

DOPING EFFECT ON ELECTRICAL PROPERTIES OF POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE) FILMS

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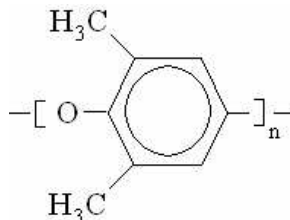
In this paper, the electrical properties of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) films have been studied. Electrical characterizations were realized on the base of dc conductivity – temperature measurements together with its variation with doping ratio. The dark conductivity measurements were carried out under vacuum of 10^{-5} Torr. The electrical conductivity of the polymer prepared in sandwich structure as Al/polymer/Al was measured in over the temperature range of 30 – 235 °C. The measurements were performed on PPO samples with thickness 6.0 μm undoped and doped by tetra-n-butylammonium tetrafluoroborate in chloroform solution at a rate of 0.25 mol doped/mol PPO, 0.50 mol doped/mol PPO. The activation energies of the samples were determined as a function of the doping ratio.

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1. Introduction

Organic or inorganic polymeric materials are known insulating materials for the industrial applications [1, 2]. Although conducting polymers are insulators in their intrinsic nature they can be transformed to conductors by suitable doping [3]. In this study, the electrical properties of PPO films which can be used as semiconductor components and snap lock connectors have been studied for both undoped and doped samples. PPO is one of the most important engineering plastics exhibits a high strength, excellent heat resistance, the high glass transition temperature (T_g) and good dimensional stability [4].



Scheme 1. The chemical structure of PPO

We determined the glass transition temperature of undoped PPO both from Differential Scanning Calorimeter (DSC) and conductivity measurements. It has been shown that the glass transition temperature of the polymer, T_g can be determined conductivity measurements [5].

Furthermore, dielectric constant, dipole moment and solubility parameter were calculated by means of group contribution method. A solubility parameter which is a characteristic of a polymer is

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used in predicting the solubility of that polymer in a given solvent. For a substance of low molecular weight, the value of the solubility parameter, δ_1 , is often estimated from the enthalpy of vaporization. For a polymer, it is usually taken to be the value of the solubility parameter of the solvent producing the solution with maximum intrinsic viscosity or maximum swelling of a network of the polymer [6-8]. These procedures are time consuming. It can be also estimated by assuming that the solubility parameter of a polymer is equal to that of a lower-molecular weight analog with structure similar to the repeating unit of the polymer. It can be calculated by adding up the contributions of groups of repeating units.

Finally, morphological changes of the undoped PPO film are studied by scanning electron microscopy (SEM).

2. Experimental

2.1. Differential scanning calorimeter

Perkin Elmer DSC6 was used in this study. DSC curves were obtained using 10 mg samples, sealed in Aluminium pans, at several controlled heating rates.

2.2. Electrical conductivity

Electrical characterizations of undoped and doped PPO films were realized on the base of dc conductivity – temperature measurements together with its variation with doping ratio.

The measurements were carried out in 10^{-5} Torr vacuum. The electrical conductivity of the polymer was measured in Al / polymer / Al structure over the temperature range of 30 – 235^oC. It was performed on PPO samples with thickness 6 μ m, undoped and doped by BF_4^- in chloroform solution, 0.25 and 0.50 mol dopant per mol PPO.

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. Polymer film thickness was determined from the area formed by spreading polymer solution with known volume and concentration.

Aluminum electrodes were deposited by vacuum evaporation at 10^{-6} Torr, along the length of the glass plates, at the width of 3 mm, onto both surfaces of the samples to form a sandwich - type specimen for measurements of electrical conductivity. Pogo contacts by direct pressure on the aluminum electrodes were used to perform contact.

For the electrical characterization, conductivity of the 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. The measurements were carried out in dark. Samples were placed on top of a copper plate that is heated by a bolt heater embedded within. Temperature was recorded by Keithley DMM 196. Electrical conductivity measurements were accomplished using a programmable Keitley 617 digital electrometer / voltage source interfaced to a computer.

The temperature dependence of conductivity was measured as the temperature being increased by 4 $^{\circ}\text{C min}^{-1}$.

For determining morphological changes, before and after heating-cooling cycle, SEM (JEOL mark, JSM-5410 LV) pictures of undoped PPO films were taken.

