NEW INSIGHTS CORRELATING ABSORPTION EDGE WITH MORPHOLOGICAL FEATURES OF SOME SEMI-ALICYCLIC POLYIMIDES

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Abstract: *The present work presents the preparation of some novel semi-alicyclic polyimides based on epiclon and three aromatic diamines. The group contribution theory data reveal that the reduced polarizability provided by the alicyclic dianhydride moieties leads to polyimides with low refractive index, ranging from 1.64-1.72. The corresponding dielectric constants decrease from 2.97 to 2.71 as the polarization of the diamine part is lower. As the number of methylene groups in the diamine residue increases the transparency is enhanced, being of appreciatively 90%. The absorption edge energies, determined from by Tauc and Davis-Mott approach, can be correlated with structural and morphological heterogeneities. Magnitude of cantilever oscillation recorded during scanning provides complementary information to atomic force microscopy (AFM) topography, additional contrast of defect edges being clearly observed because control electronics does not respond instantaneously to the sharp changes in the sample height.*

The entropy of morphology, which is a statistical parameter computed from the morphological measurements, is used for describing the richness of structuring in the morphology, strongly interrelating with the degrees of order or disorder in the grain structure distribution and is intimately associated with the root mean square roughness. This is a quantification of the shape-size complexity of studied polyimide films.

Geometric properties like surface morphology or topography have both direct and indirect implications to the optical phenomena in films. The increase in the disorder leads to decrease in the optical band-gap energy and an increase in the Urbach energy (which represents a quantitative characteristic of static disorder). The effect of the disorder on the absorption edge energies parameters of investigated materials is analyzed. The obtained data have are important for selecting the proper materials as liquid crystal alignment layers or as cell culture substrates.

Keywords: *polyimide, transparency, morphology.*

1. Introduction

Polyimides are high performance materials characterized by high thermal and mechanical resistance and excellent electrical properties. However, conventional aromatic polyimides exhibit enhanced charge transfer complex, which makes these materials to absorb in the visible spectral domain. These aspects are limiting the applications of polyimides, where high transparency is needed, such as liquid crystal orientation layers and cell culture substrates. Many efforts have been made to overcome these deficiencies and the most successful one consists in utilization of aliphatic monomers in synthesis [1]. This approach leads to less probability of charge transfer interactions and thus facilitates the polymer processing, reduces the dielectric constant and increases the transparency.

Having all these in view, the present paper reports the optical and morphological analysis of some semi-alicyclic polimides. The influence of the flexibility and polarizability of diamine moiety on the transmission spectra and position of the absorption edges is studied. The Urbach rule and the Tauc and Davis-Mott method for are used to obtain the energies describing the absorption edges and the optical band-gap. The optical properties are analyzed in rapport with surface morphological aspects.

2. Experimental

The 5-(2,5-dioxotetrahydrofuryl) -3-methyl-3-cyclohexene-1,2-dicarboxylic acid anhydride (DOCDA, Merck, 98 % purity), 1,4-phenylendiamine (PPD, Aldrich, 99 %), 4,4′ -diaminodiphenyl methane (DDM, Aldrich, 99 %), 4,4′ -diaminodiphenyl ethane (DDE, Aldrich, 99 %) and 1-methyl-2-pyrrolidone (NMP, Aldrich 99.5 %, anhydrous) are used as received.

The detailed synthesis of these polymers and their basic characterization is presented elsewhere [2]. The acronyms for the studied samples are: PI1 for DOCDA/PPD, PI2 for DOCDA/DDE and PI3 for DOCDA/DDM. Polyimide films are prepared by casting NMP polyimide solutions onto quartz substrates and subsequently drying at high temperatures.

Optical transparency of the films is recorded on a SPECORD 200 Analitik-Jena spectrophotometer.

Morphological and topographical of the polyimide surface defects are investigated using a Scanning Probe Microscope (Solver PRO-M, NTMDT) with commercially available NSG10 cantilever. In order to evaluate the surface topography statistical parameters such as root mean square roughness (RMS) and entropy of morphology [3] are used.

3. Results and discussion

The refractive index ($n_{2,LL}$) of epiclon based polyimides is estimated from group contribution theory and Lorenz-Lorentz approach [4]:

$$R_{u,LL} = V_u \left(n_{2,LL}^2 - 1\right) / \left(n_{2,LL}^2 + 2\right) . \qquad (1)$$

where R_u is the molar refractivity and V_u is the molar volume.

