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The Oxidative Displacement Polymerization of 2,4,6-Tribromophenol with Copper(II)–Acetonitrile Complex

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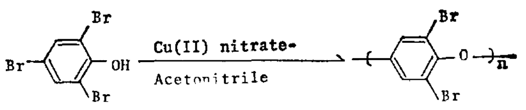
Poly(2,6-dibromophenylene oxide) was obtained easily by the reaction of 2,4,6-tribromophenol with copper(II) salt–acetonitrile complex under a mild reaction condition. The copper(II) salts used in acetonitrile influenced markedly the yield of the polymer. The polymer was formed in good yield when a 1:1 to 20:1 molar excess of 2,4,6-tribromophenol was treated with copper(II) nitrate–acetonitrile complex, whereas the polymer was not yielded with copper(II) chloride in acetonitrile. Also the yield of the polymer was found to depend on the solvent used. The differences between the present catalytic systems utilized were observed by means of electronic absorption and ESR measurements and are discussed in connection with the catalytic activities for oxidative displacement reaction of 2,4,6-tribromophenol. The phenoxy radical, considered as intermediate of the present reaction, was detected by ESR measurement when the hindered phenol was used as phenol derivatives and/or by the ESR rapid flow method for a poly(2,6-dibromophenylene oxide)–copper(II) system.

INTRODUCTION

The preparation of poly(2,6-dihalophenylene oxide) was reported at first by Hunter *et al.* (*1*). They have described the preparation and properties of silver salt of 2,4,6-tribromophenol reacted with ethyl iodide to give the corresponding polymer. Staffin and Price (*2*) have also reported the preparation of poly(2,6-disubstituted-1,4-phenylene oxide) by oxidative displacement of bromine from 4-bromo-2,6-disubstitutedphenol. A variety of reagents have been used as oxidants for halogenated-phenol (*3*).



Recently copper(II) salts in acetonitrile has been shown to be an effective oxidant for a number of compounds, including thiourea (*4*). We tried to apply this copper(II) salt–acetonitrile system to the oxidative displacement reaction of 2,4,6-tribromophenol. In a preliminary communication (*5*), it was reported that 2,4,6-tribromophenol was easily polymerized by copper(II) nitrate–acetonitrile complex.

This paper reports the polymerization of 2,4,6-tribromophenol with some copper(II) salts in acetonitrile and considers the nature of the copper(II)–acetonitrile complexes by the methods of electronic absorption and ESR measurements which are active catalysts in comparison with those of the copper(II) complexes which are not active for the oxidative displacement polymerization 2,4,6-tribromophenol. Also it was found that copper(II)–acetonitrile complex which has catalytic activity had the function of a one-electron transfer catalyst by the observation of ESR spectra

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of the radical generated from hindered phenol with copper(II) nitrate–acetonitrile and from poly(2,6-dibromophenylene oxide) with copper(II) complex by ESR flow method.

EXPERIMENTAL

Infrared spectra were recorded with a Hitachi 215 spectrophotometer as KBr disks. Electronic absorption spectra of the copper(II) complexes were measured by a Hitachi recording spectrometer Model EST-3T at room temperature using 1-cm cell. The NMR spectra of the polymers were measured in solution of carbon tetrachloride or deuterated chloroform at room temperature, using TMS as internal standard with a Varian HR 220 spectrometer. Measurement of ESR spectra was carried out with a JEOL-2BSX type ESR spectrometer with a 100 KHz modulation unit. The magnetic field was calibrated with Mn(II) ion and potassium peroxylamine disulfonate. In the case of rapid flow technique, two solutions of poly(2,6-dibromophenylene oxide) and copper(II) catalyst flowed into the mixing chamber and then the sample cell in the ESR cavity.

Materials

2,4,6-Tribromophenol was purified by recrystallization from *n*-hexane. Hydrated copper(II) salts used were reagent-grade materials and used without further purification. Solvents were purified by standard techniques.

