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Characterization and studies of electroactive properties of an organometallic polymer of iron-phthalocyanine

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An iron-phthalocyanine polymer has been characterized by infrared spectroscopy, X-ray diffraction and Mössbauer spectroscopy. The electrical properties of resistivity, dielectric constant and the thermally stimulated depolarization effect have been investigated in the temperature range 30–240°C. The depolarization of thermoelectret shows two current peaks at about 176°C and 200°C. The unpolarized sample also displays a pyroelectric current on heating, indicating the possibility of ferroelectric polarization. A temperature-dependent measurement of the dielectric constant exhibits a dielectric maximum around 180°C which is likely due to electret current peaks. The results have been compared with a monomer of iron-phthalocyanine and interpretations are made in terms of the highly delocalized π-electron system of the phthalocyanine macrocycle being further extended by polymerization.

Keywords: Metallophthalocyanines, electrical properties, sheet-like polymers, iron

INTRODUCTION

Metallophthalocyanines have attracted considerable attentions due to their interesting thermal, optical and electrical properties.[1–4] The phthalocyanine molecule represents one of the most versatile of organic systems due to its architectural flexibility. A number of structural modifications are possible within the phthalocyanine macrocycle as well as on the peripheral sites, and therefore a variety of materials can be synthesized.[5–7] It has been seen that the electrical properties of these materials are strongly governed by the chemical modifications.[8] The unique electrical properties exhibited by metallophthalocyanines are the consequence of electron delocalization. In the case of a phthalocyanine polymer, the conjugation can be further extended by polymerization. Interest in phthalocyanine polymers has been mainly focused on the stacked bridge polymers since on iodine doping they show metal-like conductivity.[9,10] The sheet-like polymers constitute another class in which two phthalocyanine macrocycles are connected together by sharing of a phenylene ring.[11] These sheet-like polymers exhibit excellent thermal and electrical characteristics due to the highly conjugated nature. It was of interest to us to study the electrical properties of a sheet-like polymer of phthalocyanine. In the present paper investigations have been made on a phthalocyanine polymer containing iron(II) as the central metal atom (FePc). The physical and electrical properties are reported and the results have been compared with a monomer of iron-phthalocyanine.

EXPERIMENTAL

Preparation of materials and characterization

Iron-phthalocyanine polymer was synthesized from the starting materials pyromellitic dianhydride ($C_{10}H_2O_6$), urea [$(NH_2)_2CO$], and ferric chloride ($FeCl_3$). Ammonium molybdate [$(NH_4)_2MO_4$] was used as the catalyst and the reaction was carried out in nitrobenzene at 200°C for 4 h. The synthesis technique employed for polymerization in the present study has been fully described elsewhere.[12] The polymeric product obtained was purified by extracting with acetone using a Soxhlet method and finally by heating at 180°C at low pressure (10^{-3} mm Hg). Samples did not undergo sublimation at this temperature while impurities like urea and pyromellitic dianhydride were sublimed. The infrared absorption spectra was recorded as a KBr pellet using a SP-1200 (Unicam Instruments Ltd, UK). An X-ray diffraction spectrograph was obtained using a Phillips X-ray diffractometer. A

Cu-K$_\alpha$ radiation source was used to record the X-ray scan. Mössbauer spectra were recorded using a Canberra Series-30. Cobalt-57 in a rhodium-matrix was used as the radiation source.

Electrical measurements

The resistance of the sample was measured by a two-probe method using a stabilized power supply and a microvoltmeter. The capacitance was measured with a standard LCR bridge at 1 and 10 kHz. All the electrical measurements were made in the temperature range 30–240°C and samples were kept at least for 30 min at each desired temperature. The method of electret formation has been previously described in detail.[13] In the present study, samples were polarized at 90°C under an electric field of 2.50 kV cm^{-1} for 2 h and the depolarization spectra were recorded at a heating rate of 6°C min^{-1}.

