Table IV
Copolymerization of 4-Hydroxybenzenesulfonyl Chloride (I) and 3,5-Dimethyl-4-hydroxybenzenesulfonyl Chloride(II)

| Mol % I | $\eta_{inh}$[b] | $T_g$ (°C) | $T_m$ (°C)[c] |
|---|---|---|---|
| 100 | 0.76 | 117 | 277 |
| 75 | 0.76 | 130 | (255) |
| 50 | 0.74 | 135 | (180) |
| 25 | 0.71 | 148 | (190) |
| 0 | 0.79 | 153 | (250) |

[a] Polymerizations carried out in HMP at 0° using 1.5 equiv of triethylamine. [b] Inherent viscosities measured as 0.5% solutions in HMP at 30°. [c] Values shown in parentheses are polymer melt temperatures, determined on a bar with a temperature gradient, for polymers which show no melting by dta.

## Experimental Section

**Reagents and Monomers.** 4-Hydroxybenzenesulfonyl chloride (I) was prepared from the reaction of sodium 4-hydroxybenzenesulfonate with thionyl chloride in the presence of a catalytic amount of DMF carried out at 60°.[5] Sodium 3,5-dimethyl-4-hydroxybenzenesulfonate was prepared from 2,6-dimethylphenol according to the method of Karrer and Leiser[14] using sulfuric acid monohydrate at 100-110°. 3,5-Dimethyl-4-hydroxybenzenesulfonyl chloride (II) was prepared from the sulfonate salt by treatment with thionyl chloride in DMF solvent.[3] The tertiary amines were distilled from potassium hydroxide and stored under nitrogen over potassium hydroxide. Solvents were purified in the usual manner and stored under nitrogen.

**Solution Polymerization.** The reactions were carried out in a dry environment under $N_2$ with stirring. The base was usually added to a solution of the sulfonyl chloride. A nonsolvent for the polymer was added after the reaction was complete and the products were thoroughly washed and dried.

**Poly(1,4-phenylenesulfonate).** To a stirred solution of 1.93 g (10 mmol) of I in 10 ml of HMP under a nitrogen atmosphere was quickly added 1.26 g (12.5 mmol) of triethylamine at 0°. A bright yellow color was produced immediately which faded in 30 sec as the solution became viscous. After stirring 6 min at 0°, the polymer was precipitated by the addition of 200 ml of water with vigorous stirring. The polymer was collected by filtration and washed on the filter with 200 ml of water and 200 ml of methanol. It was washed by stirring thoroughly in water (300 ml), methanol (3 × 200 ml) and refluxing acetone (2 × 200 ml). After drying in a vacuum oven at 70°, 1.29 g (83%) of white polymer was obtained, inherent viscosity 0.97 (0.5 g/dl of HMP solution at 30°).

*Anal.* Calcd for $C_6H_4O_3S$: C, 46.1; H, 2.6; S, 20.5. Found: C, 46.0; H, 2.7; S, 20.5.

**Melt Polymerization of I.** In a small glass reactor was placed 5.5 g (28.6 mmol) of I. Air was removed by alternately pressuring with nitrogen (10 psig) and evacuating. The system was heated at 90-100° for 2 hr with nitrogen being bubbled through the melt and the pressure maintained at 3.5 mm of Hg. After heating 2 additional hr at 100-160°, the reaction mixture solidified. At 250° it remelted and the dark, viscous liquid was heated at 250-275° for one hour. The system was cooled to room temperature under $N_2$, yielding 3.6 g (82%) of a glassy solid which showed no crystallinity by DTA, inherent viscosity 0.33 (0.5 g/dl of NMP solution at 30°): ir (film) 2.9-4.0 $\mu$ (OH), 7.3 and 8.6 $\mu$ ($SO_2$); nmr ($CDCl_3$) $\delta$ 7.12 (s, OH), 7.40 (d, $J$ = 9 Hz, protons ortho to OH), 7.8-8.4 (m, protons ortho to $SO_2$).

