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Synthesis, Characterization, and Thermal Stability of Cobalt Polymeric Phthalocyanines from 3,3',4,4'-Benzophenonetetracarboxylic Dianhydride

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ABSTRACT

Cobalt polymeric phthalocyanine and derivatives thereof were obtained by reaction of 3,3',4,4'-benzophenonetetracarboxylic dianhydride with urea, cobalt chloride, and ammonium molybdate, by saponification of imide end groups, and by esterificaton of carboxylic acid end groups. Metal content, peripheral end groups, structure, and molecular weight of the polymeric phthalocyanine compounds were determined by elemental analyses, titration of end groups, spectral data, and vapour pressure osmometer measurements (VPO). The solubility of the phthalocyanine compounds with ester end groups was examined in various solvents. The thermal stability of cobalt polymeric phthalocyanines was studied under oxidative and nitrogenous atmospheres.

1 INTRODUCTION

Metal containing polymeric phthalocyanines have been described for use as dyes[1] and industrial high-tech materials[2–7] and are also of additional interest because of their high thermostability.[8,9] Low-molecular-weight metal phthalocyanines are generally prepared in high yield by cyclotetramerization of phthalic acid derivatives, such as 1,2-benzenedicarbonitrile or benzene 1,2-dicarboxylic anhydrides, with urea and metal salts. Starting with bifunctional reactants, such as 1,2,4,5-benzenetetracarboxylic dianhydride or 1,2,4,5-benzenetetracarbonitrile, metal polymeric phthalocyanines can be prepared via polytetracyclomerization.[10–12]

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In this investigation, the structure, nature of peripheral end groups, metal content, and molecular weight of some cobalt polymeric phthalocyanines were determined by spectral data, elemental analyses, and vapour pressure osmometer measurements. The thermal stability of the compounds under oxidative and nitrogenous conditions is also reported.

2 EXPERIMENTAL

Analyses of cobalt content were carried out by breaking down 0·1 g polymer in concentrated nitric acid at high temperature, diluting with distilled water, and then titrating with 0·1M EDTA solution, using Murexid as indicator. Titration of carboxylic acid end groups of poly CoPc **2** was carried out with a Jenco model 6071 microcomputer pH-meter. Poly CoPc **2** was dissolved in an excess of 0·1M sodium hydroxide solution. The unconsumed base was titrated back with 0·1M hydrochloric acid.

IR spectra (KBr) were recorded on a BIO-RAD FTS-7 spectrophotometer. UV/VIS spectra were obtained using a Shimadzu UV-240. Elemental analyses were recorded on a Perkin-Elmer 240C. Molecular weight measurements for poly CoPc **3** were carried out with a Knauer vapour pressure osmometer, using THF as solvent. Thermogravimetric analytical studies were effected with a Dupont model 9900 thermal analyzer; a heating rate of 10°C/min was used with nitrogen and oxygen with a flow rate of 100 ml/min.

