

Mechanism Research of Copper(II)-Catalyzed Polymerization of 2,4,6-Trichlorophenols

LAISHUN SHI* and LUBING YUAN

Department of Chemical Engineering, Shandong University of Technology, Jinan 250014, and School of Chemical Engineering, Dalian University of Technology, Dalian 116012, People's Republic of China

SYNOPSIS

The copper(II)-catalyzed polymerization of 2,4,6-trichlorophenol and 2,4,6-trichloro-3-methylphenol were studied. Their polymer structures were confirmed by elemental analysis, infrared (IR), and nuclear magnetic resonance (NMR). The 2,4,6-trichlorophenoxy-copper(II) complex and 2,4,6-trichloro-3-methylphenoxy-copper(II) complex intermediates were isolated. The elemental analysis and electron spin resonance (ESR) measurement of the phenoxy-copper(II) complexes were discussed in relation to their structures. Decomposition of the phenoxy-copper(II) complex in refluxing benzene yielded poly(dichlorophenylene oxide). ESR measurements on the phenoxy-copper(II) complex in the solid state at 120°C indicated that the phenoxy radical was generated during the period of decomposition and the intensity of the ESR spectra based on the copper(II) ion decreased with the measurement time. A single-electron transfer reaction mechanism was proposed for the phenoxy-copper(II) complex intermediate. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(dihalophenylene oxide) is a new kind of high molecular weight fire-retardant agent. Especially for engineering plastics, a high molecular weight fire-retardant agent has the advantage of excellent thermal stability, a wide range of processing temperatures, good compatibility with resin, and no frosting compared with low molecular weight fire-retardant agents. In relation to a high molecular weight fire-retardant agent, Torrey and Hunter first synthesized a white amorphous polymer of poly(2,6-dibromophenylene oxide) by using iodoethane, anhydrous silver, and 2,4,6-tribromophenolate.¹ The molecular weight of this polymer is in the range of 6000–12,000 and the softening point is over 300°C. In a series of articles, Hunter and co-workers investigated this reaction more thoroughly and attempted to characterize the reaction product and concluded that the product was the corresponding poly(phenylene oxide).^{2,3} Price and co-workers found that the polymerization of 2,6-dimethyl-4-bromophenol could be initiated in the presence of a base with a variety of

oxidizing agents, e.g., $K_3Fe(CN)_6$, PbO_2 .⁴ In a patent, Stamatoff described the polymerization of unsymmetrically substituted halophenols, prepared in a manner similar to that described by Price et al., by use of peroxide or persulfate as initiators.⁵ It was also reported that the copper(II) nitrate-acetonitrile system had catalytic activity in the halogen displacement polymerization of 2,4,6-tribromophenol.^{6,7} Harrod prepared a series of phenoxy-copper(II) complexes containing a variety of halophenoxy ligands and a variety of amine ligands and investigated the properties and the thermal stabilities of these phenoxy-copper(II) complexes.⁸ Carr and Harrod also studied the solution decomposition of bis(2,4,6-trichlorophenoxy)bis(pyridine)copper(II) and presented the mechanism of the primary process which generates the phenoxy radicals.⁹

In a series of articles, we more thoroughly reported the halogen displacement reaction of 2,4,6-tribromophenol and 2,4,6-tribromo-3-methylphenol by homogeneous, heterogeneous, and oxidative coupling polymerization.^{10–15} It was revealed that the presence of a small amount of water favors the polymerization, but excess water retards the reaction when sodium methoxide is used as a base.^{13,14} The prepared copper(II) salt catalyst had maximum cat-

* To whom correspondence should be addressed.

alytic activity at a mol ratio of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ / CH_3ONa equal to 0.5. By measurement at 3518 cm^{-1} in a carbon tetrachloride solution of poly(2,6-dibromo-3-methylphenylene oxide), the reciprocal of molecular weight determined by VPO is proportional to the infrared absorbance of the terminal hydroxy group in the linear polymer.¹¹ Also, we reported the quantum chemistry computation of a series of halophenols and preliminarily probed their fire-retardant mechanism.^{10,12}

In this report, we present the results of our investigation on the polymerization of 2,4,6-trichlorophenol and 2,4,6-trichloro-3-methylphenol catalyzed by copper(II) salt. The phenoxo-copper(II) complex intermediates were isolated. Using elemental analysis, IR, NMR, and ESR measurements as the main analytical tools, the chemical structures of the polymers and complex intermediates were investigated. A single-electron transfer reaction mechanism was proposed for the copper(II)-catalyzed polymerization through the phenoxo-copper(II) intermediate.

