Effect of *N*-Methylimidazole and 3,5-Dimethylpyrazole Ligands on the Polymerization of Di(2,6-dichlorophenolato) Cu(II)/Co(II) Complexes in the Solid State

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ABSTRACT: The polymerization of 2,6-dichlorophenol (DCPH) was achieved through the thermal decomposition of copper complexes of DCPH with *N*-methylimidazole (NMIz) and 3,5-dimethylpyrazole (DMPz) ligands. Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), mass spectrometry, ultraviolet–visible spectroscopy, diffuse reflectance spectroscopy, magnetic susceptibility balance, electron spin resonance, X-ray analysis, and elemental analysis were used to characterize the complexes. The polymerization was achieved either in the solid state or in the melt. The structural analyses were performed with FTIR and NMR spectroscopy analyses. The glass-transition temperatures were determined by DSC, and the intrinsic viscosities were determined by viscosimetry. The effects of the temperature and time on the conversion percentage and viscosity of the polymers were examined. Varying the decomposition temperature during a 3-h scan showed that the DMPz complex of Cu decomposed at lower temperatures than the NMIz complex, whereas the NMIz complex yielded a higher conversion to the polymer. Complexes of DCPH with NMIz and DMPz ligands produced 1,2- and 1,4-addition products, respectively. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3797–3805, 2004

**Key words:** solid-state polymerization; transition metal chemistry

INTRODUCTION

Poly(phenylene oxide)s are polyethers with aromatic groups connected by an oxygen linkage at the backbone. They can be linear or branched, amorphous or crystalline, and high-molecular-weight or low-molecular-weight, depending on the method of synthesis, the type of transition metal used in the precursor complex, the structure of the complex, and the ortho or para position of the alkyl or halogen substituent on the starting phenol. When ortho substituents on the phenols are relatively unhindered alkyl or aryl groups, poly(phenylene oxide) is the chief product. Bulky ortho substituents such as the *tert*-butyl group lead largely to the formation of 3,3′,5,5′-tetrasubstituted 4,4′-diphenoquinone. Phenols with fewer than two ortho substituents produce branched and colored polymers through the reaction occurring at the open ortho sites.[1]

2,4,6-Trihalophenols can be polymerized into poly-(dihalophenylene oxide)s by a reaction that resembles radical-initiated displacement polymerization. Polymerization is carried out either directly in the solution after 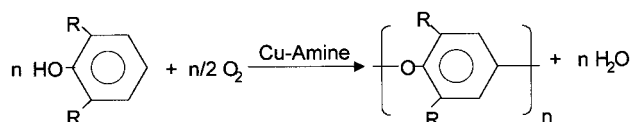the addition of all the species or by the decomposition of the isolated transition-metal complexes or inner transition-metal complexes of alkyl-substituted or trihalogenated phenols with neutral ligands. Initially, silver and copper, and more recently cobalt, nickel, and cerium, were used as transition and inner transition metals.[2–11]

The proposed reaction is as follows:

$$n\mathrm{M(OC_6H_2X_3)}_k\mathrm{L}_m \rightarrow n\mathrm{MX}_k\mathrm{L}_m + [\mathrm{-C_6H_2X_2O-}]_{n+k}$$

$$(1)$$
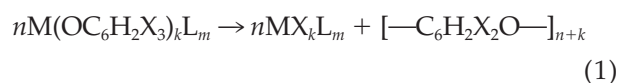
where M is the metal, L is the neutral ligand, and X is a halogen. Unhindered 4-halophenols (i.e., phenols without 2,6-disubstitution) do not polymerize under oxidative displacement conditions. Oxidative reactions at the ortho positions may consume the initiator or may interrupt the propagation step in the chain process. Hence, the more drastic conditions of Ullman ether synthesis are required.[12]

Many poly(phenylene oxide)s have been prepared in a one-step polymerization of 2,6-disubstituted phenols by oxidative coupling:[13,14]

where R is the alkyl group. Oxygen is passed through a vigorously stirred solution of the phenol and a catalyst at

about 25–50°C. A typical catalyst is composed of a copper halide and one or more aliphatic amines or pyridine (Py). The polymerization is exothermic and requires cooling to maintain the catalytic activity and to attain a high molecular weight. Poly(phenylene oxide)s are also prepared by the polymerization of 2,6-dichlorophenol (DCPH) in the presence of oxygen and a catalyst, which is a manganese, cobalt, copper, or nickel compound.[15,16]

Metal complexes have been observed to have a variety of structures. Copper(II)/N-ligand complexes[17–21] and N-ligand/transition-metal/phenolate complexes,[22–35] in which imidazoles and pyrazoles are used as the N-ligands, have been widely synthesized and characterized. Copper(II) complexes of the type L_nCu (phenolato)$_2$ (where L is a chelating N-ligand with $n = 1$ and a nonchelating N-ligand with $n = 2$ and phenolato is a phenolate substituted by halogens in the 2,4,6-positions or methoxy or nitro groups in the 2- or 4-positions)[24–28,31–36] are especially attractive because they are either studied as model systems for coordination in metalloproteins or decomposed to yield poly(dihalophenylene oxide)s.

In this investigation, the polymerization of 2,6-dichloro phenol through the solid-state thermal decomposition of the corresponding copper and cobalt complexes with N-methylimidazole (NMIz) and 3,5-dimethylpyrazole (DMPz) ligands was carried out to yield only one substituted halogen on the polymer chains [poly(chlorophenylene oxide)].

