

‘Radical-controlled’ oxidative polymerization of *m*-cresol catalyzed by μ - η^2 : η^2 -peroxo dicopper(II) complex

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Abstract

Described is an oxidative polymerization of *m*-cresol catalyzed by (1,4,7-triisopropyl-1,4,7-triazacyclononane)copper complex, from which a μ - η^2 : η^2 -peroxo dicopper(II) complex is formed under dioxygen and reacts with *m*-cresol to give ‘controlled’ phenoxy radical–copper(I) complex exclusively without formation of ‘free’ phenoxy radical. The present catalyst showed the highest activity in the metal complex catalysts reported for the polymerization of *m*-cresol with dioxygen. The resulting polymer consisted of oxyphenylene units and showed high molecular weight and high thermal stability. The high selectivity toward C–O linkage would be due to the coupling from the phenoxy radical species controlled by this catalyst. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Oxidative polymerization; *m*-Cresol; Catalyst

1. Introduction

Catalytic oxidative polymerization of phenols has received much attention as an environmentally benign method to synthesize phenolic

polymers owing to mild reaction conditions and small amounts of by-products (almost water only). Copper complexes [1,2], manganese complexes [3] or enzymes [4] catalyzed the polymerization of 2,6-dimethylphenol (DMP) to produce a linear C–O coupling polymer, poly-(2,6-dimethyl-1,4-phenylene oxide), alloys of which with polystyrene, are used as engineering plastics [5]. For DMP, two methyl groups at 2,6-positions lower the redox potential and protect the both *o*-positions. However, in the case of the polymerization of *m*-cresol (MCR), which is unsubstituted at both *o*-positions, no catalysts have afforded the C–O coupling polymers hav-

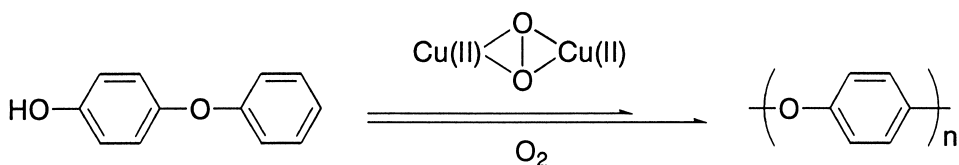
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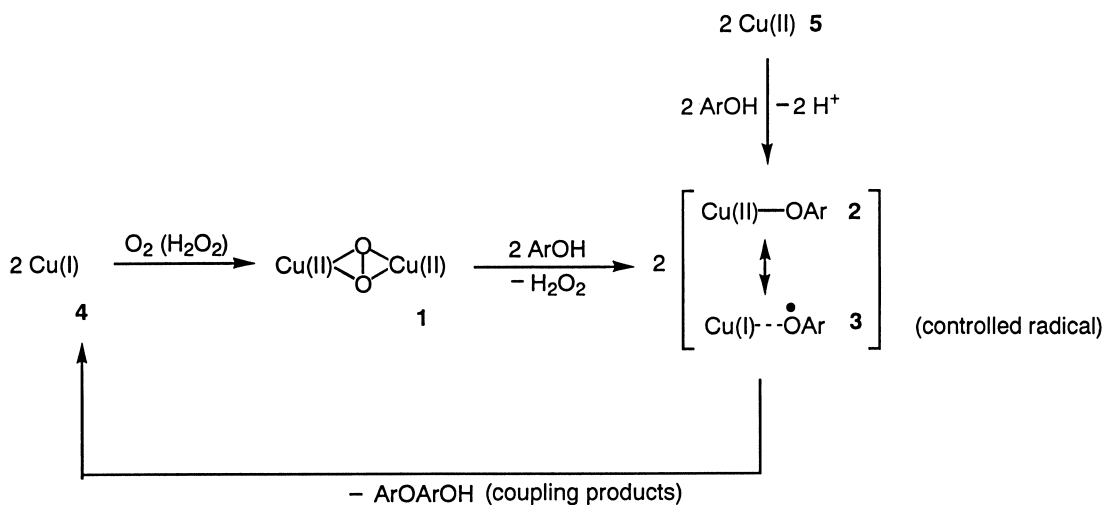


