Synthesis and characterization of poly(dihalophenylene oxides) by thermal decomposition of copper complexes with tetramethylethylenediamine and ethylenediamine ligands

H. İbrahim Ünal and Oya Sanlı
Gazi University, Department of Chemistry, Ankara, Turkey

and Duygu Kısakürek*
Middle East Technical University, Department of Chemistry, Ankara, Turkey

(*Received 25 January 1988; revised 22 April 1988; accepted 7 July 1988*)

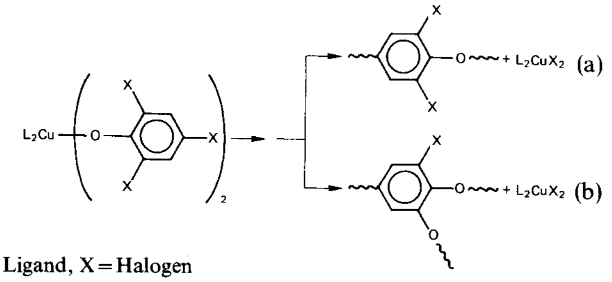
Thermal polymerization of bis(trihalophenoxo)-*N*,*N*,*N*′,*N*′-tetramethylethylenediamine copper(II) and bis(trihalophenoxo)ethylenediamine copper(II) was achieved in toluene at 70°C. The dependences of intrinsic viscosity and the percentage yield of the polymers on a sequence of increasing decomposition times of copper complexes were investigated. Structural analyses of the polymers were carried out using mainly ^{1}H nuclear magnetic resonance spectroscopy and differential scanning calorimetry. 1,4-Catenation was highly favoured over 1,2-addition in 4-bromo-2,6-dichlorophenoxide- and 2,4,6-triiodophenoxide- (with ethylenediamine ligand) and 2,4,6-triiodophenoxide- (with tetramethylethylenediamine ligand) derived polymers. However, polymers synthesized from 2,4,6-trichlorophenoxide with either ligand displayed a selectivity in favour of 1,2-catenation, whereas for 2,4,6-tribromophenoxide with ethylene diamine ligand, 1,4-catenation and *ortho* substitution took place at roughly equal rates.

(Keywords: poly(dihalophenylene oxide); glass transition temperature; intrinsic viscosity; tetramethylethylenediamine copper complex; ethylenediamine copper complex)

INTRODUCTION

It has been demonstrated that a variety of halophenols form (phenolate) copper(II) complexes[1,2]. The ease of thermal decomposition of such complexes is affected by the nature of neutral ligands on the copper. Hence, a series of bis(phenoxo)bis(pyridine) copper(II) (**1**), bis(phenoxo)-*N*,*N*,*N*′,*N*′-tetramethylethylenediamine copper(II) (**2**), bis(phenoxo)bis(ethylenediamine) copper(II) (**3**) and bis(phenoxo) copper(II) (**4**) complexes were prepared using a variety of substituted phenols and characterized previously[1,2]. The complexes prepared so far appear to be tetra-coordinated except bis(ethylenediamine) which is hexa-coordinated[2].

The synthesis and characterization of poly(dihalophenylene oxides) by thermal decomposition of bis(halophenoxo)bis(pyridine) copper(II) and bis(halophenoxo) copper(II) complexes have been thoroughly studied[1–8]. The thermal stability of the complexes with respect to the decomposition reaction:

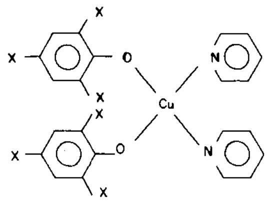


L = Ligand, X = Halogen

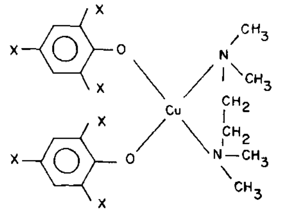
was found to be lower with ligands which increase the oxidizing power of the copper(II).

Also it was shown that chain extension occurred by rapid transfer of phenoxy ligand to the attacking polymer radical at the *para* position, leading to 1,4-addition (a), while *ortho* substitution occurred via an intramolecular process involving two adjacent phenoxy ligands at a single copper centre, leading to 1,2-addition (b) and 1,4-addition at an equal rate[5].

