Electrical and optical properties of some polyazomethine thin films prepared by a spin-coating method

A. AMIRONESEI, A. AIRINEI[a], D. TIMPU[a], V. COZAN[a], A. P. RAMBU, M. IRIMIA, F. IACOMI[*], G. I. RUSU
Department of Physics,"Al. I. Cuza" University, 11, Carol I Blvd, 700536, Iasi, Romania
[a]*"Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda, nr. 41A, 700487 Iasi, Romania, Iasi, Romania*

Three types of polymers containing azomethine units linked by ether bond, sulfone and bisfenols, were prepared, dissolved in dimethylformamide and deposited on glass slides by spin coating. The obtained transparent thin films exhibit an amorphous structure with morphology dependent on chemical structure. The study of optical absorption evidenced large direct band gaps. The sulfone presence induces an increase in the thin film band gap energy and a decrease in Urbach energy and low-energy absorption coefficient. The temperature dependence of the electrical conductivity showed that thin films have semiconducting properties with two distinct sections. The mechanism of electronic transport is described. The values of the energy band gap determined from absorption spectra were in good agreement with those calculated from the temperature dependence of the electrical conductivity. In the low temperature range, the temperature dependence of the electrical conductivity was described by the Mott variable range hopping model.

1. Introduction

Polyazomethines are known to display interesting thermal, mechanical, electrical and optical properties and are promising materials in an important number of optoelectronic applications, energy storage [1-3].

The presence of heteroatoms such as sulphur and nitrogen in the polymer backbone may increase the environmental stability [1]. Factors such as conjugation, crystallinity, linearity and doping may increase the electrical conductivity of polymers [4]. The presence of -C=N- linkages in the backbone of polyazomethines makes them stable in air and thermally resistant. It was shown that addition of oxygen atom into polyazomethine chain influences its optical properties [5].

They are alternately conjugated polymers having sp^2 hybridized nitrogen atoms in the backbone, which contribute with one electron allocated on p_z orbital to conjugated system of π electrons, and one electron pair allocated on sp^2 hybridized lone pair orbital [6].

Previous studies on electronic transport and optical properties of some poly(azomethine sulfone)s, chelate-modified polysulfones and aromatic polysulfones showed that these polymers exhibit interesting semiconducting characteristics. Some correlations between these characteristics and molecular structure of polymers have been established [7-9].

The aim of this work is to study the electrical and optical properties of some polyazomethine thin films as a function of their chemical structure.

2. Experimental part

Three types of polyazomethines were prepared by Williamson etherification method as described in [10]. The polymers contain azomethine units, sulfones and bisphenols. The azomethine units and the other components are linked by ether bond.

Polyazomethine thin films have been prepared by spin-coating method from solutions containing dimethylformamide (DMF).

The dissolution was executed at room temperature. Cleaned microscope glass slides were used as substrates for thin film depositions. The deposition process involved depositing small puddle of a certain solution onto the center of a glass substrate and then spinning the substrate at high speed (1000 rpm, 30 seconds). After spinning thin films were dried with a hot-air dryer. The procedure was repeated 5 times. Thin film thickness was measured by using a DEKTAK profilometer and was found to be in the range of 50nm -100nm. Thin film codes and chemical structure of polyazomethine thin films are presented in Table 1.

Table 1. Thin film codes

Polyazomethine chemical structure and used codes

PA
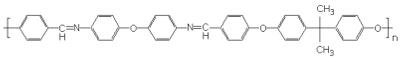
CoPAS
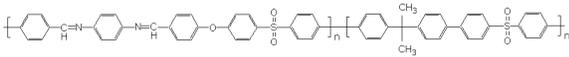
PAS
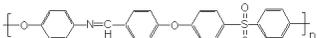
Thin film structure was investigated by using the standard X-ray diffraction technique with CuK_α radiation (λ=0.154 nm, SIEMENS DR 5000). Transmission spectra, in the spectral range 400 – 1800 nm, were recorded using an UV-VIS spectrophotometer (STEAG ETA-OPTIK).

Atomic Forces Microscopy (AFM, NT-MDT Solver Pro M) was used to investigate the thin film surface morphology and roughness.