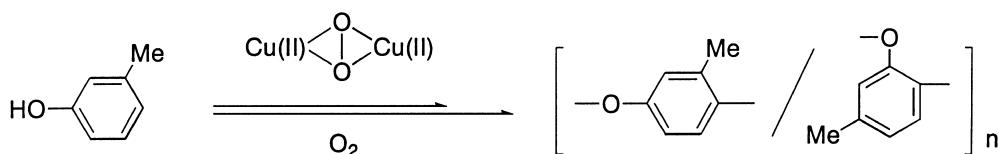
ing high molecular weights in high yields. For the polymerization of MCR with dioxygen as oxidant, copper/diethylamine complex catalyst [6] and manganese/2-aminoethanol complex catalyst [7] were merely reported and gave little amounts of the polymers (0–2%), whereas these catalysts produced the polymers from DMP in ~90% yield. Horseradish peroxidase (HRP) catalyst with hydrogen peroxide as oxidant yielded the polymer of MCR quantitatively [8], which possessed both phenylene (C–C coupling) and oxyphenylene (C–O coupling) units and did not have enough molecular weight for engineering plastics.

Recently, we have achieved highly-regioselective ‘radical-controlled’ oxidative polymerization of 4-phenoxyphenol with no substituents at 2,6-positions catalyzed by μ - η^2 : η^2 -

peroxo dicopper(II) complex to synthesize poly(1,4-phenylene oxide) showing crystallinity with a melting point (Scheme 1) [9,10]. The key point is that μ - η^2 : η^2 -peroxo dicopper(II) complex **1** [11,12] having a ‘nucleophilic’ property [13] abstracts proton from the phenol monomer to give phenoxo–copper(II) complex **2**, equivalent to phenoxy radical–copper(I) complex **3**, which are not ‘free’ radicals but ‘controlled’ radicals (Scheme 2).

In this study, the ‘radical-controlled’ oxidative polymerization of MCR was carried out (Scheme 3). As catalyst, (1,4,7-triisopropyl-1,4,7-triazacyclononane)copper (Cu(tacn)) complex was selected (Fig. 1) [9,10]. The catalytic activity was compared with that of (*N,N,N',N'*-tetramethylethylenediamine)copper (Cu(tmed)) complex, which is well known as a





Scheme 3.

highly active catalyst for the polymerization of DMP [14].

2. Experimental

Complex $\text{Cu}(\text{tacn})\text{Cl}_2$ was synthesized according to the literature [10] and $\text{Cu}(\text{tmed})(\text{OH})_2\text{Cl}_2$ complex was purchased from Tokyo Chemical Industry. Other reagents and solvents were commercially available and used without further purifications.

High-pressure liquid chromatographic (HPLC) analysis was performed on a Tosoh PD-8020 system connected to a Tosoh PD-8020 photodiode array set at 278 nm, and a YMC ODS-AM/AM-304 column was used with methanol/water eluent. Molecular weight was estimated by means of size exclusion chromatography (SEC). A Tosoh SC-8020 system equipped with a Tosoh RI-8020 differential refractometer and two Tosoh TSKGEL α -M columns was used and the measurement was performed at 60°C with *N,N*-dimethylformamide (DMF) eluent containing 0.4 wt.% LiCl. FT-IR spectra with KBr disks were recorded on a Perkin-Elmer Paragon 1000 spectrometer.

Thermogravimetric analysis (TG) was obtained on a Mac-Science TG-DTA 2000S apparatus at a heating rate of 10°C/min to 500°C under argon.

The polymerization procedure is as follows. Under dioxygen (1 atm), a mixture of MCR (130 mg, 1.20 mmol), $\text{Cu}(\text{tacn})\text{Cl}_2$ (2.3 mg, 0.0060 mmol), 2,6-diphenylpyridine (13.9 mg, 0.060 mmol), and diphenyl ether (200 mg, internal standard) in toluene (2.4 g) was kept at 40°C with vigorous stirring. During the reaction, small portions (10 mg) of the reaction mixture were sampled for determination of the MCR conversion by HPLC. After 24 h (conversion 66%), a few drops of conc. HCl aq. was added, and subsequently a large amount of methanol was poured into the reaction mixture to precipitate the polymeric material, which was collected by filtration, washed with methanol, and dried in vacuo to give 68 mg of the pale yellow powdery polymer (yield 53%).

3. Results and discussion

The polymerization catalyzed by $\text{Cu}(\text{tacn})\text{Cl}_2$ and $\text{Cu}(\text{tmed})(\text{OH})_2\text{Cl}_2$ (0.5 mol% for MCR)

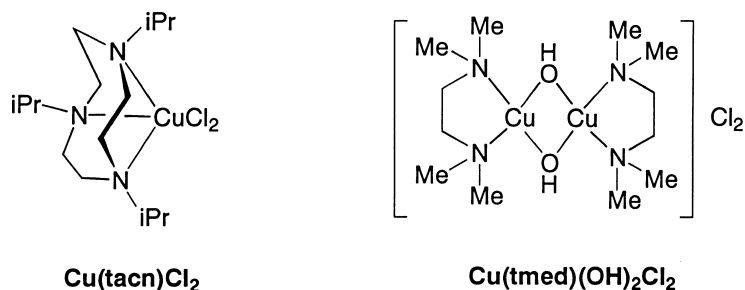


Fig. 1. Copper complexes employed as catalysts.