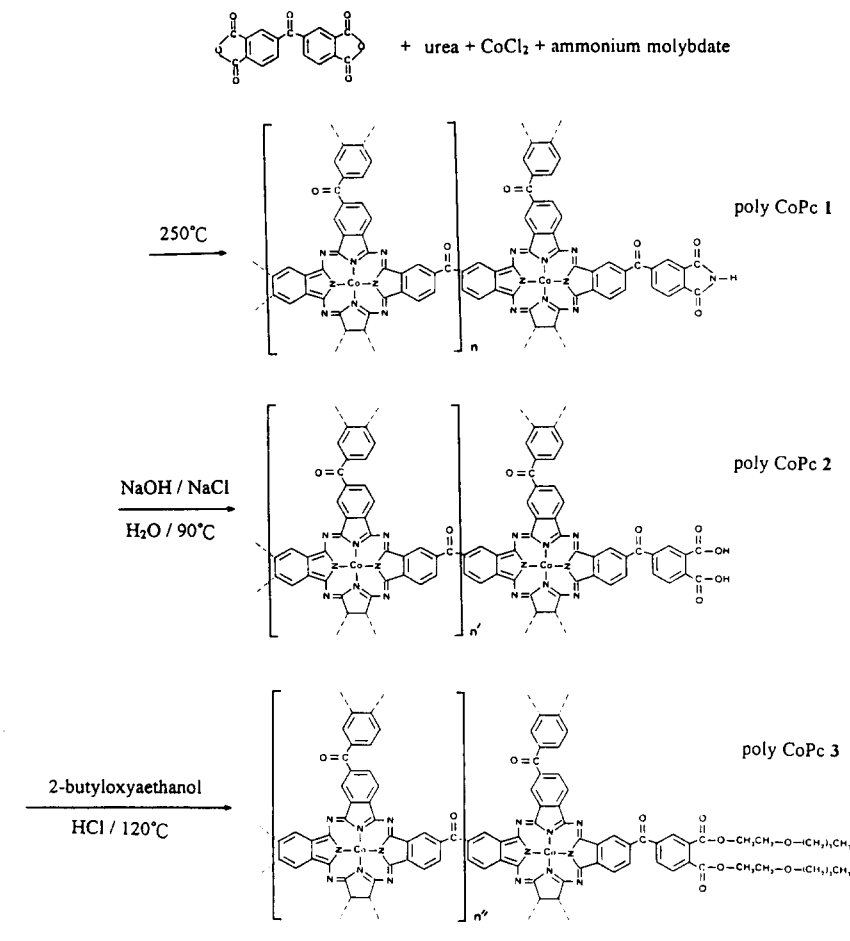
2.1 Preparation of cobalt polymeric phthalocyanine 1 (poly CoPc 1)

16·11 g (0·05 mol) 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 30 g (0·5 mol) urea, 5·95 g (0·025 mol) cobalt chloride and 0·5 g (0·0004 mol) ammonium molybdate were finely ground and heated in a sealed ampoule at 250°C for 2 h. Purification of the products was accomplished by treatment with water, acetone, and 1M hydrochloric acid. Yield 19·4 g.

Elemental analyses of poly CoPc **1**: molecular formula $C_{68}H_{28}N_{12}O_{12}Co$. Cal. for monomeric phthalocyanine, C 64·61%, H 2·22%, N 13·30%, Co 4·67%. Found: C 50·69%, H 3·44%, N 16·45%, C_0 6%.

2.2 Preparation of poly CoPc 2 by saponification of imide end groups of poly CoPc 1

15 g poly CoPc **1** was heated and stirred in a solution of 15 g sodium hydroxide and 90 g sodium chloride in 45 ml water at 90°C for 8 h. The product was then filtered and diluted with 100 ml water. After acidification with 20 ml of 1M hydrochloric acid, the precipitate was isolated and



Scheme 1

washed with water. The blue product was then dissolved in 100 ml 0·2M sodium hydroxide. After filtration, the solution was acidified with 25 ml 1M hydrochloric acid. The product, poly CoPc **2**, was isolated, washed with water and acetone, and dried at 60°C. Yield 11 g.

Elemental analyses for poly CoPc **2**: molecular formula $C_{68}H_{32}N_8O_{20}Co$. Cal. for monomeric phthalocyanine, C 60·94%, H 2·39%, N 8·36%, Co 4·41%. Found: C 55·02%, H 2·86%, N 9·02%, C_0 7%, COOH 13·7%.

2.3 Preparation of poly CoPc 3 by esterification of carboxylic acid end groups of poly CoPc 2

6 g Poly CoPc **2** was heated and stirred in a solution of 20 ml 2-butyloxyethanol and 2 ml hydrochloric acid (37%) at 120°C for 2 h. After

cooling, the solution was mixed with 40 ml of a 1:1 solution of water and ethanol. The resultant poly CoPc **3** was isolated, washed with ethanol and water, and then dried at 60°C, Yield 6·45 g.

Elemental analyses for poly CoPc **3**: molecular formula $C_{116}H_{128}N_8O_{28}Co$. Cal. for monomeric phthalocyanine, C 65·08%, H 5·98%, N 5·23%, Co 2·76%. Found: C 63·65%, H 5·08%, N 6·65%, Co 3·32%, M.W. 5075 g/mole.

