Electrical Properties of Some Transition Metallopolymer Complexes. I.

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ABSTRACT: Recently, considerable interest has been paid to polychelates of polymeric ligand with transition metal ions in order to improve their electrical properties. Some polymeric ligand complexes of Cu(II), Ni(II), and Co(II) have been synthesized, followed by chemical and physical characterization to emphasize their structure and evaluate their electrical behavior. Direct current (dc) and alternating current (ac) electrical conductivities were measured at variable temperatures (300–50 K). Relative dielectric permittivity ϵ', dielectric loss factor ϵ'', and loss tangent tan δ were measured and discussed in relation to the presence of transition metal ions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 401–407, 1999

Key words: electrical properties; metallopolymer complexes; polychelates; electrical conductivity
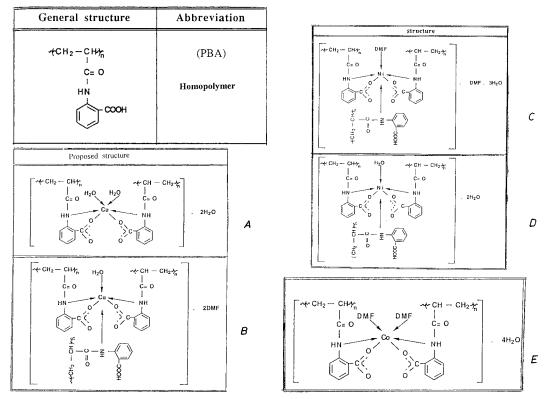
INTRODUCTION

Electrical conductivity depends mainly on the number and mobility of charge carriers that can be correlated with chemical composition and morphology of polymers.[1,2] It is of interest that the polymer morphology, its type, extent of crystallinity, and tacticity each plays a role in evaluating the electrical properties of polymers.[3] Many types of polymers have been synthesized to produce an improved electrical properties.[4–7] The presence of transition metal ions in a polymeric material may facilitate charge transportation either by crosslinking or via the hybridization of the S-P and d-orbitals.[1,2]

Recently, special attention has been directed to the study of electrical conduction of polymers containing metal ions.[8–12] Introduction of metallic ions could take place through one of the following ways.

1. The metal atoms may be a pendent from the polymer backbone and may be present as anion, as a π-complex or held by chelating ligands.[13]
2. The metal atoms may be a part of the backbone.[14] The electrical conductivity in the first group is ionic in nature and critically depends upon the water content.[15,16] The effect of hydrogen bonding and orientation of polymeric chains on its electrical conductivity has been studied by Seanor et al.[15,16] It was suggested that the transport of

Scheme 1. (A) PBA–Cu(II) acetate complex; (B) PBA-Cu(II) chloride complex; (C) PBA–Ni (II) acetate complex; (D) PBA–Ni (II) chloride complex; (E) PBA–Co (II) acetate complex.

charges through the hydrogen bonds plays an important role in evaluating the electrical properties of polymeric materials.

The aim of this work is to measure and evaluate the electrical properties of poly(2-acrylamide) benzoic acid (PBA) and their transition metallopolymer complexes, namely, Cu(II), Ni(II), and Co(II). Electrical conductivities [direct current (DC) and alternating current (AC)] and dielectric permittivity will be analyzed as a function of temperature (300–50 K).
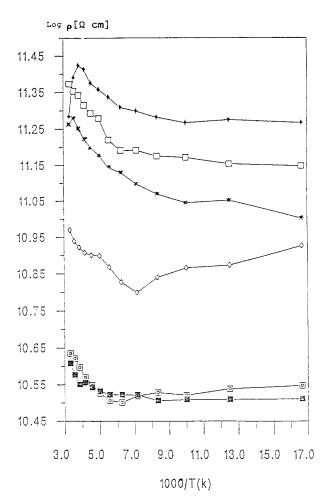
EXPERIMENTAL PROCEDURE

Preparation of Metallopolymer Complexes

Polymer complexes of the homopolymer PBA with Cu(II) acetate, Cu(II) chloride Ni(II) acetate, Ni(II) chloride, and Co acetate were prepared[17] by

dissolving a 2 : 1 molar ratio (polymer : metal salt) in dimethyle formamide (DMF). The reaction mixture was boiled under reflux for 6 h. The resulting solution was added to cold water acidified with HCl, and the formed polymer complex was precipitated, filtered, and dried under vacuum. The proposed structures of the metallopolymer complexes, which are shown in Scheme 1(A)–(E), were confirmed by chemical and physical techniques.[17]

Preparation of Samples for Electrical Measurements

Disks (1 mm thickness; 5 mm radius) were formed from fine powder compressed at 10 tons/cm^2, while vacuum (10^{-2} torr) was applied. The disks were heated in a vacuum oven at 80–90°C for 1 h and then left in vacuum desiccator. The disks are painted with highly conductive material (Ag past) as electrodes.

