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ELECTRICAL CONDUCTIVITY MEASUREMENTS IN THE RANGE OF TEMPERATURE INDUCED CONFORMATIONAL TRANSITIONS IN UNDOPED AND DOPED GLASSY POLY (PHENYL SULFONE)

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The dark conductivity in poly (phenyl sulfone) was studied. Undoped and doped films by BF_4^- in chloroform solution, prepared by cast method was investigated in the temperature range (300-430 ^oK). The dark conductivity was measured in Al/poly (phenyl sulfone)/Al sandwitch structure. The measurements were performed on poly(phenyl sulfone) samples at three different thicknesses. Some temperature dependent anomalies in the electrical conductivity changes of the poly(phenyl sulfone) samples corresponding to the second order transitions were observed.

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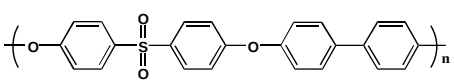
1. Introduction

Metal-insulator-metal structures based on inorganic dielectrics have been studied for a long time [1]. Dominant electrical conductivity mechanisms in such structures are described by Pool-Frenkel or Schottky models. On the other hand, the study of the properties of these structures with non-conductive polymers has started only recently [2]. Contrary to inorganic dielectrics, the polymers have lower thermal stability and their properties are strongly temperature dependent (glassy, rubbery, and plastic flow states).

Polymeric materials either organic or inorganic [3,4] are well known as insulating materials suitable for many industrial applications such as coatings adhesion, coverages, fibers, etc. Even conducting polymers in their intrinsic nature are insulators but can be transformed in conductors by suitable doping with strong acceptor and donor agents [5].

In spite of conflicts and difficulties associated with the study of the conduction mechanisms in polymeric materials, some fair results still describe gently the charge carriers migration and its variation with temperature and voltage. Sometimes, it is difficult to prove or disprove the expected conduction mechanism by direct analytical measurements because of low currents implied. Hence, different measurement techniques such as surface conductivity, dc conductivity, thermally stimulated dc current have been employed for studying the relationship between their electrical properties and chemical structure.

Poly (phenyl sulfone) is an amorphous polymer:



is used for high temperature applications because of its thermal and oxidative resistance and high glass transition temperature. It possesses much higher toughness than other glassy polymers since it has low temperature relaxation processes.

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Some energy absorbing molecular motions should exist in the polymer below glass transition i.e, β - transition, γ - transition and so on. The glass transition is called as α- transition. Above glass transition temperature, T_g, the macromolecular segments become mobile and free volume fraction in the polymer increases [6,7]. As the temperature of a polymer is lowered, the transitions are called the β-, γ-, δ- … transition [8]. The glass-, β-, γ- and δ - transition temperatures of the polymer were obtained as 480, 410, 380 and 350K, respectively, by inverse gas chromatography [9].

In this study, the electrical properties of poly (phenyl sulfone) films have been studied. Electrical characterizations were realized on the base of dc conductivity – temperature measurements together with its variation with film thickness both undoped and doped films.

The type of electrical conductivity measurement reported in the literature usually involves a simple measurement of current as a function of time, temperature, ambient atmosphere, and potential. Attempts are then made to relate the conductivity to physical processes thought to be occuring in the polymer. It is found that electrical conductivity varies exponentially with temperature, is a function of time, and may vary with electrical field: i.e.,

$$\sigma_D = \sigma_0 \exp (- E_a / kT) = f(\text{time}) = A\, f(E) \quad (1)$$

where σ_D is the dark conductivity, E_a is the activation energy, and σ_0 the preexponential factor [10]. The conductivity is obtained by measuring the current flowing through a piece of the material and using the sample dimensions to calculate σ from the equation.

$$\sigma = (d / A\, V)\, I = G \times \text{Geometric factor} \quad (2)$$

where G (= I / V) is the conductance, d is the sample thickness, A is its area, and V is the potential across the material.

2. Experimental

Undoped and doped samples under study were prepared by dropping the polymer solution in chloroform with given concentration on Corning 7059 glass substrate thoroughly cleaned using analytical pipettes in air. Aluminum electrodes were deposited by vacuum evaporation at 10^{-6} Torr, along the length of the glass plates, at the width of 3mm, onto both surfaces of the samples to form a sandwich - type specimen for measurements of electrical conduction. Contact has been performed by direct pressure of pogo contacts on the aluminum electrodes.