Oxidative Displacement Polymerization of 2,4,6-Tribromophenol

All polymerizations reported here were carried out in stirred constant-temperature water bath (30 ± 0.2°C). The standard method was as follows: to a reaction vessel equipped with a stirrer, was added copper(II) salt, 2,4,6-tribromophenol, and acetonitrile as solvent. The resulting homogeneous solution was stirred with continued vigorous agitation. The products were worked up as follows. Reaction mixture was poured into 5 vol of methanol containing a small amount of concd hydrochloric acid. The precipitated polymer was filtered off, washed with methanol. After rewashing with methanol, the polymer was dried off. (Analysis calculated for $C_6H_2Br_2O$: C, 28.84; H, 0.81; Br, 63.54. Found: C, 28.17; H, 0.89; Br, 65.50.) The filtrate was evaporated *in vacuo*, and the residue was extracted with *n*-hexane. After removing the *n*-hexane, off-white crystal was obtained. This crystal was identified as 2,4,6-tribromophenol by the methods of infrared spectrum and its melting point measurement. Intrinsic viscosity of the polymer produced was measured in Ubbelohde dilution viscometer in chloroform solution at 25°C.

RESULTS AND DISCUSSION

Oxidative Displacement Polymerization of 2,4,6-Tribromophenol with Copper(II)–Acetonitrile Complex

The oxidative displacement product of 2,4,6-tribromophenol with copper(II) nitrate–acetonitrile system was poly(2,6-dibromophenylene oxide). As reported in a preliminary communication (*5*), 2,4,6-tribromophenol was not oxidized with copper(II) nitrate in methanol. The result of the polymerization of 2,4,6-tribromophenol by copper(II) complex was presented in Table 1. It is evident from Table 1 that the yields of polymer are about 60–70% when 0.05–0.1 equivalent of copper(II) nitrate to 1 equivalent of phenol was used. However, when the ratio of copper(II) nitrate to the phenol increased more, the yield of the polymer did not increase as expected. The intrinsic viscosity of the polymer obtained at the present reaction was about 0.02 dl/g, and was not so high. The value of the intrinsic viscosity of the polymer nearly equals that of the polymer obtained from the thermal decomposition of the corresponding phenoxo–pyridine–copper(II) complex (*6*). The oxidative displacement reaction was also conducted in a nitrogen atmosphere to investigate whether exclusion of oxygen from the reaction system could affect the yield of the polymer.

Result is summarized in Table 1. When the concentration of copper(II) nitrate less

TABLE 1

Oxidation of 2,4,6-Tribromophenol with Copper(II) Catalyst[a]

Copper salt	Concn of copper salt (mole/liter)	Solvent	CH_3CN/Cu(II) (mole ratio)	Reaction time (hr)	Polymer yield (%)
$Cu(NO_3)_2 \cdot 3H_2O$	0.01	CH_3CN		2	65
	0.02	CH_3CN		0.5	42[b]
	0.02	CH_3CN		2	66
	0.02	CH_3CN		5	72[c]
	0.05	CH_3CN		2	67
	0.02	CH_3CN		2	70
	0.02	CH_3CN		2	47[d]
	0.20	CH_3CN		2	68[d]
	0.02	CH_3CN + MeOH	100	2	0
	0.02	CH_3CN + MeOH	500	2	3
	0.02	CH_3CN + *o*-dichlorobenzene	100	2	17
	0.02	CH_3CN + *o*-dichlorobenzene	76	2	14
	0.02	CH_3CN + *o*-dichlorobenzene	19	2	trace[e]
	0.10	DMSO		10	0
	0.10	DMF		10	30[f]
	0.10	HMPA		10	0
$Cu(ClO_4)_2 \cdot 6H_2O$	0.02	CH_3CN		7	trace
	0.10	CH_3CN		7	13
$CuCl_2$	0.02	CH_3CN		13	0
$Cu(CH_2COCH_2COCH_2)_2$	0.10	CH_3CN		10	9
CuCl					
(under O_2)	0.02	CH_3CN		2	0
(under N_2)	0.02	CH_3CN		2	0

[a] 2,4,6-tribromophenol; 0.2 mole/liter, solvent; 50 ml, reaction temp.; 30°C.