3 RESULTS AND DISCUSSION

3.1 Synthesis and reactions

The preparative routes for blue cobalt polymeric phthalocyanines **1** (poly CoPc **1**) and their derivatives **2** and **3** are shown in Scheme 1. Poly CoPc **1** with peripheral imide end groups was obtained by reaction of 3,3',4,4'-benzophenonetetracarboxylic dianhydride with urea, cobalt chloride, and ammonium molybdate in a sealed ampoule at 250°C for 2 h. The crude product was purified with water, acetone, and 1M hydrochloric acid. For the preparation of Poly CoPc **2**, Poly CoPc **1** was boiled in a solution of sodium hydroxide saturated with sodium chloride at 90°C for 8 h. After acidification with 1M hydrochloric acid, poly CoPc **2** with carboxylic acid end groups was precipitated, filtered, and washed with water and acetone. Subsequently, poly CoPc **2** was reacted with 2-butyloxyethanol in hydrochloric acid at 120°C for 2 h to produce poly CoPc **3** with peripheral ester end groups. This product was then washed with water and ethanol.

3.2 IR and UV/VIS spectroscopic data

The IR spectra of poly CoPc **1**, **2**, and **3**, shown in Fig. 1, provide evidence for the structural skeleton of phthalocyanine and the nature of the end groups. The intense absorption bands at 1100 cm^{-1} and 1300 cm^{-1}, corresponding to vibrations of the pyrrole or benzene rings,[13] were observed in the IR spectra of cobalt polymeric phthalocyanines. The absorption bands at 3150 cm^{-1} and 1724 cm^{-1} can be attributed to N—H and C=O vibration of peripheral imide end groups of poly CoPc **1**. A broad peak in the range 2700–3500 cm^{-1} and a sharp peak at 1712 cm^{-1}, corresponding respectively to the O—H and C=O vibration of carboxylic acid end groups, were observed in the IR spectrum of poly CoPc **2**. Absorption at 1730 cm^{-1} due to the C=O group of ester residue, and intense absorption in the 2867–2954 cm^{-1} region due to C—H vibrations of the methylene chain groups were observed in the IR spectrum of poly CoPc **3**.

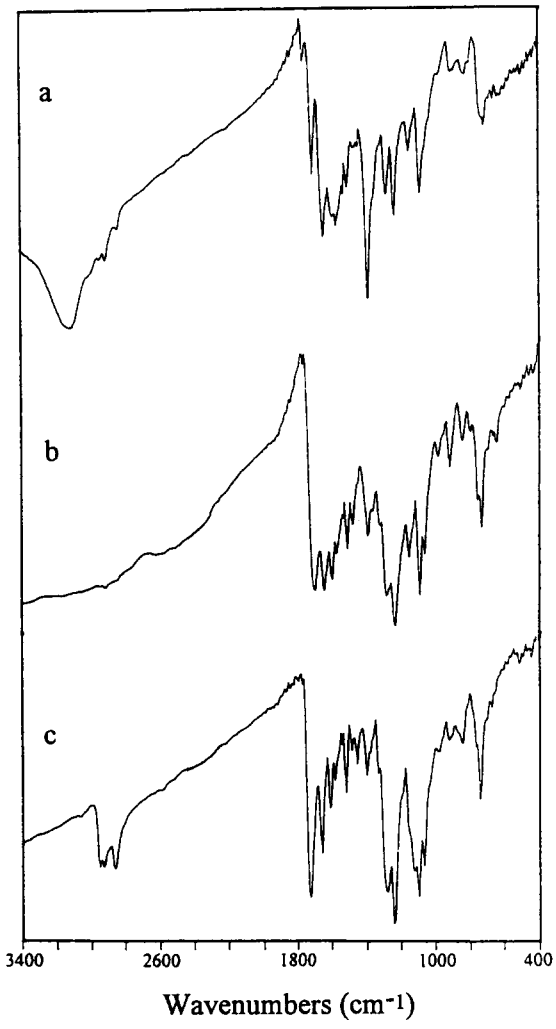


Fig. 1. IR spectra of cobalt polymeric phthalocyanines: (a) poly CoPc **1**, (b) poly CoPc **2**, (c) poly CoPc **3**.