EXPERIMENTAL

Material

2,4,6-Trichlorophenol and 2,4,6-trichloro-3-methylphenol were synthesized and purified by recrystallization from anhydrous ethanol. The melting point and chlorine content were 69.5°C and 53.57% (calcd 53.87%), 47.0°C and 50.41% (calcd 50.29%), respectively. Reagent-grade anhydrous copper(II)chloride was used after drying $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ at $110\text{--}130^\circ\text{C}$ under vacuum for 5 h. Sodium methoxide was used after sodium reaction with methanol and formed a methanolic solution of sodium methoxide. Methanol was refluxed with magnesium metal and distilled twice. Others were guaranteed reagent grade and used without further purification.

Polymerization of 2,4,6-Trichloro-3-methylphenol with Copper(II) Catalyst

A typical procedure was carried out as follows: To 35 mL of methanol in a round-bottomed flask equipped with a stirrer, a thermometer, and a cooler containing a drying tube, 0.01 mol (1.345 g) of copper(II)chloride was added. To the resulting homogeneous solution was added 5 mL of methanolic solution containing 0.015 mol (0.91 g) of sodium methoxide. A monomer (0.01 mol) of 2,4,6-trichlorophenol (1.975 g) or 2,4,6-trichloro-3-methylphenol (2.114 g) was subsequently added to the heteroge-

neous basic copper(II) system. After vigorous stirring for 3 h at the boiling point of methanol, the reaction mixture was cooled. The precipitate formed was then dissolved in 20 mL tetrahydrofuran. The solution was refluxed for 10 min at the boiling point of tetrahydrofuran and then was poured into methanol containing a small amount of concentrated HCl. The precipitate formed was then filtered and washed thoroughly by methanol and was dried *in vacuo*.

The polymers obtained were identified as the corresponding poly(2,6-dichlorophenylene oxide) and poly(2,6-dichloro-3-methylphenylene oxide) by means of IR spectra, elemental analyses, and NMR spectra.

ANAL: Calcd for $\text{C}_6\text{H}_2\text{Cl}_2\text{O}$: Cl, 44.04%. Found: Cl, 43.51%.

ANAL: Calcd for $\text{C}_7\text{H}_4\text{Cl}_2\text{O}$: Cl, 40.51%. Found: Cl, 40.31%.

Preparation of 2,4,6-Trichloro-3-methylphenoxo-Copper(II) Complex

To 35 mL of methanolic solution containing 0.01 mol (1.35 g) of copper(II)chloride, 0.02 mol monomer of 2,4,6-trichlorophenol (3.95 g) or 2,4,6-trichloro-3-methylphenol (4.228 g) was added. After 5 mL of a methanolic solution of sodium methoxide (0.02 mol, 1.08 g) was added into the homogeneous reaction mixture, the resulting heterogeneous mixture was stirred for 4 h at the freezing point of water. The solid was collected by filtration, washed with methanol, and dried *in vacuo*.

ANAL: Calcd for $\text{Cu(II)(OCH}_3\text{)(C}_6\text{H}_2\text{Cl}_3\text{O)}$: Cl, 36.55%. Found: Cl, 35.08%.

ANAL: Calcd for $\text{Cu(II)(OCH}_3\text{)(C}_7\text{H}_4\text{Cl}_3\text{O)}$: Cl, 34.87%. Found: Cl, 33.23%.

Decomposition of the 2,4,6-Trichloro-3-methylphenoxo-Copper(II) Complex

A 1-g portion of the 2,4,6-trichlorophenoxo-copper(II) complex or the 2,4,6-trichloro-3-methylphenoxo-copper(II) complex was thermally decomposed by refluxing a solution of the phenoxo-copper(II) complex in 30 mL of benzene. Following reflux for 30 min, the solution was cooled and poured into 100 mL of methanol to yield a white precipitate. This white precipitate was collected by filtration, washed with methanol, and dried *in vacuo*. The white precipitates were identified as poly(2,6-dichloro-

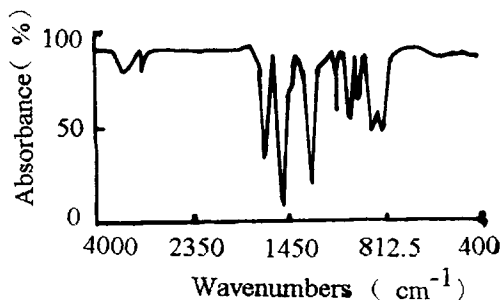


Figure 1 IR spectrum of poly(2,6-dichlorophenylene oxide).

phenylene oxide) and poly(2,6-dichloro-3-methylphenylene oxide) by their IR and NMR spectra.