[b] Intrinsic viscosity at 25°C in $CHCl_3$; 0.02 dl/g.

[c] Intrinsic viscosity at 25°C in $CHCl_3$; 0.02 dl/g.

[d] Under a nitrogen atmosphere.

[e] Heterogeneous system.

[f] Intrinsic viscosity at 25°C in $CHCl_3$; 0.01 dl/g.

than the equivalent of the phenol was used, the yields of the polymers decreased under a nitrogen atmosphere. Increasing catalyst concentration was found to increase the conversion of polymer. This finding indicates that copper(II) nitrate in acetonitrile has the function of oxidant for the present polymerization of 2,4,6-tribromophenol. Also on the basis of the result that the reaction proceeds to a considerable extent under the former reaction condition, it may be considered that this reaction includes the process that the active monomer such as phenoxy radical generated by the interaction with copper(II) catalyst acts as an initiator to another monomer.

The application of this catalyst for the preparation of other polyphenylene oxide was performed. As monomer phenol, 2,4,6-trichlorophenol and 2,6-dimethylphenol were used in the present study. When 2,4,6-trichlorophenol was reacted with copper(II) nitrate in acetonitrile at 30°C and the reaction mixture was poured into methanol, no precipitate of the corresponding polymer was produced. The evaporation of the filtrate and extraction from *n*-hexane left dark-red viscous oil. Although no further identification of the viscous oil was performed, these oils may be considered as complicated oxidation products of 2,4,6-trichlorophenol (7). On the other hand, when 2,6-dimethylphenol was utilized as monomer, tetramethyldiphenoquinone, the C–C coupling product, was yielded selectively instead of polymer, the C–O coupling product.† It was reported previously (*8*) that 2,6-disubstituted phenol was oxidized to diphenoquinone in the presence of copper(I) compound and a compound of the general formula $RCONR'_2$, where R is an alkyl, alkenyl, or aryl group and R' is an alkyl group. The present system is considered to have the same function for the oxidative coupling of 2,6-dimethylphenol as Hay's copper(I) system.

In the oxidative coupling polymerization of 2,6-dimethylphenol with copper(I)–pyridine complex under oxygen, it has been reported (*10*) the coupling products are markedly affected by the ligand ratio (mole ratio of pyridine to copper(I) chloride). It was tried to investigate the effects of the ratio of acetonitrile to copper(II) nitrate. The effect of the ratio (varying acetonitrile concentration at fixed copper(II) salt concentration) is summarized in Table 1. In order to fix the amount of solvent at 50 ml, methanol and *o*-dichlorobenzene were used when the ratio was low. In condition of low ratio, copper(II) nitrate could not be dissolved homogeneously and the catalytic system became a heterogeneous one. From the data of Table 1 the yields of polymer seem to be affected by the ratio of $CH_3CN/Cu(II)$ although the limitation of solubility of copper(II) nitrate must be considered. Increasing the ratio of acetonitrile to copper(II) nitrate favors the polymerization reaction. Furthermore an important solvent effect on the polymer yields is indicated in Table 1. When the mixed solvent of acetonitrile and methanol was used at the ratio of acetonitrile to copper(II) nitrate, 100, no polymer was yielded. And even at the ratio 500, the polymer was obtained in only 3% yield. On the other hand, the polymer yield of 17% was obtained in the solvent containing both acetonitrile and *o*-dichlorobenzene at the ratio 100. Thus the solvent may conceivably affect the structure and/or concentration of active copper(II) complex for the present oxidative displacement reaction. Particularly methanol may act as an inhibitor for oxidative displacement reaction of 2,4,6-tribromophenol catalyzed with copper(II) nitrate-acetonitrile complex. Endres and his co-workers (*9*) have described that *o*-dichlorobenzene was inert as far as coordination with copper ion is concerned. Accordingly it would be considered that in the solvent containing both acetonitrile and methanol, methanol, similar to acetonitrile, can interact with copper(II) ion although the coordinating power is thought to be weaker than acetonitrile and may form an inactive species with copper(II) ion, which has no catalytic activity for the present polymerization reaction, and causes the low yield of polymer. Already it has been reported (*5*) that by the copper(II) nitrate in methanol, no polymerization reaction had occurred.

