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ANALYSIS OF POLYARYLATE ARDEL®D-100 FILMS UNDOPED AND DOPED BY BF_4^- AS A FUNCTION OF THE DOPING CONCENTRATION

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The polyarylate films were characterized in terms of its electrical properties depending on doping effect for the films having three different dopant concentration of 0.25 mol, 0.50 mol and 1.00 mol per mol of polymer and with the constant sample thickness of 6μm. The glass transition temperatures of undoped and doped Ardel®D-100 were determined from conductivity measurements. It was aimed to observe the doping effect on glass transition temperature. In addition, dielectric constant, dipol moment and solubility parameter of undoped polymer were determined by means of group contribution method as well. The solubility parameter of polymer, δ calculated from group contribution method was compared with data found by inverse gas chromatography.

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1. Introduction

The polyarylates are copolyester of bisphenol-A and mixtures of isophthalic and terephthalic acids [1]. Numerous efforts have been made to clarify the structure–property relationships in polyarylates [2, 3], and some polyarylates are commercially available as high-performance engineering plastics [4]. Polyarylate is an amorphous aromatic polyester with high heat distortion temperature (HDT), excellent electric and mechanical properties, flame resistance, and ultraviolet resistance [5, 6, 7]. The chemical structure of these polymers is represented schematically in Fig.1.

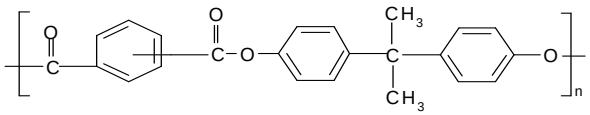

Fig.1. The chemical structure of Ardel®D-100

Polymeric materials are used extensively on spacecraft and satellites in electrical power and distribution systems, as thermal blankets and optical surface coatings, as well as mechanical support structures. The reliability of these systems when exposed to the harsh environment of space is very critical to the succes of the mission and the safety of the crew in manned-flight ventures.

The recently developed Ardel®D-100 has been reported to display outstanding performance in radiation and high temperaure environments [8]. The material, which has also good electrical and mechanical properties at cryogenic temperatures, has low specific weight and moisture absorption and may be used in electrical and electronic circuit boards, solar cells, superconductors, detectors, and in aerospace and automotive industries. Polymeric materials either organic or inorganic [9,10]

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are well known as insulating materials suitable for many industrial applications such as coatings adhesion, covers, fibers, etc. Even conducting polymers in their intrinsic nature are insulators but can be transformed conductors by suitable doping with strong acceptor or donor agents [11].

The electrical properties of Ardel®D-100 films which can be used as semiconductor components and snap lock connectors have been studied for both undoped and doped samples. It has been shown that the glass transition temperature of the polymer, T_g can be determined by using the electrical conductivity measurements [12]. We reported somewhat higher T_g to be 190^0C for Ardel®D-100 using both inverse gas chromatography and electrical conductivity measurements earlier [13]. In this study, we determined the glass transition temperature of undoped Ardel®D-100 from DSC thermogram (Perkin Elmer DSC6), but the glass transition temperatures of doped Ardel®D-100 films could not be observed in their DSC thermograms. The doping effect on the glass transition temperature was investigated by using electrical conductivity measurements. In addition, dielectric constant,dipole moment and solubility parameter were calculated by means of group contribution method.

2. Experimental

To investigate the doping effect on the conductivity, doped films by BF_4^- were investigated. 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.

Electrical characterizations were based on dc conductivity-temperature measurements and realized depending on dopant concentration. For the films having three different dopant concentration of 0.25 mol, 0.50 mol and 1.00 mol per mol of polymer at constant sample thickness of 6 μm were measured.

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. The dark conductivity measurements were carried out under vacuum at 10^{-5}Torr and dark. The measurements were carried out using a programmable Keitley 617 digital electrometer / voltage source interfaced to a computer. The conductivity measurements of the polymer samples were performed over the temperature range of 30 – 220 ^{o}C. Temperature was recorded by Keithley DMM 196. The temperature dependence of conductivity was measured at constant electrical field, the temperature being increased by 3 ^{o}C min^{-1}.

