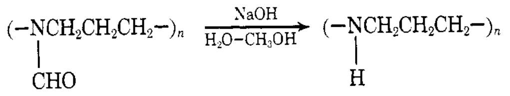
port on the preparation of linear poly(trimethylenimine).



$$(-\underset{\text{CHO}}{\text{N}}\text{CH}_2\text{CH}_2\text{CH}_2-)_n \xrightarrow[\text{H}_2\text{O}-\text{CH}_3\text{OH}]{\text{NaOH}} (-\underset{\text{H}}{\text{N}}\text{CH}_2\text{CH}_2\text{CH}_2-)_n$$

The linear poly(trimethylenimine) was found to be slightly crystalline from the X-ray diffraction spectrum.

It is interesting to compare some properties of poly(trimethylenimine) with those of crystalline poly(ethylenimine), which was prepared by the alkaline hydrolysis of poly(OZO).[9] The former is soluble in methanol and ethanol, and insoluble in water. Yet, it is very hygroscopic. Its melting point is depending upon the content of water of crystallization, *i.e.,* 74-76° for the polymer containing water of 9.3 wt % and 81-84° for that of 17 wt %. On the other hand, the latter is soluble only in hot water and shows a melting point of 58.5°.

The mechanistic and kinetic studies on the OZI polymerization are currently under progress.

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(9) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules,* **5**, 108 (1972).

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# Chemistry of Phenoxo Complexes. II. Synthesis of High Molecular Weight Poly(2,6-dichlorophenylene oxides)

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ABSTRACT: The molecular weights ($\bar{M}_n$) of poly(phenylene oxides) produced by thermal decomposition of bis(2,4,6-trichlorophenoxo)bis(pyridine)copper(II) (1) were found to increase with (i) increasing concentration of 1, (ii) decreasing concentration of free impurity trichlorophenol, and (iii) changing solvent from cumene, to toluene, to benzene. Temperature had little effect, but $\bar{M}_n$ was found to increase asymptotically to a maximum well beyond the apparent completion of reaction, as indicated by the disappearance of 1. The maximum $\bar{M}_n$ achieved by decomposition of 1 was *ca.* 80,000, but these polymers are branched at almost every unit. A substantial increase in $\bar{M}_n$ was achieved by decomposition of bis(2.4,6-trichlorophenoxo)-*N,N,N',N'*-tetramethylethylenediaminecopper(II) (2) to >150,000, but no change in the degree of branching was observed. The 4-bromo-2,6-dichlorophenoxo analogs of 1 and 2 gave polymers of still higher molecular weight and with a branching frequency of 0.1. The bromine analysis and nmr spectrum of the polymer indicated a selectivity for 1,4 over 1,2 coupling of 2:1. The 4-iodo-2,6-dichlorophenoxo analog of 1 gave results essentially identical with those of the 4-bromo derivative.

The halogenated poly(phenylene oxides) have the potential for outstanding mechanical, chemical, electrical, and thermal properties, provided they can be prepared as linear polymers of high molecular weight.[1] Such polymers have also been found to be extremely fire resistant.[2] The history of attempts to prepare useful polymers from halophenols has been long and, to a large extent, unsuccessful. Hunter and coworkers[3] reported extensive investigations of polymers prepared by decomposition of silver halophenolates and these studies have been continued more recently by Blanchard *et al.*[4] The polymers produced in these reactions are invariably branched and of modest molecular weight.

A novel synthesis of poly(phenylene oxides) by thermal decomposition of bis(halophenoxo)bis(pyridine)copper(II) complexes was described by Blanchard *et al.*[4] Although a wide variety of reaction conditions was tried, the highest molecular weight obtained was 11,000. In addition, the very low intrinsic viscosities led the authors to conclude that the polymers were all significantly branched.

A most promising synthesis of linear poly(phenylene oxides) by free-radical initiated decomposition of halophenoxides under a variety of conditions has been reported by Stamatoff.[5] In particular, it was claimed that polymerization of sodium 2,6-dichloro-4-bromophenolate with benzoyl peroxide gave linear poly(2,6-dichlorophenylene oxide) with a bromide content of *ca.* 1%. Physical properties of these polymers indicated that they were substantially linear and of quite high molecular weights, although no actual values were quoted.