Table 1 shows the solubilities of poly CoPc **1**, **2**, and **3**. Poly CoPc **1** is soluble in concentrated sulfuric acid and insoluble in organic solvents. Poly CoPc **2** is soluble in concentrated sulfuric acid and in *N*,*N*-dimethylformamide. Poly CoPc **3** could be dissolved in concentrated sulfuric acid and also showed excellent solubility in organic solvents such as acetone, chloroform, dichloromethane, *N*,*N*-dimethylformamide and dimethylsulfoxide.

The UV/VIS spectra of poly CoPc **1**, **2**, and **3** in concentrated sulfuric acid are shown in Fig. 2. These compounds all showed absorption maxima

TABLE 1
Solubility of Cobalt Polymeric Phthalocyanines **1**, **2**, and **3**

Polymer	*Solubility*[a]					
	H_2SO_4 (98%)	*DMF*	*DMSO*	*Chloroform*	*Acetone*	*Dichloromethane*
Poly CoPc **1**	+	−	−	−	−	−
Poly CoPc **2**	++	++	++	−	−	−
Poly CoPc **3**	++	++	++	++	++	++

[a] ++: completely soluble, +: partly soluble, −: insoluble.

at 780 nm in concentrated sulfuric acid. Figure 3 shows the UV/VIS spectra of poly CoPc **3** in various organic solvents. Absorption maxima were observed at 680 nm. The bathochromic shift in concentrated sulfuric acid resulted from protonation of the four outer bridging nitrogen atoms of the peripheral phthalocyanine molecules.[14] The absorption maxima of poly CoPc **3** in acidic organic solvents showed a different phenomenon, i.e. an increased absorption intensity without change of absorption maxima. Increased absorption intensity in acidic organic solvent could be due to the polarization of the phthalocyanine moiety.

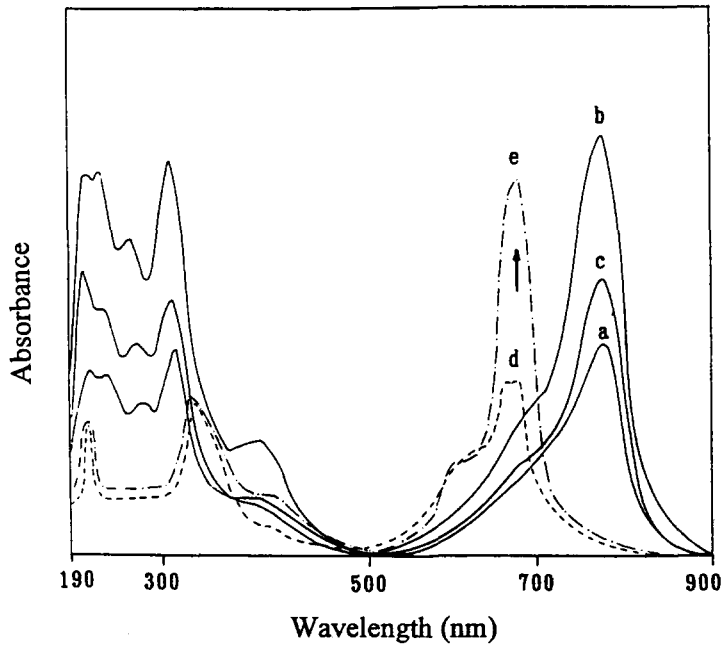


Fig. 2. UV/VIS spectra of cobalt polymeric phthalocyanines: (a) poly CoPc **1** in conc. sulfuric acid, (b) poly CoPc **2** in conc. sulfuric acid, (c) poly CoPc **3** in conc. sulfuric acid, (d) poly CoPc **3** in acetone, (e) poly CoPc **3** in acetone + hydrochloric acid (37%).