Infrared Spectrum

The IR spectra of the obtained polymers were measured as KBr disks using a Nicolet Model 20 Dx-B spectrophotometer.

NMR Spectrum

The proton NMR spectra of the polymers were obtained by using a JEOL Model Fx-90Q spectrometer. TMS was used as an internal reference. The spectra of polymers were taken in CCl_4 at room temperature.

ESR Spectrum

The ESR spectra of the phenoxo-copper(II) complexes were recorded on a Model JES-FEIXG instrument of JEOL Co. The phenoxo-copper(II) complex was placed in a sample tube, which was then attached to a vacuum line. After removal of the air in the sample tube, it was sealed off under reduced pressure, and the temperature of the ESR cavity was increased to different temperatures. The time-dependent and temperature-dependent ESR spectra were measured with the use of Mn^{2+} as the *g*-marker.

RESULTS AND DISCUSSION

Identification of the Polymer's Structure

The analytical data for the polymers shows that the polymers have the composition of $\text{C}_6\text{H}_2\text{Cl}_2\text{O}$ and $\text{C}_7\text{H}_4\text{Cl}_2\text{O}$. The IR spectrum of poly(2,6-dichlorophenylene oxide) obtained is shown in Figure 1. As shown in this figure, the absorption near 3100 cm^{-1} is assigned to the aromatic C—H stretching. Also, the bands near 1600 and 1450 cm^{-1} are assigned to

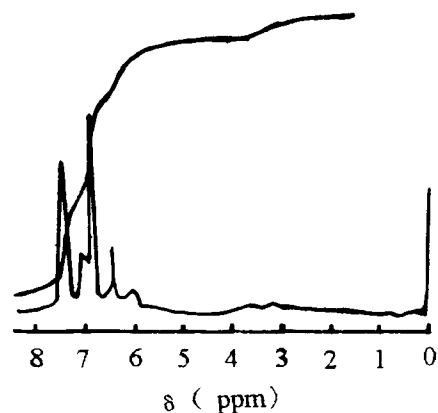
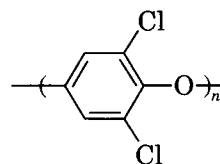


Figure 2 ^1H -NMR spectrum of poly(2,6-dichlorophenylene oxide).

the aromatic C=C stretching, the band near 1200 cm^{-1} is assigned to the aromatic C—O stretching, and the band near 1070 cm^{-1} is assigned to the aromatic C—Cl stretching. The NMR spectrum of poly(2,6-dichlorophenylene oxide) is shown in Figure 2. If the structure of the polymer is linear,



the signal of the phenyl ring protons would be observed as a singlet. The spectrum actually obtained, however, gave a different figure which allows for overlapped broad peaks around $\delta 6.45\text{--}7.45\text{ ppm}$. The observation of these peaks would indicate the presence of some phenyl rings which have different substituents. To judge from this result, it is reasonable to consider that the polymer obtained has a branched structure or an irregularity linear structure rather than a linear chain structure, e.g., resulting from addition of *ortho*-chlorine on elimination of *para*-chlorine in the phenyl ring.¹⁵

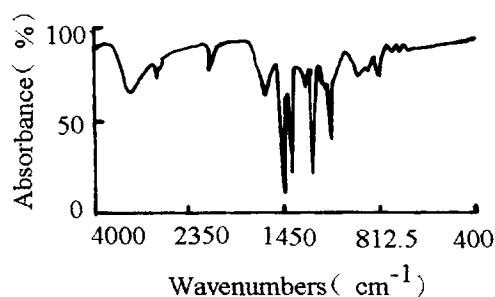


Figure 3 IR spectrum of poly(2,6-dichloro-3-methylphenylene oxide).

