

GC–MS studies on degradation of copper phthalocyanine sheet polymer

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Abstract

Synthetic metal phthalocyanine sheet polymer of copper showed exceptional thermal stability with maximum polymer decomposition temperature (PDT_{max}) 525 °C in air and 760 °C in nitrogen with char yield 91% at 800 °C in nitrogen atmosphere. Because of its excellent thermal stability, MS and GC–MS studies found to be very difficult. The present work deals with GC–MS studies on this copper phthalocyanine sheet polymer at various temperatures in the range 500–1000 °C. Tentative mechanisms for its modes of fragmentation are proposed and most probable degradation products are identified based on GC–MS studies.

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1. Introduction

Phthalocyanine is one of the most thermally stable substances [1,2]. In addition to the excellent thermal stability of phthalocyanine and its metallic derivatives, properties like chemical inertness, very high tinctorial nature, semi-conductivity, photoconductivity and catalytic activities have prompted to synthesize various types of thermally stable metal phthalocyanine polymers [3–21]. Among these studies, metal phthalocyanine polymers with repeating phthalocyanine units linked in the way, phenyl groups are linked in biphenyl showed highest thermal stability with anaerobic char yield ranging from 90 to 93% at 800 °C in nitrogen atmosphere [9]. The knowledge of mode of degradation of these polymers was found to be necessary for their high temperature applications both in oxidizing and inert atmospheres.

Literature survey indicates that most of the mass spectral studies done are on metal phthalocyanine derivatives [22–27] and, study on metal phthalocyanine polymers are found to be

meager [28]. Study on the thermally stable metal phthalocyanine polymers presented greater difficulties than the study on the metal phthalocyanine monomers because of their greater thermal stability, chemical inertness and insolubility. Thermal degradation study is not done previously on copper phthalocyanine sheet polymer. GC and GC–MS studies on the above polymer is carried out and tentative mechanisms for its degradation are proposed. Evaluation of this material with respect to its stability and the nature of degradation products is very essential for the high temperature applications such as semiconductors, photovoltaic materials, electrodes, catalysts, dyes and pigments.

2. Experimental

2.1. Materials and methods

Pure metal phthalocyanine tetracarboxylic acid of copper is synthesized by the reaction of trimellitic anhydride, copper sulphate pentahydrate, excess urea and catalyst. Then, this tetra functional monomer is polymerized by heating the monomer at 450 °C either in vacuum or in nitrogen atmosphere for 1 h. The detailed procedure is given elsewhere [15,29].

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The chemical data system model 100 solid pyrolyzer attached to the inlet of the Hewlett-Packard model 5830A chromatograph, coupled with a Hewlett-Packard model 5980 mass spectrometer is used for GC–MS analysis. A sample of ~1 mg is inserted into a quartz tube, which is then placed inside platinum foil of the pyroprobe. The pyroprobe is then inserted into the pyrolysis chamber, which can be kept at the desired temperature for a given period of time. The volatile products are flushed with helium carrier gas to the GC separation column. The GC column used 2 m long and 2 mm inner diameter glass column packed with 3% OV101 on 80/100 supercoport. During the analysis, the column temperature is heated to 60–250 °C and then maintained at the upper limit for 8 min. Helium gas flow rate is 20 ml/min. The mass spectrometer is equipped with a data acquisition system, provided mass spectral data.

3. Results and discussion

Copper phthalocyanine sheet polymer is soluble in concentrated sulphuric acid. It has high thermal resistance and nearly 1000 times higher electrical conductivity than its respective copper phthalocyanine monomer. Threshold temperature at which major decomposition occurs is typically higher than 450 °C in air. No catastrophic decomposition occurs upto

