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The influence of extended conjugation on electroactive properties of copper phthalocyanine macromolecules

Hari S Nalwa
Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, USA

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A monomer and polymer of a copper(II) phthalocyanine have been synthesized in order to develop structure–property relationships. Various electroactive properties such as dielectric constant, resistivity and thermally stimulated depolarization effects were investigated in order to examine the influence of extended conjugation.

Keywords: Copper(II) phthalocyanine, electroactive properties, extended conjugation, dielectric constant, resistivity, depolarization effects

INTRODUCTION

Metallophthalocyanines have been a subject of great interest due to their unique electrophysical properties.[1-12] Since the phthalocyanine macromolecule represents one of the most versatile organic systems from an architectural viewpoint, tremendous opportunities therefore exist to develop structure–property relationships. Various chemical modifications can be made either by introducing a central metal atom into the macrocycle or by substituting reactive functionalities at peripheral sites of the macrocycle.[13-17] Incorporation of the metal atom alters the electrophysical properties because of extended overlapping between π-orbitals; hence significant effects due to the nature of the central metal atom, particularly on the electrical properties of phthalocyanine macromolecules, have been observed.[18,19] Besides these inter- and intramacrocyclic modifications, the phthalocyanine molecule can be polymerized to extend further its π-electron system. It has been realized recently that electrophysical properties are greatly influenced by the extended π-electron delocalization.[20,21] The presence of highly conjugated π-electron systems in phthalocyanine macromolecules not only imparts unique electrical properties but also introduces exceptional thermal and chemical stability. The extended electronic conjugation can be achieved through polymerization process. It was of interest to examine how the electroactivity of copper(II) phthalocyanine macromolecules is influenced when the π-electron system is extended from a monomer to a polymer. In this paper, the electroactive properties of copper phthalocyanine macromolecules are reported.

EXPERIMENTAL

Synthesis of monomer and sheet polymer forms of copper(II) phthalocyanines was achieved by previously established methods already reported in literature.[22,23] The materials were purified and characterized by various analytical techniques. The polymers were tested in the form of pressed pellets (obtained at 9 tonnes under vacuum). The electrical measurements such as resistivity and dielectric constant were performed by procedures described earlier.[24,25] In order to study the thermally stimulated depolarization current effect, thermoelectrets were obtained by polarizing the samples at 90 °C under an electrical field of 2.50 kV cm^{-1} for 120 min and the depolarization current was recorded at a uniform heating rate of 6 °C min^{-1}. Similar polarization and depolarization conditions were employed for monomer and polymer samples. The pellets were coated with silver paste to achieve reliable electrical contacts. In the case of resistivity and dielectric constant measurements, all the samples were kept at the desired temperature for at least 30 min. Electrical measurements over the temperature range room temperature to 240 °C were made with samples sandwiched between two aluminum electrodes.

RESULTS AND DISCUSSION

The various electrical parameters such as electret data and dielectric constant measured at room temperature are listed in Table 1. The dielectric constant shows frequency dependence; it ranges from 5.3 to 6.8 D for the monomer, whilst a wide range from 10.3 to 271.7 D was observed for the polymer. The temperature versus dielectric constant plots are shown in Fig. 1 (A and B) and a dielectric maximum was recorded at 120 °C for the monomer and at 150 °C in the case of the polymer. The dielectric constants of the polymer at elevated temperatures are several orders of magnitude higher than those observed in the monomer of copper(II) phthalocyanine (CuPc) sample. Despite very significant differences in the dielectric constant at transition temperatures, it falls between 2 and 10 D just after the dielectric peak probably due to a change in the high polarizability state. Such anomalous dielectric behavior observed for the polymer seems to appear as a result of dipolar polarization since acid (—COOH) reactive functionalities are attached at the peripheral sites of phthalocyanine macrocycles, as evidenced by infrared (IR) spectroscopy.[26] Furthermore, when unpolarized samples of monomer as well as polymer were heated, evolution of a pyroelectric current was noticed, indicating that ferroelectric polarization may be another possibility. The polymer exhibited a remarkably high dielectric constant in comparison with the monomer, showing that the extended π-electron conjugation also plays a quite important role in determining the electrical parameters. The dielectric constant of the polymer is much larger than that of other conventional polymers,[27] but some other highly conjugated organic polymers show similar dielectric characteristics.[28] Voet and Suriani[29] reported a value of 4.85 D for commercial monomeric CuPc, similar to that observed in the present study.

