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Studies on phthalocyanine sheet polymers

B.N. Achar *, K.S. Lokesh

Department of Studies in Chemistry, Manasagangotri, Mysore, Karnataka State 570 006, India

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Abstract

Cobalt, nickel and copper phthalocyanine sheet polymers are synthesized by heating their respective metal (II) phthalocyanine tetracarboxylic acids at 400 °C in nitrogen atmosphere. These polymers are characterized using UV–Visible spectra, IR spectra, magnetic susceptibility, X-ray powder diffraction and thermogravimetric analysis. Electrical conductivity studies are carried out using two-probe technique in the temperature range 25–200 °C for each polymer. These polymeric materials showed room temperature electrical conductivity 10–1000 times higher values compared to earlier reported values for this type of sheet polymers.
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Keywords: Metal phthalocyanine sheet polymers; IR spectral; UV–Visible; Magnetic susceptibility measurements; Powder X-ray diffraction; Thermogravimetric study; Electrical conductivity

1. Introduction

The study of electrical conductivity on organic compounds has evoked a great deal of interest. Development of unusual organic substances with semiconductor or metal like property was expected to prove extremely useful in many major applications [1–11]. The electrical conduction in organic compounds differs in many ways from the familiar kind of metals and inorganic semiconductors like silicon and germanium [12]. However, the well-known band theory has provided essential basis of the concepts. The new feature here is that groups of atoms are chemically bonded together in discrete molecules which in turn are held together by relatively weak van der Waals' forces. Polymers having delocalized aromatic π-electrons or conjugated chains are expected to show high carrier concentration with high mobility. Phthalocyanine structure seems to be a very good model to understand many properties of the electrical conductivity of organic compounds. Semiconductor properties of phthalocyanines are known for a long time and a great deal of work has been reported in improving the electrical property of these complexes [8–11,13–18]. Attempts to improve the conductivity of phthalocyanine compounds by doping seems to decrease the chemical, thermal and mechanical properties of the doped materials and also most of the reported dopants (AsF_5, I_2, Br_2, etc.) are highly toxic [19]. Another attempt to improve the intrinsic electrical conductivity is through polymerization of the phthalocyanine molecules. One of the attempts did in this direction was to connect the peripheral benzene rings of the phthalocyanine structure through a chemical bond similar to the chemical bond present between the two benzene rings as in biphenyl. Metal (cobalt, nickel and copper) phthalocyanine sheet polymers of this type were synthesized earlier by heating metal (II) 4, 4′, 4″, 4‴-phthalocyanine tetracarboxylic acids in vacuum $\sim 10^{-6}$ Torr at 400 °C for 1 h [20]. These phthalocyanine sheet polymers showed improved room temperature intrinsic electrical conductivity of ~100–1000 times higher compared to their respective cobalt, nickel and copper parent phthalocyanines [21]. Literature survey indicates that

* Corresponding author. Tel.: +91-821-2515525; fax: +91-821-2421263.
E-mail address: bnachar@yahoo.com (B.N. Achar).

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research work on these type of polymers is meagre. Electrical conductivity of metal phthalocyanines are very sensitive to structural alterations and presence of impurities. The present work deals with the synthesis of the above type metal phthalocyanine sheet polymers using different experimental conditions. These polymers showed ~10–1000 times higher room temperature intrinsic electrical conductivity compared to the earlier reported values for this type of polymers [21]. These polymers are characterized with respect to elemental analysis, UV–Visible, IR, magnetic susceptibility, X-ray diffraction and thermogravimetric studies. The above data along with the electrical conductivity studies in the temperature range 25–200 °C are presented in this paper.

2. Experimental

2.1. Preparation of cobalt phthalocyanine sheet polymer

About 4 g of finely powdered cobalt (II) – 4, 4′, 4″, 4‴-phthalocyanine tetracarboxylic acid was taken in a reaction tube of dimension 2 cm diameter and 15 cm in length provided with an iron–constantan thermocouple, an inlet with a stop-cork and an outlet with a stop-cork. The reaction tube was carefully purged with nitrogen gas (99.98% pure) with repeated evacuation and refilling. Then it was heated to 400 °C in a current of nitrogen and maintained at the temperature of 400 ± 5 °C for 1 h and 15 min.