For the electrical characterization, dark conductivity of produced films were measured as a function of temperature using a home made liquid nitrogen vacuum cryostat having a thermocouple in good thermal contact with the sample. Samples were placed on top of a copper plate that is heated by a bolt heater embedded within. Themperature was recorded by Keithley DMM 196. Dark conductivity measurements were taken between 300-430K. The measurements were accomplished using a programmable Keitley 617 digital electrometer / voltage source interfaced to a computer.

Thicknesses of the thin poly (phenyl sulfone) samples studied were 2.00, 1.30 and 0.83 μm. Organic film thickness was determined from the area formed by spreading polymer solution with known volume and concentration. The measurements were carried out in the dark. The temperature dependence of conductivity was measured at constant electrical field 38 $kVcm^{-1}$ with the temperature being increased by 3 $Kmin^{-1}$.

3. Results and discussion

Fig. 1 shows the temperature dependence of dark conductivity (σ_d) of the undoped samples. All Al–poly(phenyl sulfone)–Al structures exhibit a dark conductivity ≥ 10^{-11} $\Omega^{-1}cm^{-1}$ at room temperature (RT).

Dark conductivity increases with temperature from 10^{-11} $(\Omega cm)^{-1}$ at RT to 5.10^{-08} $(\Omega cm)^{-1}$ at 430K for undoped films having different thicknesses. The considerable conductivity changes start after δ-transition temperature (350 K) and become almost parallel to one another throughout the temperature range of 350-430 K.

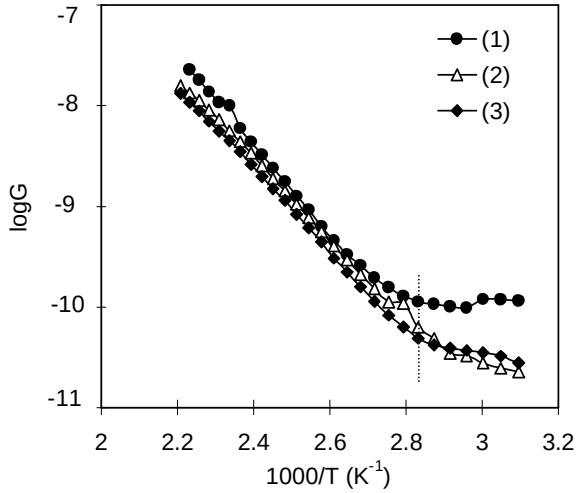

Fig. 1. Arrhenius plot of conductivity for the Al–poly (phenyl sulfone)–Al structures with different thicknesses (1) 2.00, (2) 1.30 and (3) 0.83 μm.

In Fig. 2, we show the $\log(\sigma_d)$ versus 1000/T plot for doped Al–poly(phenyl sulfone)–Al structures with different thicknesses. It appears that as the films were doped by BF_4^- in chloroform solution, the general behaviour of the conductivities are that with increasing temperature, σ_d increases in an activated way up and almost two orders of magnitude at RT and one order of magnitude at 430 K when comparing with the conductivity of undoped samples.

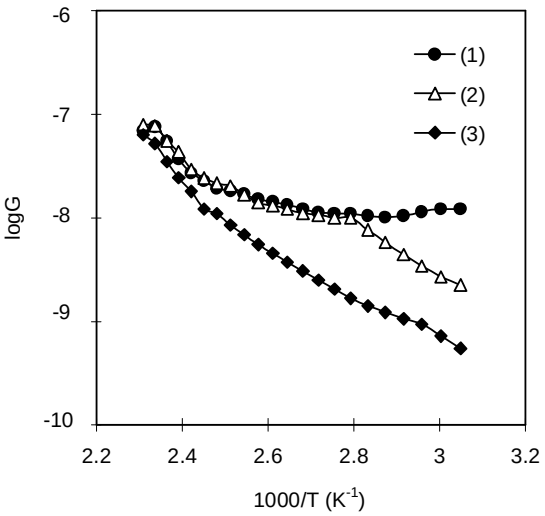

Fig. 2. Temperature dependence of conductivity of doped Al–poly(phenyl sulfone)–Al structures with different thicknesses: (1) 2.00, (2) 1.30 and (3) 0.83 μm.