RESULTS AND DISCUSSION

The infrared absorption spectrum of the FePc polymer is shown in Fig. 1. The principle IR absorption bands observed are: 420, 460, 560, 635, 725, 750, 890, 1010, 1060, 1090, 1135, 1155, 1190, 1325, 1740 and 3220 cm^{-1}. In addition to the characteristic phthalocyanine absorptions, a few new bands appeared in the polymeric system. A comparative study shows that most of the absorption bands are in good agreement with the polymer constituents except for shifts to higher- or lower-frequency regions probably due to the high conjugation of the polymer.[14,15] A medium-intensity IR band observed at 1740 cm^{-1} is associated with carboxylic functional groups attached to the peripheral sites of the phthalocyanine macrocycles. The presence of iron metal was evidenced by the appearance of a medium-intensity band at 890 cm^{-1}. In metallophthalocyanines, these metal-ion absorption bands are observed in the frequency range 888–920 cm^{-1}.[14]

The X-ray diffraction spectrum plotted in terms of intensity versus the Bragg angle (2θ is the angle of diffraction, viz. the Bragg angle) is represented in Fig. 2. The *d*-spacing values calculated from the Bragg equation were found to be 4.85, 4.39, 3.51, 3.15, 2.79, 2.68, 2.43, 2.30 and 2.13 Å with respect to the stated 2θ values. The sharp reflections only occur at 4.85 and 3.15 Å. The presence of various peaks in the X-ray diffraction spectrum indicates the crystalline state in comparison with the monomeric compound. The Mössbauer spectrum of the FePc polymer was recorded at room temperature. Experimental values and a computer-fitted curve matched closely. The experimental Mössbauer spectrum consists of a single quadrupole doublet. The isomer shift and quadrupole splitting values were found to be 0.192 and 0.732 mm s^{-1} respectively. In the case of a monomer of FePc, Mössbauer spectral values for isomeric shift and quadrupole splitting were 0.257 and 0.314 mm s^{-1} respectively.[16] Blomquist *et al.*[17] suggested that the position of the central metal atom and the substituted functionalities on the peripheral sites are quite significant, since electron-attracting groups may cause a noticeable change in the 3*d* electron population. In the present study, as evidenced by IR spectra, the functional groups attached at the peripheral sites of phthalocyanine macrocycles are carboxylic groups. Another important factor is likely to be the number of the phthalocyanine rings incorporated into the polymer.

The electrical resistivity of the FePc polymer at room temperature was found to be 7.07 × 10^{10} ohm cm.

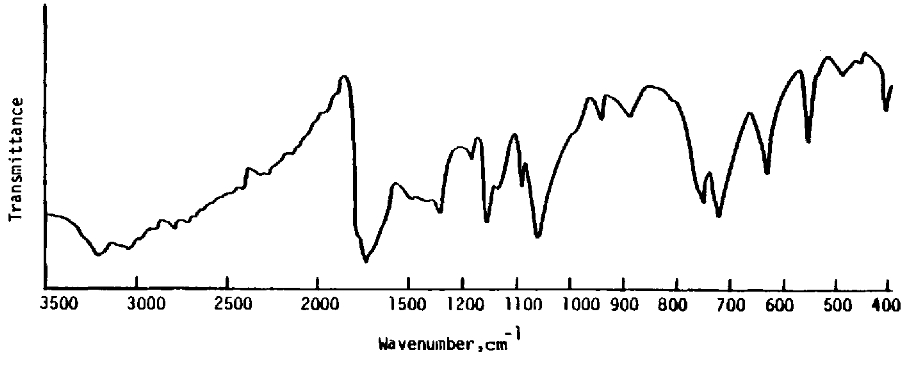

Figure 1 Infrared spectra of the iron-phthalocyanine polymer.