The IR spectrum of poly(2,6-dichloro-3-methylphenylene oxide) obtained is shown in Figure 3. As shown in the figure, the absorption near 3100 cm^{-1} is assigned to the aromatic C—H stretching. The absorption near 2930 cm^{-1} is assigned to the C—H stretching of CH_3 moieties of the polymer. Also, the band near 1596 and 1450 cm^{-1} are assigned to the aromatic C=C stretching; the band near 1200 cm^{-1} , to the aromatic C—O stretching; and the band near 1095.3 cm^{-1} , to the aromatic C—Cl stretching. The NMR spectrum of poly(2,6-dichloro-3-methylphenylene oxide) is shown in Figure 4. As also shown in this figure, a singlet signal of the CH_3 group protons was observed at δ 2.52 ppm. Similar to the spectrum of poly(2,6-dichlorophenylene oxide), the signal of the phenyl ring proton would be observed as a singlet. The spectrum actually obtained, however, allowed for overlapped broad peaks around δ 6.45–7.45 ppm. The polymer obtained has a branched structure, but the branched extent of poly(2,6-dichloro-3-methylphenylene oxide) is smaller than that of poly(2,6-dichlorophenylene oxide). This is because of the spacial hindrance of the *meta*- CH_3 group to the *ortho*-chlorine in the phenyl ring. From the points of the integral curve, the relative strength ratio obtained is 3 : 1 for CH_3 group protons to the phenyl ring proton.

Molecular weight information would be of value in the interpretation of NMR spectra. In a series of articles, we reported that the polymer molecular weight of poly(2,6-dibromophenylene oxide) and poly(2,6-dibromo-3-methylphenylene oxide) is maintained in the range of 4400–6600.¹¹ The polymer degree of polymerization is low. The order of 2,4,6-trihalophenols reactivities is as follows: 2,4,6-tribromo- > 2,4,6-tribromo-3-methyl- > 2,4,6-trichloro- and 2,4,6-trichloro-3-methylphenol.¹⁴ It is reasonable to think that the molecular weight of poly(2,6-dichlorophenylene oxide) and poly(2,6-dichloro-3-methylphenylene oxide) is low. Therefore, chlorine end groups on the polymers may contribute to the NMR because of the presence of some phenyl rings which have different substituents.

ESR Studies of 2,4,6-Trichloro-3-methylphenoxo-Copper(II) Complex

As mentioned elsewhere, it was found that 2,4,6-trichlorophenol and 2,4,6-trichloro-3-methylphenol were less reactive with the copper(II) chloride-sodium methoxide system than with bromo-substituted phenol derivatives.^{13,14} This fact may show the possibility of isolation of the intermediate complex of this reaction under mild reaction conditions. A series of bis(phenoxo)bis(pyridine)copper(II) complexes were prepared and characterized by Blanchard et al. with a variety of substituted phenols.¹⁶

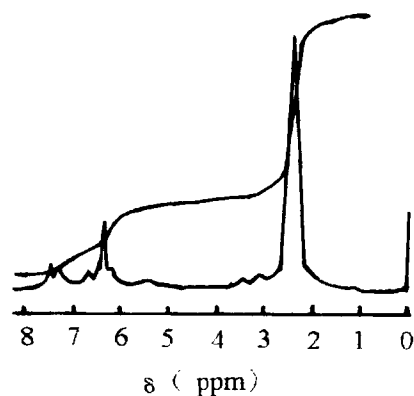
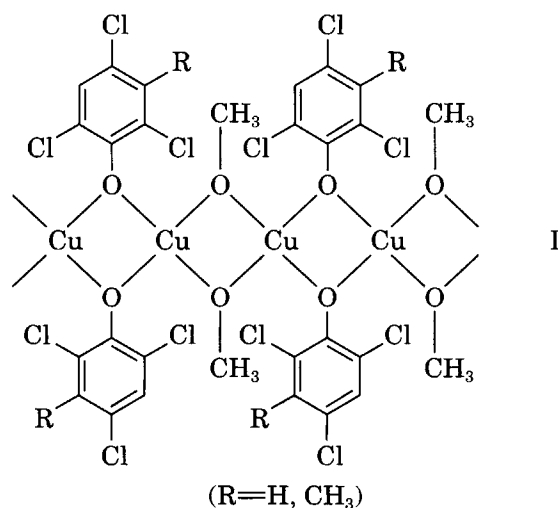


Figure 4 ^1H -NMR spectrum of poly(2,6-dichloro-3-methylphenylene oxide).