As part of a broader study of the catalytic polymerization of halophenols, we have studied the decomposition of complexed copper halophenolates in considerable detail.[6] In the present paper we give some important factors which control the molecular weights of polymers produced by decomposition of copper trihalophenolates.

## Results

**Effect of Reaction Time on Molecular Weight.** A series of concurrent reactions were performed with bis(2,4,6-trichlorophenoxo)bis(pyridine)copper(II) (1) at 70° in benzene and at a constant concentration of 50 g/l. The reactions were stopped after different reaction times and the polymer and precipitated dichlorobis(pyridine)copper(II) were recovered. Plots of the yield of product copper complex and of the $\bar{M}_n$ of the recovered polymer *vs.* reaction time are shown in Figure 1.

**Effect of Concentration on Molecular Weight.** The variation of $\bar{M}_n$ with concentration for a series of polymers produced by thermal decomposition of 1 is shown in Figure 2. Similar behavior was observed with complexes with different phenoxy or neutral ligands. Each of the runs represented in Figure 2 was allowed to react for 48 hr to ensure a maximum $\bar{M}_n$.

**Effect of Solvent on Molecular Weight.** A series of decompositions of 1, under otherwise identical conditions, was performed in benzene, toluene, and cumene. The values for $\bar{M}_n$ of the polymers produced in these reactions

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(1) I. R-T. Steinbuch, *Kunstst. Plast. (Munich),* 3, 3 (1965).

(2) H. S. Blanchard and H. L. Finkbeiner, U. S. Patent 3,256,243 (1966).

(3) W. H. Hunter and R. B. Whitney, *J. Amer. Chem. Soc.,* 54, 1167 (1932).

(4) H. S. Blanchard, H. L. Finkbeiner, and G. A. Russell, *J. Polym. Sci.,* 58, 469 (1962).

(5) G. S. Stamatoff, U. S. Patent 3,257,358 (1966).

(6) B. Carr and J. F. Harrod, *J. Amer. Chem. Soc.,* **95**, in press.

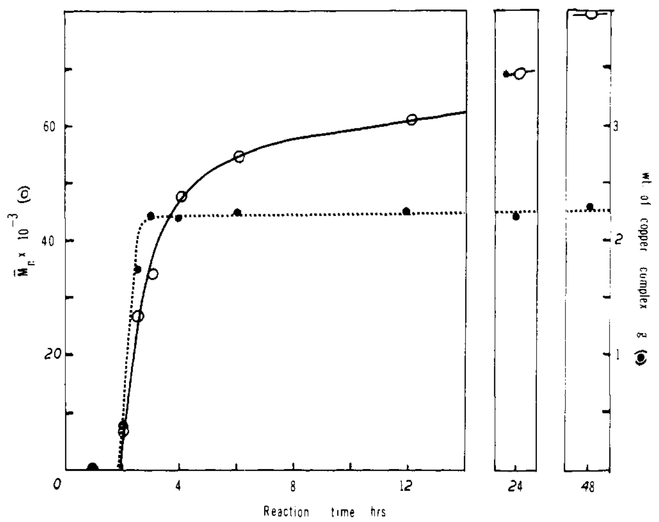

**Figure 1.** Dependence of polymer molecular weight on extent of reaction of copper complex. Initial reactant concentration: 50 g/l.; $T$ = 70° in benzene.

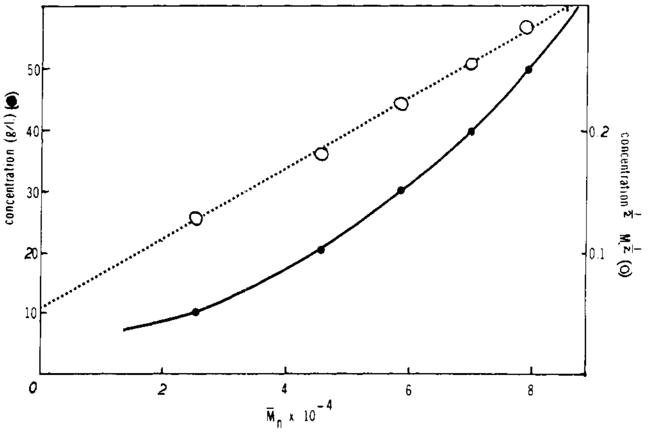

**Figure 2.** Effect of initial reactant concentration on polymer molecular weight at complete reaction at 70° in benzene.

were 80,000, 40,000, and 13,000, respectively. The reactions were carried out at 70° in air, for 48 hr and at an initial reactant concentration of 50 g/l.