Table 1
Oxidative polymerization of MCR^a

Entry	Catalyst	Time (h)	Conversion ^b (%)	Yield ^c (%)	Mn ^d	Mw ^d	Td ₅ ^e
1	Cu(tacn)Cl ₂	24	66	53	39 500	215 000	392
2	Cu(tmed)(OH) ₂ Cl ₂	24	25	0	–	–	–

^aPolymerization of MCR (1.20 mmol) catalyzed by copper complex (0.0060 mmol) and 2,6-diphenylpyridine (0.060 mmol) in toluene (2.4 g) under dioxygen (1 atm) at 40°C.

^bConversion of MCR, determined by HPLC.

^cMethanol-insoluble part.

^dDetermined by SEC.

^eTemperature at 5% weight loss, determined by TG.

was performed under dioxygen (1 atm) in toluene at 40°C (Table 1). During the polymerization, small portions of the reaction mixtures were sampled and the conversion of MCR was determined by HPLC. The time-conversion curves are shown in Fig. 2. The consumption rate of MCR using the Cu(tacn) catalyst was about 2.5 times as fast as that using Cu(tmed) one. After 24 h, the conversion for the Cu(tmed) catalyst reached only 25% and almost no polymeric products as methanol-insoluble part were obtained; all other products were methanol-soluble, indicating low molecular weight materials. From this finding and the previous data [6,7], it seems that highly active catalysts for the polymerization of DMP are not efficient catalysts

for that of MCR. This is probably because the redox potential of MCR is higher than that of DMP [15]. For the Cu(tacn) catalyst, on the other hand, the conversion reached 66%, producing pale yellow polymer in 53% yield as methanol-insoluble part. The Cu(tacn) complex is the most active catalyst in the metal complexes reported for the polymerization of MCR with dioxygen.

The present polymer was soluble in DMF, tetrahydrofuran, and chloroform, and the number- and weight-averaged molecular weights (M_n and M_w) estimated by SEC were 3.95×10^4 and 2.15×10^5 , respectively. These values were much larger than those obtained by HRP catalyst with hydrogen peroxide [8].

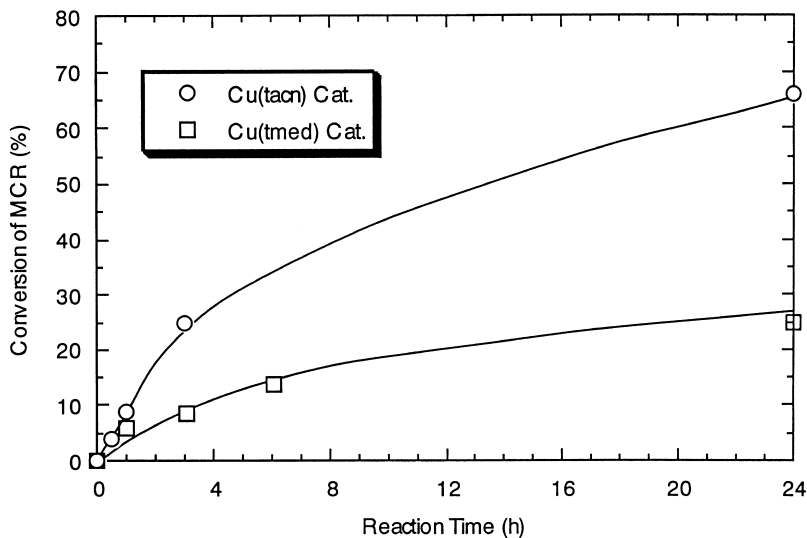


Fig. 2. Time-conversion curves for the Cu(tacn) catalyst and the Cu(tmed) one.

