

Note

Sheet polymer and its complexes: Part III—Synthesis and conductive properties of polymeric tetraphenylporphyrin and its complexes

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The polymeric porphyrin film has been prepared by polymerization of terephthalaldehyde with pyrrole. The spectra and electrical properties of its complexes with transition metals (Cu, Co, Zn, Fe, Mn, Ni) have been discussed. The polymer exhibits semi-conducting property ($\sigma_{\pi} = 5.08 \times 10^{-8} \sim 4.44 \times 10^{-3}$ s/cm) after doping with iodine.

During the past several years great progress has been made in the field of conducting organic materials based on polymeric cofacially assembled bridged porphyrins or polymer bound porphyrins in their side chains¹⁻⁴. However, so far very few investigations have been done concerning the preparation⁵ and the conductivity of the porphyrinic sheet polymer⁶. Our group⁷ reported that the polymer porphyrin film MPTBCOPP (Figure 1) prepared by interfacial polymerization of tetrakis-(4-hydroxyphenyl) porphyrin with terephthalyl chloride exhibits semi-conducting property ($\sigma_{\pi} = 4.63 \times 10^{-6} \sim 4.83 \times 10^{-4}$ s/cm) after doping with iodine.

In this paper, polymeric tetraphenylporphyrin

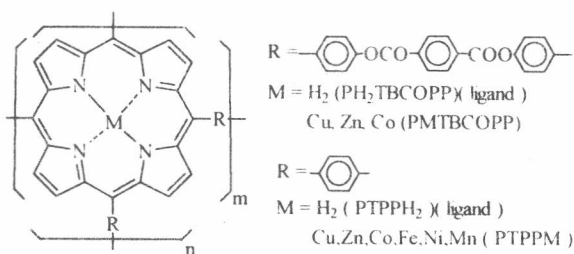
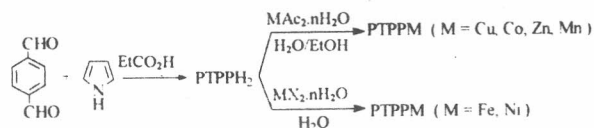


Figure 1—General structure of the sheet polymeric porphyrins

(PTPPH₂) and its complexes (PTPPM) with copper, cobalt, zinc, iron, manganese and nickel (Figure 1) have been synthesized and the effect of the length of -R- on their conductivity has been studied.

Results and discussion

The polymeric tetraphenylporphyrin and its transition metal complexes are synthesized via the following route:



In typical synthesis of low molecular weight porphyrin⁸, the yield of tetraphenylporphyrin from pyrrole and benzaldehyde derivatives is about 20%. The by-products are mainly linear polypyrrole, which could be washed away by methanol. In the synthesis of PTPPH₂, the by-products (such as polypyrrole and low molecular weight porphyrin) was washed away by methanol and chloroform separately. The yield of the polymeric tetraphenylporphyrin is more than 20%. It is suggested that the porphyrin ring is easily formed in the end of polymer. The polymeric porphyrin cannot be soluble in all organic solvents because of two-dimension structure.

IR spectra were recorded in KBr pellets: The weak absorptions of N-H stretching vibration at 3300 cm⁻¹ and δ_{HN} near 948 cm⁻¹ for the ligand (PTPPH₂) disappear or weaken in the complexes (PTPPM). The strong absorption near 1039 cm⁻¹ appears to be a characteristic absorption of all metalloporphyrins. Figure 2 shows the typical IR spectra of the polymeric porphyrin (PTPPH₂) and its complexes (PTPPFe, PTPPCo). The polymeric films of PTPPM have also been characterized by thermal analysis. Figure 3 shows the typical TG-DTA curves of the polymeric porphyrin (PTPPH₂) and its complexes (PTPPCo), which showed that the polymer was decomposed at 380°C-600°C. It is suggested that the polymer and its complexes are very stable.

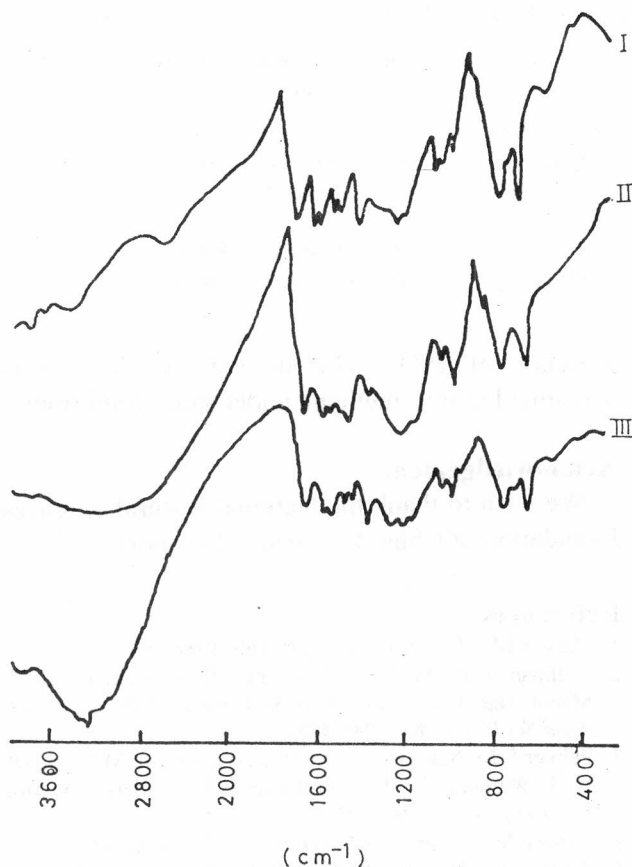


Figure 2—Infrared spectra of polymeric porphyrin (PTPPM) (I: PTPPH₂; II: PTPPFe; III: PTPPCo)

Two-point probe conductivity measurements were performed on compacted disks of the iodine-doped polymers. The conductivity of each undoped polymer is less than 10×10^{-9} s/cm, and other results are summarized in the Table 1. Iodine-doped PTPPFe shows an electrical conductivity of 4.44×10^{-3} s/cm, which is 6 orders of magnitude greater than PTPPFe and 1 order of magnitude greater than the upper limit of the reported polymeric porphyrin PMTBCOPP⁷, suggesting that the shortening of the length of -R- may promote regular arrangement of porphyrin plane in polymer skeleton, and then increase the electric conductivity of the polymeric porphyrin film.

