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Polymerisation of bis(trichlorophenolato)tri(pyridine)nickel(II) and bis(trihalophenolato)di(pyridine)nickel(II) complexes in solid state

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Abstract

The synthesis of five-coordinated bis(trihalophenolato)tri(pyridine)nickel(II) and four-coordinated bis(trihalophenolato)di(pyridine) nickel(II) complexes from an aqueous solution and their characterisation by FT-IR, X-ray, DSC and elemental analysis is described. The thermal polymerisation of these complexes was carried out in the solid state and in the melt. Structural analyses were performed using ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopic analyses. T_gs were determined by differential thermal analysis and the molecular weights by viscometric method. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Bis(trihalophenolato)tri(pyridine)nickel(II); Bis(trihalophenolato)di(pyridine)nickel(II); Solid state thermal polymerisation

1. Introduction

Poly(dihalophenylene oxide)s have been synthesised by thermal decomposition of silver salts in solution [1–4], copper complexes in solution [4–16] and in solid sate [15,18], and cobalt complex in solid state [19]. The suggested reaction mechanism is:

$$n\, M(OC_6H_2X_3)_2L_2 \rightarrow n\, MX_2L_2 + (\text{–}C_6H_2X_2O\text{–})_{2n}$$

where M is a transition metal, L is a neutral ligand and X is a halogen.

The trihalophenolate ions form crystallographically characterised complexes involving chelation through oxygen and chlorine donor atoms to cobalt(II), copper(II), nickel(II) and silver(I) ions. The six-coordinated complex of bis(trihalophenolato)di(pyridine)copper(II) and four-coordinated bis(trihalophenolato)di(pyridine)cobalt(II) have coordination through two chlorines *cis* and oxygen *trans* to copper in the octohedron [20] and to cobalt in the co-ordination through distorted tetrahedron [16–18]. The five-coordinated bis(trichlorophenolato)tri(pyridine)nickel(II) complex lies on a crystallographic two-fold symmetry axis and the geometry about the nickel described as a distorted square pyramid with one of the pyridine ligands occupying an axial position [21,24]. However, bis(trihalophenolato)di(pyridine) nickel(II) complexes are in the amorphous form.

It is well known that the ease with which the thermal decomposition occurs of such complexes is profoundly affected by the nature of the ligands and the transition metals, the coordination of the complex as well as the method of synthesis. The chemical reactions in the solid phase have been most thoroughly studied for the case of inorganic compounds [22]. Relationships governing organic reactions in the solid phase have been much less thoroughly studied. The application of these complexes, containing transition metals to solid phase polymerisation, has been recently established [15,18].

In the present study, thermal polymerisation of five-coordinated bis(trichlorophenolato)tri(pyridine)nickel(II) and four-coordinated bis(trihalophenolato)di(pyridine)nickel (II) complexes were carried out in the solid state and in the melt. There are no records in the literature about the thermal polymerisation of these complexes. This work is part of a research project aimed at finding new ways to synthesise poly(dihalophenylene oxide)s through thermal decomposition of phenolate transition metal complexes with different structures.

2. Experimental

2.1. Materials

Analytical grade 2,4,6-trichlorophenol (TCP) (Sigma and Aldrich Chemical Co. Ltd.), 2,4,6-tribromophenol (TBrP) and 2,6-dichlorophenol (2,6-DCP) (Aldrich Chemical Co.

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Ltd.) were used without further purification. The reagent grade pyridine, from Riedel-de Haen AG was used as a neutral non-chelating ligand. Commercially available reagent grade nickel sulphate hexahydrate ($NiSO_4 \cdot 6H_2O$) was used in the preparation of trihalophenolato complexes. Bromine (Br_2), purchased from Fluka AG, was used for the bromination of 2,6-DCP.

2.2. Bromination of 2,6-dichlorophenol

A solution of 0.10 mol molecular bromine and 0.15 mol KBr dissolved in 150 cm^3 distilled water was added dropwise to the solution of 0.10 mol of 2,6-DCP dissolved in a minimum amount of ethanol, with constant stirring for 2 h at room temperature. The precipitated 4-bromo-2,6-dicholorophenol was cooled on ice for 15 min, filtered, washed and dried in a vacuum oven. The structure and the purity of the product was established by ^1H NMR spectrum and melting point measurement [21,23].

