Synthesis and characterization of poly(dichlorophenylene oxide)s through solid state thermal decomposition of bis(pyridine)bis(trichlorophenoxo)copper(II) complexes

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Thermal polymerization of bis(pyridine)bis(trichlorophenoxo)copper(II) was achieved in the solid state for the first time. The time and temperature effect on polymer molecular weight, percentage yield and the structure of polymer was first studied, at constant temperature and then for constant decomposition time. Polymers were characterized by i.r., ^{1}H n.m.r. and ^{13}C n.m.r. The molecular weights of the polymers were obtained by viscometric measurements at 30°C in toluene and glass transition temperatures were obtained by d.s.c.

(Keywords: poly(dichlorophenylene oxide); solid state thermal polymerization; bis(pyridine)bis(trichlorophenoxo)copper(II) complex; intrinsic viscosity; ^{1}H n.m.r.; ^{13}C n.m.r.)

INTRODUCTION

The synthesis of poly(dichlorophenylene oxide) has been successfully carried out by the thermal decomposition of silver salts[1–3] and copper complexes[4–11] of 2,4,6-trichlorophenol (TCP) and the electro-oxidation of copper complexes of TCP[12,13] for many years. In such studies, the effect of solvent, neutral ligand and type of halogen bonded to the phenol have been determined.

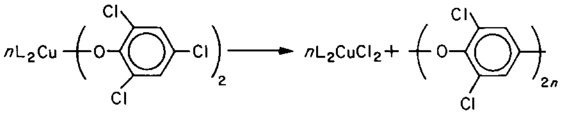
The direct synthesis of poly(dichlorophenylene oxide) was originally achieved by the decomposition of silver 2,4,6-trichlorophenolate. The suggested reaction mechanism for the smooth decomposition of the silver salt of TCP, suspended in alkyl iodides or in pure benzene, into silver chloride and an amorphous polymerized residue, was:

$$nC_6H_2Cl_3OAg \rightarrow nAgCl + (C_6H_2Cl_2O)_n$$

The same effect was produced by heating to temperatures slightly above 100°C.

In 1962, Blanchard *et al.* described the preparation and characterization of di-2,4,6-trichlorophenolate-bis-(pyridine)copper(II) complexes[4]. These complexes were decomposed under a variety of conditions yielding poly(chlorophenylene ether)s, which are highly branched as indicated by their low intrinsic viscosities.

Subsequently, Harrod carried out studies on phenoxo complexes of copper(II)[5]. A series of trichlorophenoxo complexes of copper(II) containing a variety of amine ligands was prepared. The thermal stability of the complexes with regard to the decomposition reaction:



was found to be lower with those ligands, L, that increased the oxidizing power of copper(II) and vice versa.

In this study, thermal polymerization of copper complexes of TCP with the neutral ligand pyridine was achieved in the solid state. The products obtained were characterized by i.r., ^{1}H n.m.r. and ^{13}C n.m.r. In addition, the effect of the ligand on the molecular weight of the polymer was also studied by changing the mole ratio of the ligand (pyridine) in the copper complex.

EXPERIMENTAL

Materials

Analytical grade TCP was purchased from Sigma and Aldrich Chemical Co. Ltd. The pyridine (Riedel de Hagen AG) was a reagent grade material and was used as the neutral ligand. The copper sulphate was of commercially available reagent grade. Toluene was purchased from Merck and was used as a solvent. Fractionally distilled ethanol was used as the non-solvent.

Preparation of copper complexes

Two types of bis(pyridine)bis(trichlorophenoxo)-copper(II) complexes were prepared. Complex 1 was

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prepared by mixing the following two solutions and then stirring vigorously: a solution containing NaOH (0.15 mol) and TCP (0.15 mol) in distilled water (300 ml) was slowly added to a solution containing $CuSO_4.5H_2O$ (0.075 mol) and pyridine (0.1 mol) in distilled water (300 ml). Complex 2 was prepared by mixing a solution containing NaOH (0.45 mol) and TCP (0.45 mol) in distilled water (900 ml) with a solution containing $CuSO_4.5H_2O$ (0.225 mol) and pyridine (0.45 mol) in distilled water (900 ml). In each case, the precipitated brown complexes were filtered, washed with distilled water and dried in a vacuum oven to constant weight.