Fig. 3 shows the determined activation energy values both for undoped and doped films depending on film thickness. As it can be seen from Fig. 3, the activation energies of undoped samples (1) didn't changed remarkably depending on the sample thickness at a range of 350-430 K,

above δ- transition temperatures. The activation energy was found around 0.72 ± 0.05 eV for all undoped samples. It was observed the conductivity change only at δ- transition temperature.

We calculated activation energies for the doped films below and above β–transition temperature here. From the second branch (2′) of the graphs, at a region of 410-430 K, the activation energies for different thickness were found almost the same.

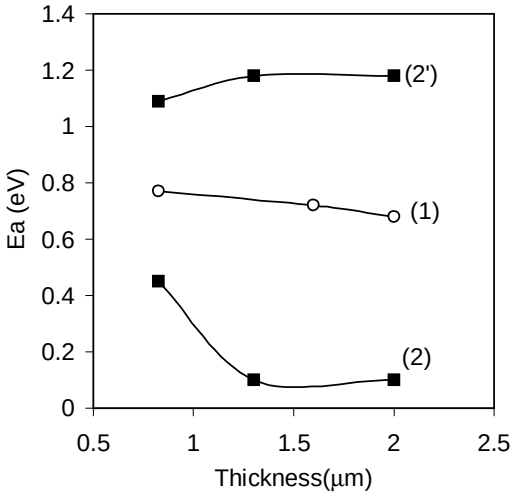

Fig. 3. Activation energies as a function of thickness of undoped (1) (350-430) and doped films from first branch (2) (380-410 K)and second branch (2′) (410-430 K) of Fig. 2.

The measurements of Arrhenius dependence of the conductivity of doped Al–poly(phenyl sulfone)–Al structure with 1.3 μm thick is shown in Fig. 4. It is clearly seen from the figure that one can see the changes on the conductivity at the points of near β- (410 K), γ- (380 K) and δ- (350 K) transition temperatures.

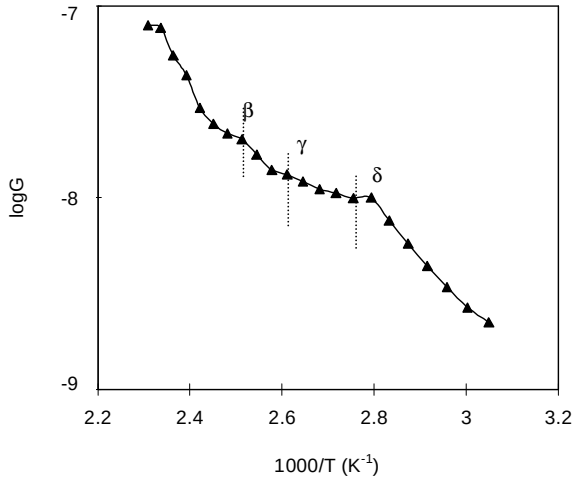

Fig. 4. Arrhenius plot of conductivity for the doped Al–poly(phenyl sulfone)–Al at the structure with 1.30-μm-thick film.

4. Conclusions

We have measured the dark conductivity in undoped and doped poly(phenyl sulfone). The electrical characteristics of the samples prepared by cast method were investigated in the temperature range of 300-430 K.

Dark conductivities increased three orders of magnitude at the temperature range studied. Moreover, an increase of the conductivity by doping up to two orders of magnitude was obtained at room temperature.

In addition, the activation energies for conductivity of the polymer were calculated from the measurements. The high value of the activation energy may be associated with ionization of deep acceptor or donor levels which become more important at higher temperature. With increasing temperature the concentration of conducting electrons increases and therefore the role of mutual interaction between electrons and between electrons and donor or acceptor centers become more important.

Finally, conductivity changes were obviously observed for the first time, at the points of δ-transition for undoped and β-, γ- and δ- transition temperatures for BF_4^- doped poly(phenyl sulfone) samples.

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