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DIELECTRIC PROPERTIES OF COPPER-PHTHALOCYANINE POLYMER

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Abstract—Dielectric properties of a sheet-like polymer of copper-phthalocyanine have been studied. Dielectric constant and dielectric loss of the compressed pellets of the samples were measured at 1, 5 and 10 kHz in the temperature range 30–240°. Dielectric constant and dielectric loss are frequency and temperature dependent. The dielectric constants recorded at the elevated temperature corresponding to the dielectric maxima were in the range of 10^5. Anomalous dielectric behaviour of highly conjugated copper-phthalocyanine polymer at low frequencies and high temperatures seems to arise from Maxwell–Wagner–Sillars polarization. It has been found that the structural changes occurring in the phthalocyanine macrocycle strongly affect the dielectric parameters. Heating of the unpolarized sample gives rise to spontaneous currents, indicating the presence of ferroelectric polarization.

INTRODUCTION

Electrical properties of metallophthalocyanines and metal chelate compounds have attracted considerable attention in recent years. Since 1948, when Eley [1] discovered their semiconductivity, they have been one of the most interesting classes of organic semiconductors. Since then, many studies have been made on photoconductivity, photovoltaic effect, photochemical reactivity, luminescence, fluorescence, photodielectric effect, etc, which depend on the highly conjugated system of the phthalocyanine molecule [2]. In addition, polymeric metallophthalocyanines have been extensively studied and in fact, they have already found industrial applications in catalysis, electrophotography, xerography, fuel cells and other semiconducting devices [3]. Polymers of metallophthalocyanines can be synthesized through metal–metal bonding or covalent bonding between the phthalocyanine rings. It has been found that metallophthalocyanines polymers exhibit unusual electrical properties and the degree of polymerization, the central metal atom, and the nature of peripheral functional groups greatly influence the electrical parameters [4]. We have studied the electrical behaviour of various monomeric and polymeric metallophthalocyanines [5, 6]. In the present article, dielectric properties of a sheet-like polymer of copper-phthalocyanine are reported.

EXPERIMENTAL

A sheet-like polymer of copper-phthalocyanine (poly-Cu-Pc) was synthesized by the Boston and Bailer method [7]. The deep blue solid polymer obtained was treated with acetone, KOH and HCl to examine the effect of these solvents on the dielectric parameters. These samples were characterized by i.r. spectroscopy to find out the structural changes occurring in the polymeric system during treatment.

The dielectric constant and dielectric loss of the powdered sample were measured using compressed pellets. These pellets were coated with silver paste to ensure the electrical contacts. Aluminium coated pellets were also used and gave the same results. Capacitance was measured by a LCR bridge (Systronics, model 921). The variation in frequency was made by an external A.F. generator (Philips, AM 2308) and bridge balance was detected through a transistorized AC microvoltmeter (Systronics, model 411). Dielectric constant (ε) was calculated from:

$$\varepsilon = CD/\varepsilon_0 A,$$

where $\varepsilon_0 = 8.85 \times 10^{-14}$ F/cm, the permittivity of the vacuum, C, D and A are the capacitance, thickness and area of the pellets respectively. Dielectric measurements were made at 1, 5 and 10 kHz as a function of temperature in the range 30–240° in a specially designed cell.

RESULTS AND DISCUSSION

In the sheet-like polymers of copper-phthalocyanine, two phthalocyanine rings are fused together by sharing a benzene ring, the hypothetical sheet-like structure of the polymer is shown in Fig. 1. The detailed characterization of the polymer is described elsewhere [8]. Figure 2 represents the logarithmic plots of dielectric constant vs frequency of various poly-Cu-Pc samples recorded at room temperature. The dielectric constant increases rapidly with decreasing frequency and higher values were recorded at the lowest frequencies. The dielectric constant ranges between 10 and 1500, which is quite high compared with the conventional polymers. Monomeric Cu-Pc exhibits a dielectric constant between 5 and 7, much lower than the polymer. This result indicates that there are remarkable changes in the dielectric parameters due to the polymerization since the π-electron system has been enhanced by the polymerization of phthalocyanine macrocycles. Figure 3 shows the temperature dependence of dielectric constant and loss at 1, 5 and 10 kHz for acetone treated samples of poly-Cu-Pc. During the dielectric measurements, all the samples were kept for 30 min at the required temperature for stabilizing the samples. There is a sharp increase in dielectric constant with increase of temperature and a dielectric maximum was observed at 150°. At the elevated tem-