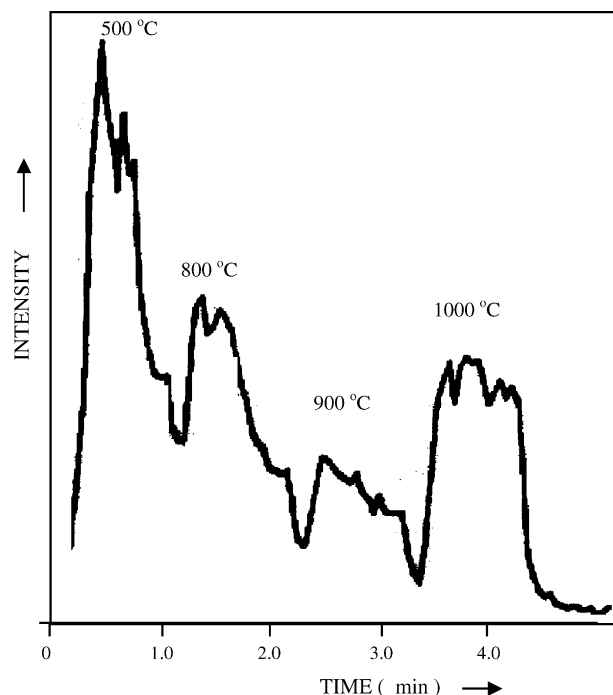


Fig. 2. Gas chromatogram of the pyrolysed products of copper phthalocyanine sheet polymer obtained in the programmed heating temperature range 500–1000 °C of the pyroprobe.

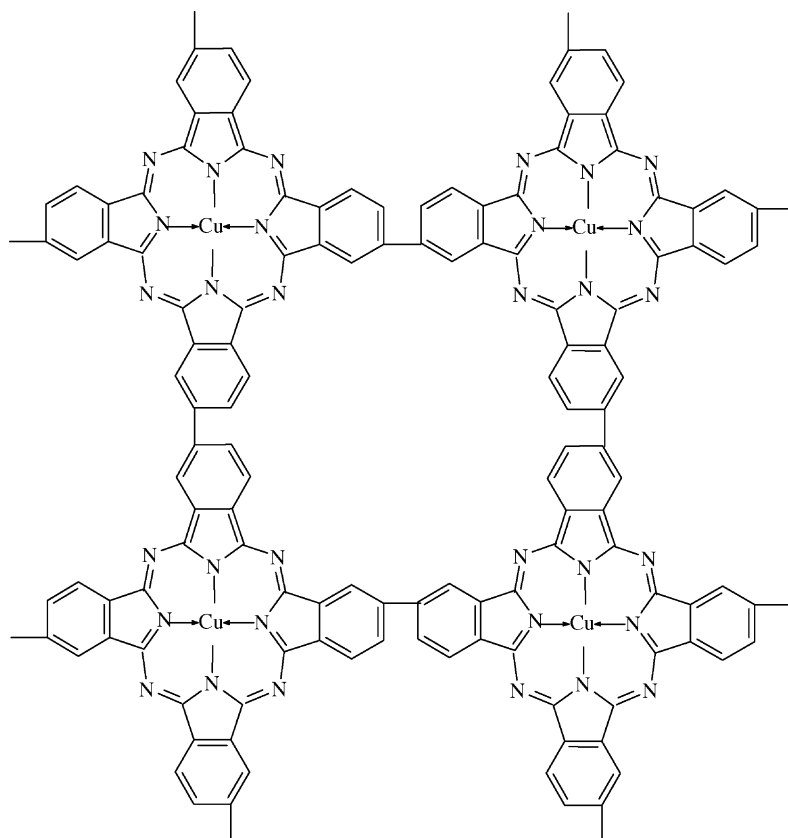


Fig. 1. Structure of copper phthalocyanine sheet polymer.