EXPERIMENTAL

Materials

DCPH was purchased from Merck and used without further purification. $CuSO_4 \cdot 5H_2O$, $CoSO_4 \cdot 7H_2O$, and NaOH were purchased from Merck and used for the preparation of the complexes. DMPz (Merck) was used as a ligand in the complexes. Toluene (Merck) was the solvent for the polymers. The ethyl alcohol (EtOH) that was used was a commercially available technical grade and was distilled before use as a nonsolvent for the polymer precipitation.

Preparation of the complexes

Complexes were prepared through the mixing of a solution containing 0.450 mol of NaOH, 0.450 mol of DCPH, and 0.450 mol of the N-ligand (NMIz or DMPz) in 900 mL of distilled water with a solution containing 0.225 mol of $MSO_4 \cdot XH_2O$ ($CuSO_4 \cdot 5H_2O$ for copper complexes and $CoSO_4 \cdot 7H_2O$ for cobalt complexes) in 900 mL of distilled water. After 2 h of vigorous stirring, the precipitated complex was filtered, washed with distilled water, and vacuum-dried to a constant weight. The general reaction for the complex formation is as follows:

$$2DCPH + 2NaOH + nN\text{-Ligand}$$
$$+ MSO_4XH_2O \rightarrow (DCP)_2M(N\text{-Ligand})_n \quad (2)$$
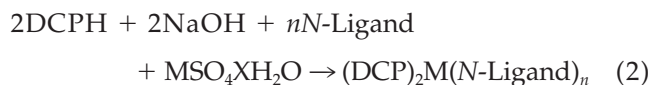
where M is Cu (X = 5) or Co (X = 7).

Characterization of the complexes

Carbon–hydrogen–nitrogen analyses (error limit = ±0.3%) of the complexes were carried out at the University College of Dublin Department of Chemistry (Dublin, Ireland) and with a Leco 932 CHNSO elemental analyzer instrument in Tübitak (Ankara, Turkey). The metal contents of the complexes were determined by standard complexometric titration (error limit = ±0.5%). A 50.0-mg sample was dissolved in a few drops of HNO_3, and the mixture was boiled until it was nearly dry to destroy the sample. This acidic sample was first dissolved in 100 cm^3 of distilled water, and then 10.0 cm^3 of a $0.0300M$ Na_2H_2EDTA solution was added. After the addition of the required amount of hexamethylethylenetetramine, the pH of the solution was adjusted to 5.10 by the addition of ammonia. The solution, containing a small amount of xylenol orange as a metal-ion indicator, was titrated with a $0.0300M$ $Zn(OAc)_2$ solution until the color changed from yellow to purple. The stoichiometry, abbreviations, and elemental analysis results for the complexes were as follows.

ELEM. ANAL. Calcd. for $(NMIz)_2Cu(DCP)_2$ (**C1**): N, 10.15%; C, 43.54%; H, 3.29%; O, 5.80%; Cl, 25.70%; M, 11.52%. Found: N, 10.36%; C, 43.55%; H, 3.30%; O, 5.44%; Cl, 25.85%; M, 11.5%.

ELEM. ANAL. Calcd. for $(DMPz)_2Cu(DCP)_2$ (**C2**): N, 9.66%; C, 45.57%; H, 3.82%; O, 5.52%; Cl, 24.46%; M, 10.96%. Found: N, 9.12%; C, 45.16%; H, 3.52%; O, 5.80%; Cl, 24.90%; M, 11.50%.

ELEM. ANAL. Calcd. for $(DMPz)_2Co(DCP)_2$ (**C3**): N, 9.74%; C, 45.94%; H, 3.86%; O, 5.56%; Cl, 24.65%; M, 10.25%. Found: N, 9.60%; C, 45.44%; H, 3.59%; O, 6.32%; Cl, 26.00%; M, 9.05%.

Infrared (IR) spectra were recorded on KBr discs with a PerkinElmer Paragon 1000 Fourier transform infrared (FTIR) spectrometer, a Nicolet 510 FTIR spectrometer, or a Shimadzu IR-470 IR spectrophotometer in the $4000–400$-cm^{-1} region.

Electronic spectra [ultraviolet–visible (UV–vis)] were taken in toluene in 10^{-4} and 10^{-3} mol/dm^3 solutions of copper and cobalt complexes, respectively, with a Hewlett–Packard 8452A diode array spectrophotometer. Absorption maxima (nm) and the corresponding molar absorptivity coefficients (L mol^{-1} cm^{-1}, in toluene) of the complexes were as follows: **C1**, 426 (1441); **C2**, 334 (1681), 380 (1538), and 500 (883); **C3**, 526 (371) and 604 (305).

Diffuse reflectance spectroscopy of **C1** was taken as the solid complex dispersed in a sample holder on a PerkinElmer 330 spectrometer with MgO as the reference.