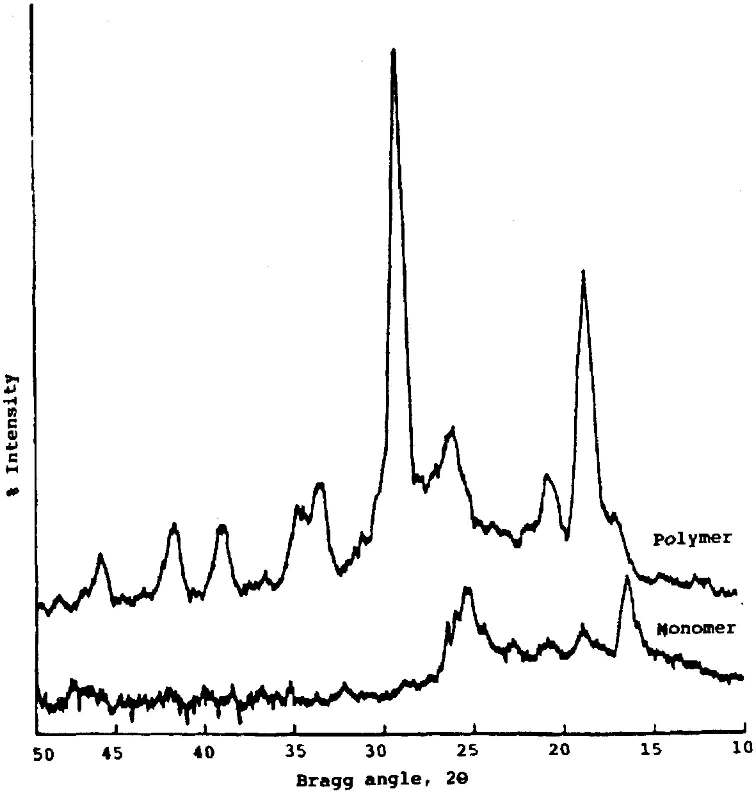

Figure 2 X-ray diffraction scans of the iron-phthalocyanine monomer and polymer.

The data plotted for log resistivity versus $1/T$ show linear behavior without any break (Fig. 3). The activation energy calculated from the plot by the Arrhenius equation is 0.40 eV (38.6 kJ mol^{-1}). The resistivity decreases as the temperature rises and at 240°C the resistivity was 2.30×10^8 ohm cm. Berlin *et al.*[18] studied several metallophthalocyanine polymers and their resistivities were reported in the range of 10^6-10^{11} ohm cm depending upon the extent of purification and degree of polymerization controlled by the different reaction conditions. A FePc monomer studied by this author showed higher resistivity as expected in comparison with the polymer. However, the carboxylic functional groups attached at the peripheral sites might act as carrier traps leading to a decrease in conductivity. The dielectric constant recorded at room temperature was in the range 40–80, outstandingly high in comparison with conventional polymers and the FePc monomer (between 5.2 and 22.7).[19] The higher dielectric constant in metallophthalocyanines is attributed to the mixing of 3*d* orbitals with the electron system of the phthalocyanine macrocycle. Polymers of metallophthalocyanines show higher dielectric constants due to the extended conjugation which would facilitate electron delocalization along the polymer chains. The temperature-dependent measurements showed a dielectric maximum at 180°C (Fig. 4). A copper-phthalocyanine polymer studied by us showed an extremely high dielectric constant (10^5) at elevated temperatures.[20] Such a dramatic difference in the dielectric constant of these two polymers presumably results from the degree of polymerization. For another polymer of iron-phthalocyanine, the dielectric constants reported were between 16 and 380 depending upon the applied pressure.[21] The dielectric behavior of metallophthalocyanine polymers has been interpreted by these authors in terms of nomadic polarization. In the present work, the possibility of ferroelectric polarization seems to be reasonable since pristine samples show a pyroelectric current on heating. However the current does not change its polarity on cooling. In the case of a true pyroelectric material, hysteresis characteristics would be observed. Therefore, the FePc polymer is a pseudopyroelectric material but the appearance of a pyroelectric current