This theory is based on the assumption that the molar volume and the molar refraction of the chain repeating unit are additive functions of composition. The low polarizability provided by the alicyclic DOCDA moieties leads to polyimides with low refractive index, ranging from 1.64-1.72.

On the other hand, knowledge of refractive index means the control of dielectric constant, ε, as shown in equation (2):

$$\varepsilon = 1.1 n_{2,LL}^2 . \qquad (2)$$

The mathematical expression (2) includes an additional contribution to ε of approximatively 10 % from the orientation and ionic polarization. The magnitude of dielectric constant is related to the ability of polarizable units from the polyimide backbone to orient fast enough to keep up with the oscillations of the alternating electric field. At the frequency used for estimation of ε' the polarization in the investigated samples comprises: (1) polarization of molecular dipoles, in particularly the imide ring, alicyclic and phenyl groups, (2) polarization of the constituent atoms and (3) electronic polarization. The introduction of the DOCDA units and flexible sequences in the diamine moieties reduces the main chain conjugation, namely disrupts the overlapping of π-orbitals with delocalized electrons through intervening sigma bonds and thus the dielectric constant is reduced. The dielectric constants of studied polyimides decrease from 2.97 (for PI1) to 2.71 (for PI3) as the polarization of the diamine part is lower.

The optical properties of these PI foils in the ultraviolet, visible and near infrared spectral range are analyzed. The combination in the PI backbone of cycloaliphatic epiclon moieties with aromatic diamine residues containing different flexible sequences leads to a transmittance of appreciatively 90 % for PI2 and PI3 over visible domain and near infrared. The transparency band is extended to UV region depending on the diamine chemical structure.

The obtained cut-off wavelengths for the investigated PIs arelower as the diamine chain length is longer and the conjugation between the aromatic rings and nitrogen atoms, assignable to the π–π* transition, is very low, namely: 317 nm for PI1, 306 nm for PI2 and 305 nm for PI3.

The optical gap energy and other energies describing the absorption edges can be determined by using the method proposed by Tauc [5] and Davis-Mott [6], relying on absorption coefficient dependence on photon energy (E):

$$\alpha = \frac{1}{d} \cdot \ln\left(\frac{1}{T}\right) . \qquad (3)$$

where α is absorption energy, d is the film thickness and T is the transmittance.

The shape of both edges is very similar to the behavior proposed by Tauc for a typical amorphous semiconductor, but is lower. Figure 1 presents the dependence of α on E.

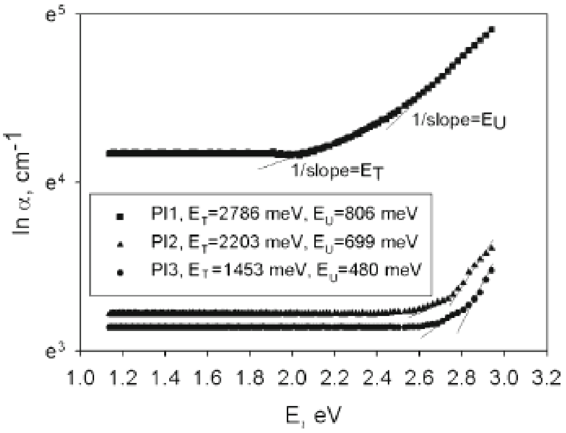

Figure 1: *Absorption coefficient dependence on photon energy for studied samples.*

Each of the absorption edges from Fig. 1 exhibits two regions with different slopes and a saturation region for higher energy. Both parts of the graphical representation follow the Urbach rule [7]:

$$\alpha \propto \exp\left(\frac{E}{B}\right). \tag{4}$$

where B becomes either Urbach energy, E_U, in the high-energy exponential region or Tauc energy, E_T, describing the low-energy exponential part of the absorption coefficient.

The values of E_U and E_T of DOCDA-based samples are obtained from the reverse of the slope of the dependence of α on photon energy from Fig. 1. As the diamine residue polarizability decreases, by introduction of flexible linkages among aromatic units, these energies are lower.

The optical band-gap, E_G, is determined from the analysis of the spectral dependence of absorption near the high absorption region, which is associated with interband transition. This is described by the following relation:

$$\alpha = const\,\frac{(E-E_G)^r}{E}. \tag{5}$$

where r is the exponential constant index and it takes typical values corresponding to different the optical absorption processes.

