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Doping type effect on electrical conductivity of Poly(2,6-dimethyl-1,4-phenylene oxide) and electrical properties of doped and undoped Poly(2,6-dimethyl-1,4-phenylene oxide) / Ardel®D-100 films

M. SERIN[a*], D. SAKAR[b], O. CANKURTARAN[b], F. KARAMAN[b]
Yildiz Technical University, [a]Department of Physics and [b]Department of Chemistry, Davutpasa Campus, 34220, Esenler, Istanbul, Turkey

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The electrical conductivity of the polymer was measured in Al/polymer/Al structure over the temperature range of 300 – 510K. The measurements were carried out under vacuum of 10^{-5} Torr and dark. The activation energies of the samples were determined. It was found that dopants such as tetra-n-butylammonium tetrafluoroborate, tetraethylammonium bromide, and tetra-n-butylammonium bromide do not increase the conductivity of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) films prepared by cast method from chloroform solution with thickness of 6.0μm and at a rate of 0.50 mol doped / mol PPO. Then, the electrical properties of undoped poly(2,6-dimethyl-1,4-phenylene oxide) / Ardel®D-100 (PPO/ARDEL) film has been studied. The glass transition temperatures of the samples were determined by conductivity measurements. It was performed on PPO/ARDEL samples doped by tetra-n-butylammonium tetrafluoroborate in chloroform solution at the rates such as 0.25 mol doped/mol (PPO/ARDEL), 0.50 mol doped / mol (PPO/ARDEL) and 0.75 mol doped / mol (PPO/ARDEL). The conductivities of PPO /ARDEL blends are increasing as much as four orders of magnitude by increasing doping concentration.

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1. Introduction

On warming, all amorphous polymers soften in a characteristic temperature range known as the glass-rubber transition region although they are stiff and glassy at low temperatures. Then, the glass transition temperature (T_g), is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states. T_g constitutes the most important mechanical property for all polymers. The physical properties such as hardness, volume, modulus (Young's module) and percent elongation-to-break undergo a drastic change at the glass transition. It is important to understand the concept of the T_g in the selection of materials for various applications [1-3].

Sometimes, we want a material that exhibits some of the properties of one polymer, and some of the properties of another polymer. Instead of going back into the laboratory and trying to synthesize a brand new polymer with all the properties we want, we try to mix two polymers together to form a blend that will hopefully have some properties of both. In recent years, there is growing interest in modifying the existing polymers rather than synthesizing new polymers [4, 5]. However, it is necessary to investigate the miscibility of new polymer blends to get desirable properties in their applications. Polymer-polymer miscibility is determined with T_g's of the polymer blend. T_g will depend on the ratio of polymer A to polymer B in the blend. Some of the most important techniques in determination of polymer-polymer miscibility are thermal analysis [6], electron microscopy [7], dynamic mechanic studies [8] and viscosimetry techniques [9].

It is known that T_g of a polymer or doped polymer can be determined by conductivity measurements [10,11]. In this study, the effect of doping type on the T_g's was investigated for PPO and then the T_g of undoped PPO/ARDEL blend was determined by electrical conductivity measurements. In addition, the electrical properties of doped PPO/ARDEL blends were investigated.

2. Sample preparation and experimental setup

Poly (2,6 dimethyl-1,4 phenylene oxide) (PPO) was purchased from Aldrich and used as received. Tetra-n-butylammonium tetrafluoroborate, tetraethylammonium bromide, and tetra-n-butylammonium bromide as dopant and chloroform were supplied from Merck AG. Electrical characterizations were realized on the base of dc conductivity – temperature measurements together with its variation with doping type.

Undoped and doped samples under study were prepared by dropping the polymer solution in chloroform with a given concentration on Corning 7059 glass substrate thoroughly cleaned using analytical pipettes in air. The resulting film thickness was 6.0 μm. Polymer film thickness was determined from the area formed by spreading the polymer solution with a known volume and concentration.

The measurements were carried out in the 10^{-5} Torr vacuum and dark. The electrical conductivity of the polymer was measured in Al / polymer / Al structure over the temperature range of 300 – 510 K.

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 conduction. Contact has been performed by direct pressure of pogo contacts on the aluminum electrodes.

The dark conductivity of produced films were measured for the electrical characterization, 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. Temperature was recorded by Keithley DMM 196. Dark conductivity measurements were accomplished using a programmable Keitley 617 digital electrometer / voltage source interfaced to a computer. The measurements were carried out in the 10^{-5} Torr vacuum and dark. The temperature dependence of conductivity was measured at constant electrical field 20 $kVcm^{-1}$ with the temperature being increased by 3 $Kmin^{-1}$.