Manahan (*10*) has observed electron exchange between copper(I) and copper(II) in acetonitrile using copper perchlorate and showed that copper(I) is stable in acetonitrile. Also it has been reported (*11*) that copper(I) chloride in some aprotic solvents under an oxygen atmosphere was detected only partly as copper(II) species by ESR measurement. From these results, the possibility of $Cu(I) \rightleftharpoons Cu(II)$ and/or Cu(II) cluster complex in acetonitrile, which state may have catalytic activity, may be suggested. To see the effect of copper(I) salt on the catalytic activity, the reaction of 2,4,6-tribromophenol with copper(I) chloride was performed under an oxygen and a nitrogen atmosphere, respectively. However, as shown in Table 1, no polymer was yielded by using copper(I) chloride in acetonitrile, which is considered to be present partly or partly all as copper(I) state under the present reaction condition.

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† The reaction mixture was chromatographed on silica gel in methylene chloride. The red crystal isolated was identified as 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone by its ir and NMR spectra. At the present time, work along this line is in progress and will be published elsewhere in the near future.

In view of the above facts, it seems reasonable to consider that copper(I) species have no catalytic activity for the present oxidative displacement reaction.

It has been reported (*12*) that dimethylsulfoxide (DMSO), dimethylformamide (DMF), and hexamethylphosphoramide (HMAP) in the place of pyridine can be used as solvent or ligand for the oxidative coupling reaction of 2,6-dimethylphenol with copper(I) chloride. It was attempted to utilize these series of solvents, DMSO, DMF, and HMPA for the present polymerization reaction with copper(II) nitrate. As seen in Table 1, copper(II) nitrate–DMSO, and –HMPA systems had no catalytic activities, but copper(II) nitrate-DMF system was found to initiate the polymerization of 2,4,6-tribromophenol though the catalytic activity is weaker than in acetonitrile. From the view of the dependence of the solvent on the polymerization of 2,4,6-tribromophenol as observed in Table 1, it is difficult to interpret the differences of the catalytic function between these copper complexes with certainty, though the absorption spectra of these copper complexes are discussed in connection with the catalytic activities in a later section of this paper.

In order to investigate the effect of the copper(II) salts, the polymerization of 2,4,6-tribromophenol with some copper(II) salts other than copper(II) nitrate in acetonitrile were carried out. Copper(II) perchlorate-acetonitrile system had catalytic activity for the polymerization of 2,4,6-tribromophenol though the catalytic activity is less than copper(II) nitrate in acetonitrile, but the polymer was not yielded by using the copper(II) chloride–acetonitrile system. When the typical chelate compound, copper(II) acetylacetonate, was used as the catalyst, the polymer was obtained in 9% yield at the present reaction condition. Thus it was found that the catalytic activities for the present reaction showed the marked dependence of the copper(II) salts used. In the light of the results obtained above, the oxidative displacement polymerization of 2,4,6-tribromophenol seems to be most favored with copper(II) nitrate in acetonitrile.