1000 °C in nitrogen atmosphere and the char yield at 800 °C is 91% [29]. The structure of copper phthalocyanine sheet polymer is given in Fig. 1. In fact, no phthalocyanine polymer heretofore synthesized showed thermal stability as high

as this polymer. Because of its excellent thermal stability, degradation does not occur at low temperature. So, GC–MS studies were carried out at high temperatures (500–1000 °C). Even at these high temperatures, the volatile products ob-

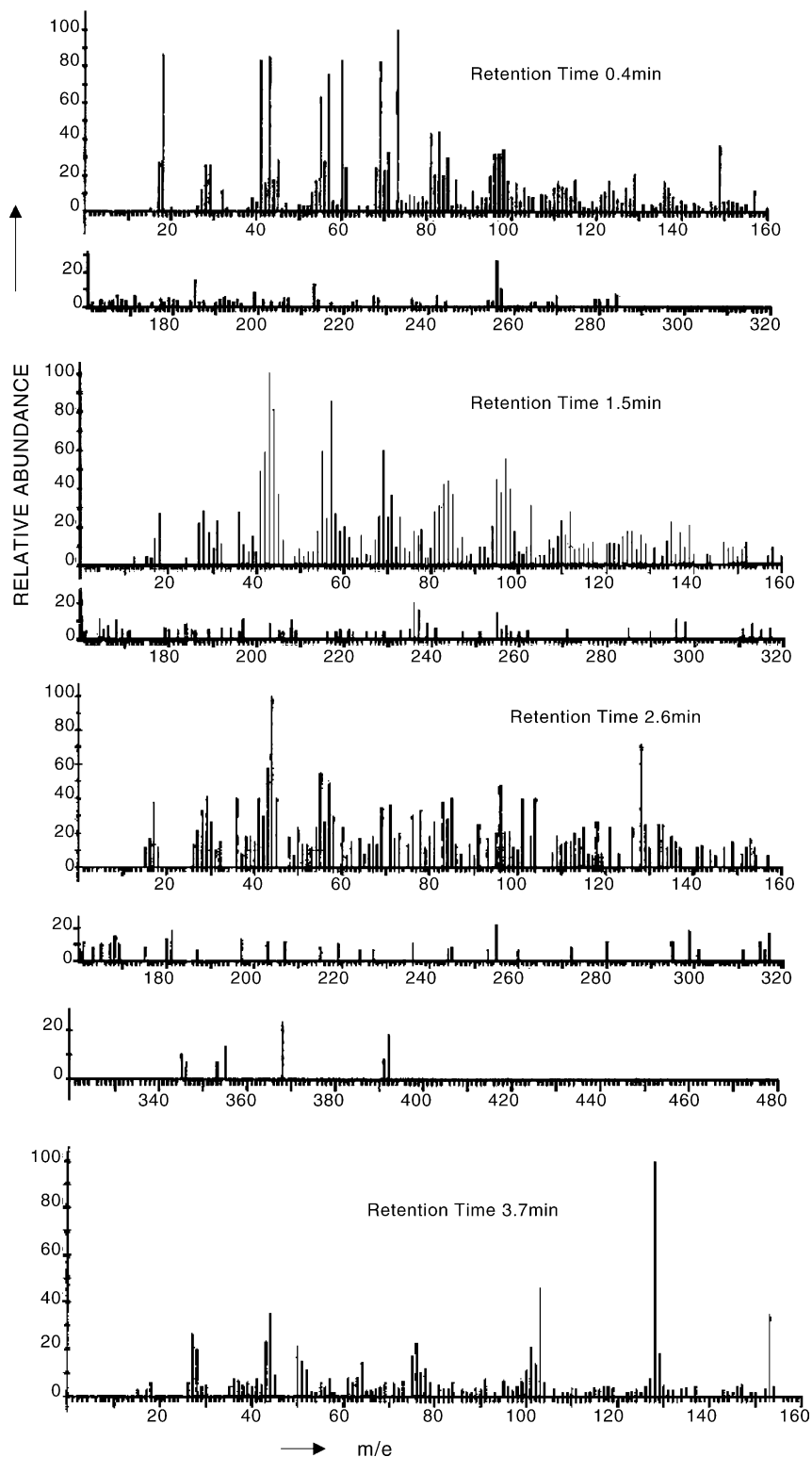


Fig. 3. Mass spectral display of copper phthalocyanine sheet polymer at various retention times.