TABLE 2
TGA and DTG of Cobalt Polymeric Phthalocyanines **1**, **2**, and **3** under Nitrogen

Polymer	Δm_{end}[a] (%)	*TGA*[b]			*DTG*
		T_{10}	T_{20}	T_{30}	DTG_{max}[c] (Δm_{rem}%)[d]
Poly CoPc **1**	49	195	467	605	61(97), 206(88), 550(74), 776(53)
Poly CoPc **2**	50	148	433	505	64(96), 188(87), 483(72), 776(52)
Poly CoPc **3**	60	343	367	381	43(99), 218(97), 367(78), 523(47), 792(40)

[a] Δm_{end}: weight in loss % at the end of the thermal analyses (950°C).
[b] TGA: T_{10}, T_{20}, T_{30}, temperature at a weight loss of 10, 20, and 30%.
[c] DTG_{max}: temperature of DTG peaks maxima.
[d] Δm_{rem}: weight remaining at the DTG_{max}.

3.3 Thermal analyses

3.3.1 TGA and DTG under nitrogenous conditions

Results of thermogravimetric analyses of the polymers under nitrogenous conditions are shown in Table 2. The thermal stabilities of poly CoPc **1**, **2**, and **3** were compared at a weight loss of 30%: poly CoPc **1** (605°C) > poly CoPc **2** (505°C) > poly CoPc **3** (381°C).

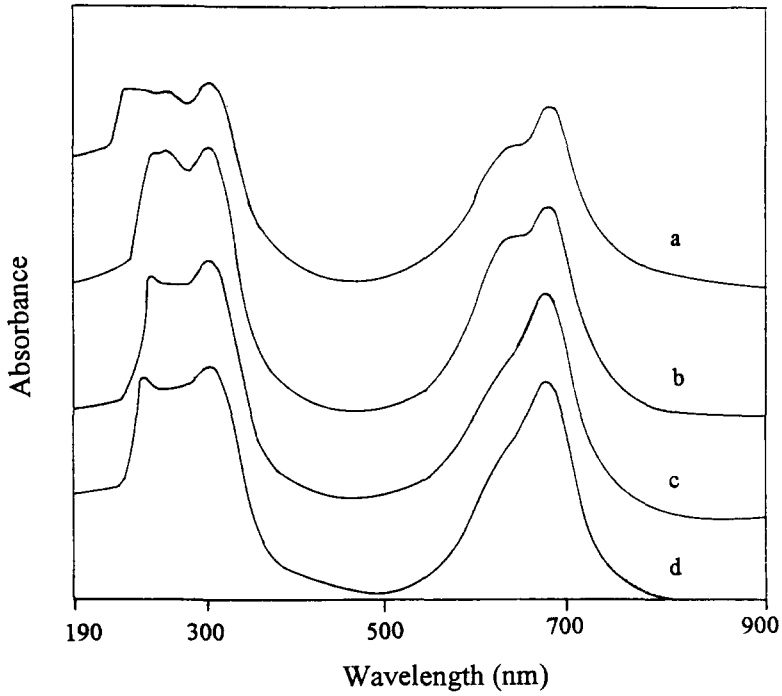


Fig. 3. UV/VIS spectra of poly CoPc **3**: (a) in chloroform, (b) in dichloromethane, (c) in DMF, (d) in DMSO.