TABLE I
MS Data for the C1 and C2

	Relative intensity (%)		
m/z	**C1**	**C2**	Assignment
42	804	137	C_2H_4N
54	569	141	C_3H_4N or C_2H_2N
63	468	1000	C_5H_3
73	104	195	C_3H_2Cl
81	1000	—	$C_4H_5N_2$
82	865	—	$C_4H_6N_2$, molecular ion $NMIz_2$
95	—	195	$C_5H_7N_2$
96	—	215	$C_5H_8N_2$, molecular ion DMPz
162	79	172	$C_6H_4Cl_2O$

A Sherwood Scientific MK I magnetic susceptibility balance was used to measure the magnetic susceptibilities of the complexes. The magnetic susceptibilities of the complexes were measured at room temperature, and magnetic moments (μ_{eff}) in a Bohr magneton were calculated. μ_{eff} values were found to be 1.81, 1.54, and 4.65 for **C1**, **C2**, and **C3**, respectively.

A JES-RE2X electron spin resonance (ESR) spectrometer from the JEOL RE series with a JEOL X-band microwave and a JEOL electromagnet equipped with a JEOL Esprit 330 ESR data system was used to take the ESR spectra of $0.100M$ **C1** in a toluene/methanol solvent mixture at the temperature of liquid N_2.

Determination of the thermal behavior of the complexes: polymer synthesis

The thermal behavior of the complexes at a scanning rate of 10°C/min for 10-mg samples was determined in air on a Thermal Analyst 2000 DSC 910S differential scanning calorimeter from DuPont.

Mass spectrometry (MS) data of the complexes were obtained with a Balzers QMG 311 quadruple mass spectrometer (heat in a tube furnace) with personal-computer control of the MS acquisition and analysis. MS data were recorded at a constant temperature of 150°C, a common decomposition temperature for the complexes.

A Stuart Scientific oven was used for the thermal decomposition of the complexes in the temperature range of 50–250°C with a temperature fluctuation of ±0.5°C. A 4.00-g sample of the complex in a glass sample holder (3.5 cm high and 3 cm in diameter) was inserted into an iron sample holder and allowed to stay in the oven for a given period of time at a given temperature. The decomposed complex was dissolved in toluene, and the insoluble residual complex was separated by filtration. Then, the polymer was precipitated with EtOH containing a few drops of HCl. The precipitated polymer was filtered, washed with EtOH, and dried *in vacuo* to a constant weight.

The thermal decomposition of **C1** and **C2** was performed at a constant temperature (200°C for **C1** and

130°C for **C2**) for different time intervals (3–48 h), or for a constant period of time (3 h) at different temperature ranges (140–250°C for **C1** and 90–200°C for **C2**). **C1** melted above 150°C, and **C2** partially melted above 110°C and melted above 200°C. The thermal decomposition of **C3** could not be achieved within the temperature range studied (up to 250°C). The conversion to the polymer and the weight loss was calculated for each decomposition set with the following equations:

$$\text{Conversion (\%)} = \frac{\text{Weight of the polymeric product}}{\text{Initial weight of the complex}} \times 100 \quad (3)$$

$$\text{Weight loss (\%)} = \frac{\begin{array}{c}\text{Initial weight of the complex} \\ - \text{ Weight of the decomposed complex}\end{array}}{\text{Initial weight of the complex}} \times 100 \quad (4)$$
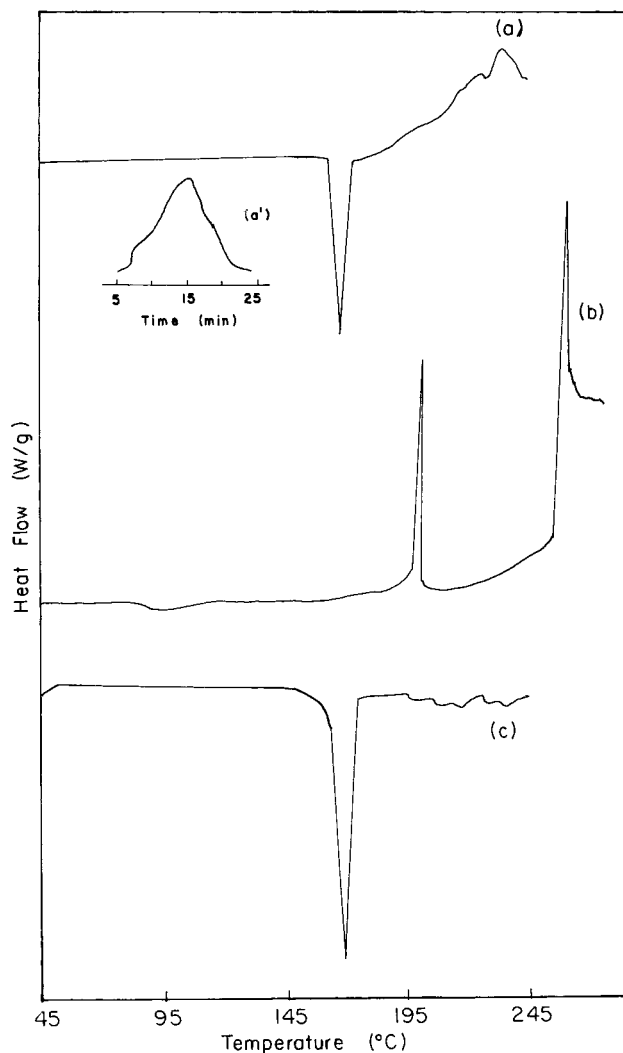