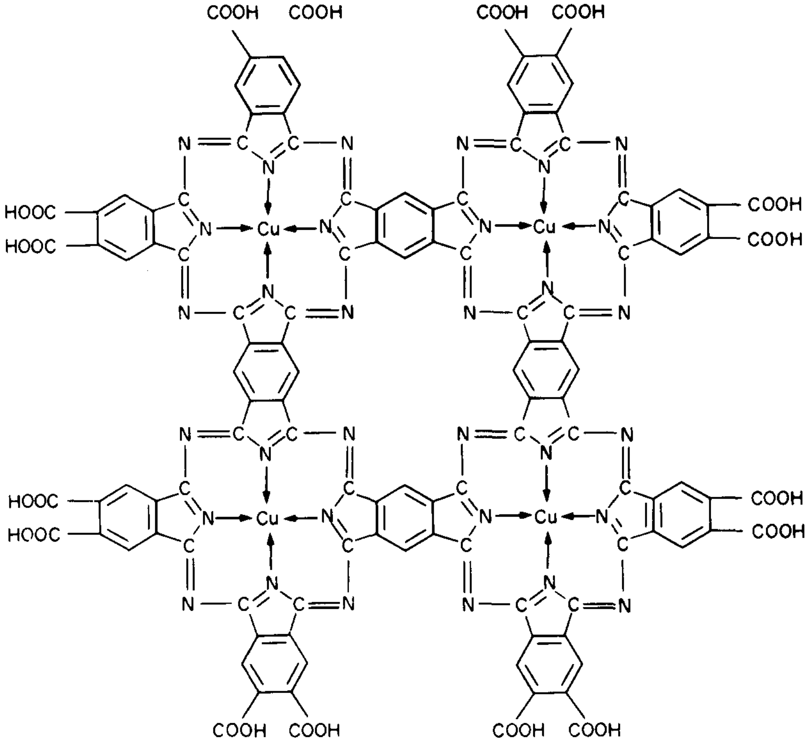

Fig. 1. Molecular structure of a sheet-like polymer of copper-phthalocyanine.

perature of 150°, the dielectric constant is enhanced approximately by four orders of magnitude. One of the interesting features noted was the sudden decrease of dielectric constant beyond 150° and its persistance between 3 and 10 in the temperature range 180–240°. Similar characteristics of dielectric loss as a function of temperature were observed with a maximum at 150°. Figure 4 shows the dielectric constant and loss vs temperature plots for KOH treated samples of poly-Cu-Pc. In this case a dielectric maximum was observed at 120°. Similar to the acetone treated sample, the dielectric constant increases sharply approaching 10^5 at 120°. Again, it remains in the range 3–10 between 180 and 240°. It seems that when the samples are heated above the temperature corresponding to the dielectric maxima, the state of high polarizability is probably destroyed, leading to the low dielectric constant. The structural changes occurring during KOH treatment probably reflects the formation of COOK from the carboxylic acid functional groups.

