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SHORT PAPER

X-ray photoelectron spectroscopy and electrical conductivity studies of metallophthalocyanine sheet polymers

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The X-ray photoelectron spectroscopy (XPS) technique has been used to characterize metallophthalocyanine sheet polymers having peripheral carboxyl groups. A comparative analysis of the XPS and electrical conductivity data of metal-free, and nickel- and copper-containing, phthalocyanine sheet polymers has been described. Metallophthalocyanine sheet polymers exhibited a maximum conductivity of about 1 S cm^{-1} on pyrolysis.

Keywords: X-ray photoelectron spectroscopy, phthalocyanine sheet polymers, metal-free, nickel, copper, electrical conductivity, pyrolysis

INTRODUCTION

Metallophthalocyanines are the most extensively studied organic materials because of their wide range of applications in many fields.[1–5] The wide variety of applications exists as a result of the unique properties that are displayed by the conjugated phthalocyanine macrocycle. The chemical versatility of the phthalocyanine macrocycle offers important opportunities to develop structure–property relationships. It would be more appropriate to view metallophthalocyanines (MPcs) as multifunctional organic materials whose electrical, optical, magnetic, thermal, piezoelectric, non-linear optical and chemical properties could be tailored for a particular end-use. The usefulness of MPcs lies in their unique physico-chemical properties coupled with excellent environmental and thermal stabilities.[6–8]

From a conductivity point of view, the phthalocyanine (Pc) macrocycle possesses a highly delocalized π-electron carbon–nitrogen backbone necessarily required for high electrical conductivity. As a consequence, for example, crystals of metal-free phthalocyanine exhibit a conductivity as high as 7.0×10^2 S cm^{-1} in the oxidized state.[9] Furthermore, a highly extended π-electron system can be built by condensing together Pc macrocycles via a polymerization process and high conductivity may be anticipated. The discovery of electrically conducting organic polymers (e.g. polyacetylene, polypyrrole, polythiophene, polyaniline, polyphenylenes, etc.) has created a great deal of attention in MPc polymers partly because of their high thermal stability and ability to be processed. Besides many other kinds of MPc polymers, sheet-like (MPc-S) polymers constitute an interesting class of conducting polymers.[10]

In this short paper, some XPS studies of MPc-S polymers are reported. The electrical conductivities of metal-free, and of metal-containing, sheet polymers are also discussed.

EXPERIMENTAL

Metallophthalocyanine sheet (MPc-S) polymers (Fig. 1) were synthesized and purified according to the method of Achar *et al.*[11] The chemical structures of the products were investigated by infrared spectroscopy techniques. Another method of characterizing these MPc-S polymers was by use of the XPS technique which is the theme of this paper. XPS spectra of the powdered samples were obtained on an X-ray photoelectron spectrometer (Model 5100 ESCA System,