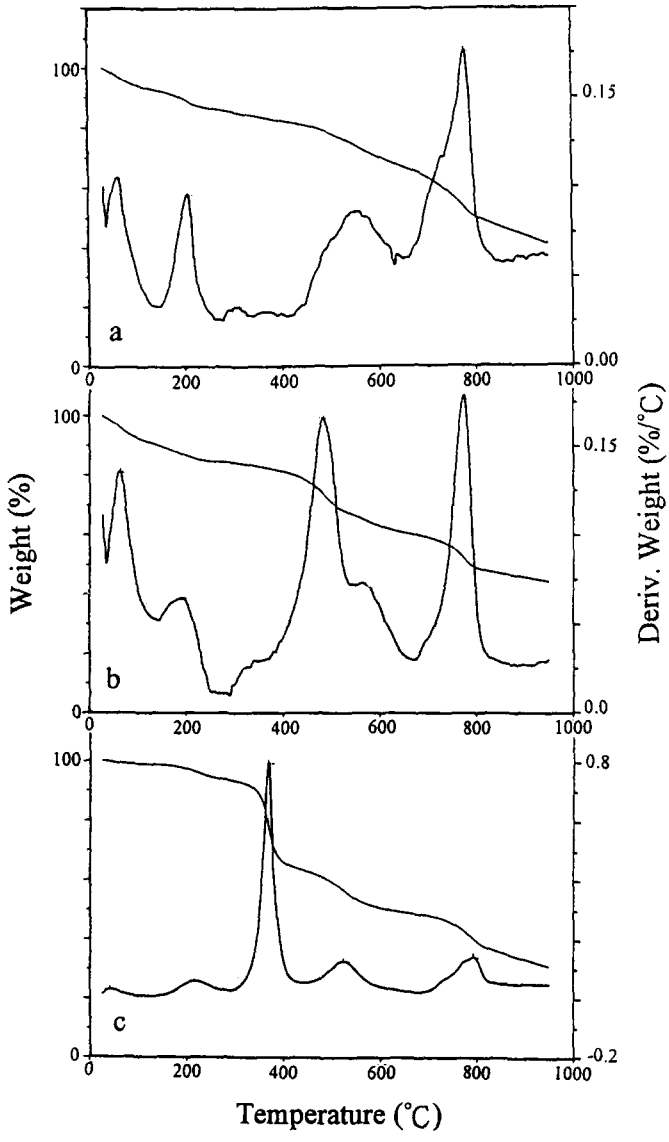


Fig. 4. TGA and DTG of cobalt polymeric phthalocyanine under nitrogen: (a) poly CoPc **1**, (b) poly CoPc **2**, (c) poly CoPc **3**.

The decomposition curves of the polymers, as shown in the DTG, show a four- to five-stage weight loss (Fig. 4). The first-stage weight loss from 42 to *c.* 200°C was *c.* 3% due to loss of absorbed water and oxygen. The weight loss of poly CoPc **2** in the range 150–250°C was *c.* 13% due to dehydration of the carboxylic acid group and formation of the anhydride.[9] Poly CoPc **3** showed approximately 30% weight loss at

TABLE 3
TGA and DTG of Cobalt Polymeric Phthalocyanines **1**, **2**, and **3** under Oxygen

Polymer	Δm_{end}[a] (%)	*TGA*[b]			*DTG*	*TGA curve*[e]	
		T_{10}	T_{20}	T_{30}	DTG_{max}[c] (Δm_{rem}%)[d]	*Turn-back range*	ΔT
Poly CoPc **1**	84	183	406	440	63(97), 211(88), 504(53)	513–440	73
Poly CoPc **2**	93	193	410	440	58(98), 185(90), 515(49)	522–422	100
Poly CoPc **3**	96	342	370	400	44(100), 219(96), 364(81)	493–373	120

[a] Δm_{end}: weight in loss % at the end of the thermal analyses (950°C).
[b] TGA: T_{10}, T_{20}, T_{30}, temperature at a weight loss of 10, 20, and 30%.
[c] DTG_{max}: temperature of DTG peaks maxima.
[d] Δm_{rem}: weight remaining at the DTG_{max}.
[e] TGA curve turn-back from a higher temperature to a lower temperature.

300–420°C, and the peak maximum of the decomposition was at 367°C, this weight loss being due to the breakdown of ester groups. The subsequent thermal decomposition showed two maxima peaks in the DTG curves (483–550°C and 776–792°C) which were due to the breakdown of the polymer structure and decomposition of the breakdown products.[9]

3.3.2 TGA and DTG under oxidative conditions

The results of the thermal analyses of the polymers under oxidative conditions are shown in Table 3. The thermal stability of the polymers under these conditions was lower than that under nitrogen. At the decomposition temperature, fast oxidative destruction occurred and the polymers were completely decomposed at 400–500°C. The temperature of the start of decomposition of the polymers was in the following order: poly CoPc **1** (410°C) > poly CoPc **2** (405°C) > poly CoPc **3** (340°C) (Fig. 5). As under nitrogen conditions, poly CoPc **2** containing carboxylic acid groups was dehydrated and the anhydride was formed at 185°C.