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# Isomerization Polymerization of 1,3-Oxazine. I. Polymerization of Unsubstituted 5,6-Dihydro-4*H*-1,3-oxazine Giving Poly(*N*-formyltrimethylenimine) and Its Alkaline Hydrolysis to Poly(trimethylenimine)

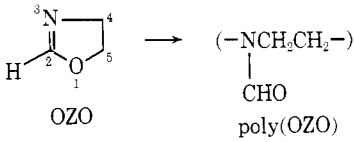
**Takeo Saegusa,* Yoshitomi Nagura, and Shiro Kobayashi**

*Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan.*

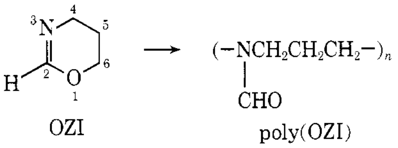
*Received December 19, 1972*

ABSTRACT: Unsubstituted 5,6-dihydro-4*H*-1,3-oxazine (OZI) is synthesized for the first time by the reaction of 3-aminopropanol with *tert*-butyl isocyanide catalyzed by AgCN. OZI was found to polymerize by various cationic initiators such as dimethyl sulfate, concentrated $H_2SO_4$, boron trifluoride etherate, ethyl trifluoromethanesulfonate, methyl tosylate, and methyl iodide. The polymer structure of poly(*N*-formyltrimethylenimine) (poly(OZI)) was established by ir and nmr spectra. The polymer was a white solid, melting point about 120°, which is soluble in water at room temperature and in polar solvents such as dimethylformamide, acetonitrile and methanol when warmed up. The solid polymer was shown to be partially crystalline by X-ray diffraction analysis. The alkaline hydrolysis of poly(OZI) gave slightly crystalline linear poly(trimethylenimine). This is the first time the linear poly(trimethylenimine) has been prepared.

Recently, we have reported for the first time the isomerization polymerization of unsubstituted 2-oxazoline (OZO), a five-member cyclic imino ether to give poly(*N*-formylethylenimine) (poly(OZO)) (eq 1).[1-4] The alkaline hydrolysis of the polymer has provided a new synthetic method of preparing poly(ethylenimine) with no branching.[3] These interesting new findings prompted us to examine the polymerization of 5,6-dihydro-4*H*-1,3-oxazine (OZI). Although several 2-substituted oxazines have been polymerized at elevated temperatures by cationic initiators to polymers having the structure of poly(*N*-acyltrimethylenimine),[5] the polymerization of unsubstituted



(1)



(2)

1,3-oxazine has not been reported so far, and even the OZI

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(1) T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, 3, 35 (1972).

(2) T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, 3, 176 (1972).

(3) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, 5, 359 (1972).

(4) T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, in press.

(5) A. Levy and M. Litt, *Polym. Lett.*, 5, 881 (1967).

Table I
**Polymerization of 5,6-Dihydro-4*H*-1,3-oxazine (OZI)[a]**

| Run No. | Initiator | Time (hr) | Polymer Yield (%) | Polymer Mol Wt | Mp[b] (°C) |
|---|---|---|---|---|---|
| 1 | $Me_2SO_4$ | 5 | 32.9 | 900 | 105–108 |
| 2 | $BF_3 \cdot OEt_2$ | 5 | 22.3 | | |
| 3 | EtOTf | 5 | 24.4 | 850 | 109–111 |
| 4 | Concentrated $H_2SO_4$ | 5 | 16.6 | | |
| 5 | MeOTs | 5 | 40.8 | 1270 | 109–114 |
| 6 | MeOTs | 24 | 57.8 | 2670 | 121–122 |
| 7 | MeOTs[c] | 24 | 66.6 | 2600 | 124–126 |
| 8 | MeOTs | 5 | 59.1 | 2580 | 113–117 |
| 9 | MeOTs[d] | 24 | 35.8 | 4160 | 119–123 |
| 10 | MeOTs[e] | 72 | 67.4 | 3440 | 120–123 |
| 11 | MeI | 5 | 79.0 | 4840 | 121–124 |

[a] OZI, 3.25–22.5 mmol; initiator, 0.02 mmol/mmol of OZI; dimethylformamide, 0.266 ml/mmol of OZI; at 80°. Purity of OZI; 98.6% for runs 1–7 and >99.9% for runs 8–11. Purity of OZI was determined by glpc analysis. [b] All melting points were measured in sealed capillary tubes. [c] Solvent, $CH_3CN$. [d] Initiator, 0.01 mmol/mmol of OZI. [e] Reaction at 50°.