At the end of this section, we wish to discuss briefly the structure of the polymer obtained. The polymer obtained by the reaction of 2,4,6-tribromophenol with copper(II)–acetonitrile system was identified as poly(2,6-dibromophenylene oxide) with the aid of its elementary analysis and infrared spectrum. However, no definite information regarding the structure of the polymer, notably the question on whether the polymer is linear chain or branched polymer, is obtained by these methods as described above. Armed with the NMR measurement of the polymer, the information on this question may be obtained. The NMR spectrum of the polymer was identical with that obtained by the polymerization of 2,4,6-tribromophenol with copper(II) chloride–sodium methoxide system (*13*). The peak at ca. $\tau = 4.6$ is assigned as the proton of OH group at the end of polymer because of its disappearance when deuterized water was added, in good agreement with the observation of NMR spectrum of the polymer obtained by the copper(II) chloride–methoxide system. If the polymer is linear chain, the peaks based on phenyl ring protons would be observed as single peaks similar to the NMR spectrum of poly(2,6-dimethylphenylene oxide) (*14*), but as evidenced in Fig. 1 the NMR spectrum of the polymer this is apparently not the case. The different groups in the region of the phenyl ring proton are observed. This observation prompts us to consider the presence of the ring protons surrounded by the different environment. Thus the polymer obtained by the copper(II) nitrate–acetonitrile system would be propagated by also the elimination of orthobromine, similar to the parabromine.

Electronic Absorption Spectra of the Copper(II) Catalysts

As described above, both copper(II) salts and solvent used for the polymerization of 2,4,6-tribromophenol extremely affect the yield of the polymer. In order to investigate some relationship between the strengths of the ligand field and the cat-

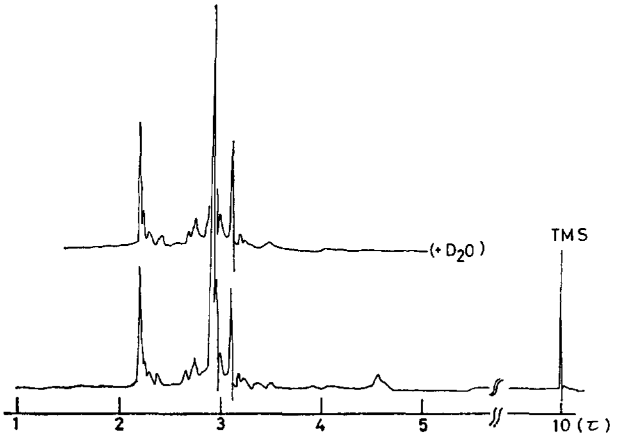


FIG. 1. NMR spectrum of poly(2,6-dibromophenylene oxide).

alytic activities of these copper(II) complexes used as catalyst, the absorption spectra in the near infrared region were observed. The electronic spectra show one broad peak in the near infrared region, which is assigned as *d–d* transition band of the copper(II) ions and composed from a combination of some *d–d* transitions. (See Fig. 2.) It is well known from a point charge approximation that a shift to a lower λ_{max} implies stronger ligand field, that is, stronger interaction of copper(II) ions with the ligand. As evidenced from the data in Table 2, the variation of the copper(II) salts used in acetonitrile causes the shift of λ_{max}. The trend of λ_{max} is as follows: the greater are the catalytic activities of the copper(II) complexes, the lower λ_{max} of the copper(II) complexes. Also the similar trend of the shift of λ_{max} was observed by the variation of solvent when copper(II) nitrate was used as copper(II) salt, with exception of methanol solvent, which cannot be ordered. When methanol was used as solvent, the λ_{max} of the copper(II) nitrate–methanol became nearly the same wave length as that of copper(II) nitrate–DMF complex, despite the difference in the catalytic activity between the two systems as mentioned above. This does not seem to be surprising in view of the large difference in solvent character, e.g., methanol is a typical protic solvent and the others aprotic ones. It may