As part of a broader study of the polymerization of halophenols, we have studied the thermal decomposition of complexed halophenolates using *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMED) and ethylenediamine (ED) as neutral ligands respectively in the present paper. However, it was not possible to synthesize polymers from bis(trihalophenoxo)bis(ethylenediamine) although various solvents and different temperatures were used. The bis(trihalophenoxo)ethylenediamine copper(II) complex (**5**) used in the polymerization has not been synthesized for this purpose before.



(1)

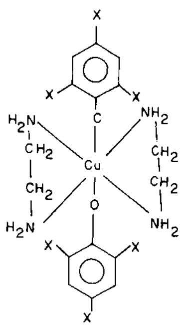


(2)

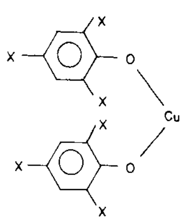
---

* To whom correspondence should be addressed

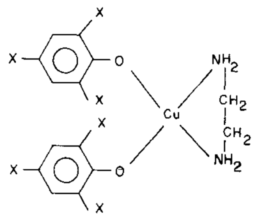
0032–3861/89/020344–04$03.00



(3)



(4)



(5)

EXPERIMENTAL

Materials

Monomers. Halogenated phenols were purchased from Aldrich, Fluka and Fisher Chemical as pure analytical grade and were used without purification. 4-Bromo-2,6-dichlorophenol was made by bromination of 2,6-dichlorophenol[7].

Ligands and copper sulphate. Ethylene diamine (ED) and *N,N,N′,N′*-tetramethylethylenediamine (TMED) were purchased from Aldrich Co. Copper sulphate ($CuSO_4 \cdot 5H_2O$) was obtained from commercial sources and used as received.

Solvents. Toluene and methanol were obtained from Merck Co. as pure analytical grade.

Synthesis of copper complexes

In the synthesis of copper complexes ED and TMED were used as neutral ligands and 2,4,6-tribromophenol (TBP), 2,4,6-trichlorophenol (TCP), 4-bromo-2,6-dichlorophenol (4Br-DCP) and 2,4,6-triiodophenol (TIP) as monomers. Complexes were prepared by mixing two solutions. In the preparation of solution (I) 0.04 mol $CuSO_4 \cdot 5H_2O$ was dissolved in water, 0.04 mol either TMED or ED was added respectively and stirred for an hour at room temperature; solution (II) containing 0.08 mol NaOH and 0.08 mol halogenated phenol in 100 cm^3 water was then slowly added to the solution (I) with vigorous stirring. In each case the resulting dark brown complexes were filtered, washed with water and dried at 30°C in a vacuum oven overnight.

The structural analyses of the copper complex were carried out by i.r. spectroscopy[2].

In the preparation of bis(tribromophenoxo)bis(ethylenediamine) copper(II) complex, the molar ratio of ethylenediamine to halogenated phenol was changed from 1/2 to 1/1. Data for their elemental analyses are listed in *Table 1*.

Synthesis of polymers

Polymers were synthesized by thermal decomposition of the respective copper complexes in toluene at 70°C. The polymerization time ranged from 3 to 48 h. Decomposition of 6.6 g/100 cm^3 complexes were carried out in a round-bottomed flask with a reflux condenser open to the air.

The appearance of turbidity in methanol was used to determine the induction period of the polymerizations.

Characterization of polymers

Polymers were characterized by viscosity measurements, n.m.r. spectroscopy and differential scanning calorimetry (d.s.c.).

Intrinsic viscosities of the polymers were determined at 30°C in toluene using an Ubbelohde viscometer, having an efflux time of 80 s.

^1H n.m.r. spectra of polymers were measured in CS_2 using a Varian EM 360, 60 MHz spectrometer, at room temperature. TMS was used as an external standard.

The glass transition temperatures (T_g) of the polymers were measured by using a Perkin–Elmer Differential Scanning Calorimeter, DSC-4, in the range 20–600°C. The scanning speed was 40°C min^{-1} and the weights of the samples were around 20 mg.

Elemental analyses were carried out by a Hewlett–Packard F and M 185 carbon–hydrogen–nitrogen analyser with flow rate of 100 $cm^3 min^{-1}$, oxidation furnace of 1050°C, reduction furnace of 500°C and column oven temperature of 80°C.

I.r. spectra dispersed in KBr discs were measured by using a Perkin–Elmer 1710 model *FT*i.r. spectrometer coupled with a PE-7500 data station.