The complexes were characterized by elemental and spectral analysis. For elemental analysis a Hewlett Packard model 185 CHN analyzer was used. The temperature of the oxidation furnace was 950°C, the temperature of the reduction furnace was 500°C, the column oven temperature was 80°C and the oven shell temperature was 60°C. The flow rate of helium was $100 cm^3 min^{-1}$. Complex 1 was found to contain (%): C, 39.67; H, 2.14; N, 3.67. Calculated for 2/3 $(C_5H_5N)_2Cu(C_6H_2Cl_3O)_2$ and 1/3 $(H_2O)_2Cu(C_6H_2Cl_3O)_2$ (%): C, 38.42; H, 2.08; N, 3.04. Complex 2 was found to contain (%): C, 42.77; H, 2.30; N, 4.37. Calculated for $(C_5H_5N)_2Cu(C_6H_2Cl_3O)_2$ (%): C, 42.99; H, 2.31; N, 4.56.

Polymer synthesis

Poly(dichlorophenylene oxide)s were synthesized by thermal decomposition of bis(pyridine)bis(trichlorophenoxo)copper(II) complexes in the solid state. The polymerization time ranged from 3 h to 7 days for complex 1 at a constant temperature of 115°C and from 3 to 48 h for complex 2 at a constant temperature of 120°C. The polymerization temperature was changed from 115 to 250°C for complex 1 for a constant time of 3 h and from 120 to 250°C for complex 2 for a constant time of 3 h. The decomposition of complexes was performed in a glass sample holder (3 cm diameter, 2.5 cm high), which was then inserted in an iron sample holder in an oven. The sample weight was 2.5 g for complex 1 and 3.7 g for complex 2.

Polymer characterization

Molecular weight determination. The weight average molecular weights ($\bar{M}_w$) of the polymers obtained by the solid state thermal decomposition of complexes were calculated using viscometric data and α and κ values given in the literature[4]. Intrinsic viscosities of the polymers were determined at 30°C in toluene using a Schott Gerate AVS 400 model automatic viscometer having an efflux time of 124 s.

I.r. spectral analysis. A Nicolet 510 model *FT*i.r. spectrophotometer was used to obtain i.r. spectra of the polymers on KBr discs.

N.m.r. The structure of the polymers was examined by ^1H n.m.r. and ^{13}C n.m.r. The spectra were obtained using a Bruker AC 80 *FT*n.m.r. spectrophotometer with a 5 ml tube for ^1H n.m.r. and a 10 ml tube for ^{13}C n.m.r. $CDCl_3$ was used as a solvent and tetramethylsilene was used as an internal reference.

D.s.c. A Perkin-Elmer DSC-4 was used to obtain the glass transition temperatures (T_gs) of the polymers. The scanning rate was $20°C min^{-1}$.

RESULTS AND DISCUSSION

The thermal decomposition of bis(pyridine)bis(trichlorophenoxo)copper(II) complexes was achieved in the solid state. The polymerization was first performed at constant time with different temperatures and then at constant temperature for different time intervals. The products obtained were characterized to obtain the percentage yield, intrinsic viscosity and $\bar{M}_w$, i.r., ^1H n.m.r. and ^{13}C n.m.r.

Percentage yield values were calculated using the following equation:

$$\text{yield }(\%) = \frac{\text{weight of the polymeric product}}{\text{initial weight of the complex}} \times 100$$

The calculation of the percentage yield for the polymerization is based on the initial weight of the complex. Since the ligand and copper are not incorporated in the polymer, the results appear to be low.