Experimental Section

Materials and measurements. Pyrrole, terephthalaldehyde and propionic acid were distilled before use. Other reagents were used without further purification.

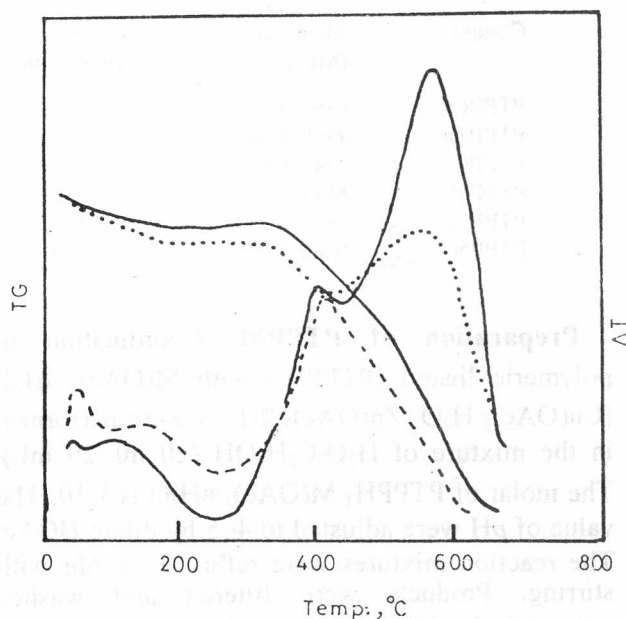


Figure 3—TG-DTA curves of PTPPH₂ (—) and PTPPCo (---)

Table I—Conductivity data of iodine-doped polymeric porphyrins

Compd	Dopant	Molar ratio	σ_{π} (S.cm ⁻¹)
PTPPMn	I ₂	1:1	1.32×10^{-6}
PTPPCo	I ₂	1:1	2.77×10^{-6}
PTPPZn	I ₂	1:1	4.04×10^{-5}
PTPPNi	I ₂	1:1	4.03×10^{-4}
PTPPCu	I ₂	1:1	1.44×10^{-4}
PTPPFe	I ₂	1:1	4.44×10^{-3}

IR spectra were recorded in KBr disks with an Alpha-centauri FT-IR spectrophotometer. Elemental analysis was performed on VarioEL elemental analyzer. Conductivity measurements were carried out using 12.9 mm (diameter) samples (compacted) and a two-point probe technique under a dry Argon atmosphere.

Synthesis of polymeric tetraphenylporphyrin (PTPPH₂) and its transition metal complexes (PTPPM). terephthalaldehyde (0.05 mole) and pyrrole (0.10 mole) were added into boiling propionic acid (500 mL). After boiling for 3 hr, the reaction mixture was cooled. The crude product was filtered and washed several times with water, ethanol and chloroform, respectively. The yield was about 90% after drying. Anal. Found: C, 77.74; H, 4.95; N, 10.89. Calc. for C₃₂H₁₈N₄·2H₂O: C, 77.73; H, 4.45; N, 11.34%.

Table II—The conditions of synthesis of PTPPM

Compd	Metal salts (ML _n)	PTPPH ₂ /Ml _n (mole ratio)	Solvent	Time	Procedure in purifying the product
PTPPCu	Cu(OAc) ₂	1/10	H ₂ O/EtOH	6h	Washed by H ₂ O,
PTPPZn	Zn(OAc) ₂	1/10	H ₂ O/EtOH	6h	and EtOH until
PTPPCo	Co(OAc) ₂	1/10	H ₂ O/EtOH	6h	no metal ions.
PTPPMn	Mn(OAc) ₂	1/10	H ₂ O/EtOH	6h	
PTPPFe	FeCl ₂	1/10	H ₂ O	36h	Washed by HCl and
PTPPNi	NiCl ₂	1/10	H ₂ O	36h	H ₂ O until no metal.

Preparation of PTPPM. Coordination of polymeric ligand (PTPPH₂) with M(OAc)₂·nH₂O [Cu(OAc)₂·H₂O, Zn(OAc)₂·2H₂O] were performed in the mixture of H₂O-C₂H₅OH (20 mL/20 mL). The molar of PTPPH₂:M(OAc)₂·nH₂O is 1:10. The value of pH were adjusted to 4~5 by dilute HOAc. The reaction mixtures were refluxed for 6hr with stirring. Products were filtered and washed separately by H₂O and ethanol for several times. Yields of 80% or better of PMTBPBSOPP were obtained after drying. Table II shows the coordination of polymeric tetraphenylporphyrin with metal salts. The coordination of polymeric ligand (PTPPH₂) with ferrous or nickel salt was different with above.

Doping of the polymeric porphyrin complexes. The iodine was dissolved into benzene, and the equal molar weight of the polymeric porphyrin complexes(PTPPM) was added. The mixture was stirred for 24 hr at 50°C and then dried *in vacuo* in

presence of P₂O₅. The doping by FeCl₃ was performed in nitromethane under same conditions.

Acknowledgement

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