On the other hand, Harrod prepared a variety of phenoxo complexes of copper(II) and discussed the thermal stability of the complexes with regard to the decomposition reaction.⁸ Such complexes are of considerable chemical interest because of the role of copper(II) in the catalytic oxidation of phenols.

Under these circumstances, we tried to isolate the 2,4,6-trichlorophenoxo-copper(II) complex and the 2,4,6-trichloro-3-methylphenoxo-copper(II) complex. Elemental analysis of the solids isolated showed it to be $\text{Cu(II)(OCH}_3\text{)}_2(\text{C}_6\text{H}_2\text{Cl}_3\text{O})$ and $\text{Cu(II)(OCH}_3\text{)}_2(\text{C}_7\text{H}_4\text{Cl}_3\text{O})$. The fact described above indicates that the present solids isolated are the copper(II) complex with 2,4,6-trichlorophenoxo or 2,4,6-trichloro-3-methylphenoxo and methoxo groups as ligands, and its structure may be polymeric rather than monomeric. Although at the present stage we have no definite information on an accurate structure of this copper(II) complex, structure I



appears to be reasonable on the basis that the copper(II) complex has generally a square-planar or an

octahedral structure, in addition to the facts obtained above. However, in the structure presented here, it is uncertain whether the copper(II) ion and the four oxygen atoms which surround it lie on the same plane. The ESR spectra of the complexes may give some information on the structure.

To study the process of thermal decomposition of the copper(II) complexes, ESR measurements of the copper(II) complexes in an outgassed, sealed tube were performed at room temperature and elevated temperature. The temperature-dependent ESR spectra of the 2,4,6-trichlorophenoxy-copper(II) complex are presented in Figure 5. At room temperature and 60°C, the characteristic signal of the copper(II) ion was observed, but the radical signal $\langle g \rangle = 2.0063$ was relatively weak. When the temperature reached 120°C, the intensity of the copper(II) ion signal became obviously weak; at the same time, the intensity of the free-radical signal became strengthened. When the temperature was increased to 140°C, the signal of the copper(II) ion disappeared; however, the intensity of the free radical became clearly strengthened.

The temperature and time-dependent ESR spectra of the 2,4,6-trichloro-3-methylphenoxy-copper(II) complex are shown in Figure 6. At the initial stage of temperature below 100°C, the ESR spectra were similar to each other both in the intensity of the copper(II) ion and the free-radical signal. On the other hand, when the temperature reached 120°C, the intensity of free radical distinctly increased. The intensity of the spectra based on the copper(II) ion decreased with the measurement time. Thereafter, however, the intensity of the free radical began to decrease.

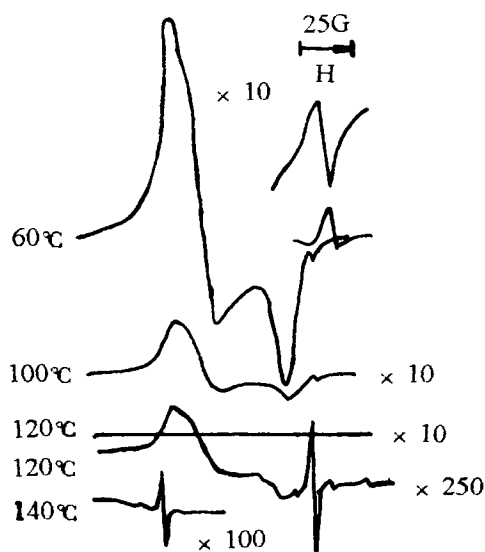


Figure 5 Variation of ESR spectra of the 2,4,6-trichlorophenoxy-copper(II) complex at different temperatures.