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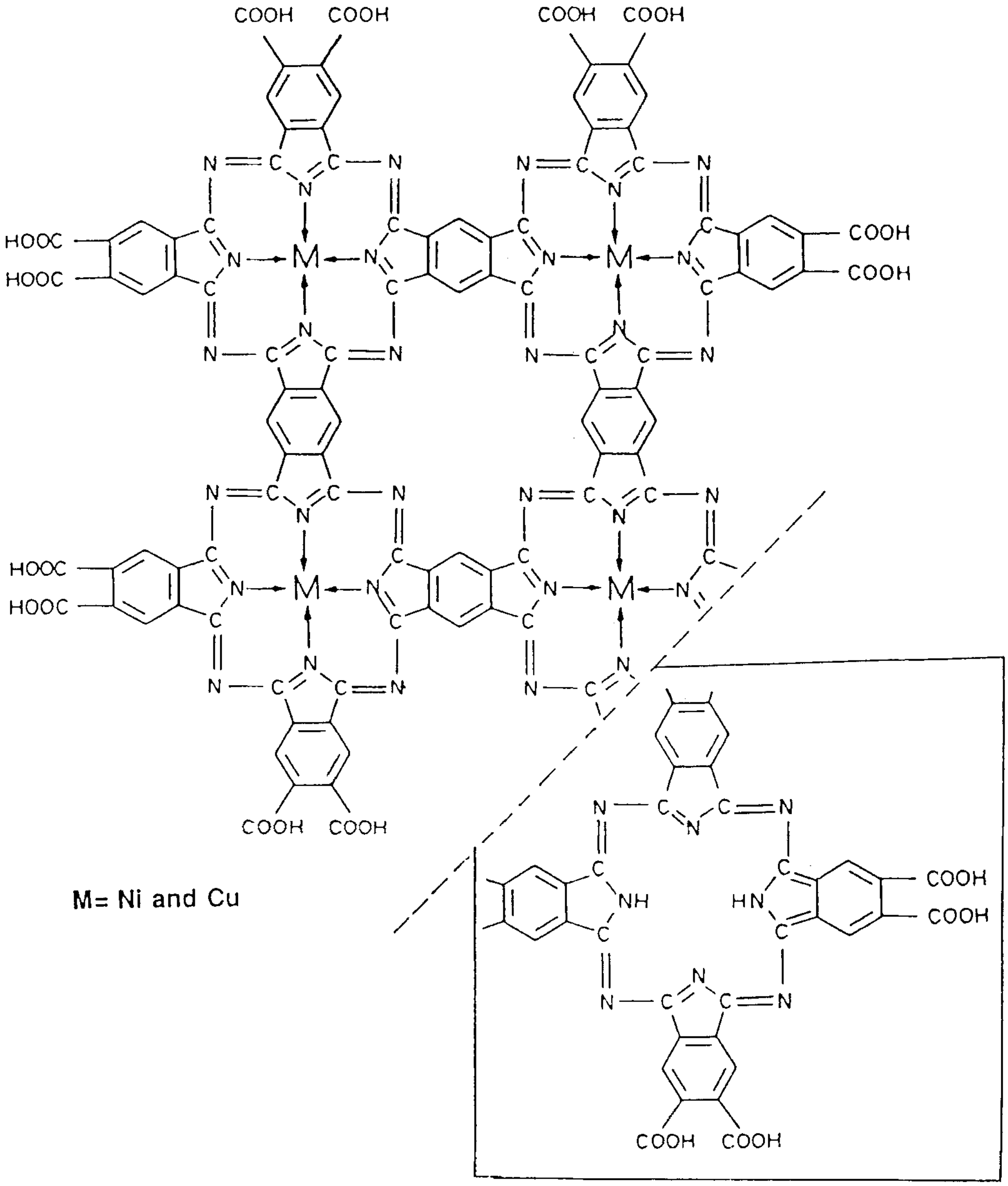

Figure 1 Structure of metallophthalocyanine-sheet (MPc-S) polymers where M represents the nickel and copper metal atoms. The structure of a metal-free phthalocyanine-sheet (H_2Pc-S) polymer is shown as an inset.

Physical Electronics) using an MgK_a X-ray radiation source (1245.9 eV photons). The room-temperature electrical conductivities of compressed pellets were measured by the two probe method and/or the standard four-probe technique of van der Pauw.[12]

RESULTS AND DISCUSSION

XPS binding energies and full width at half-maximum (FWHM) for carbon, nitrogen, oxygen, nickel and copper transitions recorded for metal-free (H_2Pc-S), nickel (NiPc-S) and copper

Table 1 XPS binding energies and full width at half-maximum (FWHM) in eV for metal-free, and nickel- and copper-containing, phthalocyanine sheet polymers

	H_2Pc-S		NiPc-S		CuPc-S	
	Position (eV)	FWHM (eV)	Position (eV)	FWHM (eV)	Position (eV)	FWHM (eV)
C1*s*	287.24	1.95	287.74	1.76	286.96	1.72
	290.76	2.54	290.87	2.55	290.36	2.60
	292.82	2.48	292.86	2.55	293.07	2.60
N1*s*	401.08	2.10	401.86	1.73	401.12	1.83
	402.42	2.22	403.17	1.76	402.49	2.00
O1*s*	533.83	2.19	534.18	1.87	533.44	1.94
	535.50	2.00	535.67	2.45	535.03	2.60
Ni($2p_{3/2}$)	—	—	858.57	1.74	—	—
Ni($2p_{1/2}$)	—	—	876.21	—	—	—
Cu($2p_{3/2}$)	—	—	—	—	935.15	1.98
Cu($2p_{1/2}$)	—	—	—	—	957.42	—

(CuPc-S) polymers are listed in Table 1. The proximity of binding energies indicates that the MPc-S polymers may have identical skeletons. The appearance of additional peaks for metal atoms in XPS spectra shows that the central metal atoms are embodied in the Pc macrocycles. The C1*s* spectrum shows three peaks. The main broad peak at 287.24 eV (H_2Pc-S), at 287.74 eV (NiPc-S) and at 286.96 eV (CuPc-S) may be assigned to $-\mathrm{N}-\overset{|}{\mathrm{C}}=\mathrm{N}-$ linkages of the pyrrole rings. The second C1*s* peak at 290.76 eV (H_2Pc-S), at 290.87 eV (NiPc-S), and at 290.36 eV (CuPc-S) probably originates from the carbons of the carboxyl groups. The third C1*s* peak at 292.82 eV (H_2Pc-S), at 292.86 eV (NiPc-S) and at 293.07 eV (CuPc-S) may be associated with the aromatic ring carbon atoms.