The specimens under study were prepared as sandwiched metal-polymer-metal structures. Al electrodes 3 mm × 3 mm in area were thermally evaporated at 10^{-6} Torr on Corning -7059 glass, along the length of the glass plates, 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. Organic film thickness was determined from the area formed by spreading polymer solution with known volume and concentration.

The activation energies of the samples were determined depending on the dopant concentration for the films at certain thickness.

3. Background

3.1. Electrical conductivity

Electrical characterizations were performed on the base of dc conductivity-temperature measurements together with its variation with doping ratio. The type of electrical conductivity measurement involves a simple measurement of current as a function of time, temperature, ambient atmosphere, and potential applied.

The electrical conductivity varies exponentially with temperature as well as with 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 [12]. 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.

$$\sigma = \left(\frac{I}{V}\cdot\frac{d}{A}\right) = G \times \text{Geometric factor} \quad (2)$$

where $G = \left(\frac{I}{V}\right)$ 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:

$$P_{LL} = \frac{\varepsilon - 1}{\varepsilon + 2} V \quad (3)$$

or

$$P_V = \varepsilon^{1/2} M \quad (4)$$

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

where P_{LL} and P_V is the molar dielectric polarization according to Lorenz 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 Lorenz and Lorenz relation, 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 [14].

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

According to Darby et. al. [14], the solubility parameter of polymers is defined by the simple correlation as follows,

$$\delta \approx 7.0\,\varepsilon \quad (6)$$

4. Results and discussion

DSC thermogram of undoped Ardel®D-100 sample was given in Fig. 2. From DSC thermogram, T_g was determined to be 187 °C.

Fig. 3. shows the temperature dependence of dark conductivity (σ_D) of the undoped and doped samples. The dark conductivity of the undoped film is equal to 5×10^{-16} $\Omega^{-1}cm^{-1}$ or higher at room temperature (RT).

Dark conductivity increases with temperature four orders of magnitude from 5×10^{-16} $\Omega^{-1}cm^{-1}$ at RT to 5×10^{-12} $\Omega^{-1}cm^{-1}$ at 190°C for undoped films having 6 μm thickness.

The general behaviour of the conductivities consists in σ_D increases in an activated way with temperature during doping process of the films by BF_4^- in chloroform solution. σ_D increases almost 2 - 5 orders of magnitude at RT and 2 - 3 orders of magnitude at 190 °C when compared with the conductivity of undoped and doped samples.

As it can be seen from Fig. 3, the conductivity changes start after glass-transition temperature [15] for undoped and doped samples but glass transition temperature changes only slightly by doping as given in Table 1.

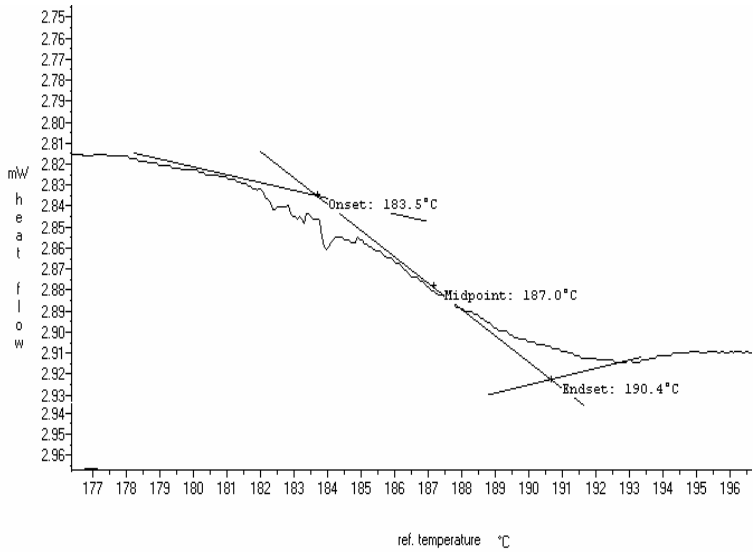

Fig. 2. DSC thermogram of undoped Ardel®D-100.