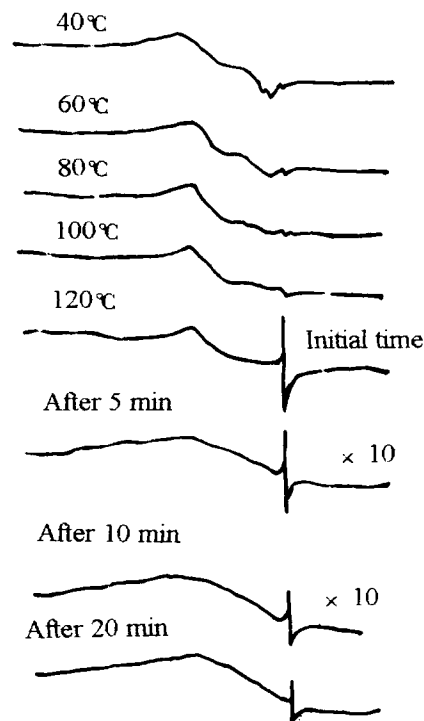
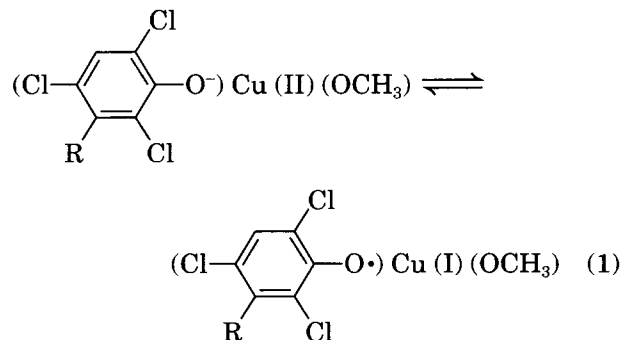


Figure 6 Variation of ESR spectra of the 2,4,6-trichloro-3-methylphenoxy-copper(II) complex at different temperatures.

These anisotropic ESR peaks may support the idea that these two copper(II) complexes deviate from square-planar structures which have symmetry axes but distorted octahedral structures. However, surprisingly, the ESR spectrum of the 2,4,6-trichlorophenoxy-copper(II) complex had one sharp peak near $\langle g \rangle = 2.0063$, which is assigned to an organic radical, in spite of the measurement at room temperature. The present sharp resonance peak appearing at $\langle g \rangle = 2.0063$ is probably due to a phenoxy radical intermediate. One plausible interpretation for this unexpected observation of the phenoxy radical at room temperature may be that the 2,4,6-trichlorophenoxy-copper(II) complex may be in an equilibrium state at room temperature as presented schematically in eq. (1):



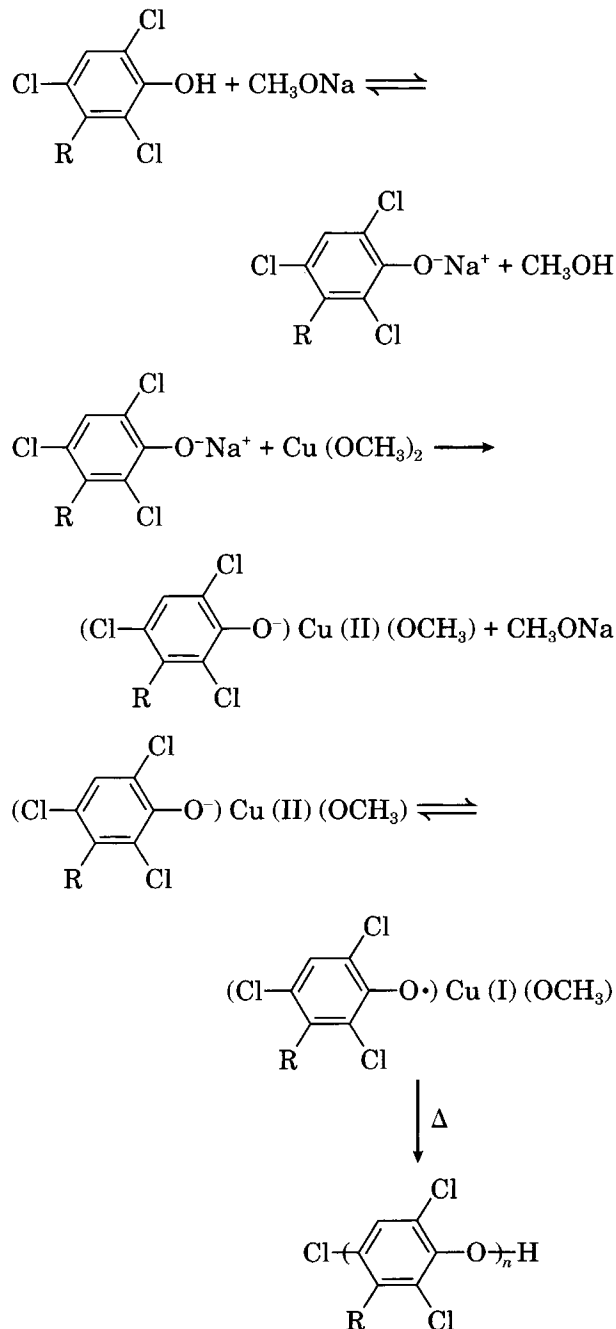
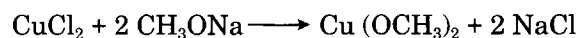
A single-electron transfer process from the phenoxide anion to the copper(II) ion in the phenoxo-copper(II) complex may be considered as an initial step of a chlorine displacement reaction of chlorophenol with the basic copper(II) complex. It was reported that the most probable initiation step for decomposition of phenoxo-copper(II) complexes involves homolysis of the Cu—O band via a ligand-to-metal charge transfer.⁸ In the oxidative coupling reaction of 2,6-dimethylphenol with a copper-pyridine complex catalyst, Price and Nakaoka postulated an electron-transfer equilibrium between the corresponding phenoxo group and the copper ion to account for the role of pyridine coordination to the copper ion in shifting the phenol coupling (C—C or C—O).¹⁷ To consider a phenoxy radical intermediate in the present reaction system seems to be reasonable from the ESR spectra of the phenoxo-copper(II) complexes.

