

SYNTHESIS OF POLYTETRAPHENYLPORPHYRIN AND ITS MANGANESE COMPLEX *

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ABSTRACT

A new polymeric tetraphenylporphyrin and its manganese complex were synthesized. Their structures were identified by examining the visible absorption, IR, $^1\text{H-NMR}$ spectra.

Porphyrins and metalloporphyrins have been studied systematically, because they play an important role in the photochemical and biochemical reactions^[1-2]. It is found that the metalloporphyrins are photosensitive and possess photovoltaic effect^[3]. With the idea of photo-splitting water into hydrogen and oxygen by means of a bipolar polymeric membrane, we have synthesized polymeric tetraphenylporphyrin.

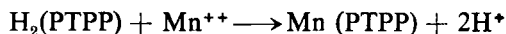
EXPERIMENTAL

1. Synthesis of polytetraphenylporphyrin (PTPP)

The synthesis of polytetraphenylporphyrin was based on the method of low molecular tetraphenylporphyrin preparation^[4]. In a 500 ml round-bottom flask, 360 ml of *n*-propionic acid, 6.17 ml (0.06 mole) of benzaldehyde and 1.34 g (0.01 mole) of terephthaldehyde were added. The mixture was stirred at room temperature until the terephthaldehyde was completely dissolved. Then 5.53 ml (0.08 mole) of pyrrole was added, and the solution was heated under reflux for 7 hours. After cooling to room temperature, it was filtered, and the black filter cake was washed thoroughly with methanol. After washing with distilled water, the black powder was dried in vacuo to give 6 g of PTPP, which was assigned as No. I.

2. Synthesis of polytetraphenylporphyrin manganese complex

The reaction of complex formation is a heterogeneous one. In a 100 ml, round-bottom flask, 50 ml of acetic acid-water solution of manganese acetate in concentration of 0.03 mol / l and 0.5 g of polytetraphenylporphyrin were added, and the mixture was heated under reflux for 6 hours, then cooled and filtered. The solid was washed with distilled water and dried in vacuo to give polytetraphenylporphyrin manganese complex product assigned as No. IV. The reaction is as follows:



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By determining the concentration difference of Mn^{++} ion before and after the reaction, the amount of complex formed was 0.12 g Mn^{++} /g PTPP or 0.34 mole Mn^{++} /mole TPP.

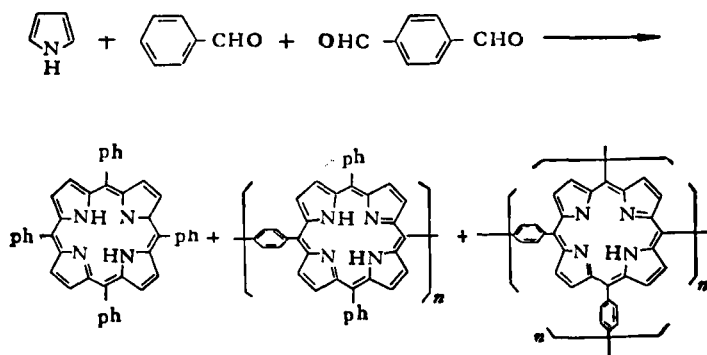
3. Determination of physical properties

Electron microscopic photograph was taken by using a DX-3A Scanning Electron Microscope. The molecular weight was determined by QX-08 Vapour Pressure Osmometer, 250 M ^1H -NMR spectra by CAMECA TSN 250 NMR apparatus, IR spectra by UR-10 IR Spectrometer and visible spectra by Specord UV-VIS Photospectrometer.

RESULTS AND DISCUSSION

1. Synthesis of polytetraphenylporphyrin

The reaction is as follows:



The product was a mixture of low molecular tetraphenylporphyrin, linear polytetraphenylporphyrin and cross-linked polytetraphenylporphyrin. Scanning electron microscopic photograph of the mixture is shown in Fig. 1.



Fig. 1 Scanning microscopic photograph of No. I ($\times 500$)

2. Determination of the structure of polytetraphenylporphyrin

The solubility of polytetraphenylporphyrin is very low, even in strong acids, strong bases.

or strong polar solvents. We extracted No. I with chloroform. After extraction, the solution was concentrated and the residue dried in vacuo, and assigned as No. II (0.1 g of No. II was obtained from 1 g of No. I). The insoluble portion was dried, and assigned as No. III.