In order to perform the electrical conductivity measurements, as a function of temperature, the obtained films were equipped with two parallel thin–film silver electrodes separated by a gap of about 2 mm and the width of each electrode was about 10 mm.

3. Results and discussion

3.1. Thin film structure and morphology

The thin film thickness (d, Table 2.) measurements evidenced different values for the three polyazomethine thin films.

X-ray diffraction patterns of thin films deposited on glass evidenced a large XRD peak typical for an amorphous structure (Fig.1).
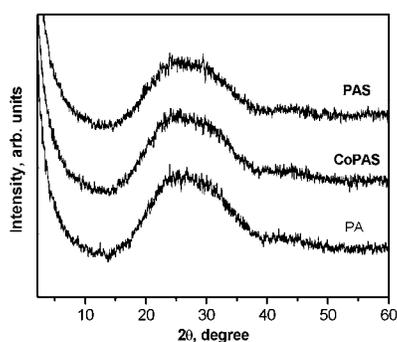

Fig. 1. XRD patterns of polyazomethine thin films

The 5×5μm AFM surface images of polyazomethine thin films are presented in Fig. 2 (a-c).

AFM images of all investigated polyazomethine films indicate high denstity structure with relatively homogeneous, smooth surfaces typical for the polymers thin films. The root mean square (RMS) roughness was found of about 5 nm for the poly(azomethine sulfone) thin films, having incorporated sulfone and ether groups (PAS,

CoPAS) in tha polymer backbone, while for the polyazomethine film (PA) the RMS value reached 21 nm.

The PA copolymer surface evidence a fibrilar morphology (Fig. 2. a) which can be explained by π-stacking presence [11].

The PAS thin film as compared to PA (Fig.2.c) shows some columnar isolated structures formed on the surface of amorphous matrix.

3.2. Optical properties

All prepared thin films were transparent with transmission reaching 65–95% and reflectivity below 20% in the low-energy range (Fig. 3. a).

The absorption coefficient, α, has been obtained from transmission (T) and reflectivity (R) measurements, according to formulae [2]:

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R)^2}{T}\right] \qquad (1)$$

The absorption spectra in the whole investigated spectral range, are shown in Fig. 3.b).

The absorption coefficient increases clearly above about 2.5 eV. The shape of these absorption edges seems to be similar to the edge of an ideal amorphous semiconductor with two exponential parts [12].

a)

b)

c)
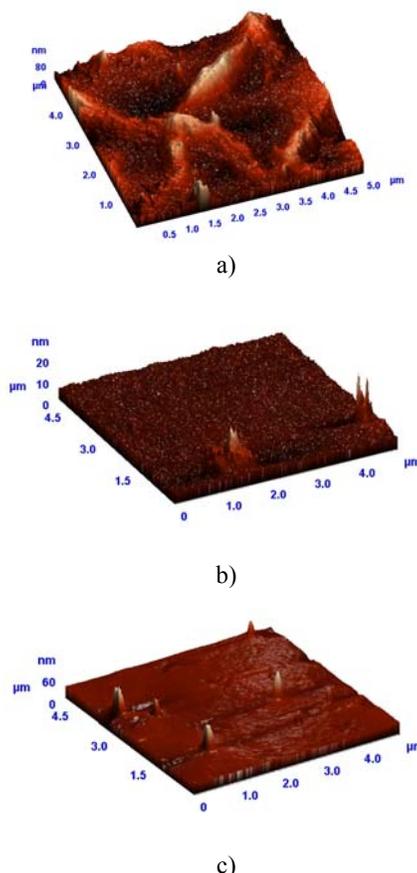
Fig. 2. 5×5μm AFM images of thin films: a)PA b) CoPAS, c)PAS

The slopes of the exponential edges follow the Urbach relation [9]: $\alpha \propto \exp(E/E_U)$. In the low energy range, the same type of relation can can be used and the low-energy parameter, ET, can be calculated..