3. Results and discussion

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

$$\sigma_D = \sigma_0 \exp(- E_a / kT) \qquad (1)$$

where σ_D is the dark conductivity, E_a is the activation energy, and σ_0 the preexponential factor [12]. The conductivity is calculated from current-voltage (I-V) characteristics using the following equation by measuring the current flowing through a piece of the material and using the sample dimensions.

$$\sigma = I L / A V \qquad (2)$$

where I is the current, L is thickness of the film, A is area of the film, and V is the voltage applied.

Electrical characterization of the films was realized on the base of dc conductivity-temperature measurements for the films undoped and doped with different type and ratio of the dopants.

In Fig. 1, it was investigated the effect of dopant type on the PPO. Fig. 1 shows the temperature dependence of dark conductivity (σ_D) of PPO undoped and doped at 0.5 mol doped/mol polymer ratio with the dopants such as tetraethylammonium bromide (TEAB), tetra-n-butylammonium bromide (TBAB) and tetra-butyl-ammonium tetrafluoroborate (TBTFB). Both undoped and doped samples exhibit a dark conductivity ≥ 3.5×10^{-15} $\Omega^{-1}cm^{-1}$ at RT.

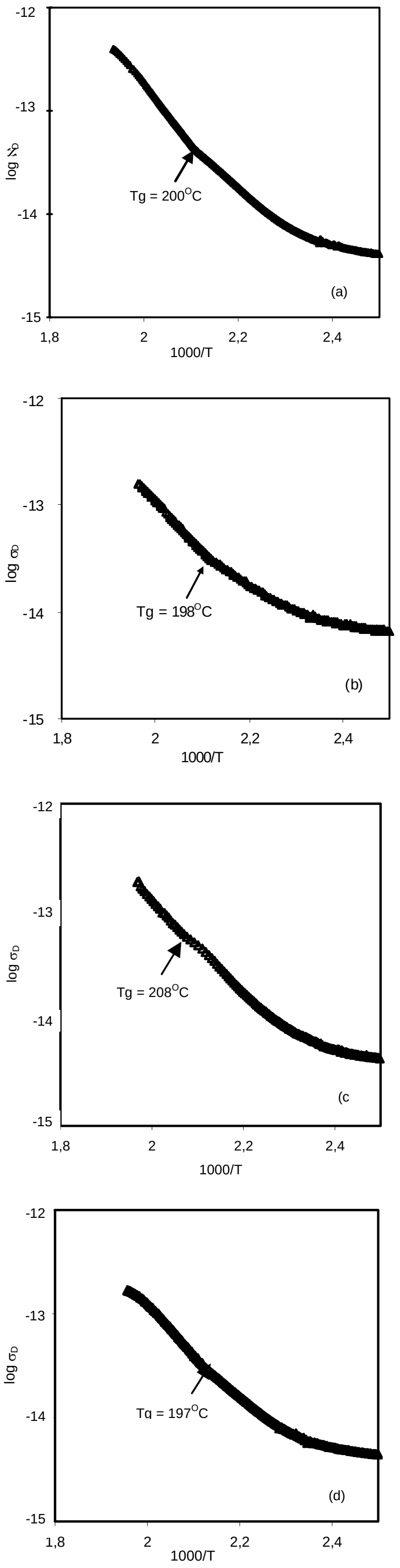

Fig. 1. Arrhenius plot of conductivity for the 6μm thickness of PPO samples undoped (a) and doped with a 0.5 mol/mol polymer ratio of tetraethylammonium bromide (b), tetra-n-butylammonium bromide (c), tetra-butyl-ammonium tetrafluoroborate (d).

For undoped films, dark conductivity increases with temperature two order of magnitude from $3.5\times10^{-15}\ \Omega^{-1}cm^{-1}$ at RT to $2.9\times10^{-13}\ \Omega^{-1}cm^{-1}$ at 235 ^{o}C.

The activation energy of undoped PPO sample was found as 1,19 eV from the first branch of the graphs at a region of 200-235 ^{o}C and 0.80 eV from second branch (160 – 200 ^{o}C) [11].

We also determined the T_g from the slope changes of the curves and the activation energies of the undoped and doped films with different dopants below and above T_g from Fig. 1 as given in Table 1.

It was determined that T_g of PPO film to be 200 ^{o}C [11], TEAB-PPO film to be 198 ^{o}C, TBAB-PPO film to be 208 ^{o}C and TBTFB–PPO film to be 197 ^{o}C. This result suggests that T_g of PPO increases as the branched alkane chain length of the ammonium bromide type dopant increases.