2.3. Preparation of nickel complexes

Nickel complexes of trihalogenated phenols were prepared in high yields from aqueous solutions of reagents. A solution of 0.2 mol NaOH and 0.2 mol trihalophenol in 400 cm^3 distilled water was slowly added to the solution containing 0.1 mol $NiSO_4 \cdot 6H_2O$ and 0.3 mol of pyridine in 400 cm^3 distilled water, with vigorous stirring. The precipitated blue complexes were recovered by filtration, washed with distilled water and dried in a vacuum oven to constant weight. The blue colour of the complex changed to yellow after drying, most probably due to the change of the water of crystallisation. However, crystallised five-coordinated complex of trichlorophenolate was always green in colour. The complexes were characterised by elemental analysis using a Carlo Erba 1108 Model carbon–hydrogen–nitrogen analyser with the oxidation furnace at 1020°C, the column oven at 65°C, the filament temperature at 190°C, a flow rate of helium gas of 120 cm^3/min and of oxygen gas of 80 cm^3/min and acetanilide as a standard. The elemental analysis of the complexes are (the experimental errors are ±0.3):

			%N	%C	%H
Complex **1**[a]	$Ni(TCP)_2Py_3$	Calculated	6.1	47.1	2.8
		Found	5.7	46.1	2.4
Complex **2**	$Ni(TBrP)_2Py_2$	Calculated	3.3	31.3	1.7
		Found	3.8	35.5	2.2
Complex **3**	$Ni(4Br\text{-}DCP)_2Py_2$	Calculated	4.0	37.8	2.0
		Found	3.7	39.0	2.1

[a] Complex crystallised.

The structural analyses of nickel complexes were carried out by FT-IR spectroscopy in KBr discs using a Mattson 1000 model. The structure of the single crystal form of the complex $Ni(TCP)_2Py_3$ was also determined by Enraf Nonious model with Molen type program, (AB-4 X-ray diffractometer).

2.4. Polymer synthesis

The thermal polymerisation of the crystalline bis(trichlorophenolato)tri(pyridine)nickel(II) (complex **1**[a]) and the amorphous bis(trichlorophenolato)di(pyridine)nickel(II) (complex **1**), the amorphous bis(tribromophenolato)di(pyridine)nickel(II) (complex **2**) and bis(4-bromo-2,6-dichlorophenolato)di(pyridine)nickel(II) (complex **3**) complexes were first performed at constant time (3 h) with different temperatures and then at constant temperature for different time intervals (3–24 h). Post-polymerisation after 3 h polymerisation in the solid state was carried out at room temperature for 24 h.

The decomposition of 5 g batches of complex was performed in a glass sample holder (4 cm in diameter with 3.5 cm height), inserted in a Dedeoğlu model oven at constant temperature. The decomposed complex dissolved in toluene and the insoluble by-product, NiX_2Py_2 was removed by filtration and then the polymer was precipitated by addition of the toluene solution to the ethanol containing few drops of concentrated HCl. The precipitated polymer was recovered by filtration and dried to a constant weight under vacuum.

2.5. Polymer characterisation

Fourier-transform infrared analysis: FT-IR spectra were recorded on a Mattson 1000 model spectrophotometer with the polymers dispersed in KBr discs.

Nuclear magnetic resonance analysis: ^1H NMR and decoupled ^{13}C NMR spectra were recorded on a Bruker GmbH DPX-400, 400 MHz high performance digital FT-NMR, using $CDCl_3$ as a solvent and TMS as an internal reference.

Differential thermal analysis: The glass transition temperatures (T_g) were determined with the use of a Perkin–Elmer DSC-4 differential scanning calorimeter. The scanning rate was 10°C/min for 6–10 mg polymer samples.