Figure 1 DSC thermograms of (a) **C1**, (b) **C2**, and (c) **C3**.
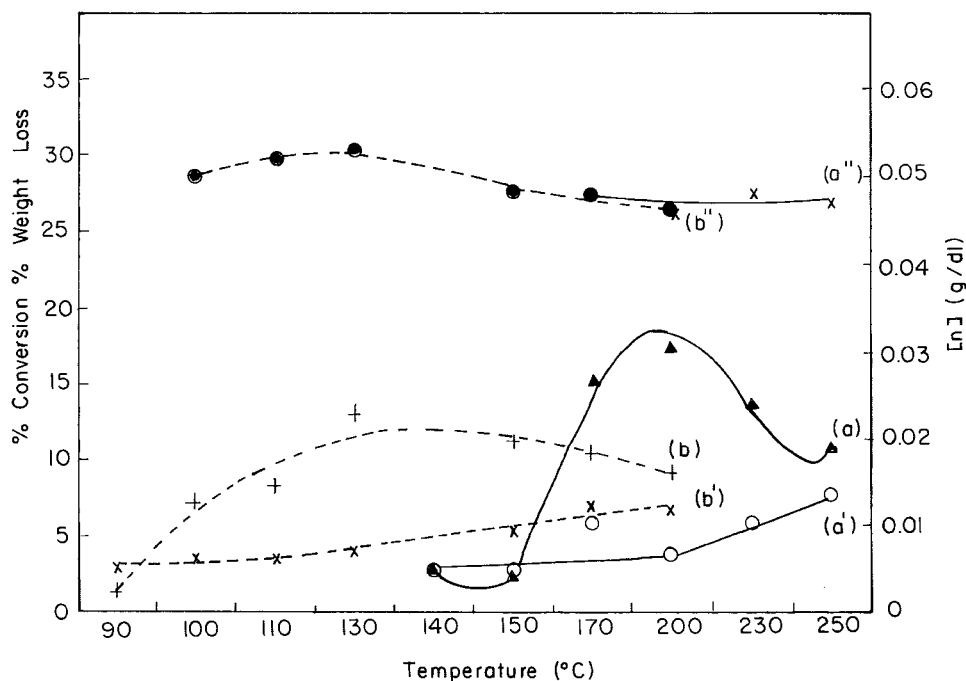
Figure 2 Changes in the conversion percentage, (′) weight-loss percentage, and (″) [*n*] with the temperature: (a) **C1** and (b) **C2**.

The calculation of the conversion percentage for the polymerization was based on the initial weight of the complex. Because the ligand and the metals were not incorporated into the polymer, the results appeared to be low.

Caracterization of the polymers

IR spectra were recorded on a Nicolet 510 FTIR spectrometer and a Schimadzu IR-470 IR spectrophotometer in the 4000–400-cm^{-1} region with samples dispersed in KBr discs.
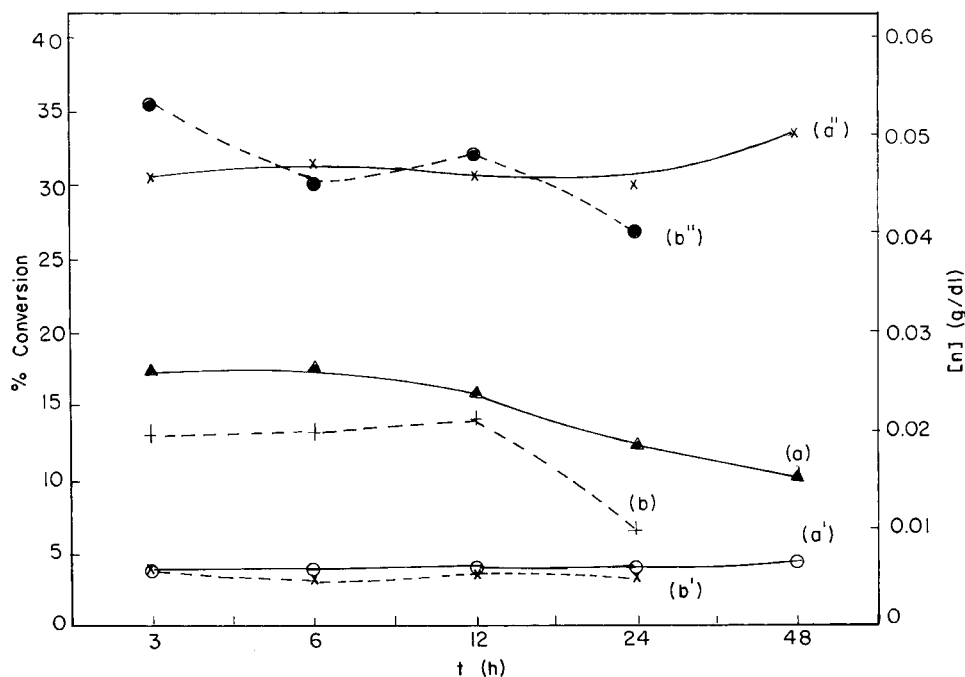

