalyzed by the copper-pyridine complex is shown in Fig. 1. After mixing the solution of MGP with a solution of a catalytic amount of the copper-pyridine complex, a linear oxygen uptake with time is observed after an induction period. The reaction is in a stationary state, the oxygen uptake being based on the oxidation of MGP. The oxygen uptake corresponds to the polymerization of MGP, since the polymer is the only reaction product.

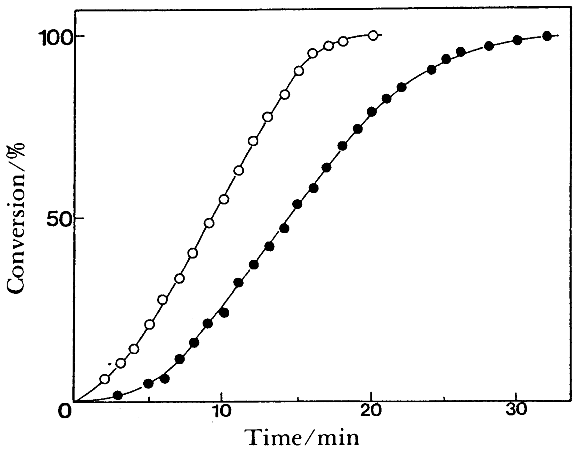


Fig. 1. Polymerization curves of MGP and DMP in benzene solution. ○: MGP, ●: DMP at 30 °C under oxygen atmosphere [Cu]=0.01 mol·l^{-1}, Pyridine 20 vol% in benzene solution.

The IR spectra of the polymers showed that the new absorptions 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}H NMR spectra were in complete agreement with those of MGP (see Experimental section).

MGP was also copolymerized with DMP. The fraction of MGP units in the copolymers and the intrinsic viscosity of the copolymers are shown in Fig. 2. Figure 2 indicates that MGP is copolymerized with DMP with a similar reactivity, but that the molecular weight of

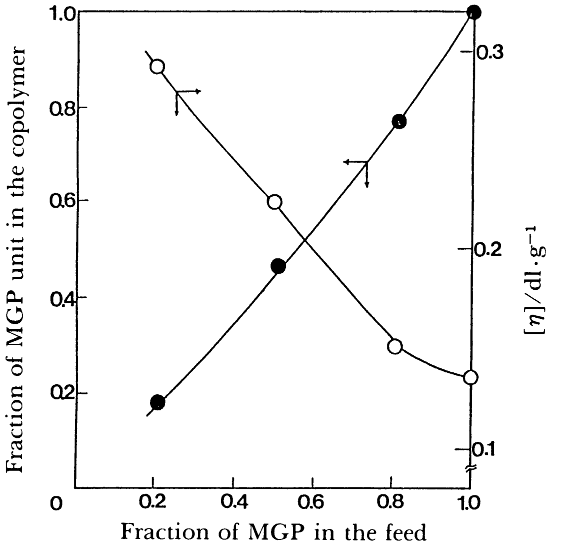


Fig. 2. Effect of the feed fraction of MGP on the composition and the intrinsic viscosity of the copolymer.

the copolymer decreases with the increase in the fraction of MGP units.

The initiation mechanism of the oxidative polymerization of phenols with the copper-pyridine complex is considered to be the following:[2] the coordination step of the phenol to the Cu(II) catalyst, the electron-transfer step from the coordinated phenol to the Cu(II) ion, the dissociation step of the activated phenol from the catalyst, and the reoxidation step of Cu(I). The previous authors have also reported[2] that the polymerization of the phenols proceeds according to a Michaelis-Menten mechanism; the following kinetic constants are estimated: the intermediate formation constants of phenol and the catalyst, *K* (the reciprocal of the Michaelis constant), and the reaction-rate constant, *k*:

$$\text{Phenol} + \text{Cu(II)} \overset{K}{\rightleftarrows} \text{Phenol-Cu} \xrightarrow{k} \text{Activated phenol} + \text{Cu(I)} \qquad (1)$$

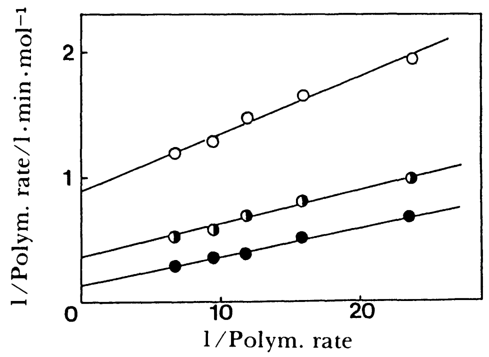


Fig. 3. Lineweaver-Burk plots for the polymerization. ○: DMP, ○: DMP-MGP (feed fraction 0.5), ●: MGP, [Cu]=1 mmol·l^{-1}, in benzene solution at 30 °C under oxygen atmosphere.