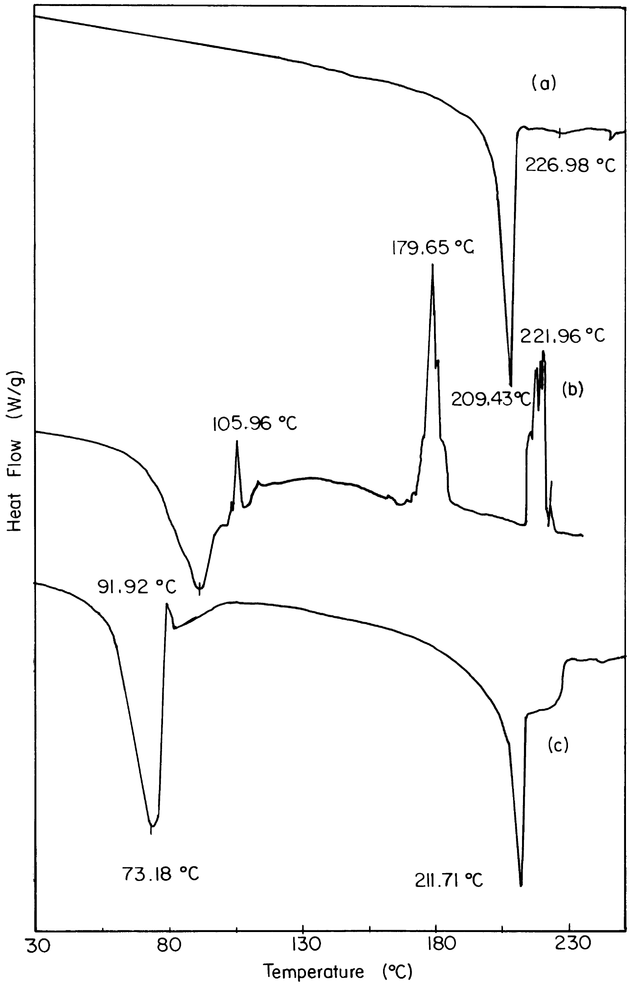

Fig. 1. DSC thermograms of: (a) complex **1**, (b) complex **2** and (c) complex **3**.

Intrinsic viscosity measurements: Intrinsic viscosities of the polymers were determined at 30°C in toluene using Schott Gerate AVS 400 Model automatic viscometer having an efflux time of 124 s.

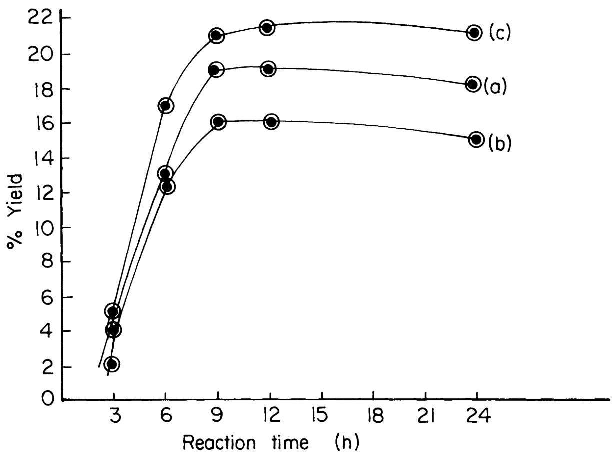

Fig. 2. Change in % yield with reaction time at constant decomposition temperature of complexes: (a) **1** at 180°C, (b) **2** at 100°C and (c) **3** at 175°C.

3. Results and discussion

FT-IR spectra of bis(trichlorophenolato)di(pyridine)-nickel(II) (complex **1**), bis(tribromophenolato)di(pyridine) nickel(II) (complex **2**) and bis(4-bromo,2,6-dichlorophenolato)di(pyridine)nickel(II) (complex **3**) complexes are similar to those of copper complexes given in the literature [5], exhibiting the characteristic absorption of C–N stretching at about 1060 cm^{-1} and the disappearances of phenolic O–H peaks around 3500 cm^{-1}. The single crystal structure of bis(trichlorophenolato)tri(pyridine)nickel(II) complex, $\mathrm{Ni(TCP)_2Py_3}$, was determined as square pyramidal by X-ray analysis. The five-coordinated complex lies on a crystallographic two-fold symmetry axis, with a geometry about the nickel as a distorted square pyramid, with one of the pyridine ligands occupying an axial position. The closest Ni···Cl distance is 3.441 Åbelow the base of the pyramid, at the van der Waals contact limit regarded as non-bonding. The N–Ni–N and O–Ni–O angles are 177.0 and 164.1°, respectively, as given in the literature [24]. $\mathrm{Ni(TCP)_2Py_2}$, $\mathrm{Ni(TBrP)_2Py_2}$ and $\mathrm{Ni(4Br\text{-}DCP)_2(Py)_2}$ are amorphous complexes with yellow colour.

The results of elemental analyses for the synthesised amorphous complexes have high carbon percentages. This can be explained by the presence of trapped TBrP and 4Br-DCP, as confirmed by DSC thermograms (Fig. 1). The DSC thermogram of complex **1**[a] showed one endothermic peak at 209°C, indicating the melting of the complex within the temperature ranges studied (Fig. 1a). However, there were three exothermic peaks around 106, 180 and 222°C, indicating new bond formations taking place and only one endothermic peak around 92°C corresponding to the melting point of trapped TBrP (m.p. 87–89°C), for complex **2** (Fig. 1b). In the DSC thermogram of complex **3**, two endothermic peaks were observed. The first peak was due to melting of trapped 4Br-DCP around 73°C (m.p. 65–68°C), and the second peak due to the melting of the complex around 212°C. There was also one exothermic peak around 82°C, due to new bond formation (Fig. 1c).