Figure 3 Changes in the conversion percentage, (′) weight-loss percentage, and (″) [*n*] with the decomposition time at constant decomposition temperatures: (a) **C1** and (b) **C2**.
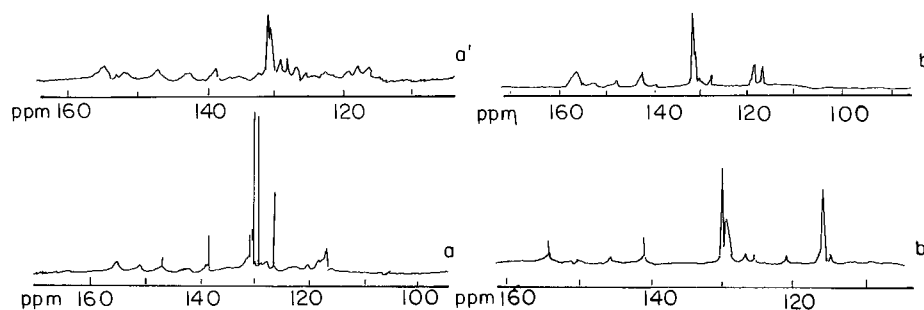
Figure 4 (a,b) Proton-coupled and (a′,b′) decoupled ^{13}C-NMR spectra for (a) **P1** and (b) **P2**.

The viscosity of 10.0 g/dL solutions of polymers in toluene at 30°C was measured on a Schott Geräte AVS 400 automatic viscometer equipped with a Schott Geräte CT 1150 thermostat.

The ^{1}H-NMR and ^{13}C-NMR spectra of the polymeric samples were recorded in deuterated chloroform on a Bruker GmbH DPX 400-MHz high-performance FT-NMR spectrometer.

A DuPont Thermal Analyst 2000 DSC 910S differential scanning calorimeter with a scanning rate of 10°C/min was used to determine the glass-transition temperature (T_g) of the polymers (10-mg samples under a nitrogen atmosphere).

RESULTS AND DISCUSSION

Structure and stoichiometry

The elemental analysis results correlate well with the suggested formula for the complexes.

The FTIR spectra of **C1**–**C3** exhibited the expected ligand vibrations; the differences from the spectra of the free ligands were due to complex formation. The broad peak in the free NMIz ligand in the 3000–3500-cm^{-1} region was simplified by coordination to Cu(II), being replaced by a single peak at 3100 cm^{-1}. The multiple peaks of the free DMPz ligand in the 2600–3300-cm^{-1} region (due to strong hydrogen bonding) were also simplified by coordination to Cu(II) or Co(II) and observed as a strong peak around 3350 cm^{-1} in each case. In general, absorption bands in the range of 3000–3100 cm^{-1} were due to C—H stretching of the ring, bands in the range of 2700–3100 cm^{-1} were due to C—H of CH$_3$ groups, bands at 1250–1350 cm^{-1} were due to the C—N stretching of *N*-ligands. In the 1600–2000-cm^{-1} region, weak bands arising as overtones of C—H out-of-plane deformation bands of the benzene ring could be clearly observed in the spectrum of **C1**. Absorption bands in the range of 1460–1580 cm^{-1} were due to C=C ring stretching; bands around 1220 cm^{-1} were due to C—O stretching of phenolic groups.

The intense absorption in UV–vis spectra of **C1** and **C2** (CuN$_2$O$_2$ coordination) was assigned to a charge-transfer transition, and the weak absorptions at longer wavelengths were assigned to d–d transitions.[35,37,38] The charge-transfer transition of this type was reported to be a phenolate-to-copper charge transition;[37,38] for a series of complexes of the type *trans*-[CuOPh$_2$(Py)$_2$] (where OPh is halogenated phenolate), it was found that the charge-transfer band moved to higher energy as the halogen substituents on phenolate became more electron-withdrawing (under the assumption that the structures of the complexes were similar). The UV–vis spectrum of **C1** was the same as its diffuse reflectance spectrum, indicating that the coordination was the same in the solid state and in solution. The electronic spectrum of **C3** showed a very similar pattern and ϵ values close to those of (NMIz)$_2$Co(TCP)$_2$ (where TCP is 2,4,6-trichlorophenolate).[35,36] The magnetic susceptibility data of the complexes also were as expected for the assumed coordination environments.

The ESR spectrum of **C1** gave $g_\parallel$ at 2.28 and $A_\parallel$ at 174 G, with $g_\perp$ splitting into superhyperfine components. These values are consistent with the parameters of a CuN$_2$O$_2$ donor type.