RESULTS AND DISCUSSION

Effect of reaction time on percentage conversion

The effect of reaction time on the yield of recovered polymers from the phenoxo complexes of copper(II) containing two different amine ligands are shown in *Figure 1*. It was readily seen that when ED was the ligand the percentage yield of the polymer increased as the atomic weight of the substituted halogens decreased, i.e. going from TIP to TBP to 4Br-DCP and TCP. The same trend was observed when the ligand was changed to TMED.

Table 1 Data for the elemental analysis of (a) bis(tribromophenoxo)bis(ethylenediamine) copper(II) and (b) bis(trichlorophenoxo)ethylenediamine copper(II) complexes

	N (%)		H (%)		C (%)	
Complex	Calculated	Found	Calculated	Found	Calculated	Found
(a) $(ED)_2Cu(TBP)_2$	6.64	7.30	2.37	2.30	22.76	22.70
(b) $(ED)Cu(TCP)_2$	5.42	5.40	2.32	2.30	32.53	32.20

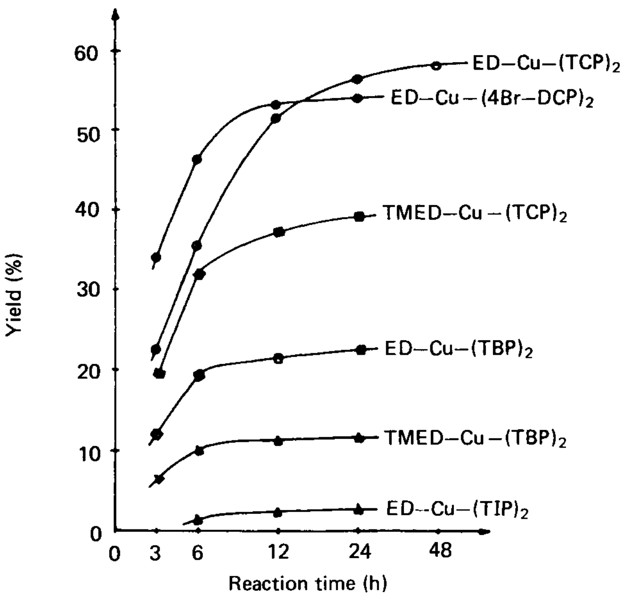


Figure 1 Dependence of the percentage yield of polymer on the extent of reaction of copper complexes with different ligands for various substituted halogens in toluene at 70°C

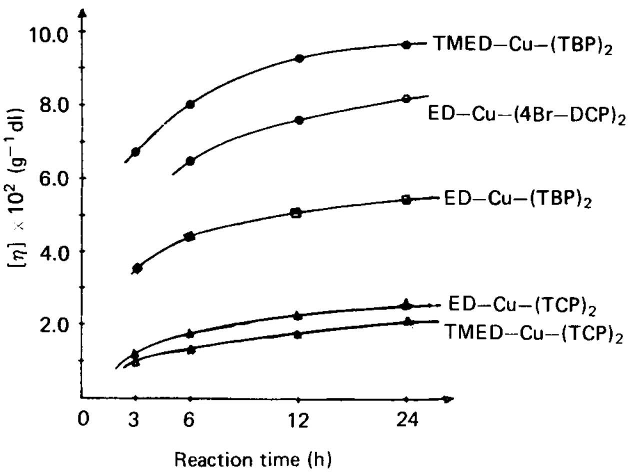


Figure 2 Effect of the extent of reaction of phenoxo copper(II) complexes on their intrinsic viscosities at 70°C in toluene

Effect of reaction time on intrinsic viscosity

A series of thermal decompositions of phenoxo copper complexes was performed under identical conditions for different reaction times, in toluene at 70°C. As can be seen from *Figure 2* the intrinsic viscosities of the polymers increased as the reaction time was increased up to 12 h. The polymer obtained from tribromophenol with either ligand has higher intrinsic viscosity compared to their corresponding trichlorophenol monomer. However, the increase was higher when the ligand was changed to TMED from ED, and also the bromine atom, in the *para* position only, yielded the highest value in intrinsic viscosity among the halogenated phenols when the ligand was ethylenediamine.