Fig. 2 shows the Tauc plot and the correct values of E_G, namely 3.51 eV for PI1, 3.73 eV for PI2 and 3.78 eV for PI3, respectively. It can be noted that these values increase with decreasing the polarizability of the diamine residues. The values of optical band-gap energy higher than 3.26 eV are a good indicative of transparent polyimide films.

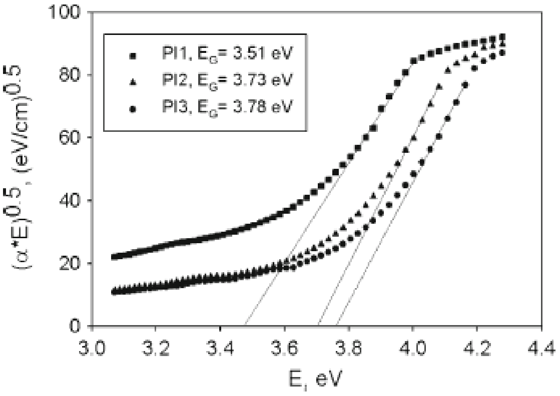

Figure 2: *The Tauc dependence of studied samples*

Since the optical band-gap and energies describing the absorption edges are dependent on the polymer atomic structure, a correlation with morphological aspects is made in the following paragraphs.

In Fig. 3 height and amplitude images exhibit pronounced structural and morphological heterogeneities. Magnitude of cantilever oscillation recorded during scanning provides complementary information to AFM topography, additional contrast of defect edges being clearly observed because control electronics does not respond instantaneously to the sharp changes in the sample height.

The surface morphology of the PI1 film shows crack-like defects, suggested by the dotted lines. These defects can be induced by various factors. Structural breaks or discontinuities of the polymer chains seem to cause a film to experience a local increase in the intensity of a stress field, favoring the formation of cracks.

PI2 sample exhibits ring-shaped morphological defects, having diameter ranging between 105 and 277 nm. The defects are found to be local deformation zones, showing considerable optical anisotropy and a microstructure strongly influenced by the adhesion condition to the substrate. The failure strain decreases with increasing coverage of these nano-scale surface defects. The reason for the early failure is the increased occurrence, or high probability for crazes to propagate into island domains [3]. These surface defects like island domains (seen for polyimide PI3) are sudden changes in the local film thickness. Therefore, at their boundaries (see the corresponding amplitude image), a large stress gradient or stress concentration is generated. These domains serve as stress concentration points. The entropy of morphology is another statistical parameter, measuring the richness of structuring in the morphology, strongly interrelating with the degrees of order or disorder in the grain structure distribution.

Fig. 4 presents the variation of RMS roughness and entropy parameters with respect to the investigated polymer structure.