The thermal decomposition of nickel halophenolate complexes in solid state were achieved either at constant temperature with different time intervals, ranging from 3 to 24 h; or at constant time of 3 h with variation of temperature. The yields of polymers were based on the initial weight of the complexes, where the neutral ligands and nickel were not incorporated into the polymer [5].

The polymers yields vs time curves for the (poly(dichlorophenylene oxide)), **P1**, (poly(dibromophenylene oxide)), **P2**, and mixed halogenated (poly(dihalophenylene oxide)), **P3**, at constant temperature of 180, 100 and 175°C, respectively, showed initially a slow increase up to 9 h and then reached a plateau (Fig. 2). Among the synthesised polymers, **P3** had the highest and **P2**, the lowest yield values. The effect of reaction time on intrinsic viscosity values of the polymers are listed in Table 1. The intrinsic viscosity values of the polymers were almost similar, except for **P3**, which

Table 1
Percent conversion and [η] values of polymers at different times, keeping the decomposition of complexes **1**–**3** at 180, 100 and 175°C, respectively

Time (h)	Complex #	% Conversion	[η] (dl/g)	M_w ($\times 10^{-3}$
3	1	4.1	0.040	20.0
	2	2.2	0.020	–
	3	4.8	0.047	17.3
6	1	13.0	0.041	21.5
	2	13.1	0.020	–
	3	16.6	0.048	18.4
9	1	19.0	0.040	20.0
	2	16.0	0.020	–
	3	21.4	0.053	25.2
12	1	18.8	0.042	23.2
	2	15.0	0.018	–
	3	21.5	0.052	23.7
24	1	17.0	0.041	21.5
	2	14.9	0.018	–
	3	21.3	0.053	25.2

Table 2
Percent conversion values of polymers obtained a different temperatures, at the end of 3 h polymerisation time

T (°C)	Polymer #	% Conversion	[η] (dl/g)	M_w ($\times 10^{-3}$
100	2	2.2	–	–
110	2	6.2	–	–
113	2	15.6	0.022	–
113[a]		19.2	0.020	–
115	2	27.0	0.020	–
120	2	38.9	0.018	–
160	2	41.9	0.021	–
170	3	0.2	–	–
175	3	4.8	0.047	17.2
175[a]		7.4	0.051	22.3
180	3	21.5	0.049	19.7
	1	4.1	0.040	20.0
185	3	35.4	0.049	19.7
185	1	17.4	0.041	21.5
185[b]	1	18.6	–	–
185[a]	1	21.1	0.042	23.2
190[c]	3	26.0	0.051	22.3
190	1	26.4	0.042	23.2
195	1	34.3	0.039	18.5
200	2	41.6	0.020	–
200[c]	1	19.8	0.041	21.5
200[c]	3	16.5	0.049	19.7
205[c]	1	7.4	0.042	23.2
210[c]	1	7.6	0.038	17.1
220[c]	1	10.8	0.042	23.2
	3	29.7	0.051	22.3
250	2	39.0	–	–

[a] Post-polymerisation at room temperature for 24 h.

[b] Complex **1** crystallised [20].

[c] Molten complex.

shows a slight increase with time (Fig. 3). Although the amounts of the decomposed complexes increased with time in all cases, the intrinsic viscosity values were slightly affected. This could be due to the interference of the formation of by-product, NiX_2Py_2, and to the diffusion of the formed polymer products.

The changes in the percent yields of three polymers with temperature are listed in Table 2. Sharp increases in the percent yields were observed for polymers **P1**–**P3** up to 34, 42 and 35%, respectively (Fig. 4). The sharp increases of the percent decomposition of the complexes **1** and **3** up to the melt was followed by a decrease and then an increase. The behaviour of complexes **1** and **3** in the melt could be due to the beginning of endothermic processes thus hindering the polymerisation and causing a drop in percent conversion. As the temperature increased to higher values, the endothermic effect on polymerisation was reduced, consistent with their DSC thermograms in the same temperature ranges (Fig. 1a and c).