3. Theory

3.1. Electrical conductivity

The type of electrical conductivity measurement involves a simple measurement of current as a function of time, temperature, ambient atmosphere and potential. Electrical conductivity varies exponentially with temperature as follows:

$$\sigma_D = \sigma_0 \exp(-E_a / kT) \tag{1}$$

where σ_D is the dark conductivity, E_a is the activation energy, and σ_0 the preexponential factor [9]. 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.

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

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

3.2. Group Contribution Method

The relation among molar polarization, dielectric constant and dipole moment of a dielectric is given as follows,

$$P_{LL} = \frac{\epsilon - 1}{\epsilon + 2} V \tag{3}$$

or

$$P_V = \epsilon^{1/2} M \tag{4}$$

$$P_{LL} - R_{LL} = \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \frac{M}{\rho} = \frac{4}{9} \pi N_A \frac{\mu^2}{kT} \approx 20.6 \mu^2 \quad (\text{at } 298 \text{ K}) \tag{5}$$

where P_{LL} and P_V is the molar dielectric polarization according to Lorentz and Lorenz and Vogel respectively, ϵ is the dielectric constant, V is the molar volume per structural unit, M is the molar mass per structural unit, R_{LL} is the molar refraction according to Lorentz and Lorenz, n is the index of refraction, ρ is the density, N_A is the Avogadro number, μ is the dipole moment and k is the Boltzmann constant [10]

Application of equation (3) and (4) permits the calculation of the dielectric constant ϵ if the structural units are known.

According to Darby et. al. [10], solubility parameter of polymers is defined by the simple correlation,

$$\delta \approx 7.0 \epsilon \tag{6}$$

4. Results and discussion

As a preliminary step, we characterized PPO in the temperature range from 40 °C to 250 °C by DSC. DSC thermogram of undoped PPO sample was given in Fig.1. In this way we determined that the glass transition temperature (T_g) for this material is at 198°C. Measurements using heating rates of 5 °Cmin⁻¹ was employed to obtain this value.

Fig.2. shows the temperature dependence of dark conductivity (σ_D) of the undoped and doped samples. The considerable conductivity changes start after glass transition temperature [11]. Therefore, T_g was found to be 200 °C for undoped PPO film from Fig. 2.

Dark conductivity increases with temperature two order of magnitude which is from $3.5 \times 10^{-15} \Omega^{-1} \text{cm}^{-1}$ at RT to $2.9 \times 10^{-13} \Omega^{-1} \text{cm}^{-1}$ at 235 °C for undoped film having 6µm thickness.

In Fig. 2, 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 when comparing conductivities of the doped samples with the undoped samples. It seems they have almost the same magnitude at RT and increased by doping one order of magnitude at 235 °C.

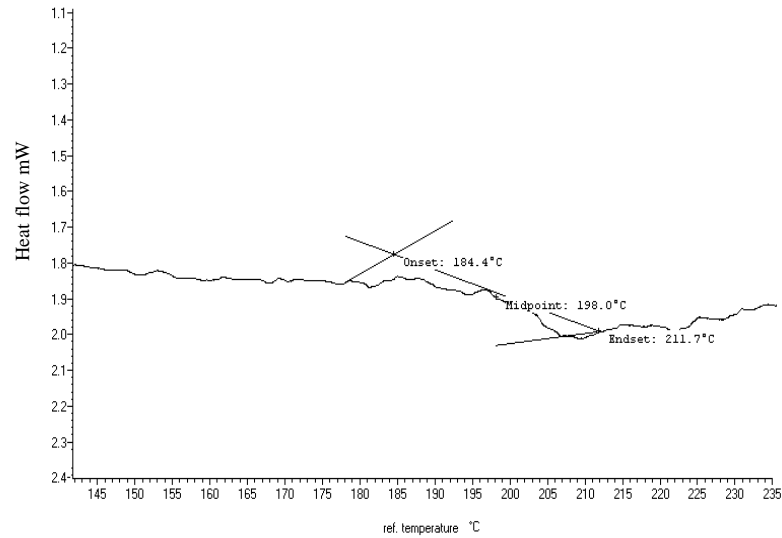


Fig. 1. DSC thermogram of undoped PPO

We calculated the activation energy of the undoped film below and above T_g glass transition temperature here. From the first branch of the graphs, at a region of 200 – 235 °C, the activation energy was found 1.19 eV and 0.80 eV from second branch (160 – 200 °C).