Secondly, it was shown in Fig. 2 the dark conductivity Arrhenius plots of the undoped ARDEL, PPO and PPO/ARDEL blend in composition of 50/50 by weight.

The activation energy of undoped ARDEL sample was found as 1.60 eV from the first branch of the graphs at a region of 190-235 ^{o}C and 1.00 eV from second branch (160 – 190 ^{o}C) [10]. For undoped PPO /ARDEL blend, it was determined as 1.12 eV from first branch (215 – 235 ^{o}C) and 0.77eV from second branch (160 – 215 ^{o}C) as seen in Table 1.

Thirdly, it was investigated the effect of dopant concentration on the conductivity of PPO /ARDEL blend. In Fig. 3, Arrhenius plots of these samples were shown. Doped samples were obtained by adding tetra-n-butylammonium tetrafluoroborate in chloroform solution at a rate of 0.25, 0.50 and 0.75 mol doped/ mol PPO/ARDEL. According to Fig. 3, dark conductivity increases with temperature two order of magnitude from $8.0\times10^{-15}\ \Omega^{-1}cm^{-1}$ at room temperature (RT) to $3.0\times10^{-13}\ \Omega^{-1}cm^{-1}$ for undoped films, and to $3.5\times10^{-11}\ \Omega^{-1}cm^{-1}$ depending on the doping ratio at 240 ^{o}C.

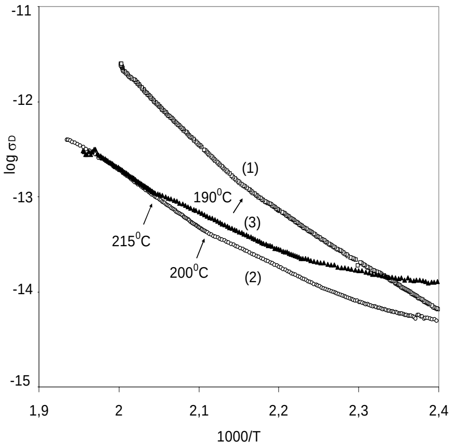

Fig. 2. Arrhenius plot of conductivity for the undoped ARDEL (1), PPO (2) and PPO /ARDEL blend (3) samples with 6 μm thickness.

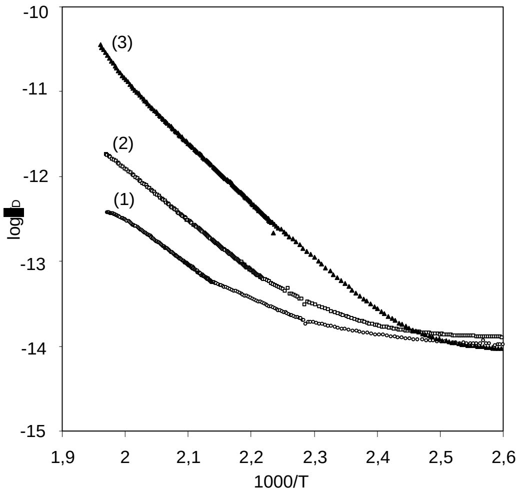

Fig. 3. Arrhenius plots of conductivity for the PPO/ARDEL doped by tetra-n-butylammonium tetrafluoroborate in chloroform solution at a rate of 0.25 (1), 0.50 (2) and 0.75 (3) mol doped / mol PPO/ARDEL samples with 6 μm thickness.

Table 1. The effect of dopant type on glass transition temperature of PPO and activation energies of the undoped ARDEL, PPO and PPO/ARDEL and doped PPO samples.

Samples	T_g (^{0}C)	ΔEa_1 (eV)	ΔEa_2 (eV)
Undoped ARDEL	190	1,60	1,00
Undoped PPO	200	1,19	0,80
Undoped PPO / ARDEL	215	1,12	0,77
PPO doped with TEAB	198	0,93	0,58
PPO doped with TBAB	208	0,94	0,79
PPO doped with TBTFB	197	1,02	0,72

4. Conclusions

It has been shown in Fig. 1 that there is no significant difference on increase of the conductivity related to dopants type. From Fig. 2, it was found that the T_g of PPO /ARDEL blend is higher than that of both ARDEL and PPO. Some favorable specific interactions may be responsible from the increase of T_g of the blend. It was observed also that the conductivities of PPO /ARDEL blends are increasing as much as four orders of magnitude by increasing doping concentration as seen in Fig. 2 and 3.

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[*] Corresponding author: merihserin@yahoo.com