The maximum molecular weights, calculated by using K and α values given in literature [23], for polymers **P1** and **P3** are 2.3×10^4 and 2.5×10^4, respectively. A slight increase in molecular weights of the polymers **P1** and **P2** was observed at the melting point of the complexes **1** and **2**

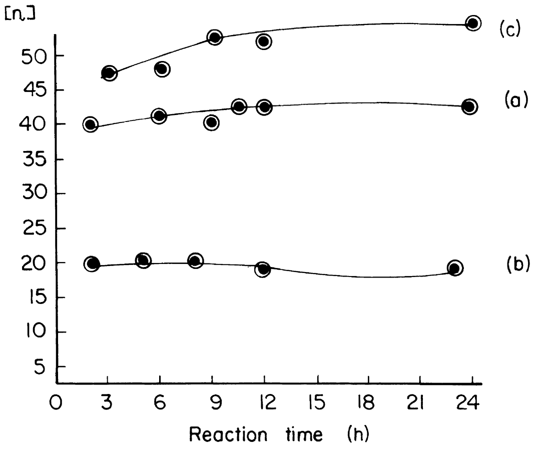

Fig. 3. Change in [η] with reaction time of polymers: (a) **P1**, (b) **P2** and (c) **P3** at constant decomposition temperatures.

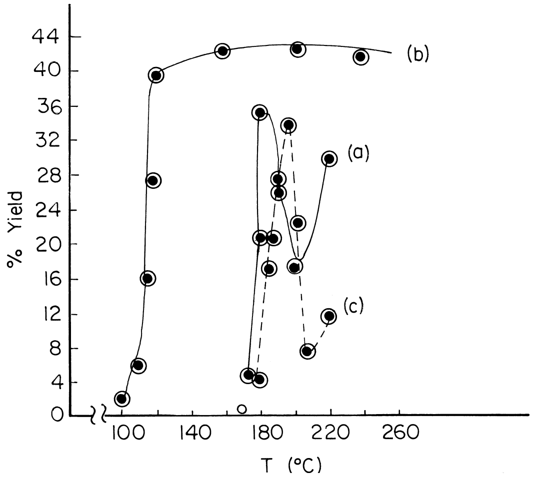

Fig. 4. Change in % yield of poly(dihalophenylene oxide)s with temperature at the end of 3 h: (a) **P1**, (b) **P2** and (c) **P3**.

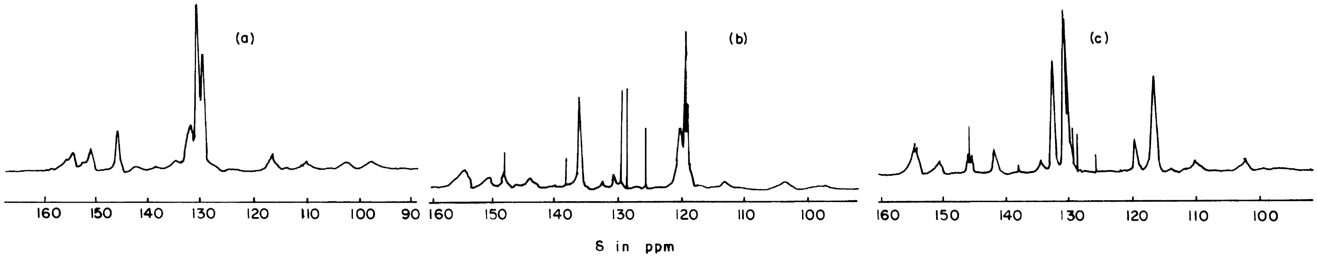

Fig. 5. Proton-decoupled ^{13}C NMR spectra of: (a) **P1**, (b) **P2** and (c) **P3**.

where there were decreases in the percent conversions. A further increase in temperature caused decrease in both percent conversion and molecular weights, followed by an increase in both. These percent conversion and molecular weight dependence on temperature, could be due to the higher mobility of the monomers, where the rate of decomposition slowed down because of the endothermic melting processes. This effect was partially overcome at higher temperature and caused an increase in the percent conversion.

The absorption bands in the FT-IR spectra of polymers **P1**–**P3** were in the range 1474–1626 cm^{-1} due to C=C ring stretchings; at 1115–1268 cm^{-1} due to C–O absorption; at 1064–911 cm^{-1} due to C–O–C stretchings; at 885–806 cm^{-1} due to out of phase C–H bendings and at 752 cm^{-1} due to C–Br absorption as given in the literature [11,13,17–19,21]. ^{13}C NMR proton decoupled spectra of the polymers **P1**–**P3** are displayed in Fig. 5a–c, respectively. Three basic structures can be drawn for each polymer. The theoretical ^{13}C NMR chemical shift data for the main three possible addition products of each polymer were calculated from the related correlation tables given in literature [25]. The binary relations between the observed and calculated data for polymers, **P1**–**P3** are displayed in Figs. 6–8, respectively.