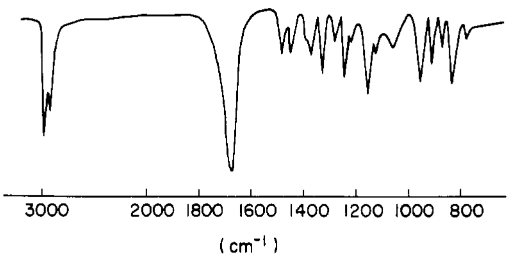


Figure 1. Ir spectrum of 5,6-dihydro-4*H*-1,3-oxazine (OZI) (neat).

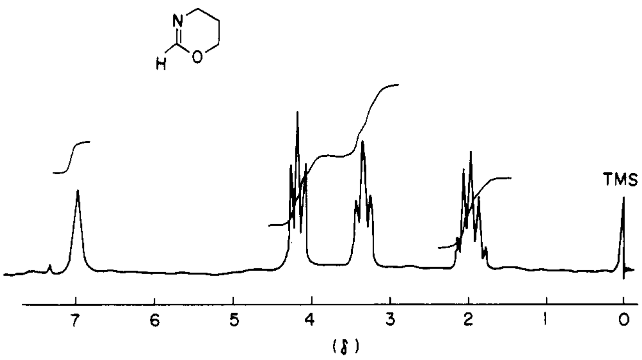


Figure 2. Nmr spectrum of 5,6-dihydro-4*H*-1,3-oxazine (OZI) (in $CDCl_3$).

monomer itself has been an unknown compound until we recently succeeded first in the preparation of OZI[6]. The present paper deals with the preparation and polymerization of OZI, and the alkaline hydrolysis of the product polymer to poly(trimethylenimine).

## Experimental Section

**Reagents.** Ethyl formate, *tert*-butylamine, *n*-pentane, pyridine, diethyl ether, $CD_3OD$, $POCl_3$, and AgCN are commercial reagents and were used without purification. 3-Aminopropanol, methyl tosylate (MeOTs), dimethyl sulfate ($Me_2SO_4$), methyl iodide (MeI), and $BF_3 \cdot OEt_2$ were purified by distillation under nitrogen before use. Dimethylformamide and acetonitrile were dried on molecular sieves 4A (Union Carbide) and then distilled under nitrogen. Ethyl trifluoromethanesulfonate (EtOTf) was prepared by the reaction of $Et_2SO_4$ with $CF_3SO_3H$, bp 115° (lit.[7] bp 115°). *tert*-Butyl isocyanide (*t*-BuNC) was prepared by dehydration of *N*-*tert*-butylformamide with $POCl_3$ according to Ugi's procedure.[8]

**Preparation of OZI.** The mixture of 0.62 mol (46.5 g) of 3-aminopropanol, 0.74 mol (61.4 g) of *t*-BuNC, and 0.031 mol (4.15 g) of AgCN was stirred at 80–90° for 3 hr under nitrogen. Then, the reaction mixture was subjected to vacuum distillation to give 35 g (66% yield) of OZI. OZI was further purified by repeated distillation and kept on molecular sieves 4A under nitrogen, bp 54–56° (56 mm). *Anal.* Calcd for $C_4H_7NO$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.66; H, 8.44; N, 16.80.