Figure 1 Variation of log ρ versus $1000/T$ of (*) homopolymer (PBA), (■) Cu(II) acetate complex, (□) Cu (II) chloride complex, (◆) Ni(II) acetate complex, (◇) Ni(II) chloride complex, and (⊠) Co(II) acetate complex.

Electrical Measurements

DC Conductivity

The electrical resistivity measurements were carried out according to ASTM-D 257.[18] The sample was set up in a cryogenic system (CSA 202, from Air Products). A series of dc voltage (50–400 V) was applied on the sample, and the corresponding currents values were recorded by a digital electrometer (Keithly 616) as a function of temperature (300–50 K). The electrical resistivity values for each sample (ρ) were measured as a temperature dependence, as shown in Figure 1.

AC Conduction

The measurements of capacitances are carried out according to ASTM-D 150.[18] The painted

disk was placed in the cryostat chamber, and it was connected directly to the ac Bridge (Autobalance Precision Bridge, Wyne Kerr B 331). The variation of sample capacitance as a function of temperature was recorded, and the corresponding dielectric constant ϵ' and conductance G were calculated and presented as shown in Figure 2(a)–(f).
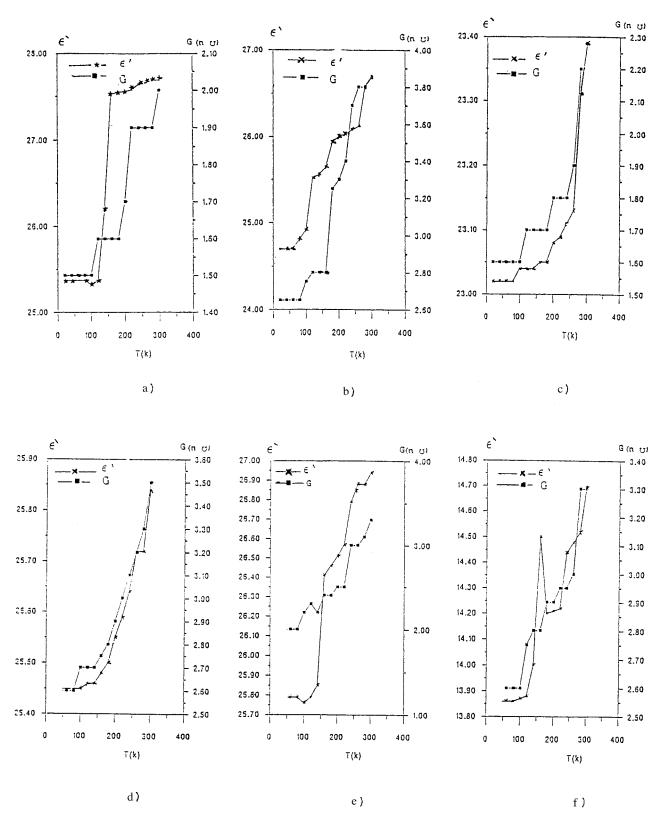
RESULTS AND DISCUSSION

DC Conductivity

The main principle in which electrical properties are described is to measure the electrical conductivity (σ) or resistivity (ρ) as a function of temperature T, as follows:

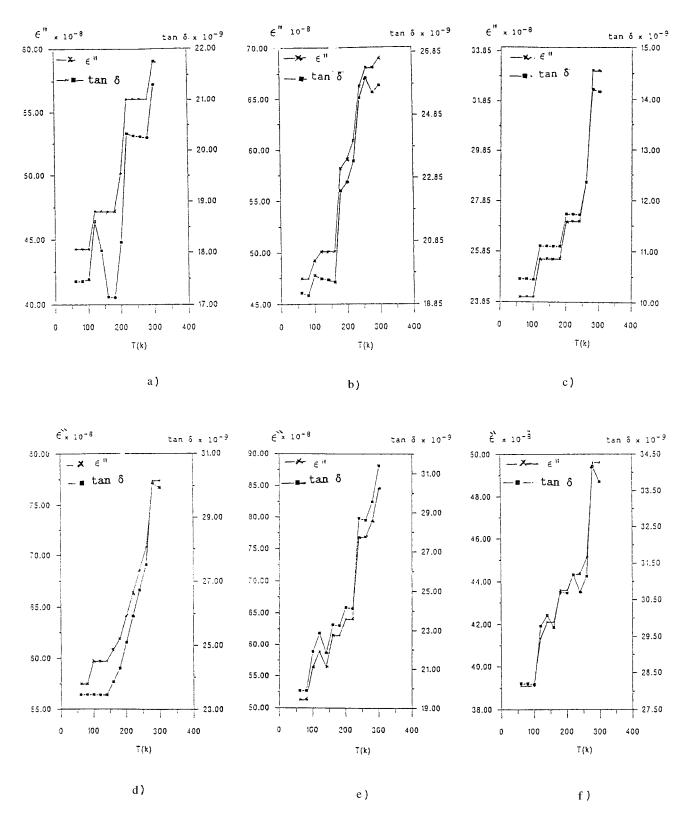$$\sigma = \sigma_0 e^{-E_A/\kappa T} \tag{1}$$