For semiconductor materials it is possible to calculate the band gap energy, E_g, from relation given by formula [7]:

$$\alpha \cdot E = A\left(E - E_g\right)^r \qquad (2)$$

where α is the absorption coeficient, A is a parameter independent of photon energy, E, E_g represent photon and band gap energies. Exponent r accepts two values 1/2 or 2 connected with direct and indirect band to band transition.

Type of the transition in the investigated thin films is

determined by subscript r = 1/2. Such approach leads to equation:

$$\left(\alpha E\right)^2 = f(E) \qquad (3)$$

Delimitation value of the energy band gap, E_g, is determined from linear approximation of equation (3), as was mentioned for amorphous semiconductors (Fig.3. c) [2].

By extrapolating the linear portions of equation (3) to $(\alpha h \nu)^2 = 0$ the values of E_{g0} can be determined. The parameters of absorption edges: E_g, E_U and E_T were determined for the studied thin films and are shown in Table 2.
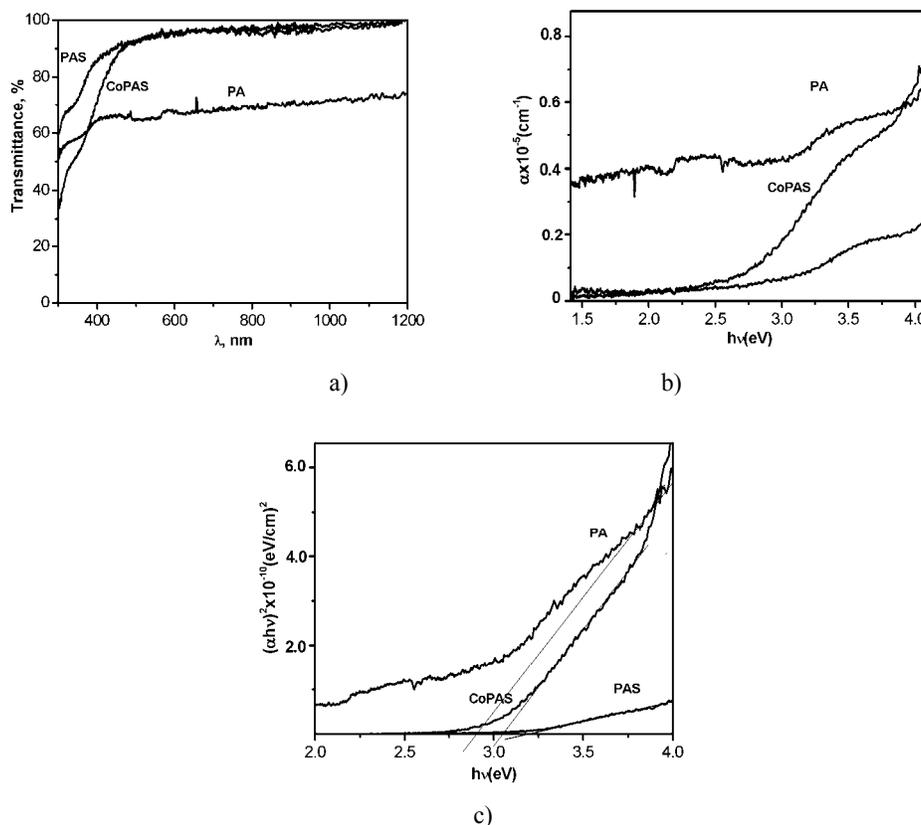

a)   b)

c)

Fig. 3. Thin film optical spectra: a) Transmittance spectra; b)Absorption coefficient; c) Linear approximation of absorption edges of thin films

The slightly increase in the absorption with decreasing energy and the high E_T value (Fig.3. b); Table 2) indicate the important role of the localized states inside the energy gap. These localized defect states inside the gap are mainly due to electron–phonon interaction. The existence of polarons in polymer compounds can be a result of possible structure defects, responsible also for the increase in absorption. The Urbach energy changes from 0.41 eV for the copolymer (containing bisphenols and sulfones) CoPAS to about 1.42 eV for the polymer PA.

The different possible conformations of polymer chain increase the density of defect states. The structural disorder defects resulting from different lengths and orientations of polymer chains may be responsible for the amorphous character of absorption edge and amorphous structure evidenced by XRD and AFM studies.