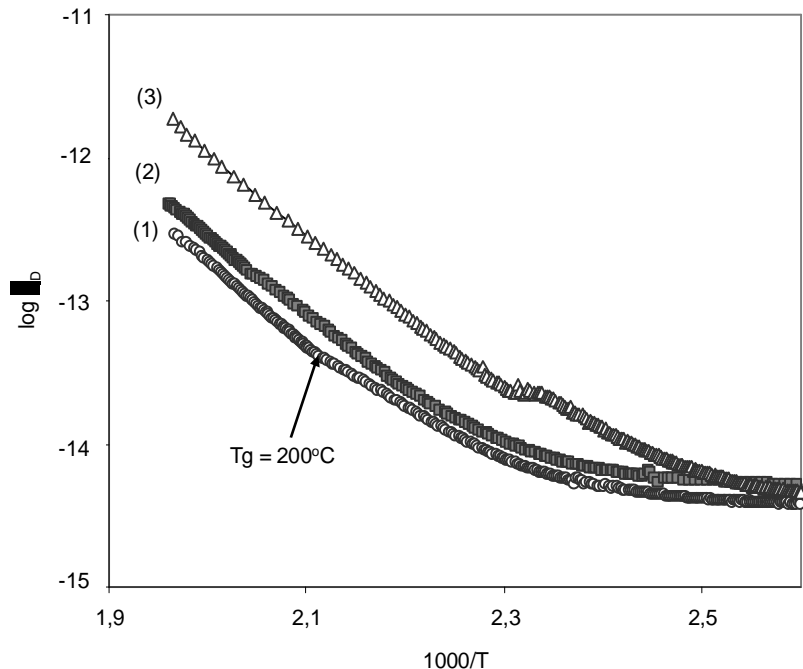


Fig. 2. Arrhenius plot of conductivity for the PPO samples; undoped (1) and doped by tetra-n-butylammoniumtetrafluoroborate in chloroform solution rate of 0.25 (2), 0.50 mol doped/mol PPO (3) with thickness 6.0 μm .

Dielectric constant and dipole moment of PPO determined to be $\epsilon_1 = 2.79$ from Eq. 3, $\epsilon_1 = 2.60$ from Eq. 4, and $\mu = 0.43$ Debye from Eq. 5, by group contribution method, respectively. By using the average value of ϵ_1 and ϵ_1 , the solubility parameter of polymer, δ_2 calculated to be 9.23 $(\text{cal.cm}^{-3})^{1/2}$.

SEM pictures of undoped PPO before and after conductivity measurements were given in Fig. 3. It seems that the morphology of PPO did not changed with heating between 30 and 235 °C.

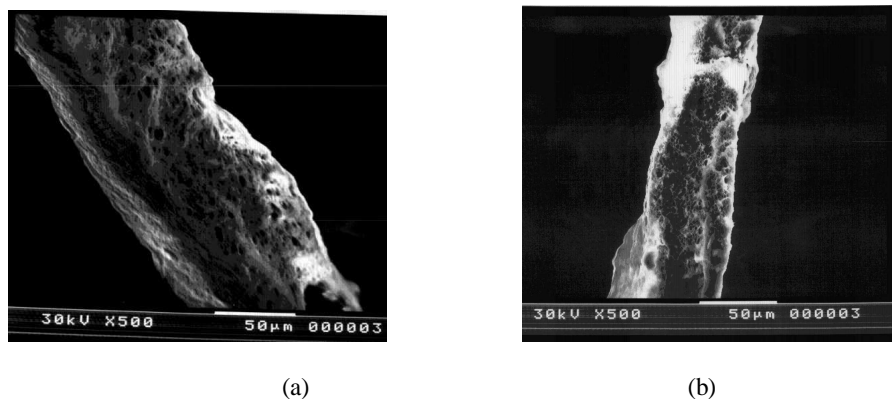


Fig. 3. SEM pictures of undoped PPO films before (a) and after (b) conductivity measurements

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