Comparisons of the VIS absorption spectra and ^1H -NMR spectra between No. II and the known low molecular tetraphenylporphyrin were made. From Fig. 2, it can be seen that the five peaks both in TPP and in No. II appear at similar wavelength. The absorption

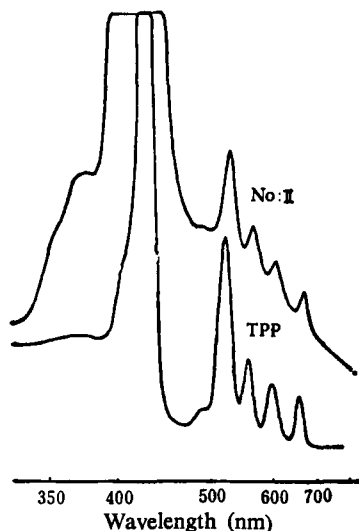


Fig. 2 VIS spectra of TPP and No. II

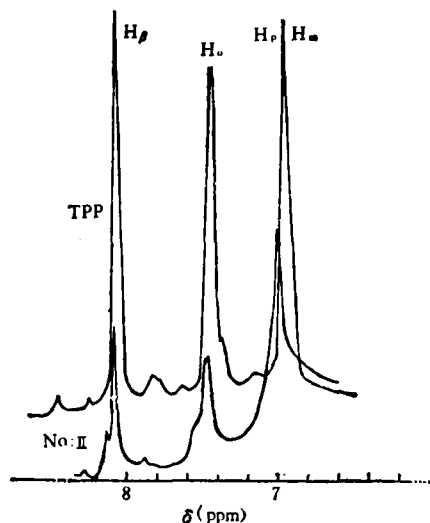


Fig. 3 ^1H -NMR spectra of TPP and No. II (solvent CDCl_3 , 60°C). In Fig. 3. H_β , H_o , H_m and H_p indicate the hydrogen atoms at the position of porphyrin and ortho, meta and para positions of benzene respectively

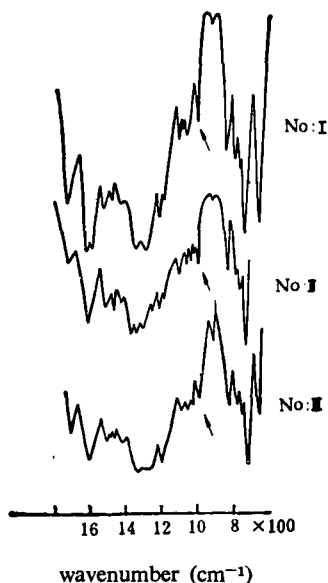


Fig. 4 IR spectra of No. I, No. II and No. III

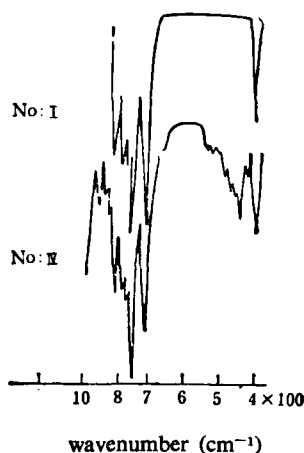


Fig. 5 IR spectra of No. I and No. IV

peak for Hp of PTPP in Fig. 3, shifts 0.004 ppm to lower magnetic field from the peak for Hp of TPP. This is due to the TPP linking to form a polymer.

The comparison of the IR spectra of No. I, No. II and No. III (see Fig. 4) shows that the absorption peak at 970 cm^{-1} is the characteristic ring skeleton vibration of porphyrin^[5].

The number average molecular weight of No. II determined by VPO is 3,667.

Visible absorption spectra, ^1H -NMR spectra IR spectra and molecular weight determination all showed that No. II is linked by tetraphenylporphyrin unit.

It can be seen from Fig. 4 that the characteristic absorption peak of 970 cm^{-1} is also found in No. III. This indicates that No. III also consists of tetraphenylporphyrin unit.

3. IR spectra of polytetraphenylporphyrin manganese complex

The IR spectra of complex are shown in Fig. 5. The absorption band due to $\nu_{\text{N-Mn}}$ is found in the lower wavenumber of $340\text{--}370\text{ cm}^{-1}$, which indicates that the Mn^{++} ion is linked to the ring of porphyrin.

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