Figure 2 represents the log resistivity versus $1/T$ plot for the monomer of CuPc. The sample has a resistivity of $\sim 1.55 \times 10^{11}$ ohm cm and this decreases as a function of temperature up to 150 °C but increases as the temperature is further raised. The Activation Energy (E_a) calculated from the plot was found to be 1.12 eV (108.0 kJ mol^{-1}) in the temperature range 20–150 °C and 1.38 eV (133.1 kJ mol^{-1}) between 150 and 240 °C. The electrical resistivity reported by a number of groups for CuPc ranges between 10^{11} and 10^{14} ohm cm depending upon the nature of material and the measurement techniques employed.[30–33] The present results are in good agreement. Interestingly enough, polymeric CuPc has a

Table 1 Dielectric constant measured at room temperature and thermally stimulated depolarization current parameters of monomeric and polymeric copper phthalocyanines

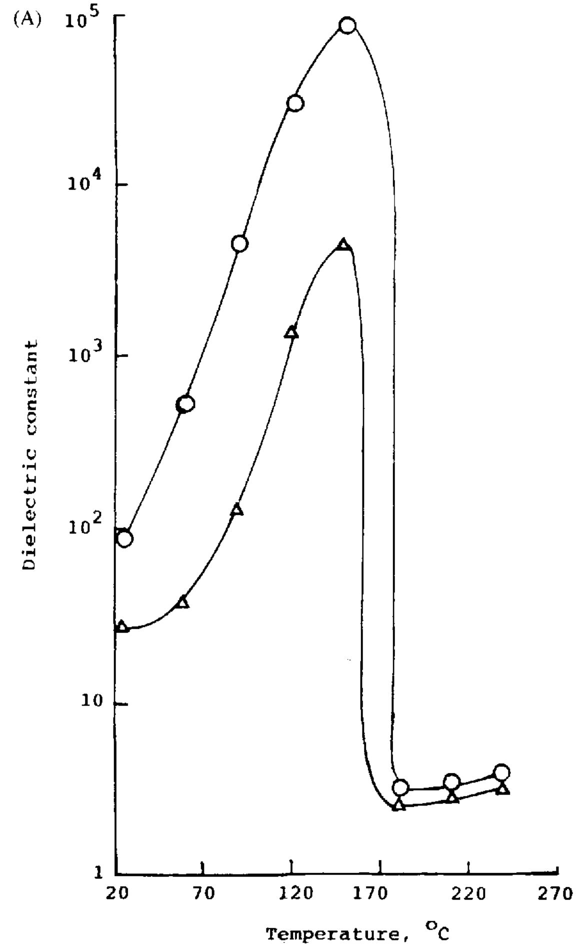
(A) Dielectric constant

Frequency (kHz)	Dielectric constant (D) Monomer	Polymer
0.5	6.8	271.7
1	6.4	89.9
5	6.2	39.3
10	5.9	25.7
50	5.3	10.3

(B) Depolarization kinetics parameters[a]

Sample	T_{max} (°C)	I_{max} (A)	E_a (eV)	τ_0 (s)	τ_{300} (s)	$\tau_{T_{max}}$ (s)
CuPc	180	$\sim 10^{-9}$	0.36[b]	4.8124×10^{-2}	5.4355×10^{4}	4.9078×10^{2}
PolyCuPc	170	$\sim 10^{-7}$	0.50[c]	6.8510×10^{-4}	1.7479×10^{5}	3.3793×10^{2}