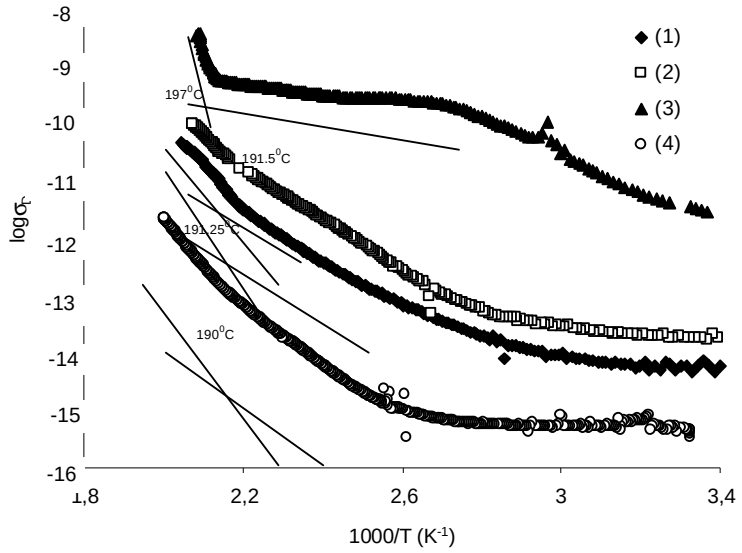

Fig. 3. Arrhenius plot of conductivity for the undoped (4) and doped with 0.25 mol/mol polymer (1), 0.5 mol/mol polymer (2), 1.00 mol/mol polymer (3) ratio Ardel®D-100 samples with 6 μm thickness, above (first branch) (1) and below (second branch) (2) glass transition temperature

We have calculated the activation energies for the undoped and doped films above (first branch) (1) and below (second branch) (2) glass transition temperature. Fig. 4 shows the determined activation energy values both for undoped and doped films depending on doping concentration. The activation energy was found 1.65 eV above and 1.07 eV below glass transition temperature, T_g, for undoped samples.

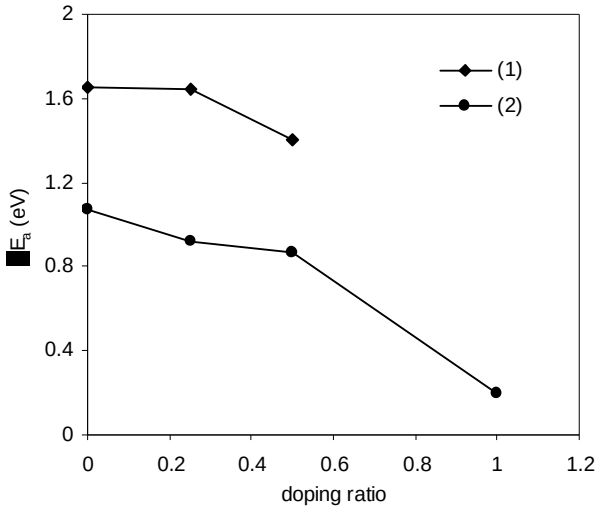

Fig. 4. Activation energies as a function of doping ratio of 0.25 mol/mol polymer, 0.5 mol/mol polymer and 1.00 mol/mol polymer. ΔE_{a1}, from first (1) (190-220 ^oC) and ΔE_{a2}, second (2) (190-110 ^oC) branch of Fig. 1.

Table 1. The effect of doping on glass transition temperature and activation energies of the Ardel®D-100 samples.

Doping ratio	T_g (^0C)	ΔE_{a1} (eV)	ΔE_{a2} (eV)
0.00	190.00	1.65	1.07
0.25	191.25	1.64	0.92
0.50	191.50	1.40	0.87
1.00	197.00	-	0.20

The dielectric constant, and the dipole moment of Ardel®D-100 were determined to be $\varepsilon_1 = 2.91$ from Eq. 3, $\varepsilon_2 = 3.04$ from Eq. 4, and $\mu = 0.902$ Debye from Eq. 5, by group contribution method, respectively. By using the average value of ε_1 and ε_2, the solubility parameter of polymer, δ, calculated to be 10.8 $(cal.cm^{-3})^{1/2}$ is comparable with the value reported in the literature to be 11.6 $(cal.cm^{-3})^{1/2}$ got by inverse gas chromatography [16].

Conclusions

The doping effect of BF_4^- in polyarylate Ardel® D-100 films has been investigated. Softening temperature and activation energy were measured as a function of dopant concetrantion. A significant increase of T_g with dopant concentration and a decrease of the activation energy were revealed.

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