The effect of ligand on the structure of the polymer

The structures of the poly(dihalophenylene oxides) were determined from their ^{1}H n.m.r. spectra (*Figures 3* and *4*). Polymers were more linear except the one resulting from the decomposition of bis(tribromophenoxo)ethylenediamine copper(II) complex. The spectrum had two intense lines; the one at $\delta = 7.0$ may be assigned to the protons of 2,6-dibromo-1,4-phenylene oxide units and the line at $\delta = 7.7$ to the 5-protons of 2,4-dibromo-1,6-phenylene oxide units, indicating 1,2- and 1,4-addition during polymerization took place at equal rates. However the lower-field peaks are not so sharp in the other cases, indicating that 1,4-catenation is favoured over 1,2-catenation, except the ones obtained from TCP with either ligand. It is observed that 1,2-addition is more favoured and the broad higher-field lines could be due to polymerization through 2,4- and 2,4,6-positions on the same 2,4,6-trichlorophenols.

CONCLUSIONS

It has previously been suggested that the nature of the neutral ligand should strongly influence the thermal stability of the starting complex[1,2]. It was reported also that the order for stabilization of Cu(II) was ethylenediamine > pyridine through the study of the effect

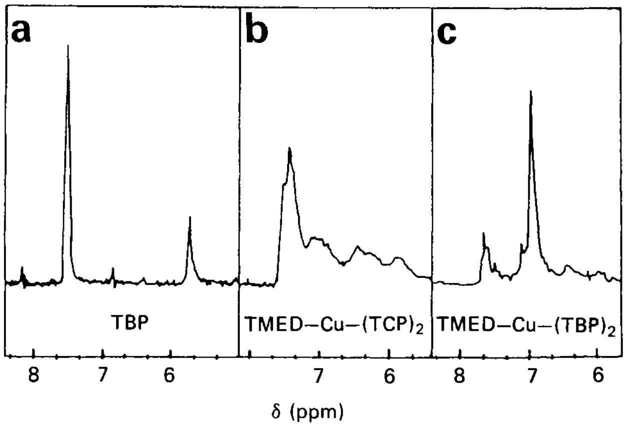


Figure 3 ^{1}H n.m.r. spectra of: (a) tribromophenol; (b, c) the polymers derived from the decomposition of (b) trichlorophenoxo and (c) tribromophenoxo copper(II) complexes with N,N,N',N'-tetramethylethylenediamine as the ligand

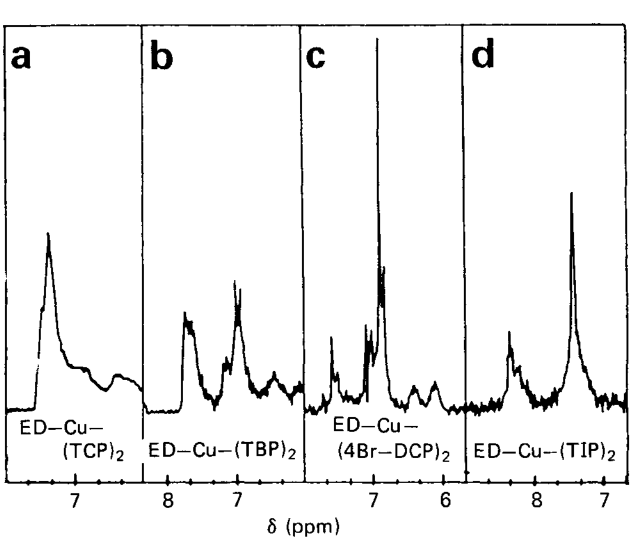


Figure 4 ^{1}H n.m.r. spectra of the polymers synthesized from the decomposition of (a) trichlorophenoxo, (b) tribromophenoxo, (c) 4-bromo-2,6-dichlorophenoxo, and (d) triiodophenoxo copper(II) complexes with ethylenediamine as the ligand

Table 2 Data for induction periods

Ligand	Induction period (min) TCP	Induction period (min) TBP
Pyridine[4]	30	–
Ethylenediamine	56	28
N,N,N′,N′-tetramethylethylenediamine	45	18

Table 3 Intrinsic viscosities and glass transition temperatures for poly(dihalophenylene oxides) derived from various halophenoxo copper complexes with different ligands in 24 h reaction times

Ligand	Trihalophenol	$[\eta]^a$ (dl g^{-1})	T_g (°C)	C_p (cal deg^{-1})
TMED	TCP	0.022	283	2.66
TMED	TBP	0.096	270	1.66
ED	TCP	0.026	280	3.18
ED	TBP	0.056	278	0.43
ED	4Br-DCP	0.082	250	–

[a] In toluene at 30°C

of amine ligands on the redox potentials of the Cu(II)/Cu(I) system[9]. Later a correlation was found to exist between the thermal stability of phenoxo copper complexes and the position of the amine ligand[2]. Although oxidation potentials for tetramethylethylenediamine complexes have not yet been reported, TMED would be expected to stabilize copper(II) relative to Cu(I) whereas a monodentate ligand is expected to stabilize Cu(I) relative to Cu(II).