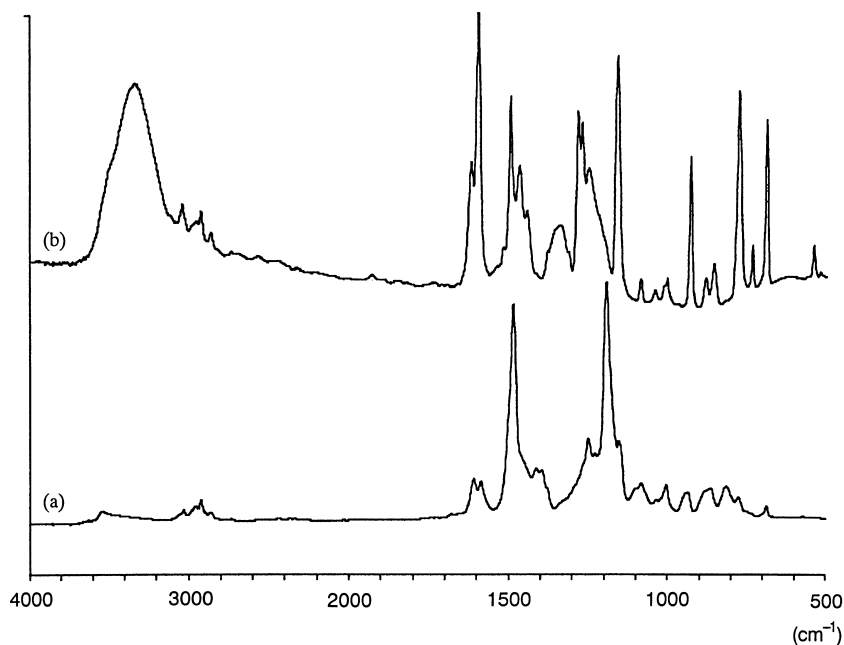


Fig. 3. FT-IR spectra of the polymers obtained for the Cu(tacn) catalyst (a) and MCR (b).

The polymer structure was estimated by FT-IR spectroscopy (Fig. 3). The polymer obtained for the Cu(tacn) had a broad peak at 3537 cm^{-1} due to O–H vibration, which was much smaller than that of MCR, indicating that this polymer

possesses little amounts of phenylene units. Two characteristic peaks detected at 865 and 816 cm^{-1} will be ascribed to C–H deformation vibrations of 1,2,4-trisubstituted benzenes. A small peak seen at 778 cm^{-1} would be at-

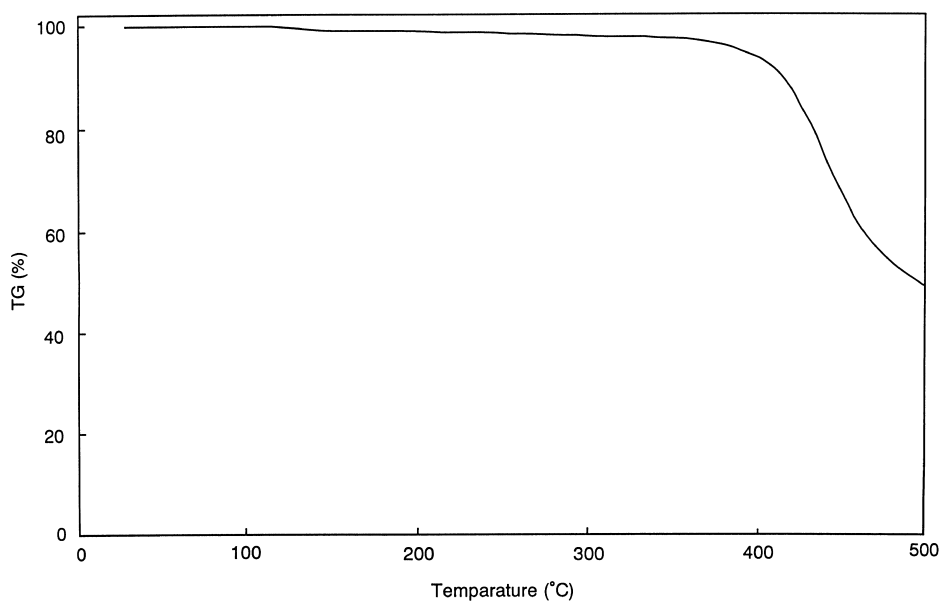


Fig. 4. TG trace of the polymer obtained for the Cu(tacn) catalyst.