Similarly nickel and copper phthalocyanine sheet polymers were prepared using their corresponding metal phthalocyanine tetracarboxylic acid derivatives.

Anal. for cobalt phthalocyanine sheet polymer, $C_{32}H_{12}N_8Co$: Calc. C, 67.73; H, 2.13; N, 19.75; Co, 10.39. Found: C, 68.02; H, 2.24; N, 19.56; Co, 10.52%. IR absorption bands (cm^{-1}): 728s, 756w, 770w, 874w, 899w, 941w, 1067m, 1090m, 1119w, 1165m, 1289w, 1329m, 1420w, 1603w.

For nickel phthalocyanine sheet polymer, $C_{32}H_{12}N_8Ni$: Calc. C, 67.76; H, 2.13; N, 19.75; Ni, 10.35. Found: C, 68.06; H, 2.31; N, 19.98; Ni, 10.52%. IR absorption bands (cm^{-1}): 727s, 756w, 770w, 875w, 899w, 947w, 1064m, 1091m, 1119w, 1166m, 1288w, 1331m, 1419w, 1606w.

For copper phthalocyanine sheet polymer, $C_{32}H_{12}N_8Cu$: Calc. C, 67.18; H, 2.11; N, 19.58; Cu, 11.2. Found: C, 67.54; H, 2.24; N, 19.97; Cu, 11.32%. IR absorption bands (cm^{-1}): 727s, 754w, 770w, 874w, 899w, 943w, 1063m, 1090m, 1119w, 1165m, 1288w, 1329m, 1419w, 1603w.

2.2. Elemental analysis

Elemental analysis for carbon, hydrogen and nitrogen were made by Regional Sophisticated Instrumentation Center, CDRI, Lucknow, India. The metal contents of the metal phthalocyanine sheet polymers were determined by decomposing a known amount of the polymer using H_2SO_4–HNO_3 mixture, followed by careful evaporation and calcination [22].

2.2.1. Physical measurements

UV–Visible spectra were recorded in 15 M sulphuric acid using Systronics type-117 model spectrophotometer with 1 cm silica cells, Systronics, Ahmedabad, India. IR spectra were recorded in Nujol–mull using Shimadzu 8201PC FT-IR spectrometer, Japan. Magnetic susceptibility measurements were done using the Gouy magnetic balance consisting of the type NP-53 electromagnet with DC power supply type NP-1053 and a Keroy semimicro balance supplied by Universal Scientific Company, Bombay, India. Pure mercury tetrathiocyanato cobaltate (II) was synthesized and used as a calibration standard [23]. A JEOL-JDX-8P X-ray diffractometer was used to study powder X-ray diffraction pattern of the samples. Powdered sheet polymers were compressed into pellets of 1.3 cm diameter and thickness ranging from 0.15–0.25 cm, using Perkin–Elmer KBr Die under a pressure of 500 kg/cm^2. The Carver laboratory Press Model – diaton capacity was used for applying the pressure. The diameter and thickness of the pellets were determined by using a screw gauge readable upto 0.005 cm. Conducting silver paint (ELTECKS preparation No. 1228-C) was coated on both flat surfaces of the pellets and the electrical contacts to the samples were made using the same silver paint to the electrodes. The electrical contacts were checked to verify the ohmic connection and resistance measurements were done from 25 to 200 °C using DOT 402 Digital Milli Ohm Meter and DOT 425 Insulation Resistance Tester, Bhandari Electronics and Electricals, Bangalore, India. Thermogravimetric analyses were done in a DuPont model 990 thermogravimetric analyser using 10–15 mg of sample. A heating rate of 10 °C/min was used, both in air and nitrogen atmospheres at a flow rate of 100 ml/min.

3. Results and discussion

The metal phthalocyanine sheet polymers of cobalt, nickel and copper have dark bluish to purplish colours. The elemental analysis for carbon, hydrogen, nitrogen and metal agreed very well with the theoretical calculation for the proposed structure, Fig. 1.