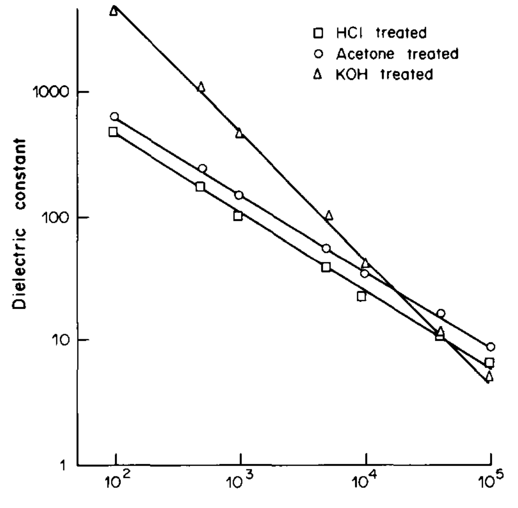

Fig. 2. Logarithmic plots of dielectric constant vs frequency at room temperature.

The HCl treated samples of poly-Cu-Pc showed a dielectric maximum at 90°, both for dielectric constant and loss as represented in Fig. 5. A tremendous difference in the dielectric parameters has been observed at the elevated temperatures in comparison to the other samples, in the present case the dielectric constant is much lower. These changes in the dielectric behaviour are due to the demetallization of the copper from the phthalocyanine rings. The i.r. spectra of these samples have been recorded and discussed [8]. A medium intensity i.r. absorption band at 920 cm^{-1} was observed in the samples other than the HCl treated sample; this absorption is characteristic of metallophthalocyanines. It indicates that HCl has reacted with copper and the polymer is now metal-free. Complex formation takes place between the copper and chloride ions and copper salt separates out leaving behind the metal-free-phthalocyanine system. Further, this result was substantiated by the elemental analysis, since the HCl treated sample showed no traces of Cu ions. This evidence indicates that the presence of metal in the phthalocyanine system greatly influences the dielectric parameters. Such variation in the dielectric characteristics of the phthalocyanines having same π-electron system may depend upon the inter-

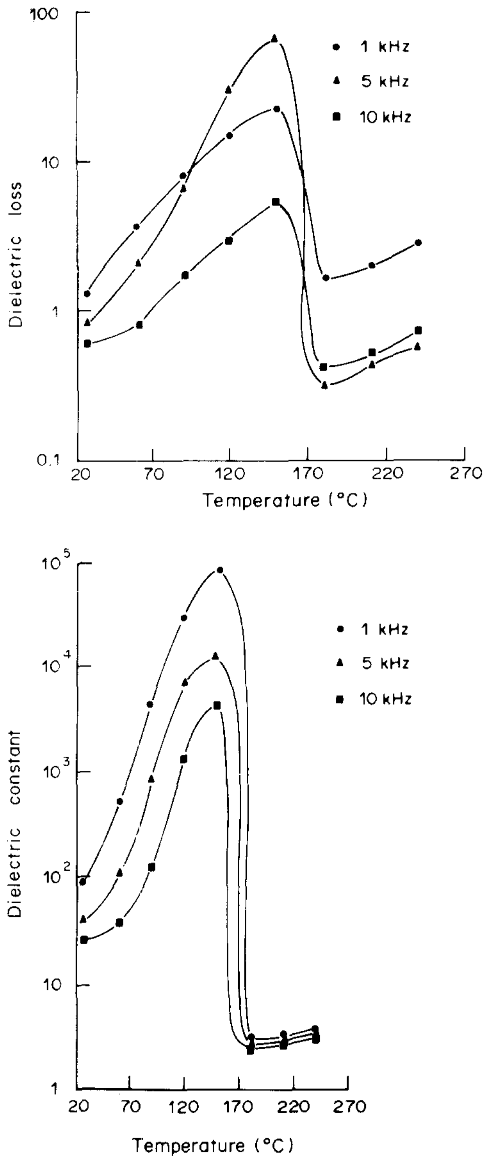

Fig. 3. Dielectric constant and dielectric loss plots as a function of temperature of acetone treated poly-Cu-Pc sample.

molecular differences, since in metal-phthalocyanine there is relatively stronger intermolecular overlap of the π-orbitals.