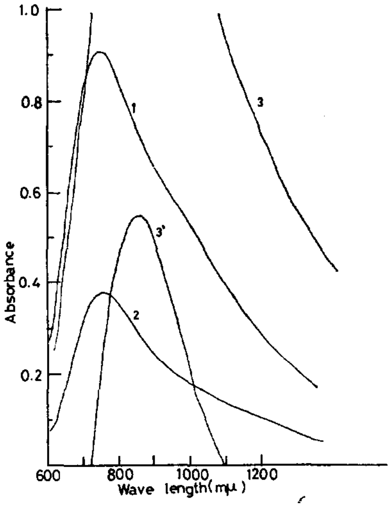


FIG. 2. Electronic spectra of the copper(II) complexes: (1) $Cu(NO_3)\cdot 3H_2O$–CH_3CN; (2) $Cu(ClO_4)\cdot 6H_2O$–CH_3CN; (3) $CuCl_2\cdot 2H_2O$–CH_3CN (3′ absorbance, 1–2).

TABLE 2

λ_{max} AND ϵ_{max} OF COPPER(II) COMPLEX[a]

Copper(II) complex	λ_{max} (nm)	ϵ_{max}
$Cu(NO_3)_2\cdot 3H_2O$–CH_3CN	735	45.0
–DMF	800	37.8
–DMSO	850	33.2
–HMPA	885	48.5
$Cu(ClO_4)_2\cdot 6H_2O$–CH_3CN	765	19.7
$CuCl_2\cdot 2H_2O$–CH_3CN	860	88.0

[a] Copper(II) salt; 0.02 mole/liter.

be unreasonable, rather, to compare directly the shift of the absorption spectra of the system in methanol solvent with the system in the other solvent, and to correlate with the catalytic activities. However, it may be qualitatively considered that λ_{max} of the copper(II) complexes which have catalytic activities for the present polymerization tend to shift to shorter wave length from the observation of electronic spectra. It is of interest to note that the same trend on the shifts of λ_{max} is observed for the copper(II) complexes as catalyst of oxidative coupling polymerization of 2,6-dimethylphenol (*11*).

ESR Spectra of the Copper(II) Complexes and Reaction Intermediate

The observation of the electronic spectra of the series of copper(II) complexes called us to test another method for inferring details about the differences between the series of the copper(II) complexes in connection with the catalytic activities. ESR measurement may provide some information regarding these copper(II) complexes. To find out information on the nature of the species formed when copper(II) salts are dissolved in acetonitrile, the ESR spectra of the complexes were observed. We took here the typical two copper(II) salts, copper(II) nitrate and copper(II) chloride, the former in acetonitrile catalyzes the polymerization of 2,4,6-tribromophenol and the latter does not. The ESR spectra of these two copper(II) complexes at 77°K are shown in Fig. 3, together with the partial enlargements of these spectra. ESR spectra of the two complexes indicate that these complexes are paramagnetic at liquid nitrogen temperature. The anisotropic spectra based on copper(II) ions were not observed even at 77°K, and we obtained the ESR spectra with one nearly symmetrical broad peak for the present two copper(II) complexes. These observations may indicate that both complexes have distorted octahedral symmetry about the copper(II) ions rather than square planar complexes whose ESR spectra show generally the anisotropic absorption.

More significant concern for the purpose of our present study is to observe the differences between the two ESR spectra in order to connect the nature of two complexes with the catalytic activities of the present displacement reaction. In the high magnetic fields of the ESR spectrum of copper(II) nitrate–acetonitrile complex (solid line), some peaks superposed upon the broad peak based on copper(II) ions are observed. The enlargement peak in the upfield is also shown on Fig. 3. But no peak in addition to the broad peak appeared in the case of copper(II) chloride–acetonitrile complex (dotted line). The superimposed peaks observed in the copper(II) nitrate–acetonitrile complex would be due to the superhyperfine coupling which occurred from the interaction of the nitrogen atoms of the ligands with