3.1. UV–Visible and IR spectra

UV–Visible absorption spectra of cobalt, nickel and copper phthalocyanine sheet polymers are recorded in the range 200–850 nm using 30 N sulphuric acid. All the polymers showed absorptions at 214–228, 298–306,

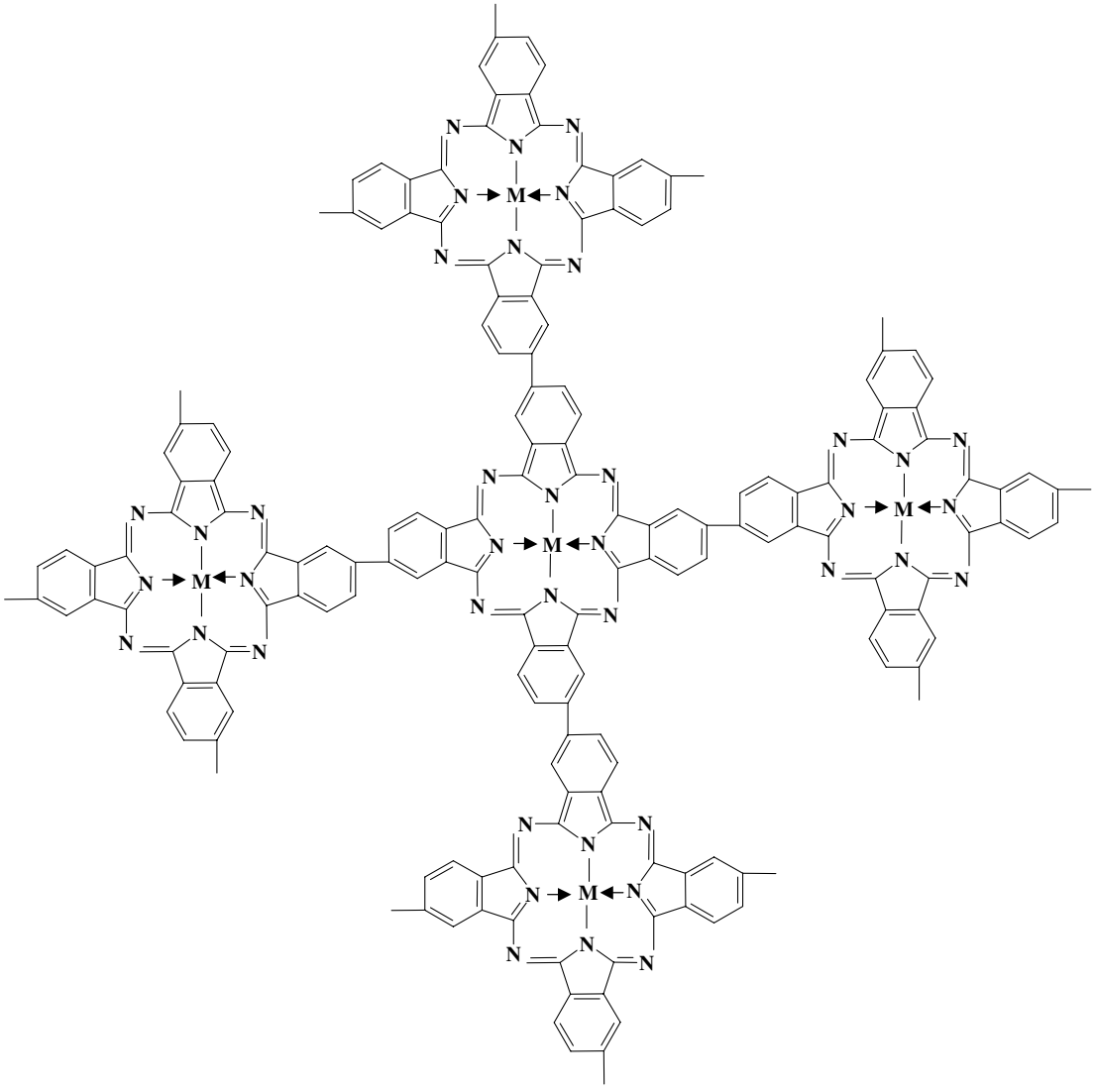

Fig. 1. Structure of metal phthalocyanine sheet polymer (metal=Co, Ni, and Cu).