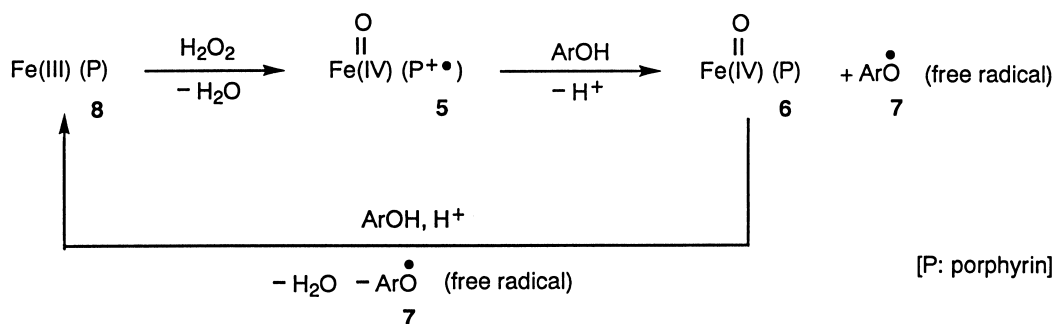
tributed to the C–H vibrations of 1,2,3-substituted benzenes. From these data, the present polymer seems to consist mainly of 3-methyl-1,4-oxyphenylene and/or 3-methyl-1,6-oxyphenylene units and to contain a small amount of other units, e.g., 3-methyl-1,2-oxyphenylene units. On the other hand, the previous study on the HRP-catalyzed polymerization of MCR [8] showed that the resulting polymer was of a mixture of phenylene and oxyphenylene units (nearly 1:1 unit ratio) and had a large peak at 770 cm^{-1} as well as two peaks at 865 and 815 cm^{-1} in the IR spectrum.

A TG trace of the polymer obtained for the Cu(tacn) catalyst is shown in Fig. 4. Weight loss was scarcely detected up to 350°C , and the temperature at 5% weight loss (T_{d_5}) was 392°C , which was much higher than that reported for the HRP catalyst (337°C) [8]. These data suggest that the Cu(tacn) catalyst prevented the C–C coupling, yielding poly(phenylene oxide) with high molecular weight and high thermal stability.

The polymerization mechanism for the Cu(tacn) catalyst is postulated as follows (Scheme 2). First, copper(II) complexes **5** of Cu(tacn)Cl₂ react with MCR or oligomers of MCR to give phenoxy–copper(II) complexes **2**, equivalent to phenoxy radical–copper(I) complexes **3**. An excess of 2,6-diphenylpyridine having no coordination ability to copper atom was added in order to neutralize hydrogen chloride generated from the starting complex. C–O selective coupling takes place via **2** and/or **3** to

produce copper(I) complexes **4**. Complex **4** was found to generate $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo}$ dicopper(II) complex **1** under dioxygen [16]. A similar complex **4** was proved to react not only with dioxygen, but also with hydrogen peroxide to form a similar complex **1**. It was reported that complex **1** reacted with HBF₄ to yield hydrogen peroxide [16], and the reaction of the similar complex **1** with 4-fluorophenol gave complex **2** [13]. These previous studies strongly indicate that, for the Cu(tacn) catalyst, ‘nucleophilic’ $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo}$ dicopper(II) complex **1** is formed and reacts with phenols to regenerate intermediates **2** or **3** and hydrogen peroxide. Hence, the free radical coupling pathway would be completely excluded in this catalytic cycle.

For the HRP catalyst (Scheme 4), it was reported that Fe(III) complex **8**, the resting state, reacts with hydrogen peroxide to give Fe(IV) = O (porphyrin cation radical) complex **5**, and **5** abstracts a hydrogen atom of substrate to afford Fe(IV) = O complex **6**, which subsequently abstracts a hydrogen atom of another molecule of substrate to regenerate complex **8** [17]. It was also reported that HRP reacts with hydrogen peroxide and 2-*tert*-butyl-4-methoxyphenol to give the free phenoxy radicals **7** [18]. These data indicate that, for the HRP catalyst, ‘radical’ active oxygen complexes **5** and **6** are formed and abstract hydrogen atoms of MCR or oligomers of MCR to give the free phenoxy radicals **7**, followed by regeneration of the resting state **8**. Therefore, the polymerization catalyzed by HRP proceeded via the free-radical



Scheme 4.

coupling, giving both the C–C and C–O coupling.

4. Conclusion

In this paper, the ‘radical-controlled’ oxidative polymerization for production of aromatic polyether with regulated structure was extended to the polymerization of MCR. The Cu(tacn) catalyst showed to be the most active in the metal complex catalysts reported for the polymerization of MCR with dioxygen, and produced the poly(phenylene oxide) with high molecular weight and high thermal stability. The selectivity toward C–O coupling would be regulated by the Cu(tacn) catalyst, from which a ‘nucleophilic’ μ - η^2 : η^2 -peroxo dicopper(II) complex is formed under dioxygen and reacts with MCR to give ‘controlled’ phenoxy radical–copper(I) complex exclusively without formation of ‘free’ phenoxy radical. Hence, the prevention of C–C coupling seems to increase the molecular weight and thermal stability of the resulting polymer.

Acknowledgements

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