The percentage yields of polymers obtained from complex 1 show almost no change over the time and temperature interval studied. The value was found to be 55%. Post polymerization and periodical stirring of the reaction medium did not have any effect on the percentage yield either. The same is true for complex 2 except for the initial time and temperature, where the percentage yield for the polymer obtained at 120°C for 3 h was 0.74% as for the same polymer left for 24 h post polymerization. For complex 2, the percentage yield was ~51% in other situations. In both complexes, however, the percentage yield in the melt (250°C) is the same as that in the solid state.

The molecular weights of the polymers obtained from complex 1 and complex 2 were around 22 000 ($[\eta] = 0.039 dl g^{-1}$) and 30 000 ($[\eta] = 0.043 dl g^{-1}$), respectively. The molecular weights of the polymers obtained from the copper complexes show no proportional change with time or temperature. The molecular weight is almost constant for every temperature and time interval. The polymers have high T_g values (170°C).

Figure 1 shows the *FT*i.r. spectrum of the polymer obtained from complex 1. The polymer is characterized by bands at 1380, 1400, 1560 and $1600 cm^{-1}$ (C=C stretchings), 950, 1000 and $1030 cm^{-1}$ (C–O–C stretchings), 1110, 1140, 1200 and $1240 cm^{-1}$ (C–O stretchings), and 820 and $860 cm^{-1}$ (out-of-plane C–H bendings). The spectrum of the polymer obtained from complex 2 was similar. ^{13}C n.m.r. spectra (both coupled and decoupled)

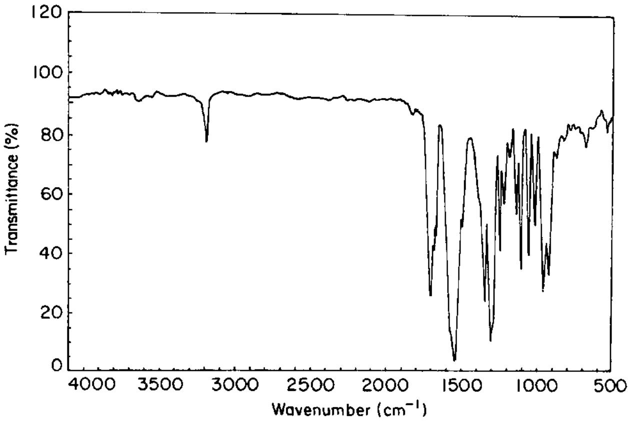

Figure 1 *FT*i.r. spectrum of the polymer obtained from complex 1

of the polymers are shown in *Figure 2*. Theoretical ^{13}C n.m.r. chemical shift data for the main three possible 1,2- or 1,4-catenation products of TCP were calculated using the appropriate correlation tables[14]. The binary relations between the observed and calculated data for the polymers obtained from complex 1 and complex 2 are shown in *Figures 3* and *4*, respectively.

It could be predicted that a polymer chain of TCP having a high degree of structural regularity (*Figures 3a* and *4a*) could exhibit a fairly simple ^{13}C n.m.r. spectrum, i.e. that of the simple repeating unit, depending on the complexity of the monomer. Hence, *Figures 3b* and *c* and *Figures 4b* and *c* should display fairly complex spectra. The observed and calculated ^{13}C n.m.r. spectra of the polymers show that all of the structures are possible. No one structure is preferred.

The ^{1}H n.m.r. spectra are shown in *Figure 5*. The peak at 6.8 ppm is due to the protons of 2,6-dichloro-1,4-phenylene oxide units (1,4-catenation) and the peak at lower field at 7.3 ppm is due to the protons of 2,4-dichloro-1,6-phenylene oxide units (1,2-catenation). Broader peaks at higher field indicate the presence of both 1,2- and 1,4-addition for the same monomeric unit. As can be seen from the spectra 1,2- and 1,4-additions take place at about equal rates. The broad peak at higher fields (6.5–5.5 ppm) indicates the high degree of branching.