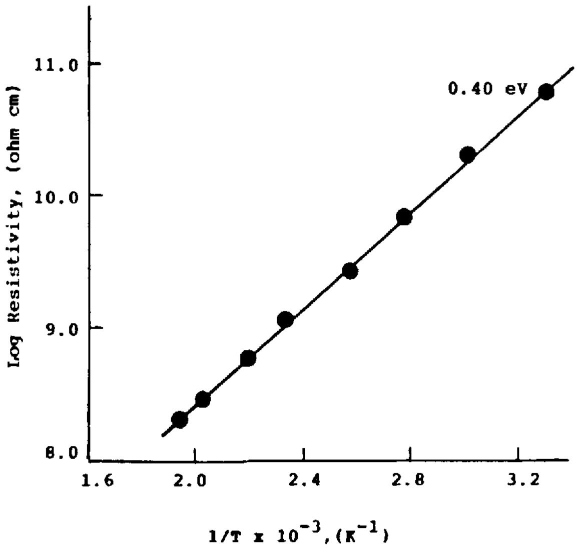

Figure 3 Log resistivity versus $1/T$ plot for the iron-phthalocyanine polymer.

in the unpolarized state indicates the possibility of ferroelectric polarization. Besides the ferroelectric polarization, the polar groups may contribute to the high polarizibility leading to these interesting dielectric properties.

Figure 5 shows the thermally stimulated depolarization current (TSD) spectra of the FePc polymer. The sample, depolarized at a heating rate of 6°C min^{-1}, exhibits two current peaks: one around 176°C and the other around 200°C. The dielectric constant measurements performed as a function of temperature also show a dielectric maxima around 180°C. Possibly this transition temperature involves dipoles. The depolarization kinetics parameters calculated for the thermoelectret are listed in Table 1. The activation energies (E_a), calculated from the initial rise method,[22] are 0.44 (42.5 kJ mol^{-1}) and 0.50 eV (48.2 kJ mol^{-1}) for the 176 and 200°C TSD peaks respectively whilst the unpolarized sample has an E_a value of 0.62 eV (59.8 kJ mol^{-1}). The E_a values were also determined by the Bucci–Fieschi–Guidi method.[23] A straight line was obtained when the log of remaining charge divided by current at a particular temperature was plotted against $1/T$. The E_a values calculated from this method were 0.48 and 0.62 eV (46.3 and 59.8 kJ mol^{-1}) for the TSD peaks of 176 and 200°C respectively. The E_a values determined by these two methods are in good agreement. Comparing these TSD spectra with the monomer of FePc, it may be noted that the magnitude of the current was higher in the polymer. The monomer sample showed no TSD peak but only a continuous increase in current as a function of temperature. However, several polarization processes occur during the electret formation but mainly dipolar and space-charge polarizations are considered significant.[24] The FePc polymer contains polar groups at the peripheral sites so dipolar polarization seems to contribute to the TSD effect. During thermoelectret formation the dipoles become oriented and, on heating, disorientation of dipoles