The polymerization rates in a steady state for MGP and DMP were plotted with the feed phenol concentrations; their reciprocals (Lineweaver-Burk plot) show linear relationships, as in Fig. 3, supporting this mechanism. The *K* and *k* values calculated from the slopes and intercepts of the straight lines are given in Table 1.

The *K* value for MGP is smaller than that for DMP because the bulky 2-substituted geranyl group hinders the coordination of MGP to the copper catalyst. However, the *k* for MGP is larger than for DMP, leading to the relatively high polymerization rate of MGP.

Table 1. Kinetic Parameters for the Polymerization of MGP and DMP

Feed monomer fraction of MGP	*K* / l mol^{-1}	*k* / min^{-1}	k_e / min^{-1}
0	1.0	0.14	0.31
0.5	0.69[a)]	0.25[a)]	—
1	0.10	0.67	0.46

a) Apparent values.

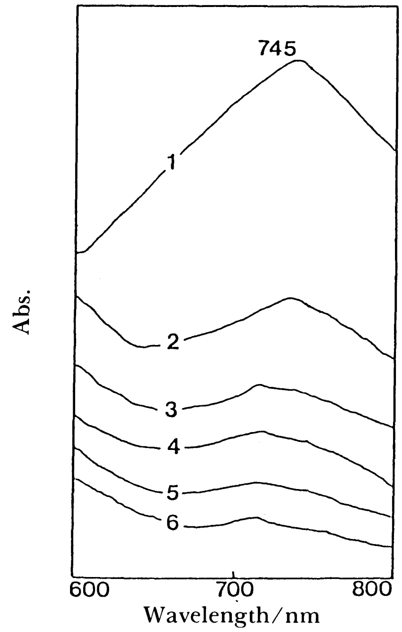
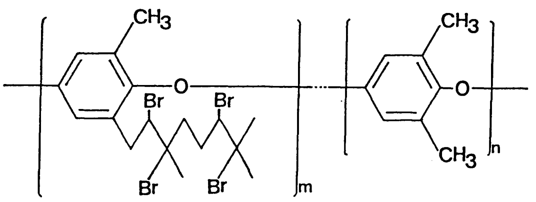


Fig. 4. Visible spectral change of the reaction mixture with time [Cu]=5 mmol·l, [MGP]=0.1 mol·l, in pyridine solution 1; without MGP, 2: 0.5 min, 3: 1.5 min, 4: 3.5 min, 5: 5,5 min, 6: 13.5 min.

This high reactivity of MGP was further studied spectroscopically. 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, it turned brown, which corresponds to the Cu(I) complex formation or the electron transfer from the phenol to the Cu(II) catalyst. The change in the visible absorption is shown in Fig. 4. The measurement of the decrease in d-d absorption at 745 nm under an oxygen-free atmosphere provides the rate constant (electron transfer step: k_e). The k_e value given also in Table 1 is larger for MGP, which agrees with the result for *k*. This behavior is consistent with the overall polymerization as has been shown in Fig. 1. The step represented by *k* or k_e is the rate-determining step in this polymerization.

The oxidation-peak potential of the phenols was measured by cyclic voltammetry and is given in Table 2. This indicates that MGP is more readily oxidized than DMP, a finding which agrees with the kinetic and spectroscopic results. The electron-donating 3,7-dimethyl-2,6-octadienyl group probably reduces the oxidation peak-potential of phenol and enhances its reactivity in the polymerization.



Scheme 3.

Table 2. Oxidation-Peak Potential

Phenol	Volt
MGP	0.34
DMP	1.6

The 3,7-dimethyl-2,6-octadienyl groups in the polymer showed enough chemical reactivity, e.g. for the addition of bromine. Two bromine molecules were introduced per monomer unit of the polymer; i.e., >98% of the geranyl group was reacted with bromine. The brominated polymer is interesting for its self-extinguishing property.

The oxygen- and nitrogen-permeability coefficients are given in Table 3. The gas permeability of the MGP copolymer is comparable with that of poly[oxy-(3,5-dimethyl-1,4-phenylene)], and the copolymer shows a good permselectivity.

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Table 3. Gas Permeablility (P, cm^3(STP)cm/cm^2·s·cmHg) of the MGP Copolymer Membrane[a)]

Membrane	$10^{10}\cdot P_{O_2}$	$10^{10}\cdot P_{N_2}$	P_{O_2}/P_{N_2}
MGP copolymer	5.4	1.1	4.9
Poly[oxy(3,5-dimethyl-1,4-phenylene)][b)]	15.8	3.8	4.2

a) Fraction of MGP units in the copolymer; 80 mol%.
b) H. Yasuda and Kj. Rosengren, *J. Appl. Polym. Sci.*, **14**, 2839 (1970).

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