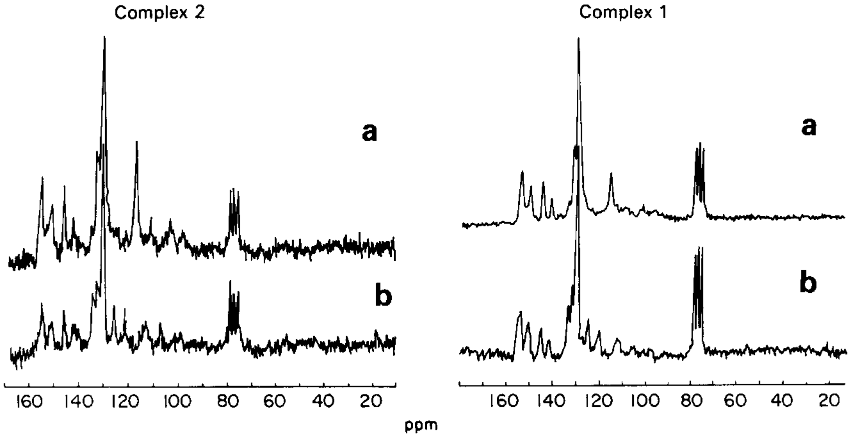

Figure 2 ^{13}C n.m.r. spectra of the polymers obtained from complex 1 and complex 2: (a) decoupled; (b) coupled