Poly-Cu-Pc polymers have outstandingly high dielectric constants compared to the values between 1.9 and 35, most often noted for conventional polymers [9]. There are several reasons associated for the appearance of such an interesting dielectric behaviour in the highly conjugated system of metallophthalocyanines. First, there exists spontaneous polarization in the samples, an essential characteristic of a ferroelectric material [10]. Sometimes, parasite currents are observed in the unpolarized samples due to the electrochemical processes occurring between the metallic electrodes and the sample. These parasitic currents also increased sharply with temperature similar to the conduction current and are reversible in nature. In order to eliminate such problems,

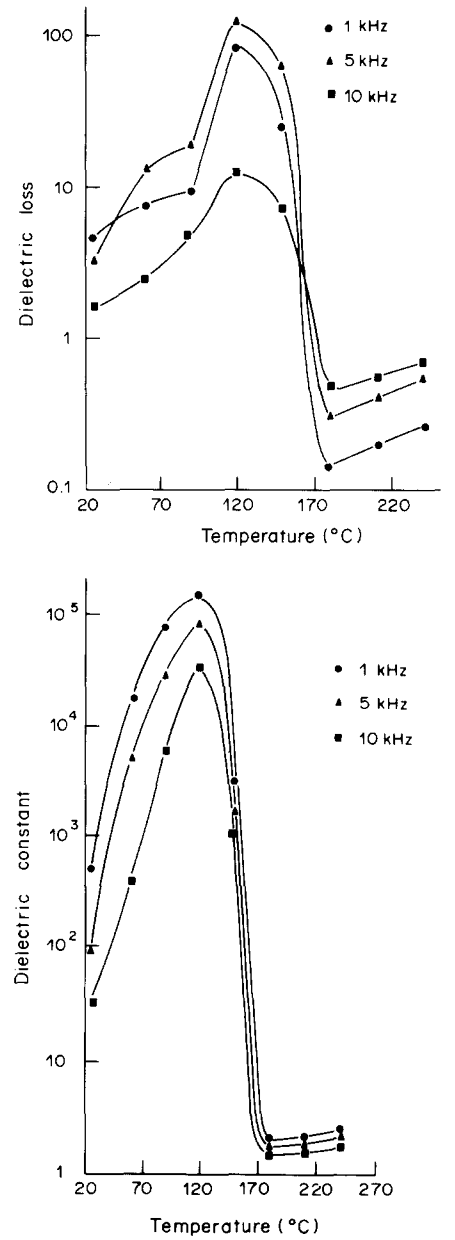

Fig. 4. Dielectric constant and dielectric loss vs temperature curves of KOH treated poly-Cu-Pc sample.

metal-electrodes often are deposited on the sample by evaporation since electrode-sample contacts play an important role in the determination of the electrical properties. Poor electrical contacts may lead to irreproducible results. In the present case, aluminium electrodes were deposited on the pellets by evaporation under vacuum. When the unpolarized samples were heated at the uniform rate of 6°/min, the evolution of spontaneous current was observed as shown in Fig. 6. Current increases remarkably with increase of temperature and a current maximum was observed at 120°. This temperature dependece of the spontaneous current indicates the pseudopyroelectric nature of the samples, since during cooling of the samples, this pyroelectric current was not found to reverse in polarity. The reversal of the pyroelectric