As reported previously,[7] the product copper complexes differed dramatically in the three solvents. In benzene, the product was almost entirely dichlorobis(pyridine)copper(II), in cumene almost entirely $\mu_4$-oxo-$\mu$-hexachlorotetrakis[pyridinecopper(II)]. In toluene the product was *ca.* 90% of the former and 10% of the latter complex.

**Effect of Temperature on Molecular Weight.** Several runs were performed at different temperatures, with other conditions kept constant. The results of these runs are summarized in Table I. The decompositions at 20° were left for about 1 year to achieve complete reaction, those at higher temperatures were left for several days.

**Effect of Trichlorophenol on Molecular Weight.** Preliminary studies of the decomposition of **1** and the molecular weights of the resulting polymers showed that internally consistent behavior was usually observed for a given batch of **1**, but that different preparations tended to give quite scattered results. In particular, the ultimate $\bar{M}_n$ for a series of decompositions, under identical conditions, of several samples of **1**, prepared at different times and with different degrees of purity, varied over a range approaching a factor of two. The complete removal of free trichlorophenol from **1** is virtually impossible without recourse to extraordinary measures to exclude water during recrystallization and preparation of reaction mixtures. Since free phenol was likely to affect the molecular weight of the polymer, the influence of added phenol on the $\bar{M}_n$ of the polymers produced by decomposition of **1** was investigated.

Table I
Effect of Temperature on Molecular Weight

| Concn (g/l.) | Solvent | Temp (°C) | $\bar{M}_n$ |
|---|---|---|---|
| 40 | Toluene | 20 | 24,000 |
| 40 | Toluene | 60 | 16,700 |
| 40 | Toluene | 90 | 16,600 |
| 50 | Benzene | 20 | 80,000 |
| 50 | Benzene | 70 | 80,000 |

Figure 3 shows the variation of $\bar{M}_n$ for a series of decompositions of **1** in the presence of various amounts of trichlorophenol. It is evident that $\bar{M}_n$ is extremely sensitive to small amounts of added phenol, but is much less sensitive at higher loading levels. Such behavior is characteristic of the effect of a transfer agent, or of a chain stopper. The fact that the molecular weight was still 7600 at the 1.0-g loading of added phenol, a ratio of *ca.* five ligand phenoxides per added phenol, favors the hypothesis that the phenol behaves as a transfer agent.

The batch of **1** used to obtain the data shown in Figure 3 was subject to less stringent purification than that used for the data in Figures 1 and 2. This may account for the lower molecular weight of the sample without added phenol, compared to that expected on the basis of Figures 1 and 2.

Infrared spectra of the polymers, produced in the presence of added phenol, are shown in Figure 4 and indicate a progressive increase in the hydroxyl content of the polymer with increasing added phenol. It is of interest that the hydroxyl content of the polymer produced without added phenol is significant. A sample of polymer produced from a highly purified sample of **1** gave no detectable absorption in the hydroxyl region.

**Molecular Weights of Polymers from Decomposition of Other Complexes.** A saturated benzene solution of bis(trichlorophenoxo)-*N,N,N′,N′*-tetramethylethylenediaminecopper(II) (**2**) (*ca.* 20 g/l.), was left at room temperature for 5 months. At the end of this time the solution was almost colorless and large crystals of dichloro(*N,N,N′,N′*-tetramethylethylenediamine(copper(II) had precipitated. The polymer recovered from the solution had an $\bar{M}_n$ of 161,000.

A similar decomposition of bis(4-bromo-2,6-dichlorophenoxo)bis(pyridine)copper(II) (**3**) (5 g/l. at 71° for 24 hr) yielded a polymer of $\bar{M}_n$ = 126,000. A duplicate experiment in toluene gave a polymer of $\bar{M}_n$ = 130,000. Although these polymers were of lower molecular weight than that produced from **2**, they were only partially soluble in benzene, or toluene, at room temperature. They did dissolve on warming in the latter solvents.