Thermal behavior of the complexes and polymerization

Copper complexes decompose to give poly(chlorophenylene oxide) when they are subjected to high temperatures. The polymerization of DCPH by the decomposition of copper complexes proceeds by a weight loss, which indicates the evolution of some gaseous products during the decomposition reaction. The MS results imply that the gaseous products mainly originate from the *N*-ligand in the case of **C1**. The structure of this complex has been proposed to be elongated and octahedral, with the DCP ligand acting as a bidentate ligand.[34] In the case of **C2**, the opposite trend has been observed. The loss of DCP is now more significant. A tetragonal geometry has been proposed for **C2**. Thus, for this complex, the DCP ligands act as monodentate ligands and can be lost more readily, as indicated by the MS results. Intense and characteristic peaks present in the mass spectra are summarized in
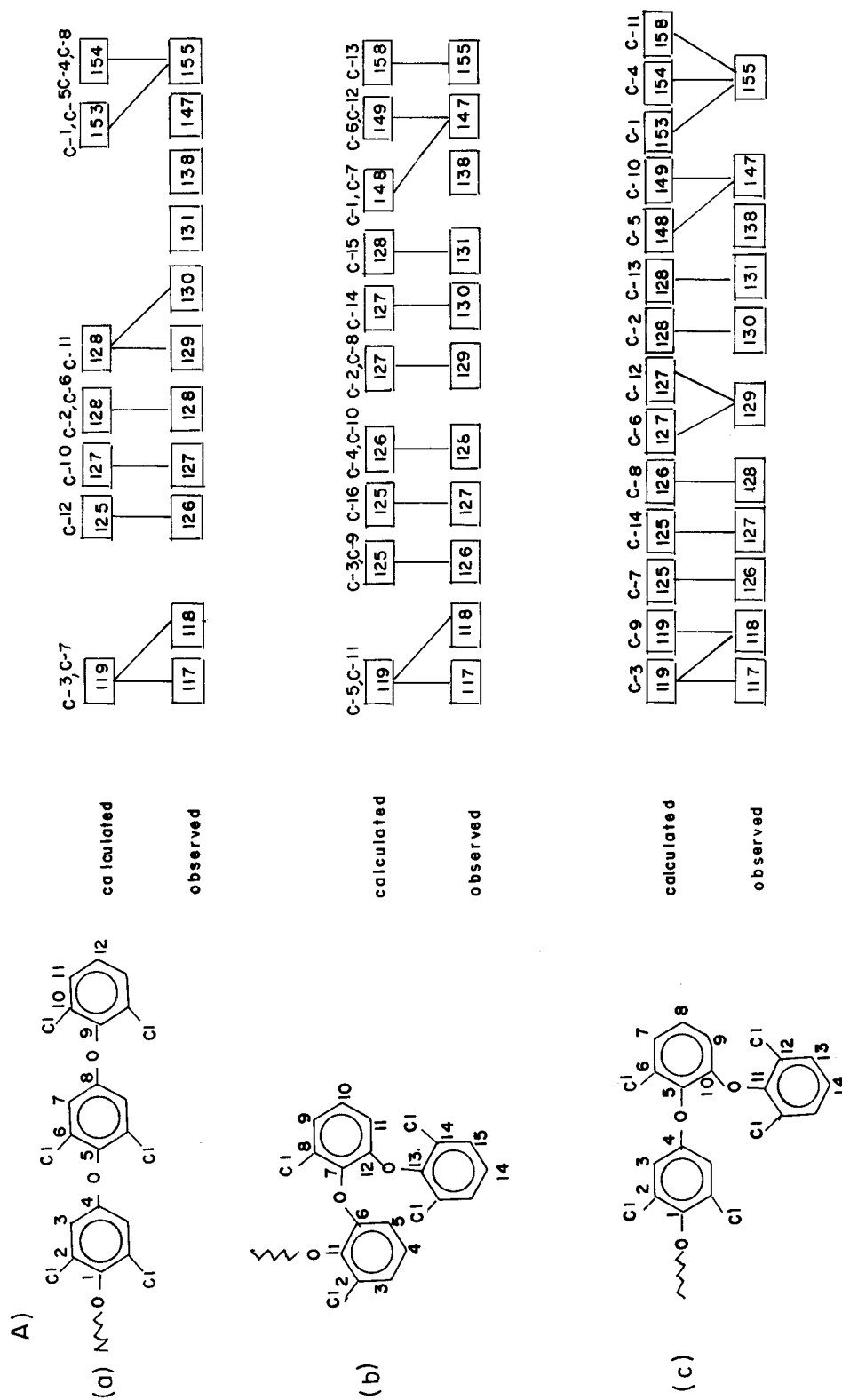
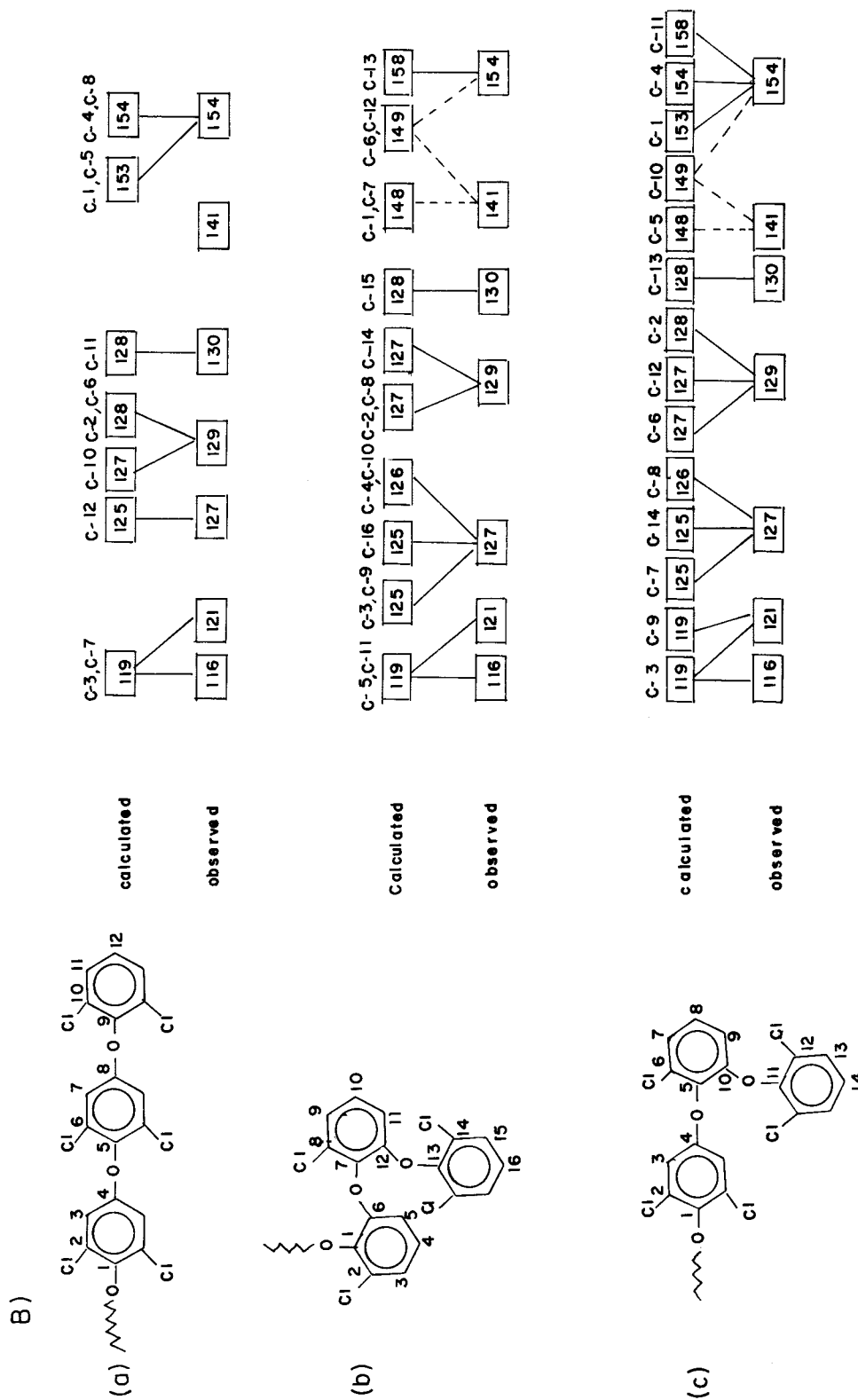Figure 5   Binary relationship between the observed and calculated data for (A) **P1** and (B) **P2**.
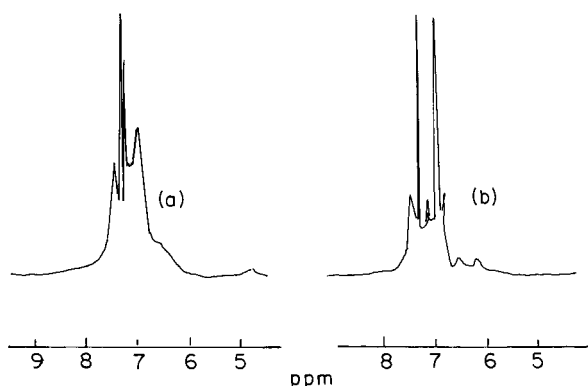
Figure 5 (*Continued on previous page*)