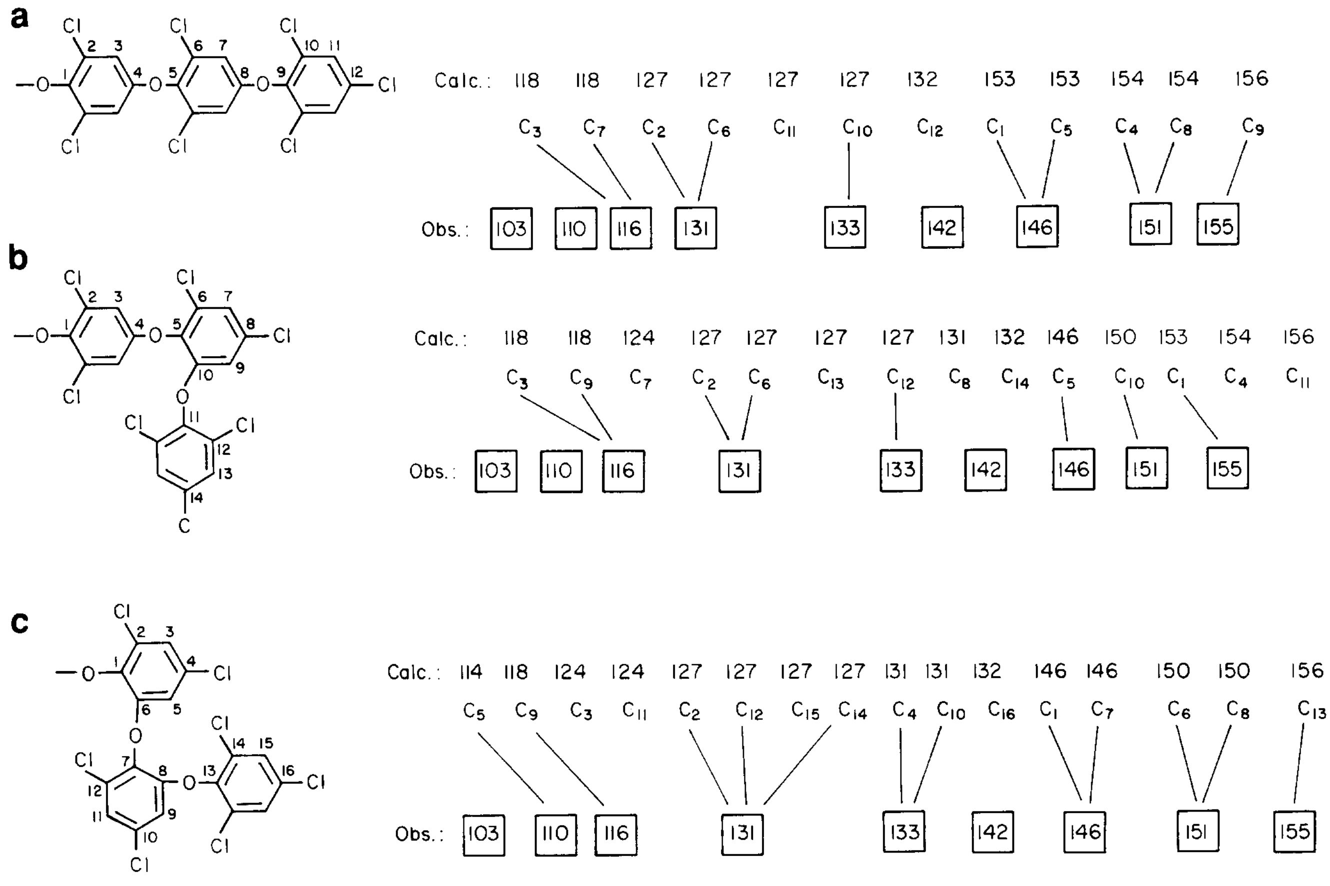

Figure 3 ^{13}C n.m.r. shift data for the polymer obtained from complex 1

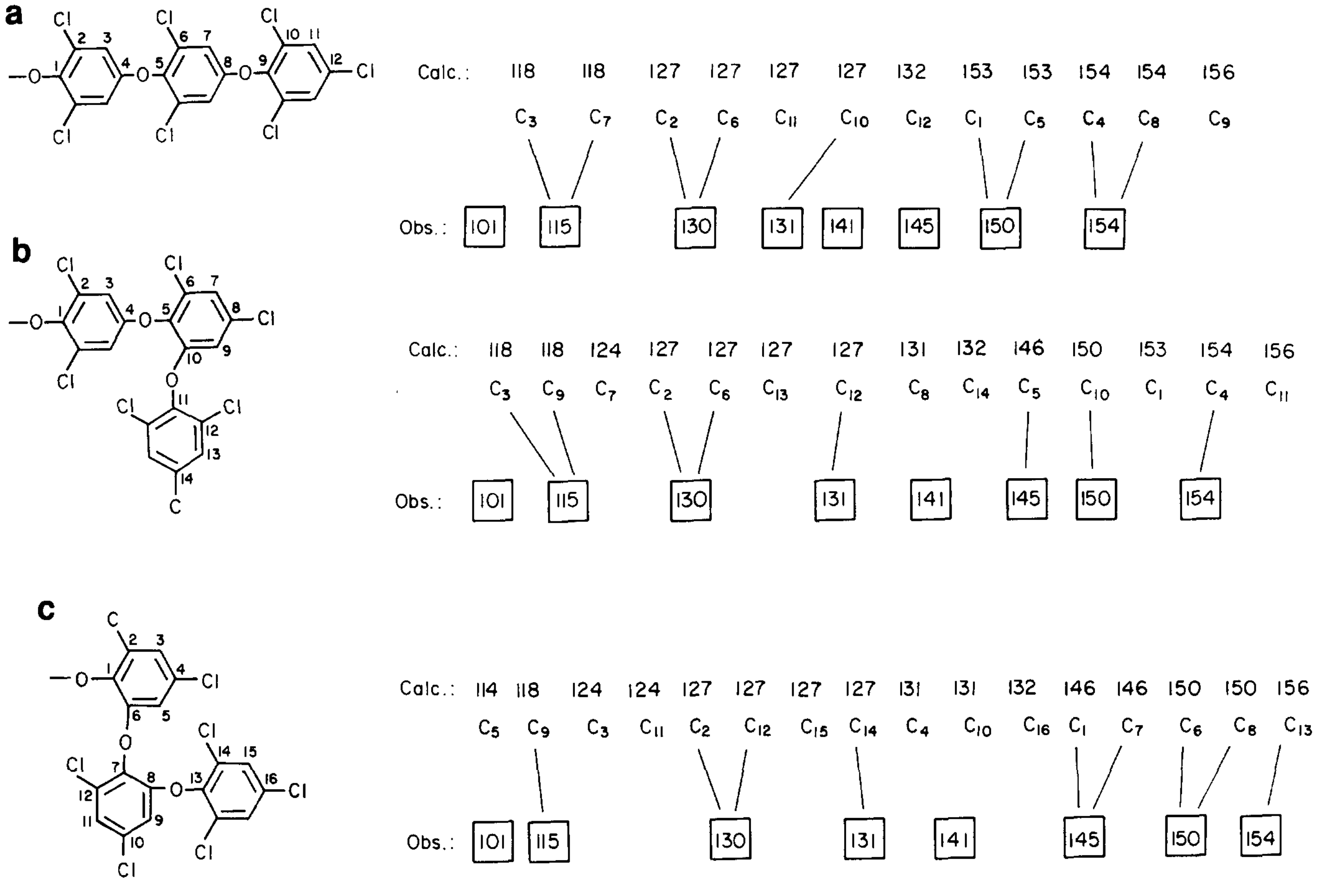

Figure 4 ^{13}C n.m.r. shift data for the polymer obtained from complex 2

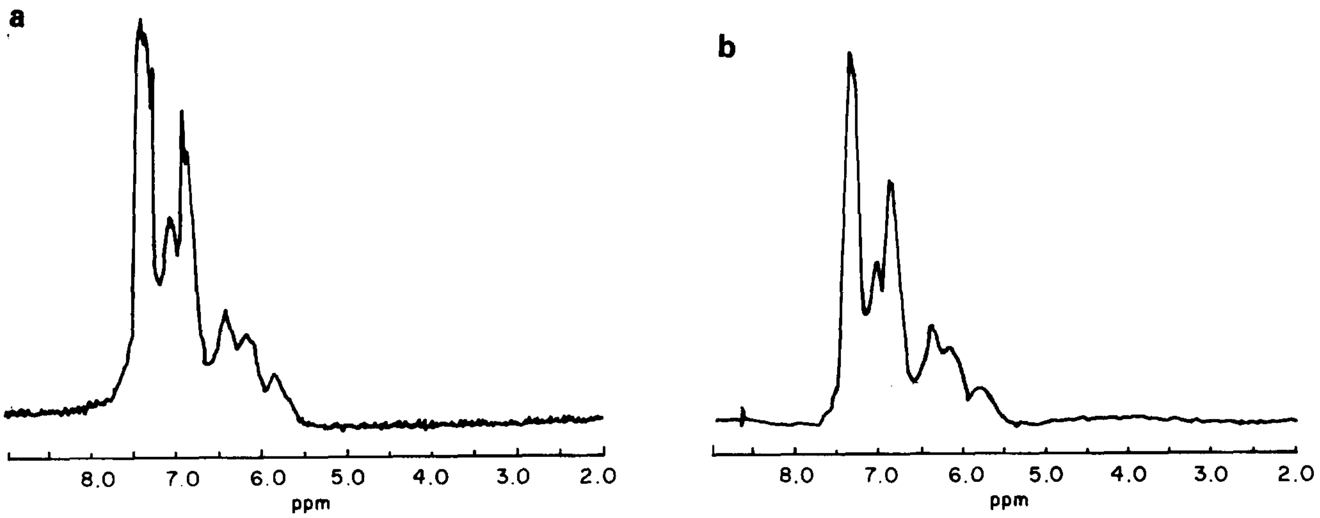

Figure 5 ^{1}H n.m.r. spectra of the polymer obtained from (a) complex 1 and (b) complex 2

CONCLUSIONS

Copper complexes of TCP with the neutral ligand pyridine were decomposed for the first time in the solid state to give poly(dichlorophenylene oxide). For both complexes studied the polymerization proceeds through 1,2- and 1,4-additions almost equally. The polymers are highly branched and have high T_g values (170°C). The process leads to $\bar{M}_w$ values between 20000 and 30000. The time and temperature interval studied have no effect on the percentage yield and $\bar{M}_w$.

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