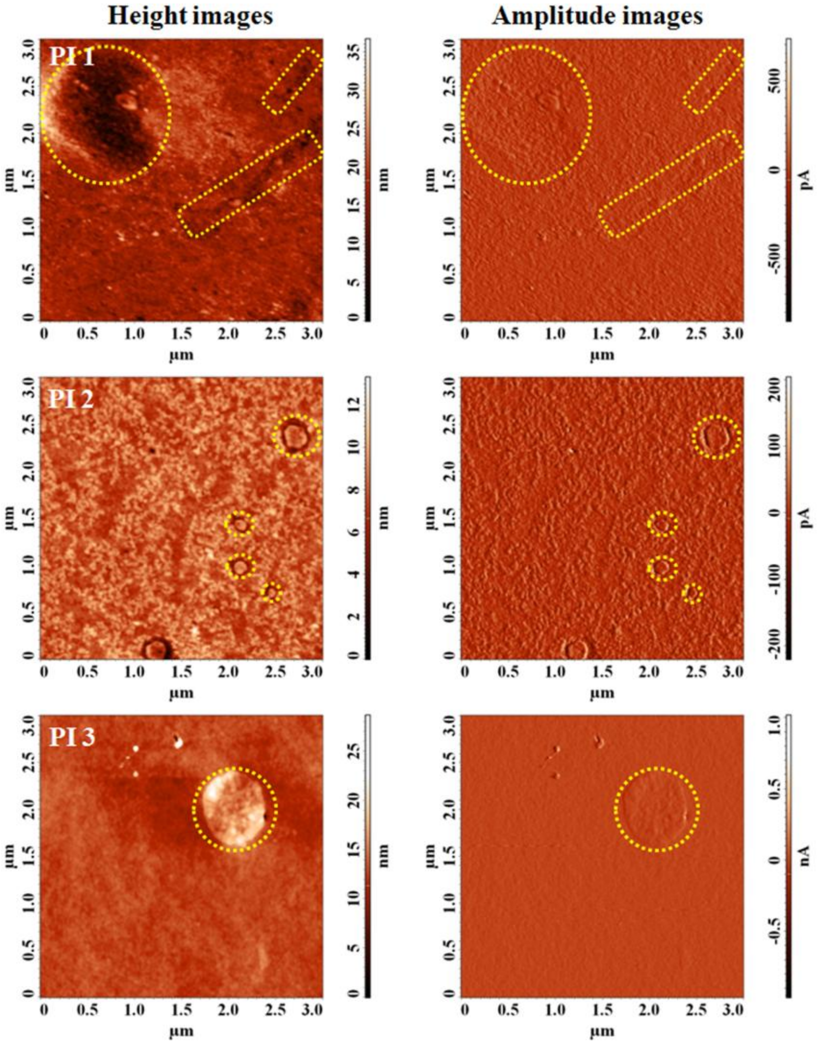

Figure 3: *Height and the corresponding amplitudeimages obtained for studied films, highlighting different defects of the surface morphology*

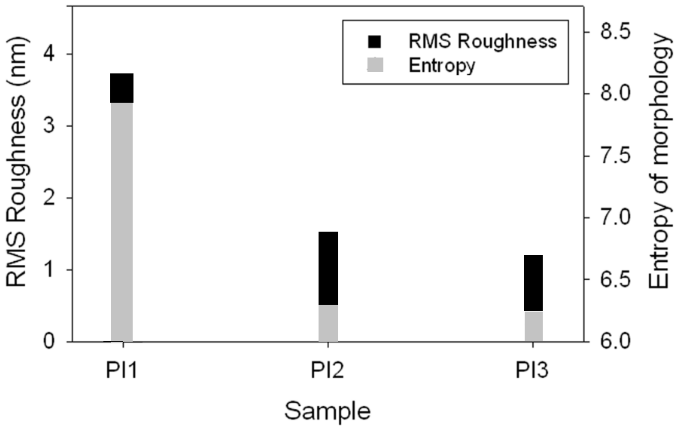

Figure 4: *Variation of RMS roughness and entropy parameters with respect to polyimide structure*

Both variables show a similar trend, following each other in their evolutions. Therefore, the higher roughness obtained for polyimide PI1 can be associated with more disorder (entropy) in the morphology. In contrast, the insignificant variation in surface height achieved for PI2 and PI3 films equates to lower relief diversity.

Geometric properties like surface morphology or topography have both direct and indirect implications to the optical phenomena in films [8]. The increase in the disorder leads to decrease in the optical band-gap energy and an increase in the Urbach energy (which represents a quantitative characteristic of static disorder), the effect of the disorder on the optical parameters already being reported in thin films [9]. Considering this aspect, in correlation with the high transparency and optical band-gap obtained for PI3 film it can be noticed that this material is the most recommended for microelectronics or bio-technologies [10-12] implying flexible and transparent substrates.

4. Conclusions

The refractive index determined from group contribution theory is low - values typical for transparent polymeric materials. The transparency of the samples which contain methylene and ethylene groups in the diamine units (PI2 and PI3) is appreciatively of 90% over visible and near infrared domain.

Reduction of the charge transfer interactions caused an increase of the optical band-gap energy from 3.51 eV for PI1, 3.73 eV for PI2 and 3.78 eV for PI3, respectively.

The energies describing absorption edges are related to the localized states induced by the polymer atomic structure. Possible structure defects like the break or torsion of polymer chains, generated by the kink linkages from the diamine segments or by the non-coplanar structures of the dianhydride moieties, seem to be responsible for the slight increase in capacity of absorption generated by them in the low-energy absorption domain.

The obtained optical and morphological features of PI3 film recommends this sample as being good candidate for microelectronics as liquid crystal orientation layers or for tissue engineering as guided cell growth substrates.

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