The N1*s* spectrum consists of two components indicating the existence of two chemical environments for nitrogen atoms. The low-binding-energy N1*s* peak at 401.08 eV (H_2Pc-S), at 401.86 eV (NiPc-S) and at 401.12 eV (CuPc-S) is probably associated with the nitrogen atoms of the pyrrole rings. The high-binding-energy peak at 402.42 eV (H_2Pc-S), at 403.17 eV (NiPc-S) and at 402.49 eV (CuPc-S) involves azo bridged nitrogens having $-\mathrm{C}-\mathrm{N}=\mathrm{C}-$ type linkages.

The features of the O1*s* region spectrum are particularly applicable to the C1*s* spectrum. The deconvolution gives two component peaks. The O1*s* low-binding-energy peak is attributed to the oxygens of $-\mathrm{COOH}$ groups. The second O1*s* peak probably results from water molecules based on a formula of $C_{120}H_{40}N_{32}O_{32}M_4 \cdot 8H_2O$ that has been suggested by Achar *et al.*[11] The XPS spectral features suggest inclusion of metal atoms in the Pc macrocycles and the associated XPC binding energies for nickel and copper are given in Table 1. The XPS binding energies are in agreement to those reported in the literature for MPc monomeric and polymeric compounds.[13-16] A sheet-like structure as depicted in Fig. 1 may be expected for H_2Pc-S, NiPc-S and CuPc-S polymers although the XPS data cannot be used to confirm this.

The H_2Pc-S, NiPc-S, and CuPc-S polymers as synthesized show electrical conductivities of 2.45×10^{-6}, 8.44×10^{-5} and $1.12 \times 10^{-5}\ \mathrm{S\ cm^{-1}}$ respectively.[17] The electrical conductivities of these polymers measured after various types of treatments are summarized in Table 2. After the polymers had been cured at 200°C for six days under vacuum their conductivities declined indi-

Table 2 Electrical conductivities of metal-free, and nickel- and copper-containing, phthalocyanine sheet-polymers recorded at room temperature

	Electrical conductivity ($\mathrm{S\ cm^{-1}}$)		
Polymer	Undoped state[a]	Doped state[b]	After pyrolysis[c]
H_2Pc-S	2.53×10^{-13}	7.24×10^{-5}	3.20×10^{-4}
NiPc-S	2.23×10^{-6}	8.57×10^{-2}	1.06
CuPc-S	6.12×10^{-9}	3.26×10^{-3}	7.21×10^{-2}

[a] Undoped state represents the samples treated at 200°C for six days under vacuum. [b] Undoped samples doped with sulphuric acid. [c] Pyrolysis carried out at 480°C following the method of Venkatachalam *et al.*[15]

cating that the previous high electrical conductivity resulted either from the water molecules and/or from impurities. Doping with sulphuric acid raises conductivity as high as $8.57 \times 10^{-2}\ \mathrm{S\,cm^{-1}}$ for the NiPc-S polymer. The increased conductivity after doping following curing is a consequence of highly polar carboxyl (-COOH) groups attached at the peripheral sites of the Pc macrocycles which act as carrier traps and hence partially circumvent charge carrier mobility compared with pyrolised samples. Pyrolysis of MPc-S polymers at 480°C under an inert atmosphere[15] shows a significant increment in conductivity, and a maximum conductivity of about $1\ \mathrm{S\,cm^{-1}}$ was observed for the NiPc-S polymer. Venkatachalam *et al.*[15] reported a conductivity value of $2.3\ \mathrm{S\,cm^{-1}}$ for the NiPc-S polymer and the present results are in good agreement. Poly(copper octacyanophthalocyanine) shows a conductivity *ca* 5–$8\ \mathrm{S\,cm^{-1}}$ on thermal treatment as reported by Lin and Dudek.[18] In another study, Walten *et al.*[16] reported that Pc polymers, prepared from bisphthalonitrile monomers, exhibit electrical conductivity of about $1\ \mathrm{S\,cm^{-1}}$ after curing at about 600°C. Therefore, for MPc polymers that have terminal carboxyl (-COOH) or cyano (-CN) groups, pyrolysis seems to be a very effective method of generating high-conductivity MPc polymers, since curing causes further polymerization leading to the formation of a highly conjugated network. High electrical conductivity in MPc-S polymers also appears as a result of an extended conjugated system due to the decarboxylation and because of the formation of free radicals.

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