The observations revealed that polymer **P1** has the most probable structure given in Fig. 6b. The ^{1}H NMR spectrum (Fig. 9a) of polymer **P1** was characterised by the peak at $\delta = 7.3$, due to the protons of 2,4-dichloro-1,6-phenylene oxide units and the broader peaks at higher field indicating the presence of both 1,2- and 1,4-addition at the same monomeric unit, suggesting that 1,2-addition is predominant over 1,4-addition.

The observed and calculated shift data of the polymers **P2** and **P3** indicated that both structures, (Figs. 7b,c and 8b,c), respectively, were possible. The ^{1}H NMR spectrum in Fig. 9b revealed that the peaks at $\delta = 7.68$–7.75 and $\delta = 7.19$–7.26 were due to the fifth and third protons,

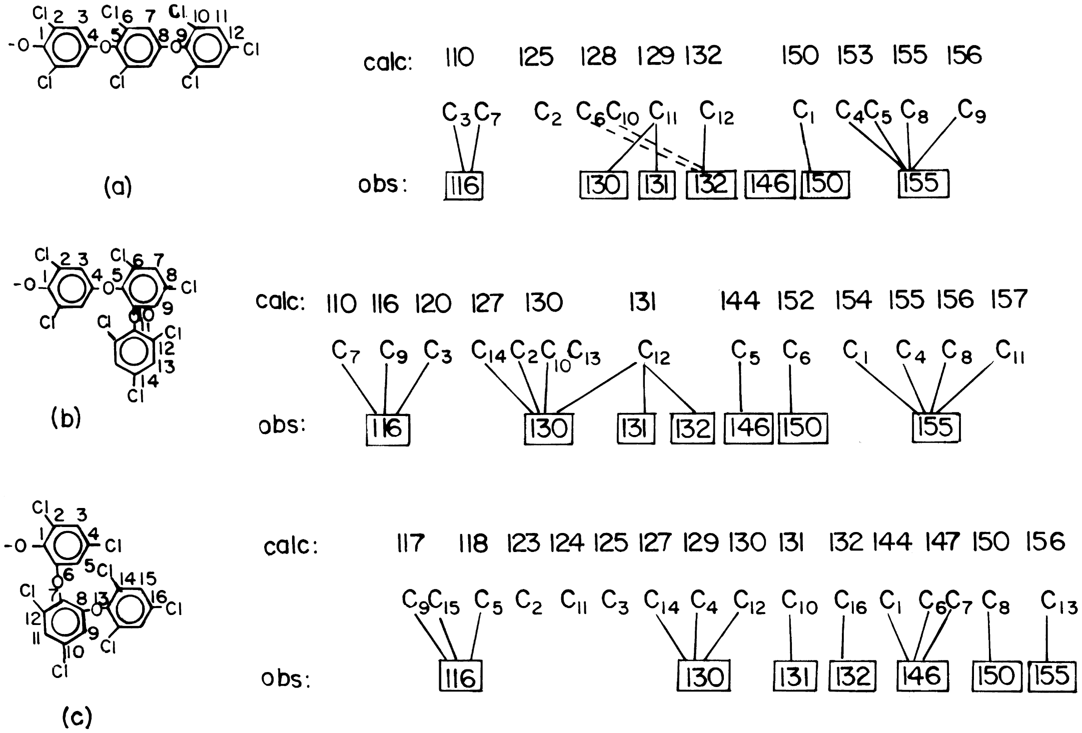

Fig. 6. Schematic representation of the observed and calculated ^{13}C NMR of **P1**.