**Polymerization of OZI.** Polymerization was carried out under dry nitrogen in a sealed tube using dimethylformamide or $CH_3CN$ as solvent. The polymerization reaction proceeded homogeneously. After polymerization, an excess amount of methanol was added to the reaction mixture and volatile materials were evaporated under reduced pressure at 50°. The residue gave polymer, which was dissolved in methanol and precipitated by pouring the methanol solution into diethyl ether. Purification by reprecipitation was repeated twice and the polymer was dried *in vacuo* at 130°. *Anal.* Calcd for $C_4H_7NO$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.48; H, 8.43; N, 16.15. Other details may be found in Table I.

**Alkaline Hydrolysis of Poly(OZI).** To 10 ml of 50% aqueous methanol, 0.725 g of poly(OZI) (mol wt 2670 by vapor pressure osmometer) and 0.60 g of NaOH were dissolved. The homogeneous solution was stirred at 95° for 3 hr. A pale yellowish solid precipitated at the end of the reaction. The precipitate was washed throughly with water and purified by reprecipitation twice with about 2 ml of methanol (solvent)-large excess amount of diethyl ether (precipitant) system. Then, it was dried *in vacuo* at 90° to give 0.334 g (69%) of poly(trimethylenimine). *Anal.* Calcd for $C_3H_7N \cdot (H_2O)_{0.32}$: C, 57.23; H, 12.24; N, 22.24. Found: C, 57.52; H, 11.96; N, 21.91.

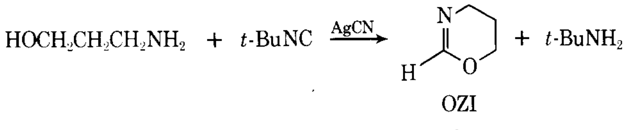
**Nmr Measurement.** All nmr spectra were taken on Hitachi R-24 or R-20B spectrometer in $CDCl_3$ using $Me_4Si$ as an internal standard, in $CD_3OD$ using $CHCl_3$ as an internal standard, and in $D_2O$ using $Me_4Si$ as an external standard.

**Molecular Weight Determination.** The molecular weight of the polymer was measured by a vapor pressure osmometer (Hitachi Perkin-Elmer Model 115) in dimethylformamide at 55°.

**X-Ray Diffraction.** X-Ray diffraction spectra of the powdery polymer were taken by using Rigaku Denki Model SC-10.

## Results and Discussion

**Preparation of OZI.** Some 2-substituted 5,6-dihydro-4*H*-1,3-oxazines were prepared by cyclodehydrochlorination of *N*-(3-chloropropyl)amides or by cyclodehydration of *N*-(3-hydroxypropyl)amides, and these 1,3-oxazines were found to be polymerized.[5] Synthesis of unsubstituted 5,6-dihydro-4*H*-1,3-oxazine (OZI), however, has long been unsuccessful. Recently, we have found a novel method to synthesize OZI, in which a single-step reaction of 3-hydroxypropylamine with *t*-BuNC in the presence of AgCN catalyst produced OZI in high yield. The details of this method will be described elsewhere.[6] It is necessary for the polymerization to prepare the monomer of high purity. Fortunately, the above reaction was clean and selective. The purification of OZI was successfully accomplished by repeated fractional distillation.



The ir and nmr spectra of OZI are shown in Figures 1 and 2, respectively. The ir spectrum shows bands at 1650 cm$^{-1}$ (>C=N-), 1150 cm$^{-1}$ (C-O-C) and 1125 and 1040 cm$^{-1}$ (skeletal), which are at lower frequencies compared with the corresponding absorption bands of 2-alkyl- or aryl-substituted OZI.[5] A similar observation was already noted also in the case between unsubstituted and 2-substituted 2-oxazolines.[1] The nmr spectrum exhibits a formyl proton (singlet at δ 7.02, 1 H), *O*-methylene protons

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(6) Y. Ito, Y. Inubushi, M. Zenbayashi, S. Tomita, and T. Saegusa, *J. Amer. Chem. Soc.*, in press.

(7) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 173 (1956).

(8) I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).