Decomposition of bis(4-bromo-2,6-dichlorophenoxo)-*N,N,N′,N′*-tetramethylethylenediamine (**4**) (25 g/l. in benzene at 25° for 4 months), yielded a polymer that was largely insoluble in benzene, or toluene. Because of its insolubility, the molecular weight of this polymer was not determined.

**Some Other Properties of the Polymers.** All of the polymers, without exception, produced by decomposition of **1** and **2** were highly branched. The nmr spectra of these polymers (Figure 5a) were poorly resolved and complex, due partly to a substantial concentration of free radicals

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(7) B. Carr and J. F. Harrod, *Can. J. Chem.*, 50, 2792 (1972).

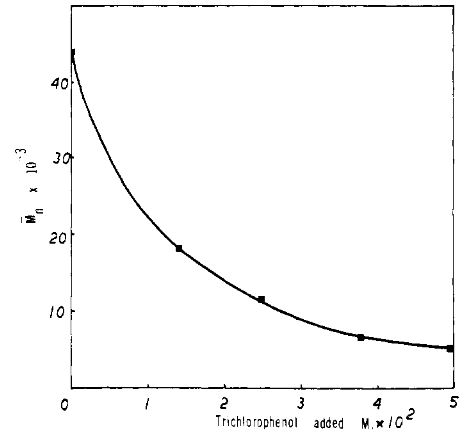
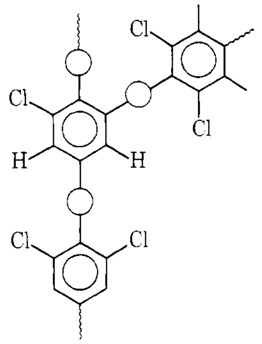


Figure 3. Effect of added trichlorophenol on molecular weight of polymer at complete reaction at 70° in benzene. Initial reactant concentration: 50 g/l. (0.08 *M*).

in the polymers and possibly partly due to restricted segment motion in these highly branched molecules.

Polymers resulting from decompositions of 3 and 4 were substantially more linear than those from 1 and 2 as indicated by their nmr spectra (Figure 5b). The most intense line in the latter ($\tau$ 3.1) may be reasonably assigned to the protons of 2,6-dichloro-1,4-phenylene oxide units. The lower field doublet ($\tau$ 2.46) is assigned to the 5-proton of 4-bromo-2-chloro-1,6-phenylene oxide units. A second doublet due to the 3-proton is presumably obscured at $\tau$ 2.8. The higher field lines are assigned to branch units of the kind 5 and 6.



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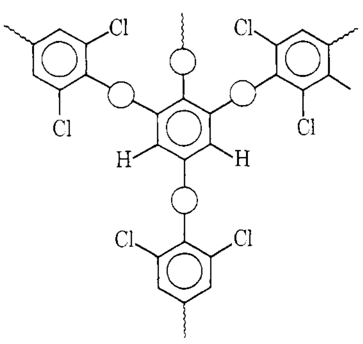


6

Chemical analysis of the polymers from 3 and 4 showed that they contained *ca.* 8% bromine and 38% chlorine, corresponding to a Br:Cl ratio of *ca.* 1:10. The copper complexes from decomposition of 3 contained *ca.* 4% chlorine and 36% bromine corresponding to a Cl:Br ratio of 1:4. Far-infrared spectroscopy showed these products to be a mixture of dichloro- and dibromobis(pyridine)copper(II).

The nmr spectrum of a polymer prepared by decomposition of bis(4-iodo-2,6-dichlorophenoxo)bis(pyridine)copper(II) (7) was very similar to that of the polymer derived from 3 or 4 (Figure 5c). Integration of this nmr spectrum indicated a branch to linear unit ratio of 1:10 and a selectivity for 1,4 relative to 1,1 coupling of 2:1. Both of the latter values are virtually the same as for polymers from 3 or 4. Chemical analysis of the iodo polymer showed the presence of 14% iodine and 20% chlorine, corresponding to an I:Cl ratio of 1:5.

The intrinsic viscosities of several polymers prepared in the present study are summarized in Table II.