where σ_0 is the prefactor (in limit $1/T = 0$), E_A is the activation energy, and κ is Boltzman's constant.

It is observed that within the temperature range (300–50 K), the value of log ρ decreases as the temperature decreases (Fig. 1), reaching a limit value at a lower temperature for the homopolymer (PBA) and the corresponding metallocomplexes. This trend could be attributed to the reduction of carrier phenon scattering rate, and, hence, an increase in mobility should occur. This may be partially compensated by carrier freeze out with a rate, depending upon the type and morphology of the polymer. Also, when cooling down to 50 K, an increase in resistivity was observed, which may be due to a reduction of free carrier contributing to the dominant conduction mechanism. This is accompanied by a competing mechanism caused by reduction in carrier phenon scattering rate. Also, the transfer of carriers to lower energy states will enhance the localized hopping conduction rate.

The electrical conductivity of the homopolymer (PBA) and their derivatives of metallotransition complexes showed an insulation behavior; therefore, it does not indicate an improvement in their electrical conductivities. This fact is in agreement with some previous reports[19–23] concerning electrical properties of polychelates.

Figure 2   Variation of dielectric constant ϵ' and conductance G versus $T(k)$ of (a) homopolymer (PBA), (b) Cu(II) acetate complex, (c) Cu(II) chloride complex, (d) Ni(II) acetate complex, (e) Ni(II) chloride complex, and (f) Co(II) acetate complex.

Figure 3 Variation of dielectric loss ϵ'' and tan δ versus $T(k)$ of (a) homopolymer PBA, (b) Cu(II) acetate complex, (c) Cu(II) chloride complex, (d) Ni(II) acetate complex, (e) Ni(II) chloride complex, and (f) Co(II) acetate complex.

It was noticed that the resistivity ρ decreases with temperature, as shown in Figure 1. This can be explained on the basis of the following:

1. The carriers may be injected from the metallic contacts (electrodes) to the bulk materials, thus giving false indications of the intrinsic property of the polymer[2];
2. an orientation effect, which may occur when an external electric field is applied, which includes other parameters, such as sample grain size, grain orientation, or the applied pressure during preparation of disk[19];
3. The existence of hydrogen-bonded water molecules with the polymer[20,21];
4. the presence of impurities, disorder, and/or solvent traces in the polymer, as well as the nature and thickness of the disk sample, which could give rise a such behavior[22]; and
5. the thermal expansion of polymeric matrix, which leads to breaking of the network of conductive particles, which, in turn, leads to an increase in resistivity as the temperature increases.[23]

AC Conduction

The frequency dependence of conductivity, capacitance, dielectric loss factor, and loss tangent tan δ are often used to investigate various types of conduction process, interfacial polarization, and junction characteristics.

Dielectric permittivity ϵ', conductance G, dielectric loss factor ϵ'', and loss tangent tan δ of the homopolymer PBA and their metallic transition complexes are presented in Figure 3(a)–(f). It was observed that dielectric permittivity ϵ' decreases as the temperature T decreases, which may be attributed to the freezing out of the motions of chain segments.[24–26]

This might not be the case if ϵ' was measured in the dc conditions. In this situation, ϵ' might not be much affected by reducing the temperature of the sample due to the previously mentioned freezing out mechanism. In our case, the dipole moment contributing to the value of ϵ' will only be responding to the applied frequency at a fairly high temperature.

However, the dielectric loss ϵ'' decreases with a higher rate compared with ϵ' as the temperature is reduced, based on the previously mentioned explanation. The decreasing value of tan $\delta = \epsilon''/\epsilon'$

upon cooling confirms the last statement. This is shown in Figure (3).

CONCLUSION

The addition of transition metal ions, for example, Cu(II), Ni(II), and Co(II) to polymeric material has an insignificant effect on the electrical properties of the prepared complexes. This is due to the presence of metallic ion rather than the backbone of the polymeric chain. From the ac and dc measurements, it was concluded that the resistivity values of polymeric complexes acquire a more or less constant values at certain temperature (165 K). On the other hand, the dielectric constant and dielectric loss decreased upon cooling.

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