By a method analogous to that for 2,4,6-trichlorophenol and 2,4,6-trichloro-3-methylphenol, we attempted the preparation of the 2,4,6-tribromophenoxo-copper(II) complex and the 2,4,6-tribromo-3-methylphenoxo-copper(II) complex. Under a variety of conditions, including low temperature (over -10°C), we have not been able to isolate the desired complexes, but rather have obtained the corresponding polymers. Such a fact indicates that the formed 2,4,6-tribromophenoxo-copper(II) complex and 2,4,6-tribromo-3-methylphenoxo-copper(II) complex are very reactive and leads us to believe that the corresponding polymer must be an important step in this reaction. Thus, the reactivity of 2,4,6-trihalophenol or 2,4,6-trihalo-3-methylphenol with the basic copper(II) catalyst may be controlled by the formation ability of the corresponding phenoxo-copper(II) complex and by ease of the decomposition of the complex.

It is of interest to attempt thermal decomposition of the present 2,4,6-trichlorophenoxo-copper(II) complex and the 2,4,6-trichloro-3-methylphenoxo-copper(II) complex. The phenoxo-copper(II) complexes were decomposed in benzene at 80°C . As a result of its decomposition, poly(2,6-dichlorophenylene oxide) and poly(2,6-dichloro-3-methylphenylene oxide) were obtained.

Although at the present stage we have no information on the propagation step of this reaction, it seems reasonable to assume that a first-order phenoxy radical generated through a single-electron transfer within a phenoxo-copper(II) complex attacks the *para* or *ortho* position of the other phenoxo group and that the halogen atom is eliminated by the Cu(I) present in the system, as reported by Carr and Harrod.⁹

On the basis of the results mentioned above, we believe that the following mechanism for the present polymerization is the likely one:



CONCLUSIONS

1. Poly(2,6-dichlorophenylene oxide) and poly(2,6-dichloro-3-methylphenylene oxide) could be obtained by copper(II)-catalyzed

- polymerization of 2,4,6-trichlorophenol and 2,4,6-trichloro-3-methylphenol. Their polymer structures were confirmed by elemental analysis, IR, and NMR measurements.
- The 2,4,6-trichlorophenoxy-copper (II) complex and the 2,4,6-trichloro-3-methylphenoxy-copper(II) complex intermediates were isolated. The elemental analysis and ESR measurements of the phenoxy-copper (II) complexes were discussed in relation to their structures.
 - Decomposition of the phenoxy-copper(II) complex in refluxing benzene yielded poly-(dichlorophenylene oxide).
 - The ESR measurements on the phenoxy-copper (II) complex in the solid state at 120°C indicated that the phenoxy radical was generated during the period of decomposition and intensity of the ESR spectra based on the copper(II) ion decreased with the measurement time.
 - A single-electron transfer reaction mechanism was proposed for the copper(II)-catalyzed polymerization through the phenoxy-copper(II) complex intermediate.

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