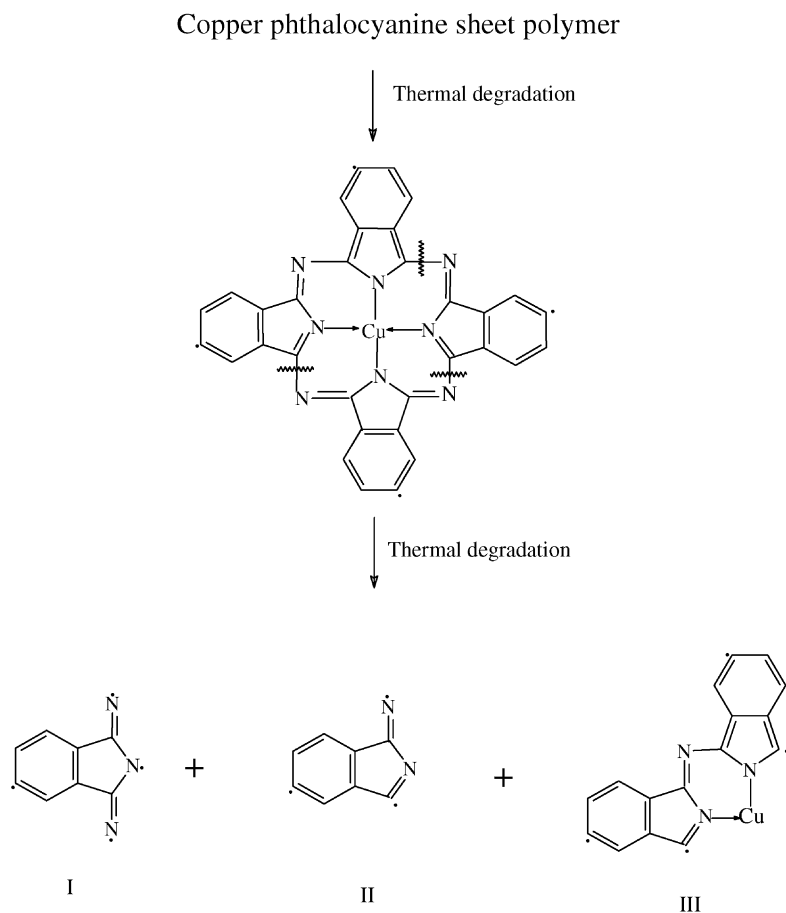


Fig. 4. The tentative mechanism of fragmentation of copper phthalocyanine sheet polymer under high thermal conditions.