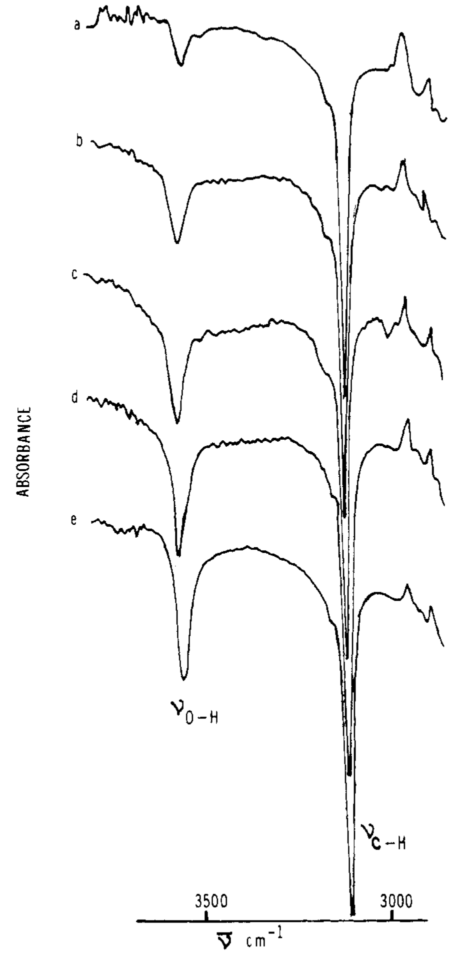


Figure 4. Infrared spectra of polymers prepared in the presence of varying amounts of added trichlorophenol. [$C_6H_3Cl_3O$]: (a) none, (b) 0.0125 *M*, (c) 0.015 *M*, (d) 0.0375 *M*, (e) 0.05 *M*. Polymers derived from same reactions as data of Figure 3.

The infrared spectra of 20 polymer samples, produced by decomposition of 1 or 2, with molecular weights in the range 10,000–150,000 were measured. No detectable difference was discernible between these spectra in the range 3000–475 cm$^{-1}$.

The infrared spectra of polymers from 1 and 2 exhibit a very strong band at 770 cm$^{-1}$ which is completely absent from the polymers derived from 3 and 4. The band is presumably characteristic of the 2,4-dichloro units in the polymers from 1 and 2. The 770-cm$^{-1}$ band is also absent from polymer derived from 7. The infrared spectra of polymers from 3, 4, and 7 showed only minor differences from each other.

## Discussion

**Polymerization Mechanism.** The polymerization mechanism has been discussed in detail in a preceding paper.[6] The evidence for the participation of phenoxy radicals is overwhelming. Further evidence suggests that these radicals react rapidly with phenoxocopper(II) species to produce quinol ethers and copper(I) intermediates, which subsequently abstract halogen from the quinol ether to regenerate phenoxy radical and yield product halocopper(II). All of the results reported in the present paper find ready explanation in terms of the above mechanism, and indeed may be taken as added confirmation of certain aspects.

**Polymer Molecular Weights.** It is evident, from the present study, that advantage may be taken of several experimental variables to augment the molecular weights of polymers produced by decomposition of phenoxocopper complexes. The key variables which control molecular weight are reactant concentration, reaction time, autox-

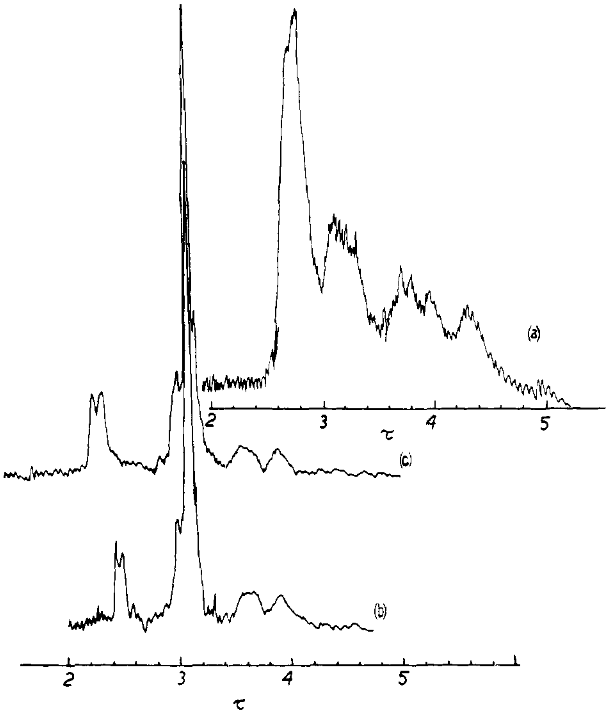
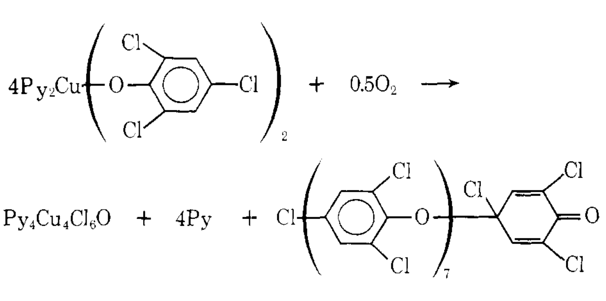