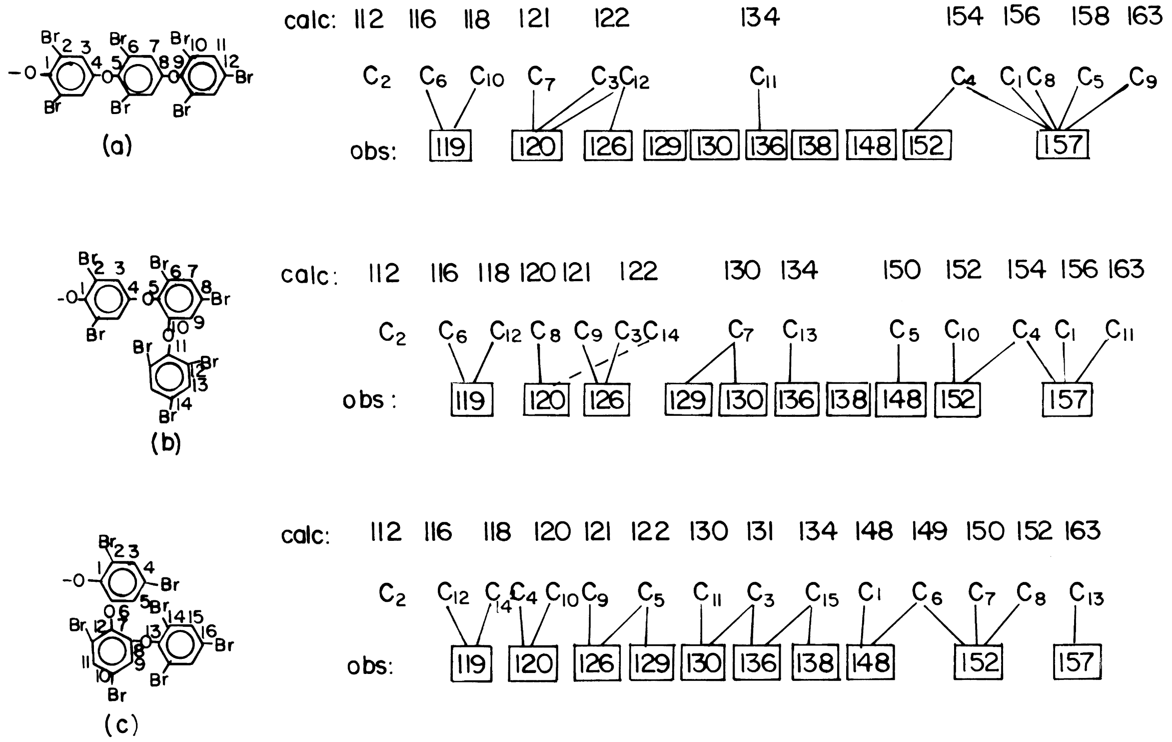

Fig. 7. Schematic representation of the observed and calculated ^{13}C NMR of **P2**.

respectively, of 2,4-dibromo-1,6-phenylene oxide units (1,2-addition); the peaks at $\delta = 7.03$–7.10 were due to the protons of 2,6-dibromo-1,4-phenylene oxide units (1,4-catenation), and the broader peaks at higher field indicated the presence of both 1,2- and 1,4-addition at the same monomeric unit, leading to mainly 1,2-addition. In the ^{1}H NMR spectrum of polymer **P3** (Fig. 9c) the peaks at $\delta = 7.51$–7.56 and 7.1–7.2 were due to the fifth and third protons, respectively, of 4-bromo-2-chloro-1,6-phenylene oxide units (1,2-addition); the peaks at $\delta = 6.88$–6.95 due