The phthalocyanine polymers **1**, **2**, and **3** showed an interesting phenomenon under oxidative condition, i.e. the TGA curves showed a decrease of temperature prior to complete decomposition of the polymers. The order of the 'turn-back' range of temperature was: poly CoPc **3** > poly CoPc **2** > poly CoPc **1**. As noted in the literature,[15,16] metal phthalocyanines have the ability to absorb oxygen, and can be used as an oxidative catalyst. Therefore, as the oxidative thermal decomposition was initiated, the polymers absorbed oxygen. When the decomposition proceeded to some extent, the oxygen began to be desorbed, resulting in the absorption of heat, with corresponding decrease in temperature.[17]

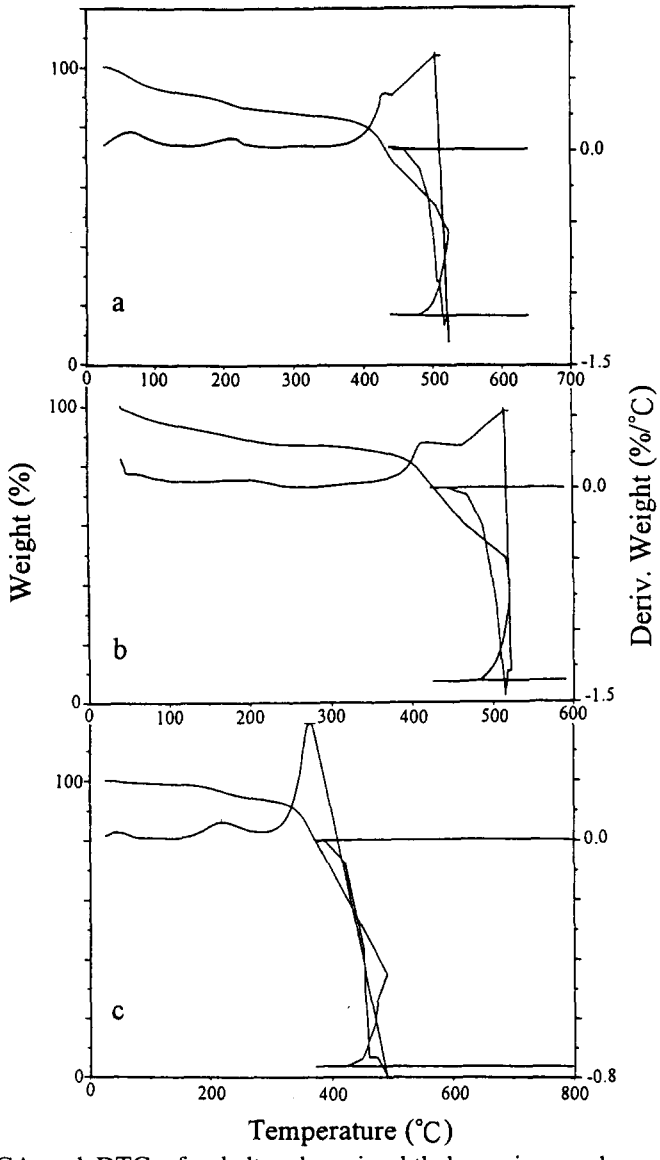


Fig. 5. TGA and DTG of cobalt polymeric phthalocyanines under oxygen: (a) poly CoPc **1**, (b) poly CoPc **2**, (c) poly CoPc **3**.

4 CONCLUSION

Cobalt polymeric phthalocyanines were obtained by reaction of 3,3',4,4'-benzophenonetetracarboxylic dianhydride with urea, cobalt chloride, and ammonium molybdate. Poly CoPc **3** with ester end groups was prepared by

esterification of poly CoPc **2** with 2-butyloxyethanol using hydrochloric acid as catalyst.

Results of thermal analyses showed that the thermal stability of the polymers under oxygen and nitrogen decreases in the order: poly CoPc **1** > poly CoPc **2** > poly CoPc **3**. The TGA and DTG curves showed that the thermal decomposition of the polymers operates under different breakdown mechanisms in nitrogenous and oxidative conditions. Under oxidative conditions, the TGA curves showed decrease of temperature before complete decomposition of polymers.

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