**Figure 5.** Nmr spectra of polymers derived from decompositions of (a) trichlorophenoxo, (b) 4-bromo-2,6-dichlorophenoxo, and (c) 4-iodo-2,6-dichlorophenoxo complexes.

idation behavior of the solvent, hydrogen-transfer properties of the solvent, or impurities, and the nature of the halogen substituents on the phenol.

Since the degree of polymerization is proportional to the square root of reactant concentration, there is little to be gained by going beyond the higher concentrations used in the present study. The same may be said for the time of reaction.

The effect of solvent autoxidation is very complicated. The dramatic effect of solvent autoxidation on the nature of the copper complex product has been reported in detail previously.[7] In cumene, the product of decomposition of 1 is entirely $\mu_4$-oxo-$\mu$-hexachlorotetrakis[pyridinecopper(II)]. A reaction of the stoichiometry shown in eq 1 would lead to polymer with average degree of polymerization equal to eight. This is far lower than the experimentally observed value of *ca.* 80 and there must clearly be organic radicals involved in the autoxidation cycle which are capable of propagating polymer chains by chlorine abstraction. Without more detailed knowledge of these processes, it is not possible to decide whether the reduction in molecular weight observed on changing from benzene to cumene as reaction solvent is due to diminished capacity to scavenge halogen in the propagation step, or to increased activity of the solvent as a hydrogen-transfer agent.

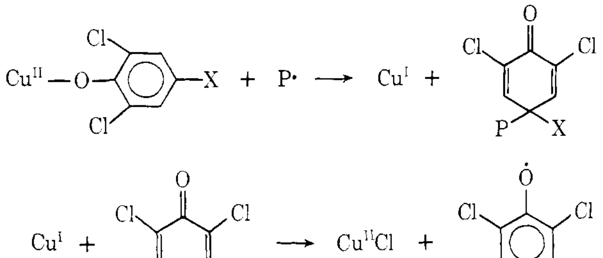


(1)

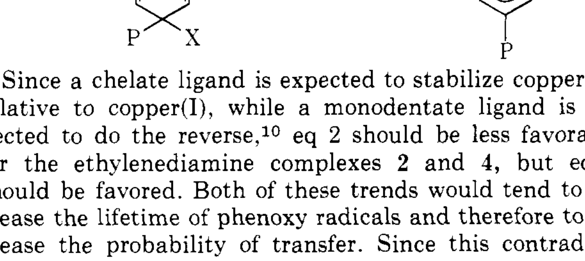
The effect of added trichlorophenol on the $\bar{M}_n$ of polymer produced by decomposition of 1 is almost certainly an example of hydrogen atom transfer. That hydrogen atom transfer can occur between phenols and phenoxy radicals is well established.[8] If it is assumed that molecular weight is limited only by transfer and that the reactant complex was contaminated by *ca.* 2% of free trichlorophenol, the data from Figure 3 in a log-log plot give a good straight line with a negative slope close to unity. Although not conclusive, this does suggest that transfer due to impurities is more important than kinetic termination in determining molecular weight under the conditions used in the present work.

Another illustration of the importance of hydrogen transfer in these reactions is the failure to produce polymer in certain ether solvents. For example, decomposition of 1 in air-free tetrahydrofuran yields trichlorophenol and a copper(I)-phenoxo complex.[9] Although the details of this reaction have not been elucidated, it is most likely that hydrogen transfer from solvent is so fast that phenoxy radicals are too short-lived to propagate.