[a] T_{max} is the TSD peak temperature, I_{max} is electric current at T_{max}, τ_0 is the relaxation time constant, τ_{300} is the relaxation time at 27 °C, $\tau_{T_{max}}$ is the relaxation time at T_{max}, E_a is activation energy. [b] 34.7 kJ mol^{-1}. [c] 48.2 kJ mol^{-1}



higher resistivity, of the order of 1.34×10^{13} ohm cm, than the monomer. The resistivity decreases as the temperature increases, unlike the monomer. The E_a value determined from the Arrhenius equation was approximately 1.00 eV (96.4 kJ mol^{-1}). Inoue *et al.*[34] reported a value of 1.60×10^8 ohm cm with an E_a of 1.00 eV (96.4 kJ mol^{-1}). However, a lower resistivity of 10^{12} ohm cm has been reported by Terentiev.[35] A wide variation in the resistivity of the polymers has been noticed depending upon the starting materials and the synthetic conditions. CuPc polymers prepared from pyromellitonitrile have been found to exhibit lower resistivity than those synthesized from acid or acid anhydrides.[36] In the present investigation, pyromellitic dianhydride was used for polymer synthesis resulting in the incorporation of acid (—COOH) groups at the peripheries of the phthalocyanine macrocycles. The residual groups of the —COOH type act as carrier-traps leading to higher electrical resistivity than monomer CuPc. However, it is likely that extended π-electron delocalization in polymers must lower resistivity due to increased conjugation by polymerization.

The thermally stimulated depolarization (TSD) current spectra of the monomer and polymer were obtained under identical conditions (Fig. 3). The monomer showed a TSD peak at 180 °C whilst the polymer peak was at 170 °C. The details for the TSD parameters are listed in Table 1. The E_a calculated

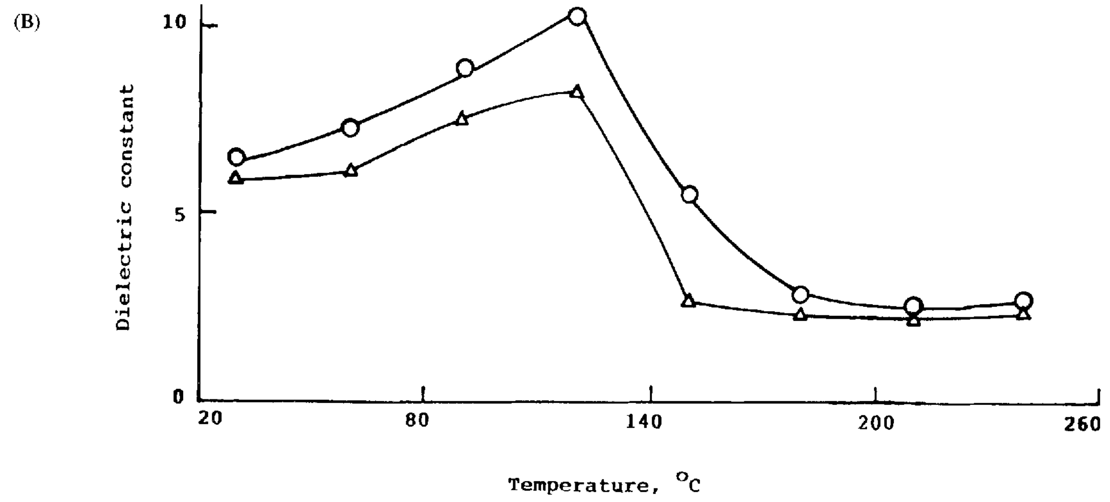


Figure 1 Dielectric constant versus temperature plots of (A) copper(II) phthalocyanine polymer and (B) copper(II) phthalocyanine monomer, recorded at 1 kHz (○) and 10 kHz (△).

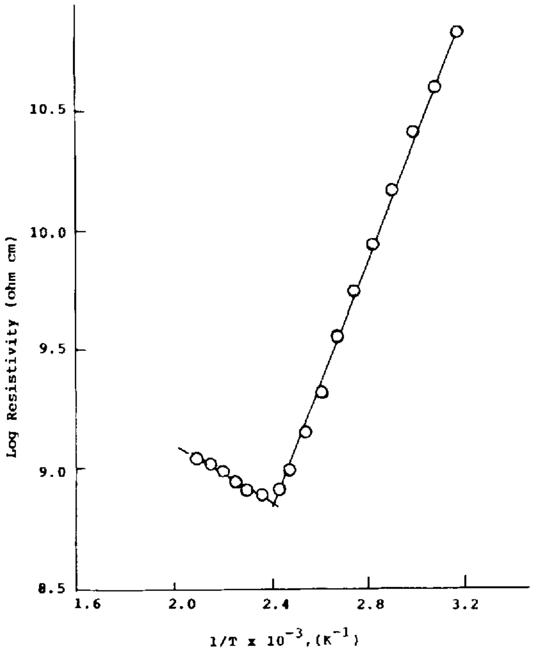


Figure 2 Log resistivity versus $1/T$ plot of copper(II) phthalocyanine monomer.