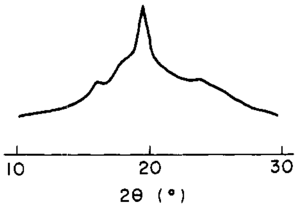


**Figure 3.** X-Ray diffraction diagram of poly(*N*-formyltrimethylenimine).

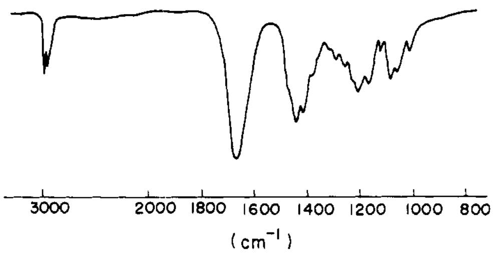


**Figure 4.** Ir spectrum of poly(*N*-formyltrimethylenimine) (KBr).

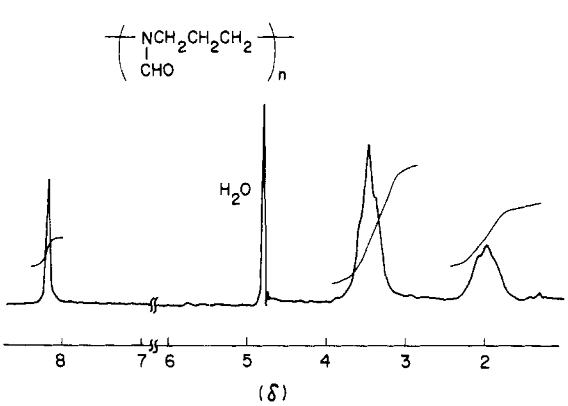


**Figure 5.** Nmr spectrum of poly(*N*-formyltrimethylenimine) (in $D_2O$).

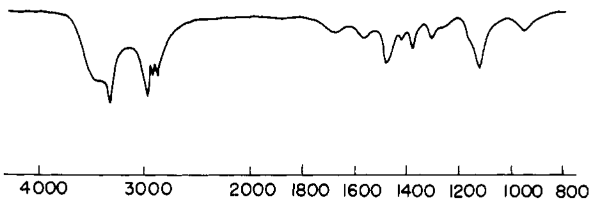


**Figure 6.** Ir spectrum of poly(trimethylenimine) (KBr).

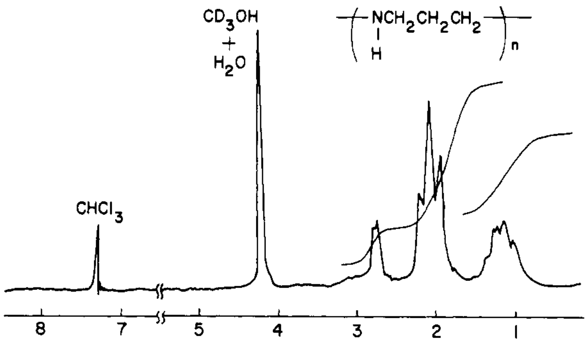


**Figure 7.** Nmr spectrum of poly(trimethylenimine) (in $CD_3OD$).

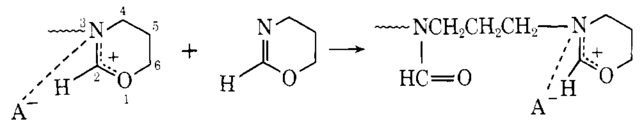
(triplet centered at $\delta$ 4.17, 2 H), *N*-methylene protons (triplet at $\delta$ 3.36, 2 H) and *C*-methylene protons (quintet centered at $\delta$ 1.95, 2 H), respectively.