The energy gap of thin films changed from 2.90 eV (PA) for the polymer containing bisphenol to 3.20 eV for the polymer containing sulfones (PSA). The greatest value of E_g indicates short conjugated parts in polymer chain,

while the smalest one indicates larger conjugation parts. The weak level of low-energy bands in PAS and CoPAS is due to smaller density of delocalized states.

3.2. Electrical properties

It was observed experimentally that samples with a stable solid-state structure can be obtained by subjecting them to a heat treatment consisting of several successive heating/cooling cycles within a determined temperature range, ΔT, characteristic for each polymer [7].

Presuming that the temperature dependence of the electrical conductivity, σ, can described by the expression [7]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \qquad (4)$$

where E_a is the thermal activation energy of electrical conduction, σ_0 is a parameter depending on the polymer nature and k_B represents Boltzmann's constant, the $ln\sigma = f(10^3/T)$ plots were were investigated for all thin films.

The experimental results shown that after two heatings and coolings, in the temperature range ΔT = 300K - 473 K, the temperature dependence of the electrical conductivity becomes reversible (Fig. 4. a).

For heat-treated samples the $ln\sigma = f(10^3/T)$ plots show two distinct sections: a section with a smaller slope, within the lower temperature range (extrinsic domain), and a section with larger slope (intrinsic domain), within the higher temperature range (Fig. 4. a, b). There is a characteristic temperature, T_C, delimiting the two sections, dependent on the polymer structure.This temperature ranges from 321K for PA and CoPAS thin films to 330K for PAS thin film.

Similar results were obtained in a previous paper on poly(azomethine sulfone)s and was suggested that the electronic transport in thin films can be described by using the model based on energy bandgap representation [7].

Based on equation (4), the values of the band gap Eg were calculated from $ln\sigma = f(10^3/T)$ plots within the intrinsic domain, $E_g = 2E_a$ (Table 2)[7].

In comparison with previous studied poly(azomethine sulfone)s thin films, PA, PAS and CoPAS thin films have higher electrical conductivities, their semiconducting characteristics being determined by their specific molecular structure.

In the low temperature range, the temperature dependence of the electrical conductivity can be described by the Mott variable range hopping model.
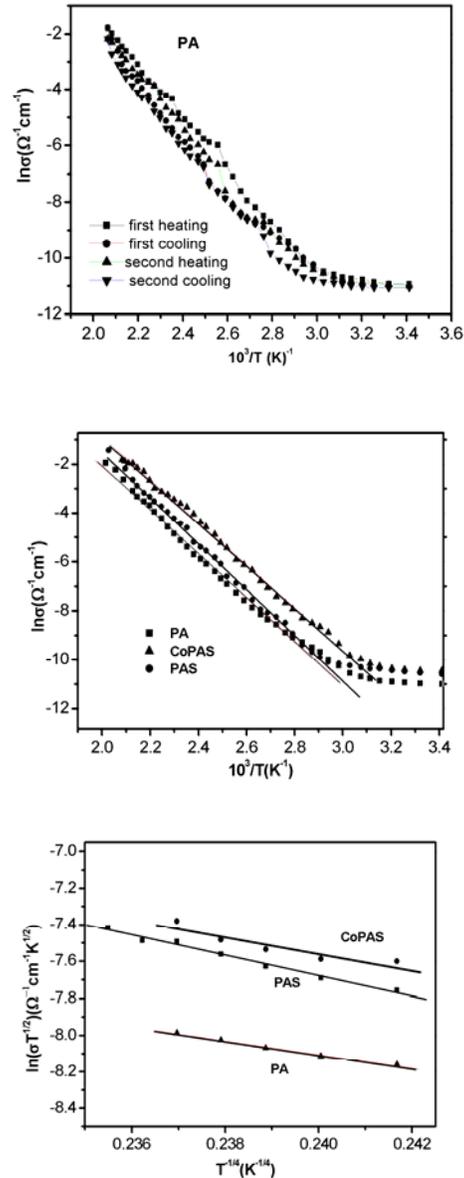

Fig.4. The electrical conductivity as a function of temperature:a) Temperature dependence during heat treatment; b) $ln\sigma = f(10^3/T)$ plots, intrinsic domaine; c) $ln(\sigma T^{1/2}) = f(T^{1/4}$ plots, extrinic domaine

Tab. 2. Characteristic parameters of thin films: thin film thickness, d; band gap energy, E_g; activation energy, E_a; Urbach energy, E_U; low energy parameter, E_T; Mott parameters, σ_0' and T_0.