The molecular weights of the polymers produced in this work were very insensitive to the rate of initiation. Thus, although the induction period for decomposition of 1 in benzene at 70° was reduced from 90 to 0 min by addition of a trace of $CBr_4$, the molecular weights of the polymers were identical. The same was true for reactions accelerated by free-radical initiators. The reasons for the higher molecular weights obtained by decomposition of 2, 3, and 4, relative to 1, must be related to an increase in propagation efficiency relative to transfer, or to radical chain termination. Since, to a first approximation, the propagating radicals are the same in all four cases, the difference must occur in the rate at which these radicals attack the coordinated phenoxide ligand (eq 2, $P\cdot$ = polymer radical), or the rate at which the copper(I) intermediate abstracts halogen from the quinol ether (eq 3). If transfer is the dominant molecular weight limiting process, eq 2 is critical. If a hitherto unidentified radical termination is dominant, either eq 2 or 3 may be critical. In view of the overall greater reactivity of 3 relative to 1, it is easy to reconcile the high molecular weights obtained from 3 with the greater reactivity of a bromine, relative to a chlorine, in both reactions 2 and 3. This is not the case with complexes 2 and 4, which show a much lower reactivity than their pyridine analogs.



(2)



(3)

Since a chelate ligand is expected to stabilize copper(II) relative to copper(I), while a monodentate ligand is expected to do the reverse,[10] eq 2 should be less favorable for the ethylenediamine complexes 2 and 4, but eq 3 should be favored. Both of these trends would tend to increase the lifetime of phenoxy radicals and therefore to increase the probability of transfer. Since this contradicts the experimental molecular weight evidence, we are inclined to favor the alternative possibility that the complexes 2 and 4 are less susceptible to hydrolysis, or more

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(8) L. R. Mahoney and M. A. Darooge, *J. Amer. Chem. Soc.*, 92, 890 (1970).

(9) J. F. Harrod, unpublished results.

(10) B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 2007 (1961).

**Table II**
**Intrinsic Viscosities of Poly(phenylene oxides)**

| Reactant | Reaction Solvent | $[\eta]$[a] | $\bar{M}_n$[b] |
|---|---|---|---|
| 1 | Benzene | 0.038 | 26,000 |
| 1 | Benzene | 0.054 | 34,000 |
| 1 | Benzene | 0.054 | 47,000 |
| 1 | Benzene | 0.066 | 54,000 |
| 1 | Benzene | 0.073 | 61,000 |
| 1 | Benzene | 0.073 | 69,000 |
| 1 | Toluene | 0.043 | 39,000 |
| 2 | Toluene | 0.112 | 130,000 |
| 2 | Benzene | 0.112 | 126,000 |

[a] In $CH_2Cl_2$ at 25°. [b] Toluene at 30°.

efficiently separated from phenol by recrystallization, and thus less contaminated with free phenol.

**Degree of Branching in Polymers.** It has long been concluded that the polymers resulting from dehalogenation of trihalophenoxides are highly branched. This fact is supported by the anomalously low intrinsic viscosities, such as those reported in Table II. Although branching is also evident from the nmr spectra of these polymers, the spectra have not been unequivocally interpreted because of their complexity and poor resolution. The chemical shifts in these polymers are also variable, depending on the method of synthesis and history of the material. This is perhaps due to the variability of the residual free radical concentration. These free radicals are detectable by esr and are in much higher concentration in polymers from **1** and **2** than from **3** and **4**, or **7**. The latter polymers give sharp spectra that may be assigned with little equivocation. It is also quite evident that **7** gives polymer with both the same branching ratio and the same positional selectivity for coupling, as do **3** and **4**. The branching ratio of 1:10 for these polymers is probably still too high for them to have useful physical properties.

The nmr spectra of polymers from **1** and **2** are quite dramatically different from those described above. Although unequivocal assignment of these spectra has not been effected, it may be reasonably assumed that the higher field peaks are due to branch units, by analogy with polymers from **3**, **4**, and **7**. Given this assumption, it is evident that the branching ratio for these polymers is very high (*ca.* 1:3). Examination of models of branch units such as **5** and **6** makes it very evident that motion of the benzene rings involved in the branch is severely hindered. It is probable that at very high branching ratios all segmental motions are restricted and that this contributes to the considerable line-broadening evident in Figure 5a.