**Polymerization of OZI.** The polymerization of OZI was successfully performed by various cationic initiators as shown in Table I. Because dimethylformamide and acetonitrile were found to be good solvents for the polymerization of OZO,[1] they were used as solvent also in the present study. All of the reactions proceeded in homogeneous systems, which was interestingly compared with the OZO polymerization where the polymer precipitated in all cases.[1]

Typical cationic initiators such as $BF_3 \cdot OEt_2$ and concentrated $H_2SO_4$ gave gummy polymers, whereas alkylating agent initiators such as $Me_2SO_4$, EtOTf, MeOTs, and MeI gave solid polymers. The molecular weight and polymer yield increased when the reaction time was prolonged. Monomers of higher purity gave higher molecular weight polymers and higher yields (expt 8-11). The polymerization of OZI is characterized by its higher reactivity in comparison with that of 2-substituted monomers, *e.g.*, OZI polymerized readily at 50°, whereas the polymerization of 2-alkyl- and aryl-substituted monomers were carried out at elevated temperatures, at least at 130°.[5]

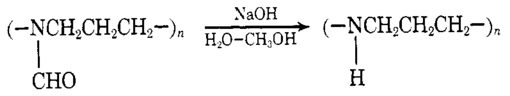
**Characterization of Polymer.** The OZI polymer is a white solid melting *ca.* 120° and was shown to be partially crystalline by its X-ray diffraction spectrum (Figure 3). Based on the ir and nmr spectra, the polymer structure of poly(*N*-formyltrimethylenimine) (poly(OZI)) was established. The ir spectrum of the polymer (Figure 4) has a characteristic band of amide group at 1660 cm$^{-1}$ (>N–CH=O). Its nmr spectrum (Figure 5) shows a singlet at $\delta$ 8.14 (formyl proton, 1 H), a triplet-like broad signal centered at $\delta$ 3.44 (*N*-methylene protons, 4 H) and a broad signal centered at $\delta$ 1.94 (*C*-methylene protons, 2 H).

All the above data have led reasonably to the structure of poly(*N*-formyltrimethylenimine) (eq 2). The formation of this type of polymer indicates that OZI undergoes the cationic ring cleavage at the $C_6$–O bond followed by isomerization to the amide in a similar manner to the polymerization OZO.[2] Furthermore, the alkaline hydrolysis of the polymer provided additional evidence for the proposed structure (*vide infra*).



The polymer was soluble in water at room temperature and also in organic solvents such as dimethylformamide, acetonitrile and methanol when warmed to about 60°. This solubility character is quite different from that of poly(OZO). Poly(OZO) is soluble only in water and insoluble in most organic solvents.[1]

**Alkaline Hydrolysis of Poly(OZI).** The alkaline hydrolysis of poly(OZI) proceeded readily in 50 vol % aqueous methanol solution of NaOH at 95°. After 3 hr the reaction was complete and a solid precipitated (see Experimental Section). The ir and nmr spectra of the solid are shown in Figures 6 and 7, respectively. The nmr spectrum was taken in $CD_3OD$ using $CHCl_3$ as an internal standard. The ir spectrum shows bands at 3250 ($\nu_{NH}$), 1550 ($\delta_{NH}$), 1480 ($\delta_{CH_2}$), 1115 ($\nu_{C-N}$), and 3400 cm$^{-1}$ ($\nu_{OH}$) due to water of crystallization. The nmr spectrum possesses a broad singlet at $\delta$ 2.73 (N proton, 1 H), a triplet centered at $\delta$ 2.07 (*N*-methylene protons, 4 H), and a broad multiplet centered at $\delta$ 1.20 (*C*-methylene protons, 2 H). A sharp singlet at $\delta$ 4.80 also indicates that the polymer contains water of crystallization. These spectral data confirm the poly(trimethylenimine) structure for the hydrolyzed polymer. So far as we know this is the first report on the preparation of linear poly(trimethylenimine).



$$(-\underset{\text{CHO}}{\underset{|}{\text{N}}}CH_2CH_2CH_2-)_n \xrightarrow[H_2O-CH_3OH]{NaOH} (-\underset{\text{H}}{\underset{|}{\text{N}}}CH_2CH_2CH_2-)_n$$

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)

**B. G. Carr, J. F. Harrod,* and P. van Gheluwe**

*Chemistry Department, McGill University, Montreal, Canada.*

*Received February 15, 1973*

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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