Code	d nm	E_g eV	E_U eV	E_T eV	E_a eV	σ_0'×10^{-5} $\Omega^{-1}cm^{-1}$	T_0×10^{-6} K
PA	100	2.90	1.42	10.52	1.46	1.46	1.99
CoPAS	70	3.05	0.41	0.61	1.51	2.41	4.21
PAS	50	3.20	0.48	1.16	1.62	2.03	9.23

Conform to the Mott model, the electrical conductivity can be expressed by the formula [7]:

$$\sigma = \sigma_0' T^{-1/2} \exp\left(-\frac{T_0}{T}\right)^{1/4} \qquad (5)$$

where σ_0' and T_0 are the Mott characteristic parameters.

In Fig. 4. c) are shown the experimental $ln(\sigma T^{1/2}) = f(T^{1/4})$ plots. The Mott parameters were determined from the experimental linear plots. Their values are presented Table 2 and are lower comparing with those observed for other polyazomethines.

The results obtained suggest that the presence of sulfones in the polymer backbone determines increases in energy band gap, activation energy and Mott parameters values and that the presence of bisphenols has the opposite effect.

5. Conclusions

Spin-coating method appeared to be an effective tool to prepare good quality polyazomethine thin films. The chemical structure influenced the energy band gap values, thickness and surface structure. It could be concluded that the investigated polyazomethine thin films are amorphous semiconductor with wide energy band gaps.

It was found that the model based on the energy bandgap representation is suitable for explaining the electronic transport mechanism in the higher temperature range and that at lower temperatures the conduction mechanism can be discussed in terms of Mott variable range hopping conduction.

The values of some characteristic parameters were correlated with the molecular structures of the polymers. The values of the energy bandgap determined from absorption spectra are in good agreement with those calculated from the temperature dependence of the electrical conductivity.

References

[1] A. G. El-Shekeil, H. A. Al-Saady, F. A. Al-Yusufy, Polym. Intern. **44**, 78 (1997).
[2] M. Palewicz, A. Iwan, J. Doskocz, W. Strek, D. Sek, B. Kaczmarczyk. B. Mazurek, Polym. Bull. **66**, 65 (2011)
[3] M. Grigoras, O. Catanescu, J Macromol. Sci. Polym. Rev. **44C**, 131 (2004).
[4] A. O. Patil, A. J. Heeger, F. Wudl, Chem. Rev., **88**, 192 (1988).
[5] B. Hajduk, J. Weszka,V. Cozan, B. Kaczmarczyk, B. Jarzabek, M. Domañski, Arch. Mater. Sci. Eng. **32**, 2, 85 (2008)
[6] J. Weszka, H. Bednarski, M. Domański, J.Chem. Phys. **131**, 024901 (2009)
[7] G.I. Rusu, A. Airinei, M. Rusu, P. Prepelita, L. Marin, V. Cozan,I.I. Rusu, Acta Mater. **55**, 433 (2007).
[8] G.I. Rusu, I. Caplanus, L.Leontie, A. Airinei, D. Mardare, I.I. Rusu. Acta Mater. **49**, 553 (2001).
[9] B. Jarzabek, J. Weszka, M. Domanski, J. Jurusik, J. Cisowski, J Non-Cryst Solids **354**, 856 (2008).
[10] L. Marin, V. Cozan, M. Bruma, Polym. Adv. Technol., **17**, 554 (2006).
[11] M.Cazacu, C. Racles, A Vlad, G. Calin,; D.Timpu, F. Iacomi, J. Optoelectrn. Adv. Mater., **2**(2) 294 (2010).

_____

[*] Corresponding author: f_iacomi@yahoo.com