Figure 6 ¹H-NMR spectra of (a) **P1** and (b) **P2**.

Table I. The weight loss observed for **C1** is considerably lower than that of **C2**. The loss of DCP from **C1** becomes significant and comparable to that of **C2** only at temperatures above 170°C.

The thermal behavior of the complexes was studied by differential scanning calorimetry (DSC; Fig. 1). A DSC thermogram of **C1** showed a sharp melting peak at 169°C with an onset at 164°C. The isothermal treatment of **C1** at 150°C showed an exothermic peak due to the polymerization process, which was complete within 20 min [Fig. 1 (a′)].

The decomposition of **C1** in bulk was studied between 140 and 250°C at a constant decomposition time of 3 h (Fig. 2). The conversion was 2.70% at 140°C. The decomposed complex was in the melt state above 170°C, and a maximum conversion of 17.4% was obtained at 200°C. As the complex melts, the diffusion of the molecules is much easier; this can explain the sudden increase in the conversion from 2.30% at 150°C to 15.2% at 170°C. The conversion was 10.9% at 250°C [Fig. 2(a)]. The decrease in the conversion as the temperature exceeded 200°C might have been due to the loss of the ligands as well as the decomposition of the newly formed products as the temperature increased.

The DSC thermogram of **C2** [Fig. 1(b)] shows two sharp exothermic peaks at 182 and 276°C. To understand the nature of the first exothermic peak, which is assigned to the polymerization process as for **C1**, we performed a DSC–IR study. The complex was subjected to DSC, and just after the first exothermic peak was observed, the capsule was removed so that we could take the IR spectrum of the sample as a KBr disc without separating the decomposition products. The polymer formation was indicated by C—O—C peak formation in the 900–1030-cm⁻¹ region, whereas the original complex exhibited no peak in this range. The peak around 3300 cm⁻¹ in the original complex, which was due to the DMPz ligand, disappeared in the decomposed complex, and this indicated that DMPz left the complex structure during decomposition and evaporated (this was also implied by the MS spectra).