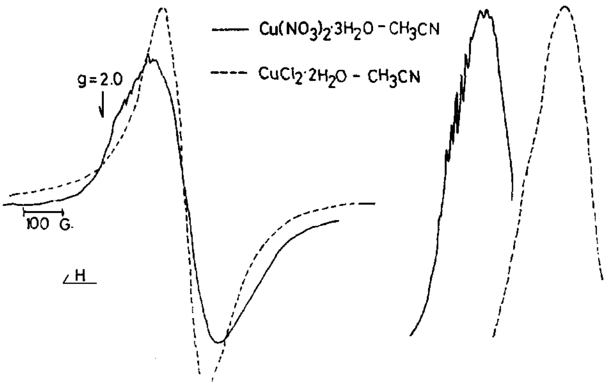


FIG. 3. ESR spectra of copper(II) complexes at 77°K.

unpaired electron of the copper(II) ion. Because of no appearance of this superhyperfine coupling in the ESR measurement of the copper(II) nitrate–methanol system, the possibility that the nitrogen atoms of nitrate anions participate with the structure of the superhyperfine coupling seems to be ruled out. Based on the observation of the ESR spectra, it is evident that in the copper(II) nitrate–acetonitrile system the unpaired electron on the copper(II) ions is delocalized to the nitrogen atoms of the acetonitrile, on the other hand, the unpaired electron does not reach the nitrogen atoms through the copper(II) ion–nitrogen atoms interaction in the case of the copper(II) chloride–acetonitrile system. This finding is compatible with the fact that the nitrate anion is more ionic and labile than the chloro anion in the copper(II) salts (*15*), and may be interpreted in connection with the difference of catalytic activities of the two copper(II) complexes. That is to say, in the copper(II) nitrate–acetonitrile system, as the nitrate anions are easily removed, the copper(II) complex, which have copper(II) ion–acetonitrile bonds and are assumed as active catalyst for the present polymerization, can be formed more easily than the copper(II) chloride–acetonitrile system. The trend of shift of $\lambda_{\max}$ reported in an earlier section is compatible with the results of ESR measurement. Thus the copper(II) salts which have catalytic activities interact with acetonitrile stronger than those which have not. In a previous section, it was reported that copper(II) perchlorate in acetonitrile catalyzes the oxidative displacement of 2,4,6-tribromophenol although the activity is not so strong as copper(II) nitrate. Also it is well known (*15*) perchlorate anion similar to nitrate ion is difficult to coordinate with the metal ion because of its large electronegativity. Accordingly the same interpretation for the catalytic activity of the copper(II) perchlorate–acetonitrile system as the copper(II) nitrate would be possible.

It has been well established that generally in the process of the oxidation of phenol derivatives, the corresponding phenoxy radicals are generated as the reaction intermediates. Staffin and Price (*2*) have reported that in the polymerization reaction of 4-bromo-2,6-dimethylphenolate ion with a number of oxidizing agents such as ferricyanide ion, lead dioxide, the likely course for the propagation step in the polymerization is the displacement of bromine ion by phenoxy radical. On the other hand, it has been reported (*4*) that the oxidation reaction of thiourea proceeds with formation of a red complex which was considered as paramagnetic species. These findings prompt us to investigate the possibility of the formation of the corresponding phenoxy radical in the course of the reaction of the phenol derivatives with copper(II)–acetonitrile system. As phenol derivative, we took 2,6-di-*tert*-butyl-4-methylphenol. The ESR spectrum of the radical generated from the mixture of the phenol and copper(II) nitrate–acetonitrile complex is presented in Fig. 4. It is evident (*5*) that the ESR spectrum is identified as 2,6-di-*tert*-butyl-4-methylphenoxy radical, and the present copper(II) nitrate–acetonitrile complex has the function as the one-electron transfer reagent. However, the corresponding phenoxy radical could not be observed when 2,4,6-tribromophenol was used at present measurement condition. It may be possible to observe the corresponding phenoxy radical by ESR measurement if the more appropriate condition, for example, rapid flow system, is chosen for the ESR measurement. Waters and his co-workers (*16*) have reported that the ESR spectra of