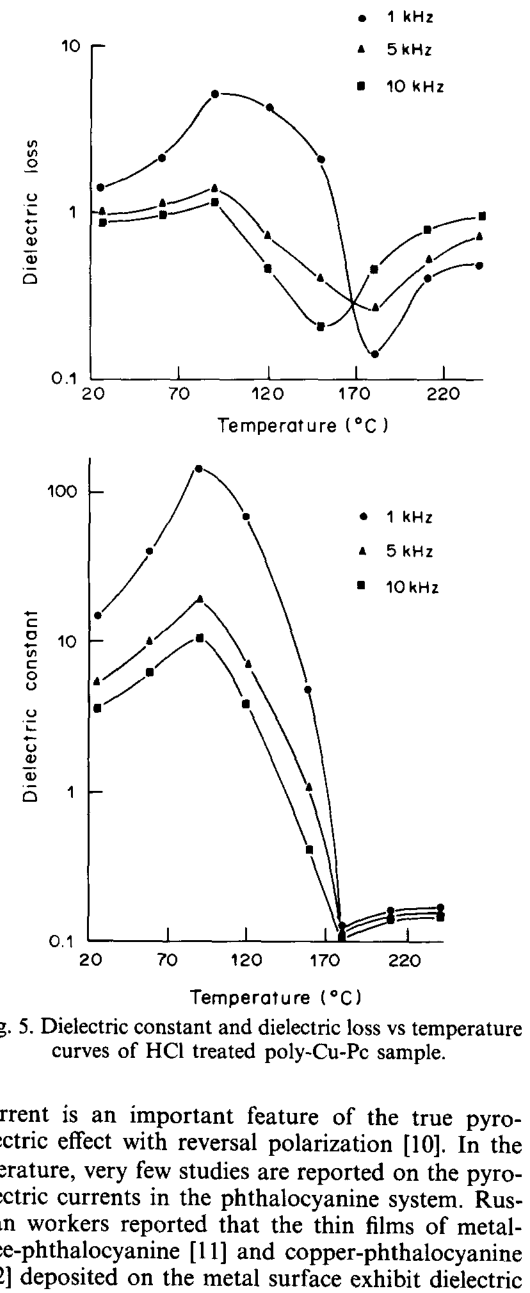

Fig. 5. Dielectric constant and dielectric loss vs temperature curves of HCl treated poly-Cu-Pc sample.

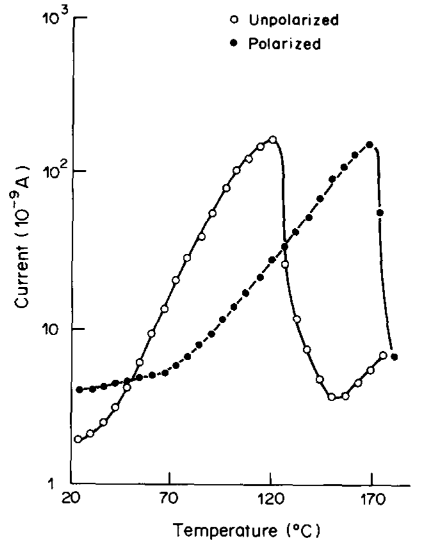

Fig. 6. Spontaneous current (○) as a function of temperature recorded at the heating rate of 6°/min and thermally stimulated depolarization current (●), for the sample polarized at 90° under an electric field of 2.5 × 10^3 V/cm for 2 hr and depolarized at the rate of 6°/min.

current is an important feature of the true pyroelectric effect with reversal polarization [10]. In the literature, very few studies are reported on the pyroelectric currents in the phthalocyanine system. Russian workers reported that the thin films of metal-free-phthalocyanine [11] and copper-phthalocyanine [12] deposited on the metal surface exhibit dielectric properties similar to a ferroelectric material. However, such dielectric behaviour has not been studied in polymers of the metallophthalocyanines so far. The present experiments provide proof for the occurrence of spontaneous polarization in poly-Cu-Pc samples. As seen from the chemical structure of the polymer (Fig. 1), carboxylic acid functional groups are present at the peripheral sites of the phthalocyanine rings. The presence of –COOH groups is evidenced by i.r. spectroscopy. The characteristic COOH groups absorption bands occur at 1330, 1420, 1600 and 1740 cm^{-1} [8]. These dipolar groups are capable of producing high polarizability, which is favourable for the occurrence of the spontaneous polarization. When poly-Cu-Pc samples were polarized at 90° under an electric field of 2.50 × 10^3 V/cm for 2 hr and the thermally stimulated depolarization current spectrum was recorded at 6°/min, a current maximum occurs at 170° (Fig. 6). Unpolarized as well as polarized samples show currents of equal magnitude, however, after thermoelectric treatments, the current maximum shifts from 120° to 170°.