The phenoxo complexes containing chelating ligand would be exceptionally resistant to thermal decomposition, which should increase the induction period of polymer formation (*Table 2*). Hence the order for stabilization of Cu(II) should be ED > TMED > pyridine in the complexes.

The polymer isolated from the decomposition of trihalophenoxo copper complex was in very low yield when TIP was used as halogenated phenol. However, an increase in the yield was observed as the size of the substituted halogen(s) was decreased in the following sequence TCP > 4Br-DCP > TBrP > TIP with either ligand.

The poly(phenylene ethers) constitute a series of polymers that can be modified easily by the placement of various halogen substituents in the 2,4,6-positions of the phenylene ring. Also it has long been concluded that the polymers synthesized from dihalogenation by trihalophenoxides are highly branched due to their anomalously low intrinsic viscosities (*Table 3*). Later it was proved that branches were largely monomeric and of modest molecular weight[3,5,7]. The ^{1}H n.m.r. spectra of various samples of poly(dihalophenylene oxide) indicated differences in structure between the polymers produced by decomposition of copper(II) trihalophenoxide complexes with either ligand (*Figures 3* and *4*).

As previously reported, the linear poly(2,6-dihalo-1,4-phenylene oxides) exhibited the expected sharp singlet in the ^{1}H n.m.r. spectra, together with some minor peaks (*Figures 3c, 4c* and *4d*). Polymerization of 4-bromo-2,6-dichlorophenoxide, yielding a linear polymer, indicated a high selectivity for displacement of bromine rather than chlorine in *para* position (*Figure 3c*). Polymerization of 2,4,6-tribromophenoxide with ED as ligand yielded a polymer containing substantial amounts of both 1,2- and 1,4-linked phenylene units (*Figure 4b*). However, a linear structure was previously also reported for tribromophenoxide with either ligand[3] or without any ligand[5,6,8].

In the case of trichlorophenoxide, 1,2-addition was favoured over 1,4-addition with either ligand (*Figures 3b* and *4a*). However, 1,2- and 1,4-catenation, taking place at equal rates, was reported with pyridine ligand or without any ligand[3,5,8].

Examination of molecular models revealed that runs of 1,2-enchained segments were considerably more restricted in their degrees of motional freedom than were runs of 1,4-enchained segments[9]. The restriction could be partly due to the steric interference of substituents on adjacent phenylene rings. It was also suggested that 1,2-coupled units were essentially locked in position and probably could move as the whole polymer molecules moved[9]. Investigation of T_g values indicated that the highest values corresponded to TCP with either ligand and TBP with ligand ED, as expected from their structure for these rigid polymers (*Table 3*).

The present study indicates that in the decomposition of halophenoxo copper(II) complexes ligands can influence the structure of the derived polymer.

ACKNOWLEDGEMENT

One of us (D.K.) would like to thank METU Research Fund for the partial support of the work.

REFERENCES

1 Blanchard, H. S., Finkbeiner, H. and Russell, G. A. *J. Polym. Sci.* 1962, **58**, 469

2 Harrod, J. F. *Can. J. Chem.* 1969, **47**, 637

3 Carr, B. G., Harrod, J. F. and Van Gheluwe, P. *Macromolecules* 1973, **6**, 498

4 Carr, B. G. and Harrod, J. F. *J. Am. Chem. Soc.* 1973, **95**, 5707

5 Harrod, J. F., Van Gheluwe, P., Kısakürek, D. and Shaver, A. *Macromolecules* 1981, **14**, 565

6 Harrod, J. F. and Shaver, A. *Macromolecules* 1982, **15**, 676

7 Kısakürek, D., Binboğa, N. and Harrod, J. F. *Polymer* 1987, **28**, 1967

8 Türker, L. and Kısakürek, D. *Br. Polym. J.* 1988, **20**, 131

9 Harrod, J. F. and Van Gheluwe, P. *ACS Symp. Ser.* 1979, **104**, 52