421–427, 706 (shoulder) and 785–791 nm. Similar absorptions for their parent metal phthalocyanine complexes are observed at 206–224, 302, 430–438, 692–710 and 740–760 nm [24]. The bands are broader and less intense compared with the spectra of their respective monomers. The deep blue colours of the polymers are due to the $\pi \rightarrow \pi^*$ transitions which may be assigned to bands observed at 706–791 nm. All these absorption bands appeared at higher wavelengths than their corresponding parent phthalocyanine complexes except the absorption band at around 430 nm. Broader and lesser intensity appearance of the bands with shifting to lower or higher wavelengths support the polymeric nature of the material.

The polymerization reaction involving the conversion of metal phthalocyanine tetracarboxylic acid to metal phthalocyanine sheet polymer has been followed by analyzing the samples at the regular intervals of time by IR spectral studies. Disappearance of the absorption peaks corresponding to the carboxylic acid groups 2500–3000, 1750, 1710, 1420, 1300–1200 and 920 cm^{-1} are taken as the completion of polymerization reaction. Time required for complete conversion of the monomers to the phthalocyanine sheet polymers are found to be 1 h and 15 min. The characteristic phthalocyanine skeletal absorption bands at 750, 906, 947, 1060, 1088 and 1116 cm^{-1} are observed in the polymeric materials indicating the presence of phthalocyanine structures intact [25]. However, these bands are observed with a loss of fine structure and decreased intensities compared to their respective parent phthalocyanine compounds, which is also supporting the polymerized nature of the materials.

3.2. Magnetic susceptibility measurements

Magnetic susceptibility measurements of cobalt, nickel and copper phthalocyanine sheet polymers have been

investigated in the solid state at ambient temperature and varying magnetic field strengths ranging from 1.02 to 3.58 kG. The χ_M values reported in Table 1 are the product of the magnetic susceptibility and molecular weight of the repeating unit of the polymer backbone structure. The experimental data are in agreement with the paramagnetic nature of the copper and cobalt complexes as well as the diamagnetic nature of the nickel complex. The nature of variation of the magnetic susceptibility values with field strength are presented in Fig. 2 and the data are summarized in Table 1.

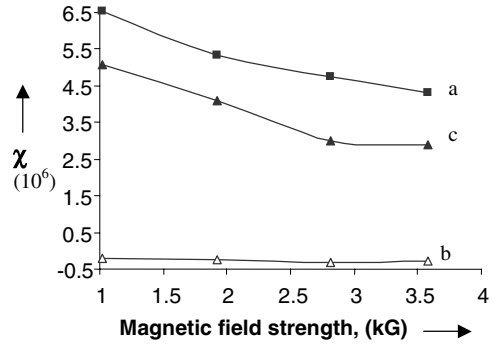

Fig. 2. Variations of magnetic susceptibilities (a) cobalt, (b) nickel and (c) copper phthalocyanine sheet polymers with field strength.

3.3. X-ray diffraction studies

The powder X-ray diffraction study of cobalt, nickel and copper phthalocyanine sheet polymers were done over the range 2θ angles 0–45°. The diffraction patterns of these polymers showed qualitatively similar spectrographs. Three peaks observed, one sharp peak with maximum intensity and other two are not well resolved broad peaks with less intensity. The interplanar spacings calculated based on these peaks gave values (in Å): 3.43, 6.905 and 14.309 for cobalt; 3.405, 7.58 and 14.59 for nickel and 3.38, 7.58 and 13.86 for copper phthalocyanine polymers. The shapes of the X-ray diffraction spectrographs indicate that these polymers are amorphous in nature.

3.4. Thermogravimetric studies

The dynamic thermogravimetric analytical data for cobalt, nickel and copper phthalocyanine sheet polymers showed exceptional thermal stability, which indicated very good agreement with the earlier published data [21]. Maximum polymer decomposition temperatures in air found to be 500, 502 and 520 °C for cobalt, nickel and copper phthalocyanine sheet polymers respectively. The corresponding maximum decomposition temperatures with char yield at 800 °C in nitrogen atmosphere are found to be respectively 852 °C and 90%, 888 °C and 92% and 750 °C and 90%, for the three polymers.