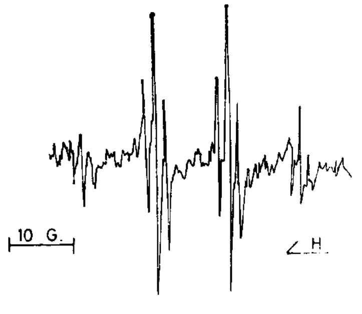


FIG. 4. ESR spectrum of 2,6-di-*tert*-butyl-4-methylphenoxy radical.

short-lived alkyl- and alkoxy-substituted phenoxy radicals could be obtained by flowing benzene solution of the corresponding phenols through bed such as silver oxide or lead dioxide. Most free aryloxy-radicals have so transient an existence that for the measurement of their ESR in solution at room temperature it is necessary to use a flow technique whereby free radicals, at a steady concentration, are passed through the cavity of an ESR microwave detecting system. In this way, Stone and Waters (*17*) have measured the ESR spectra of even the simplest of aryloxy radicals in aqueous solution by oxidizing phenols with ceric sulphate, whereas Dixon and Norman (*18*) have successfully used hydrogen peroxide–titanous chloride mixtures. The rapid-flow method stimulated renewed interest in investigation of the intermediate of the oxidative displacement of 2,4,6-tribromophenol and acetonitrile solution of copper(II) nitrate were mixed in the ESR cavity. However, no ESR signals were detected within the measurement condition used. Next we tried to observe the radical generated from poly(2,6-dibromophenylene oxide) with copper(II) nitrate–acetonitrile by the method of flow technique. The ESR signal considered to generate from the polymer was observed at near $g = 2.0$, though the signal detected is very weak (small S/N ratio) as shown in Fig. 5. From these results, it may be considered that the radical generated from the 2,4,6-tribromophenol monomer could not be observed because of its short lifetime.

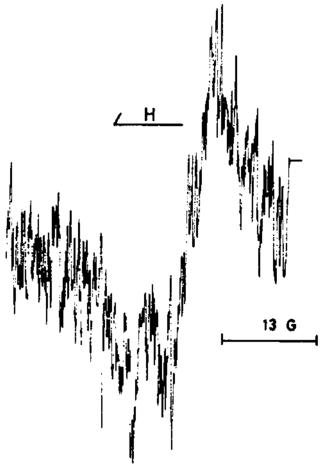
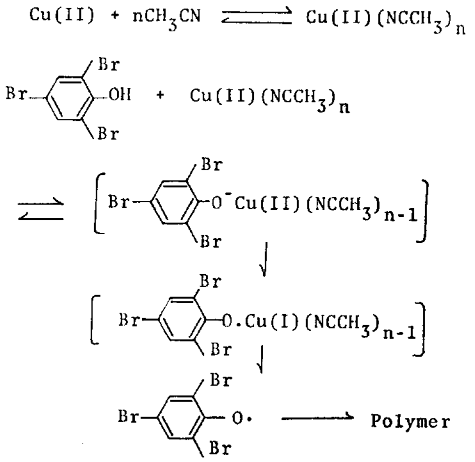


FIG. 5. ESR spectrum of poly(2,6-dibromophenylene oxide) with copper(II) nitrate–acetonitrile.

On the basis of the results mentioned above, we believe the following initial step for the present oxidative displacement polymerization is the likely one. From the observation of the paramagnetic copper(II)–thiourea complex reported by Zatko and his co-workers (*4*), the possibility of the presence of the similar complex containing 2,4,6-tribromophenoxo group would be considered as presented in the above scheme. The phenoxo–copper(II) complex may play a vital role as pointed out in the case of polymerization of 2,6-dimethylphenol with copper(II)-amine complex (*6*).



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