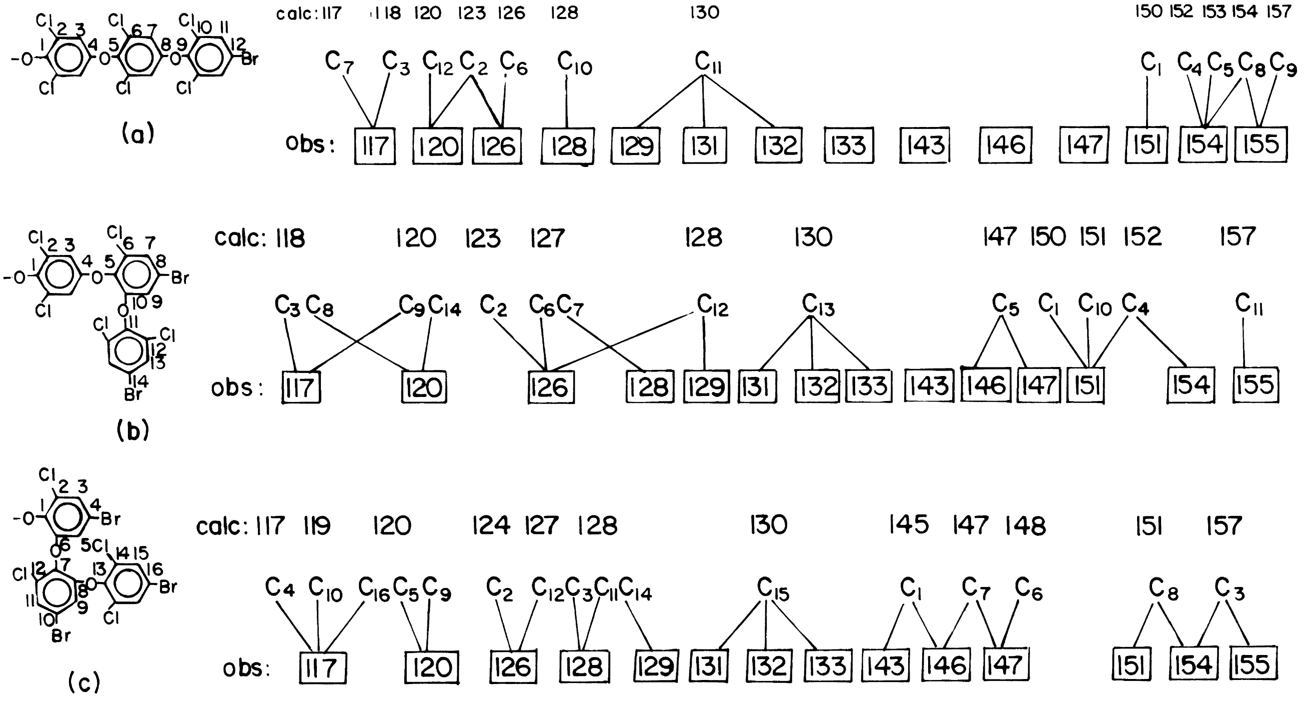

Fig. 8. Schematic representation of the observed and calculated ^{13}C NMR of **P3**.

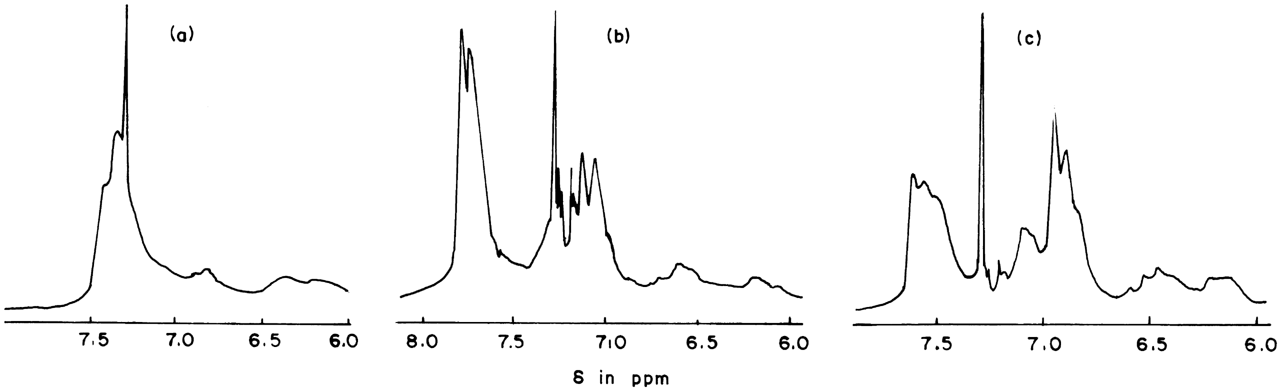

Fig. 9. ^{1}H NMR spectra of: (a) **P1**, (b) **P2** and (c) **P3**.

to protons of 2,6-dichloro-1,4-phenylene oxide units (1,4-addition), and the broader peaks at higher field due to the presence of 1,2- and 1,4-addition at the same monomeric unit, indicating that 1,2- and 1,4-addition were taking place at about equal rates leading to a branched structure.

The glass transition temperatures of **P1**–**P3** in the range 190.2–208.1°C (Table 3), indicated high rigidity,

4. Conclusions

Bis(2,4,6-trichlorophenolato)tri(pyridine)nickel(II), bis(2,4,6-trichlorophenolato)di(pyridine)nickel(II), bis(2,4,6-tribromophenolato)di(pyridine)nickel(II) and bis (4-bromo-2,6-dichlorophenolato)di(pyridine)nickel(II) complexes can be thermally polymerised in the solid state and in the melt. The poly(dichlorophenylene oxide)s synthesised from the thermal decomposition of square pyramidal bis(trichlorophenalato)tri(pyridine)nickel(II) and square-planar bis(trichlorophenalato)di(pyridine)nickel(II) complexes had higher yields and higher molecular weights compared to the polymers obtained from the decomposition of tetrahedral cobalt(II) complex [19], and slightly lower values compared to that of the polymers synthesised from octahedral copper(II) complexes [26]. For both complexes, **1** and **2**, the polymerisation proceeds through mainly 1,2-addition, and for complex **3**, 1,2- and 1,4-addition takes place at almost equal rates. The post-polymerisation of all four complexes led to higher yields, but only the post-polymerised polymers from complexes, **1** and **3** have higher intrinsic viscosity values and calculated molecular weights. All polymers are highly rigid.

Table 3
T_g values of three polyl(dihaphenylene oxide)s

Polymer #	T_g (°C)
1	190.2
2	208.1
3	201.4

Acknowledgements

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