3.5. Electrical conductivity

The electrical conductivity data of synthesized metal phthalocyanine sheet polymers are recorded from 298–473 K and plotted log σ versus $1/T$, Fig. 3. The relevant data are presented in Table 1. The plots indicated that cobalt and nickel phthalocyanine sheet polymers are semiconducting in nature and copper phthalocyanine sheet polymer showed metallic conduction in the tem-

Table 1
UV–Visible spectral, magnetic susceptibility, X-ray and electrical conductivity data

Compound	UV–Visible spectral data (nm)	Magnetic susceptibility		Electrical conductivity ($S cm^{-1}$)		X-ray diffraction interplanar spacings (Å)
		Field strength (kG)	$\chi_M \times 10^6$	25 °C	200 °C	
Cobalt phthalocyanine sheet polymer	214, 298, 421, 707, 785	1.02	3699			3.43, 6.905, 14.309
		1.92	3036	1.35×10^{-7}	3.43×10^{-5}	
		2.81	2701			
		3.58	2450			
Nickel phthalocyanine sheet polymer	225, 306, 424, 696, 777	1.02	−113			3.405, 7.58, 14.59
		1.92	−1.44	3.80×10^{-7}	3.02×10^{-5}	
		2.81	−163			
		3.58	−167			
Copper phthalocyanine sheet polymer	222, 306, 427, 707, 791	1.02	2905			3.38, 7.58, 13.86
		1.92	2332	4.16×10^{-7}	1.38×10^{-6}	
		2.81	1720			
		3.58	1649			

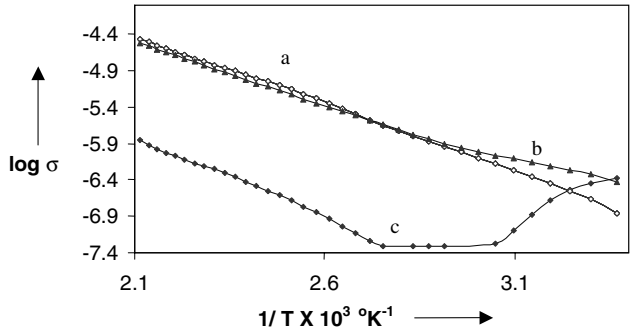

Fig. 3. Variations of electrical conductivities (a) cobalt, (b) nickel and (c) copper phthalocyanine sheet polymers with temperature.

perature range 295–323 K and semiconducting in the range 363–473 K. The conductivity of cobalt phthalocyanine sheet polymer is increased from 302–363 K followed by a gradual increase, and again becomes linear in the temperature range 383–473 K. The same type of linear variation of conductivity is seen at 296–343 and 348–473 K for nickel phthalocyanine sheet polymer. However, copper phthalocyanine sheet polymer showed three temperature regions 295–323 K corresponding to metallic conductivity and, 363–408 and 423–473 K corresponding to semiconducting properties. The linear variations of the electrical conductivities found to fit the expression:

$$\sigma = \sigma_0 e^{-E/kT},$$

where E is the activation energy, σ is the specific conductivity at T K, σ_0 is a constant and k is Boltzmann constant. The room temperature specific conductivities of cobalt, nickel and copper phthalocyanine sheet polymers are 1.35×10^{-7}, 3.80×10^{-7} and 4.16×10^{-7} Scm^{-1}, respectively. The corresponding respective observed values for the parent phthalocyanine compounds are 3.67×10^{-10}, 5.53×10^{-11} and 1.25×10^{-13} Scm^{-1}. The corresponding respective earlier observed values for cobalt, nickel and copper phthalocyanine sheet polymers are 1.40×10^{-8}, 1.81×10^{-8} and 3.80×10^{-10} Scm^{-1} [21]. The activation energies are found to be 0.116 eV (303–363 K) and 0.052 eV (383–473 K) for cobalt, 0.076 eV (296–343 K) and 0.078 eV (348–473 K) for nickel, and 0.117 eV (363–408 K) and 0.04 eV (423–473 K) for copper phthalocyanine sheet polymers respectively. Improved electrical conductivities observed for these synthesized sheet polymers are due to the greater degree of planarity achieved due to the extended sheet like structure. This extension of planarity is expected to increase intermolecular contact and interactions of 3d orbitals with the π-orbitals of the neighbouring phthalocyanine units. The change in activation energies in the different temperature ranges may be due to some structural transformations and variation in the intermolecular interactions resulting change in the electrical conductivity.

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