In the bulk decomposition of **C2** at 90°C, 1.4% polymer was obtained at the end of 3 h (Fig. 2). When the decomposition temperature was raised up 130°C, the maximum conversion was obtained (13.0%). The relatively sudden increase in the conversion at 100°C is thought to be due to the change from the solid state to a partially melted state, which allowed the molecules to diffuse more easily and caused an increase in the conversion. The decrease in the conversion to 9.20% at 200°C [Fig. 2(b)] might have been due to the loss of the phenolate ligand as well as the decomposition of the products.

No time effect on the decomposition of **C1** and **C2** at 200 and 130°C, respectively, was observed up to 12 h (Fig. 3). Then, there was a sharp decrease in the conversion down to 10.3% at the end of 48 h and to 6.50% at the end of 24 h for **C1** and **C2**, respectively [Fig. 3(a,b)].

C3 melted at 152.9°C [Fig. 1(c)] and yielded no polymeric product within the temperature range studied.

C2 decomposed at a lower temperature (90°C) than **C1** (140°C), and the cobalt complex did not decompose to give any polymer at all; this indicated the higher stability of **C1** in comparison with **C2** and the higher stability of the cobalt complex in comparison with the copper complexes. The same trend was observed in the TCP analogues of these *N*-ligand complexes.[39] NMIz complexes were more stable than the DMPz complexes, and the Co(II) complexes were more stable than the corresponding copper complexes. With the same metal and *N*-ligand, the DCP complexes required higher decomposition temperatures than the TCP analogues and did not have higher conversions.

Characterization of the polymers

All of the polymers were characterized by 1443-, 1560-, and 1607-cm⁻¹ C=C stretching frequencies, 910-, 950-, 1006-, and 1033-cm⁻¹ C—O—C stretching, 1181-, 1115-, 1143-, 1204-, and 1245-cm⁻¹ C—O stretching, and 855- and 821-cm⁻¹ out-of-plane C—H bending frequencies. The peak at 3084 cm⁻¹ was assigned to C—H stretching of the benzene ring, and the peak at 3500 cm⁻¹ was attributed to the phenolic end groups.[5,9]

Proton-coupled and decoupled ¹³C-NMR spectra of the polymers are displayed in Figure 4. Theoretical ¹³C-NMR chemical-shift data for the main three possible 1,2- or 1,4-addition products were calculated with appropriate tables.[40] The binary relations between the observed and calculated data for the two polymers are displayed in Figure 5(A,B) for polymers from **C1** (**P1**) and **C2** (**P2**), respectively. Within the three possible structures of the DCPH polymers, the 1,4-addition product was expected to show a simple spectrum with a simple repeating unit. ¹³C-NMR shift data calculations showed that for **P1**, all

of the structures seemed to be possible, indicating that both 1,2- and 1,4-additions took place at the same time (Fig. 5). **P2** correlated well with structure a, having a simple spectrum as expected for a 1,4-addition product; however, structures b and c could not be completely discarded.

To clarify the ^{13}C-NMR results, we also took ^{1}H-NMR spectra of the polymers. The ^{1}H-NMR spectra clearly reveal that **P1** and **P2** [Fig. 6(a,b), respectively] were different in their patterns, having different relative intensities for the two main peaks. The peak at 7.4 ppm was due to the 1,2-addition product, and that at 6.9 ppm was due to the 1,4-addition product.[14,17,23,33,34] Thus, **P1** seemed to have slightly more 1,4-addition than 1,2-addition, whereas in the product of **P2**, 1,4-addtion was predominant. **P2** also showed branch units at high fields. The peak at 7.1 ppm in **P1** indicated the presence of both 1,2- and 1,4-addition at the same monomeric unit. Hence, ^{1}H-NMR suggests that 1,2- and 1,4-addition took place at the same time for **P1**, and 1,4-addition was predominant in **P2**.

The intrinsic viscosities for **P1** were almost constant as the temperature [Fig. 2(a″)] and time [Fig. 3(a″)] changed. However, **P2** showed a maximum intrinsic viscosity, at a maximum conversion, of 0.053 dL/g, followed by a decrease to 0.046 dL/g as the conversion decreased at 200°C. As time increased, the intrinsic viscosity decreased gradually to a value of 0.040 as the conversion decreased with time.

T_g's of **P1** and **P2** were 160 and 185°C, respectively, indicating that they were rigid polymers.

CONCLUSIONS

Elongated and octahedral **C1** and tetragonal **C2** complexes can be thermally polymerized in the solid state, whereas the **C3** complex does not decompose under the same conditions. Copper complexes decompose with a weight loss because of the loss of phenolate ligand and N-ligand. The loss of the N-ligand is more significant in **C1**, and phenolate loss predominates in **C2**. The initial decomposition temperature of **C1** is higher than that of **C2**, indicating the higher stability of **C1**. The conversion values are lower for **C1** than for **C2** up to 170°C, and then the conversion significantly increases as the temperature increases because of the higher diffusion rate in the melted complex (**C1**). The polymerization time and temperature have nearly no effect on the intrinsic viscosity for **C1**, whereas for **C2**, the maximum value (0.053 dL/g) is achieved at the maximum conversion at 130°C and decreases over a longer period to a minimum value (0.040 dL/g). **C1** tends to give polymers that are both 1,2- and 1,4-addition products, whereas **C2** gives mainly 1,4-addition products. Both polymers are rigid, having high T_g values.

On the basis of these results and the results of complementary studies,[39] we can conclude that DMPz complexes are less stable and better for the lower temperature polymerization of DCP or TCP.

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