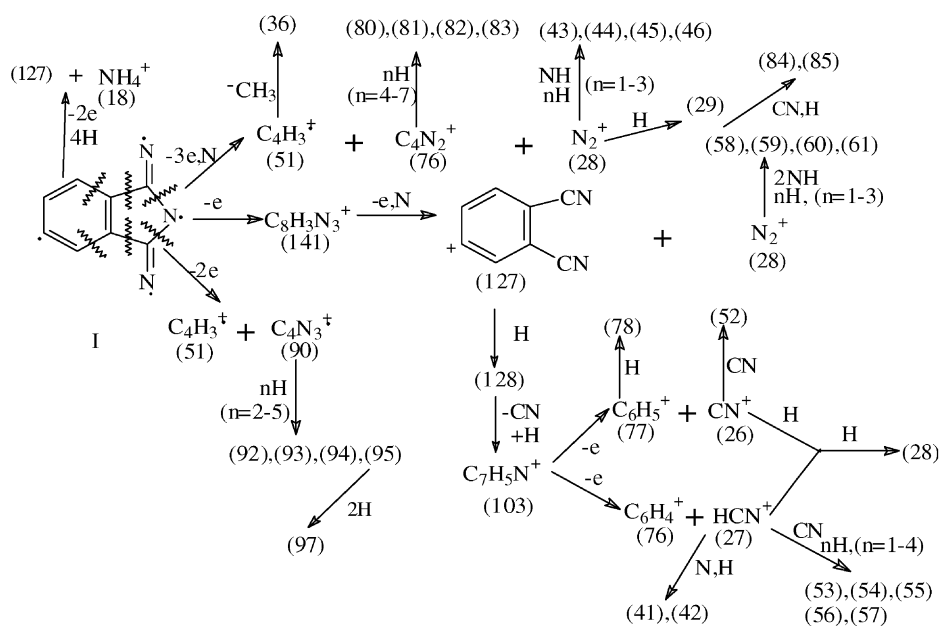


Fig. 5. The tentative mechanism of modes of fragmentations of copper phthalocyanine sheet polymer inside the ionization chamber of the mass spectrometer.

(Fig. 5). Majority of the pyrolysed products of the polymer with their relative abundance equal greater than 40% correspond to m/e 18, 29, 36, 41–45, 55, 57, 60, 64, 67, 69, 73, 81, 83–85, 92, 95, 97, 98, 101, 104 and 128. The most probable molecular formulae for the above ions are NH_4^+ or H_2O^+ , N_2H^+ or CH_3N^+ , C_3^+ , CHN_2^+ , CH_2N_2^+ , CH_3N_2^+ , CH_4N_2^+ or N_3H_2^+ , N_3H_3^+ , $\text{C}_2\text{H}_3\text{N}_2^+$, $\text{C}_2\text{H}_5\text{N}_2^+$, N_4H_4^+ , C_5H_4^+ , C_2HN_3^+ , $\text{C}_2\text{H}_3\text{N}_3^+$, $\text{C}_2\text{H}_7\text{N}_3^+$, $\text{C}_4\text{H}_5\text{N}_2^+$, $\text{C}_4\text{H}_7\text{N}_2^+$, $\text{C}_4\text{H}_8\text{N}_2^+$, $\text{C}_4\text{H}_9\text{N}_2^+$, $\text{C}_4\text{H}_2\text{N}_3^+$, $\text{C}_4\text{H}_5\text{N}_3^+$, $\text{C}_4\text{H}_7\text{N}_3^+$, $\text{C}_4\text{H}_8\text{N}_3^+$, $\text{C}_7\text{H}_3\text{N}^+$, $\text{C}_7\text{H}_6\text{N}^+$ and $\text{C}_8\text{H}_4\text{N}_2^+$. The base peaks observed are 73, 43, 44 and 128 at retention times 0.4, 1.5, 2.6 and 3.7 min, respectively. However, the possibility of H_2O^+ and CO_2^+ for $m/e = 18$ and 44 cannot be avoided, as these ions may also generate due to the presence of residual $-\text{COOH}$ groups in the polymerized products. Assigning the correct molecular formula for the ions based on the intensity calculations for $M+1$, $M+2$, etc., is difficult, because of the presence of other ions in these regions, also contribute to the relative intensities. The important products identified at the maximum sensitivity of the instrument are N_2 , $(\text{CN})_2$, HCN , $\text{C}_6\text{H}_5\text{CN}$ and $\text{C}_6\text{H}_4(\text{CN})_2$.

4. Conclusions

Analysis of the pyrolysed products by GC and MS indicates that the mode of fragmentation is extensively leading to the degradation of the macro cyclic copper phthalocyanine structure with more fragmentation products compared to the mass spectral data obtained by an electron beam work [24,30]. In the later case, fragmentation of the macro cyclic structure rarely occurs. The majority of the products identified in the above pyrolysed products are found to be N_2 , $(\text{CN})_2$, HCN , $\text{C}_6\text{H}_5\text{CN}$ and $\text{C}_6\text{H}_4(\text{CN})_2$. These products will be obtained only when the polymer is pyrolysed at high temperature ($>500^\circ\text{C}$) before running the GC–MS.

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