Practically, polymeric materials are almost always heterogeneous. The structural heterogeneities in polymers arise from the presence of impurities like monomer, solvent, water, etc. A heterogeneous system exhibits Maxwell–Wagner–Sillars (MWS) polarization, sometimes termed interfacial polarization, which appears to be due to the migration of charged carriers through the several phases of the dielectric leading to the accumulation of different charges at the interface [13, 14]. MWS polarization depends upon the geometry of the structural heterogeneities and usually is expected at the low frequency range. MWS type polarization has been studied in several polymers [15]; poly(vinylchloride) [16], poly(acrylic acid), poly(methacrylic acid) and poly(styrene sulphonic acid) [17] exhibit this type of relaxation. In the case of copper-phthalocyanine polymer, dielectric phenomena can be caused by MWS polarization since impurities will introduce heterogeneity. The dielectric constant decreases rapidly with increasing frequency (Fig. 2) and comparatively high ε values were recorded at lower frequencies. For poly-Cu-Pc the dielectric constant increases sharply with increasing temperature. This characteristic is also consistent with the MWS polarization mechanism since there are possibilities of creating enormous numbers of free charge carriers with increase of temperature which then will enhance the dielectric constant. Sometimes, it is rather difficult to distinguish MWS polarization from a true molecular permittivity increase. However, at low temperatures, impurities are almost immobilized corresponding to low values of dielectric parameters. In the present case dielectric behaviour can be best interpreted in terms of MWS polarization.

Metallophthalocyanine polymers have been classified as ekaconjugated polymeric systems [4] because they are highly conjugated and have a large planar structure of predominantly aromatic nature. The π-electrons are completely delocalized over the entire chain molecule. A number of ekaconjugated polymers having sufficiently high dielectric constant have been studied. For example, polyacenequinone radical polymers (PAQR) [18], show dielectric constant from 10 to 3×10^5 or even higher at elevated temperatures and pressures. Other ekaconjugated polymers exhibiting similar dielectric characteristics are metallo-organic polymers [e.g. poly-Cu(II)-*N*, *N'*-dimethyl rubeanate], poly(carbon-disulphide), quinazone polymers, pyropolymers, etc. [19]. This type of unusual dielectric behaviour of ekaconjugated polymers appears to be due to a new type of polarization called hyperelectronic nomadic polarization as suggested by Rosen and Pohl [20]. However, the present data are best interpreted in terms of ferroelectric and MWS polarization. Besides these effects, other physico-chemical changes occurring within the phthalocyanine polymeric system may lead to interesting dielectric behaviour. Also, preliminary studies performed at room temperature with pellets of poly-Cu-Pc samples did not give rise to a hysteresis loop, a characteristic of ferroelectricity. Possibly, such effects may become observable in the vacuum coated thin films rather than in thick polycrystalline pelletized samples. Further studies are being undertaken for a better understanding of the phase transition in metallophthalocyanine polymers.

CONCLUSIONS

The copper-phthalocyanine polymer exhibits very interesting dielectric behaviour. Dielectric constant and dielectric loss are frequency and temperature dependent. Treatment of samples with solvents like acetone, KOH and HCl cause structural changes in phthalocyanine ring. Particularly, HCl treated sample showed low dielectric constant because of demetallization indicating that the copper ion greatly influences dielectric parameters. An anomalous increase in dielectric constant at higher temperatures has been interpreted in terms of MWS polarization due to structural heterogeneities. Unpolarized samples upon heating exhibit spontaneous current indicating that ferroelectric polarization is another possibility to explain anomalous dielectric behaviour.

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