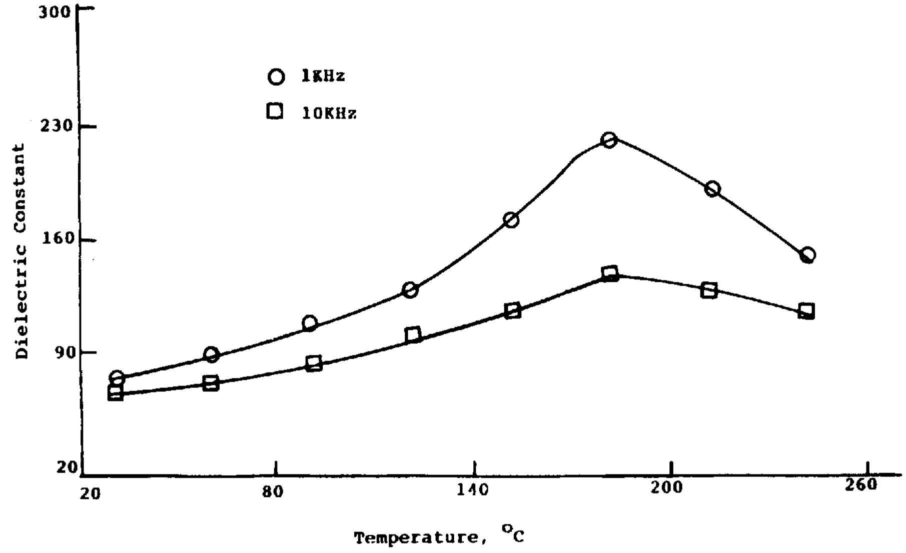

Figure 4 Dielectric constant versus temperature plots recorded at 1 and 10 kHz.

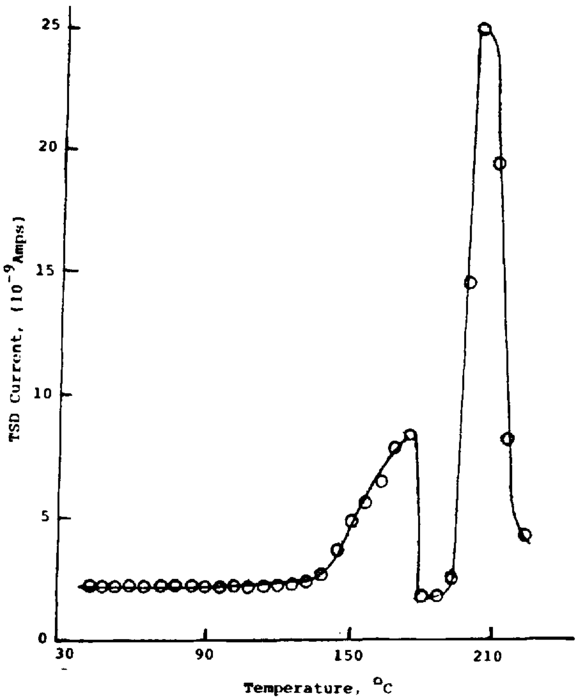

Figure 5 Thermally stimulated depolarization current (TSD) spectra of iron-phthalocyanine polymer electret. Samples were polarized at 90°C under an electric field of 2.50 kV cm^{-1} for 2 h and depolarization currents were recorded at a uniform heating rate of 6°C min^{-1}

occurs, resulting in the discharge current peaks. In addition to dipolar polarization, a space charge may be operative, likely due to the monomeric materials. However, in order to understand fully the mechanism responsible for the TSD effects, the influences of various polarization parameters such as temperature, electric field, electrode materials, time, heating rate, sample thickness, etc., on the FePc polymer need to be investigated. The ferroelectric polarization as evidenced by the appearance of pyroelectric currents may also play a significant role in the electret formation.

CONCLUSIONS

Characterization by analytical techniques shows the formation of an iron-phthalocyanine polymer. A comparative study made with the monomeric material indicates the electrical parameters like resistivity and dielectric constant are greatly influenced by the extended conjugation in the polymer. The electret and dielectric measurements show the presence of a transition around 180°C. Pyroelectric current observed for pristine samples suggest the possibility of ferroelectric polarization.

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Table 1 Depolarization kinetics data of a thermoelectret of iron-phthalocyanine polymer

			τ_{300}^{c}		$\tau_{T_{max}}$^{d}	
T_{max}^{a} (°C)	E_a (eV)	τ_0^{b}(s)	(s)	(days)	(s)	(days)
176	0.44	4.4986×10^{-3}	1.1247×10^{5}	1.3017	3.9449×10^{2}	4.5658×10^{-3}
200	0.50	1.7937×10^{-3}	4.5765×10^{5}	5.2968	3.8525×10^{2}	4.4589×10^{-3}

[a] T_{max} is the TSD peak temperature. [b] τ_0 is the relaxation time constant. [c] τ_{300} is the relaxation time at 27°C. [d] $\tau_{T_{max}}$ is the relaxation time at T_{max}.

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