from the semilogarithmic plot of depolarization current versus $1/T$ by the initial rise method[37] are found to be 0.50 (48.2) and 0.36 eV (34.7 kJ mol^{-1}) for polymer and monomer respectively. The electrical current recorded at the TSD peak temperatures shows a significant variation from 10^{-9} to 10^{-7} A resulting from the dipolarizability of the polymer, since in the monomer only space charge effects can be operative due to the absence of dipoles. It seems two different polarization mechanisms are active in monomer and polymer. It is difficult to tell from these results the exact polarization phenomena taking place during thermoelectret formation. A clearer picture of the polarization mechanism can be obtained by studying the influence of various polarization and depolarization conditions such as the electrical field, temperature, time, electrode material, sample thickness, heating rate, storage time, etc.[38] As stated earlier, the monomer and polymer exhibit a pyroelectric current upon heating without polarization, evidencing the presence of spontaneous polarization. These materials are pseudopyroelectric in nature since no reversible

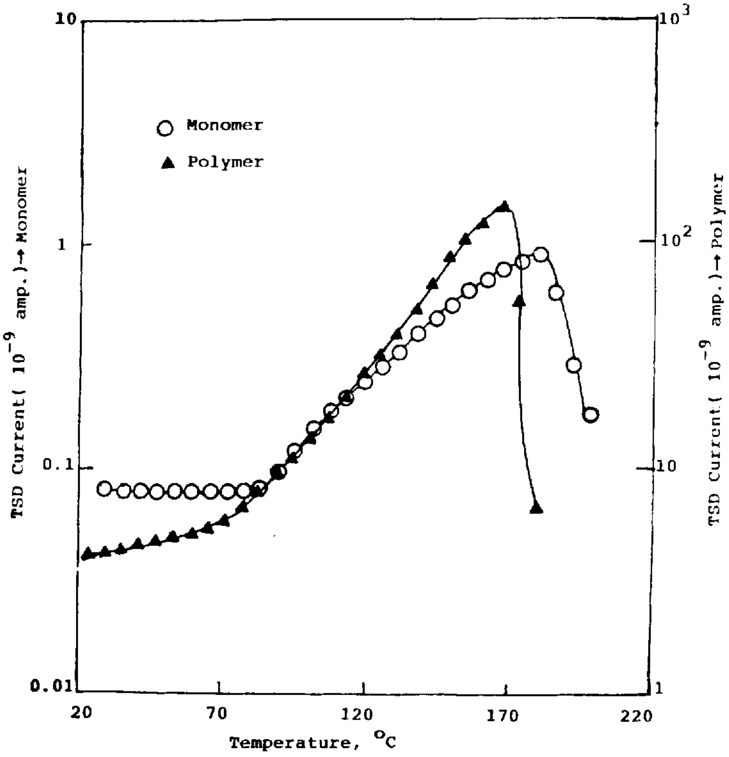


Figure 3 Thermally stimulated depolarization current spectra of copper(II) phthalocyanine monomer and polymer recorded at a uniform heating rate of 6 °C min^{-1}. Identical polarization conditions were employed for thermoelectret formation. In both cases, samples were polarized at 90 °C under an electric field of 2.50 kV cm^{-1} for 120 min.

change in polarity was observed while cooling the sample, a characteristic of pyroelectric material.[39] The significant differences between the electrical properties of the monomer and polymer of CuPc result from the extended π-electron conjugation enhanced by polymerization. The present data suggest that structure–property relationships can be developed by appropriate modifications in the molecular structure.

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