A synthesis of linear polymer by initiation of sodium 4-bromo-2,6-dichlorophenoxide decomposition with benzoyl peroxide was described by Stamatoff.[5] This polymer was reported to contain 1.1% by weight of Br. Linearity was confirmed by nmr, although no nmr spectra were reported. A polymer prepared in our laboratory according to the recipe of Stamatoff gave a nmr spectrum identical with that shown in Figure 5b. The reason for this difference in behaviour is not presently understood, but it may be due to lack of control of some unidentified parameter to which branching is highly sensitive.

One of the notable features of the reactions of the present study is the complete insensitivity of the polymer structure to any reaction parameter other than the chemical nature of the phenoxide ligand. The infrared and nmr spectra of some 20 different samples of polymers from decompositions of **1** and **2** under a wide range of reaction conditions showed no detectable differences, with the exception of changes in the -OH vibration region referred to above.

It is evident that the production of structurally perfect poly(2,6-dichloro-1,4-phenylene oxide) by the present method requires a much better ligand-transfer leaving group at the 4 position, or more selective steric blocking by the neutral ligand. Work to achieve this goal is presently continuing in this laboratory.

## Experimental Section

All of the phenoxocopper complexes used in this work were prepared by precipitation from aqueous solution as described previously.[11] Complexes were purified by repeated recrystallization from benzene-hexane mixtures in a dry atmosphere. Decomposition of complexes during recrystallization was inhibited by addition of a small amount of pyridine to the recrystallization mixture.

Solvents were refluxed over calcium hydride, distilled, and stored over molecular sieves.

Decompositions were carried out in lightly stoppered erlenmeyer flasks, immersed in a constant-temperature bath. The insoluble product–copper complexes were collected by filtration and the polymer was recovered from the filtrate by slow addition to a large excess of methanol containing hydrochloric acid. Polymers were reprecipitated several times from toluene before drying under high vacuum.

Polymers derived from 4-bromo-2,6-dichlorophenol were not completely soluble in the reaction media at room temperature and were removed from the product-copper complexes by repeated extraction with boiling toluene.

**Characterization of Polymers and Product Complexes.** The number-average molecular weights of polymers were determined by either vapor pressure osmometry (VPO), or by membrane osmometry. VPO was used for polymers of $\bar{M}_n \leq 20{,}000$. Measurements were made on benzene solutions at 25° with a Hewlett-Packard 301A osmometer, calibrated with a monodisperse polystyrene standard ($\bar{M}_n = 10{,}300$) supplied by Pressure Chemical Co. The instrument was checked for accuracy with a variety of polymers of known $\bar{M}_n$. The reproducibility was found to range from ±1% for $\bar{M}_n \sim 1000$ to ±10% for $\bar{M}_n \sim 20{,}000$.

Samples of $\bar{M}_n > 20{,}000$ were examined by membrane osmometry, using a Hewlett-Packard 502 high-speed membrane osmometer. The apparatus was fitted with 0-6 Schleicher and Schuell membranes and was operated with toluene solvent at 30°.

The instrument was calibrated with a monodisperse polystyrene standard ($\bar{M}_n = 50{,}000$) supplied by Pressure Chemical Co. Measurements on samples of known molecular weight indicated that measurements were reproducible to ±2% in the range 50,000-150,000. At the lower limit (~20,000) the branched polymers prepared in the present study diffused rather rapidly through the membranes and the $\bar{M}_n$ in this region is of much lower reproducibility (*ca.* ±10%).

Nmr spectra of polymers were measured as concentrated solutions in $CS_2$. Spectra were measured on Varian T60 and Varian HA100 spectrometers, but not much difference in quality of spectra was observed between the two instruments.

Infrared spectra of polymers were measured as dilute solutions in $CS_2$ ($\nu_{O\text{-}H}$ region), or dispersed in KBr disks, using a Perkin-Elmer 257 spectrometer. Spectra of complexes were measured in KBr disks (4000-625 $cm^{-1}$), or, for the far-infrared region, in Nujol mulls on polyethylene plates, with a Perkin-Elmer FIS-3 spectrometer. Mixtures of $Py_2CuCl_2$ and $Py_2CuBr_2$ were identified by absorptions at 235 and 178 $cm^{-1}$ (chloride) and 255 and 128 $cm^{-1}$ (bromide).

**Acknowledgment.** Financial support for this work from the National Research Council of Canada is gratefully acknowledged.

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(11) J. F. Harrod, *Can. J. Chem.*, **47**, 637 (1969).