EFFECT OF THE DIANHYDRIDE MOIETIES ON REFRACTION PROPERTIES OF POLYIMIDES BASED ON CHALCOGEN ELEMENTS

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Abstract: *This paper is focused on the analysis of optical properties of a polyimide film, which is studied for use in applications like protective covers of solar cells. The main chain of the polymer is made of a combination of imide rings, alicyclic segments, and dithiol bridges that are meant to render a proper balance among the transmittance and refraction properties. Theoretical assessment of the refraction index is performed by employing group contribution approach. Several types of alicyclic dianhydrides are combined with 4-aminophenyl disulfide and the influence of the polyimide structure on the resulted refraction is discussed. Also, optical losses in a solar cell, that uses these samples as shielding layers are determined and their impact on the conversion efficiency of the photovoltaic cell is investigated. The attained data have are a great relevance for making shielding layers with higher performance than the conventional cover glass.*
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Keywords: *polyimide, refractive index, optical losses, solar cells*

1. Introduction

The energy sector has known, in the past decades, a considerable progress of technologies involving renewable resources. For instance, the devices that harvest solar radiations for the production of electricity are more and more integrated into our daily life. Solar cells are facing challenges in terms of material performance, from those that constitute the active zone to the materials used for shielding purposes. The replacement of the cover made of rigid glass has led the attention of scientists towards polymers, owing to their advantages related to processing, flexibility, and lightweight [Hou,2019]. Regarding to this application, the other essential aspects relies on the thermal and mechanical characteristics of the polymer. A good balance between these properties is found for polyimides (PIs).

On the other hand, the conversion efficiency of the photovoltaic cell is strongly affected by the optical properties of the cover layer [Hulubei, 2019]. Light absorption and improper match of the refractive properties among the elements of the solar cell are undesirable. The optical clarity of the PI films or coatings is enhanced when introducing alicyclic segments in the main chain. Moreover, the presence of chalcogen atoms in the PI backbone is increasing the refractive index closer to that of the neighboring transparent conductive oxide (TCO). Therefore, it is expected that a combination of these elements in the polyimide structure would be beneficial for achieving the targeted optical performance for solar cells covers [Hulubei, 2019].
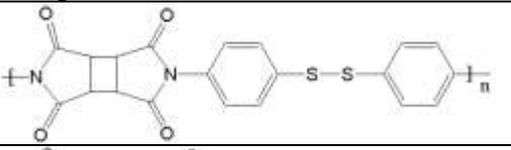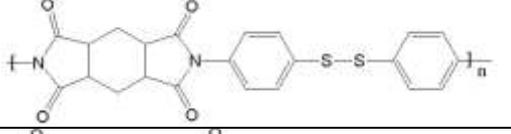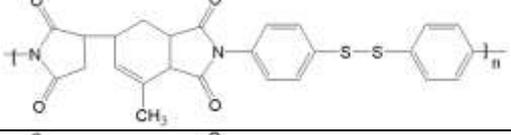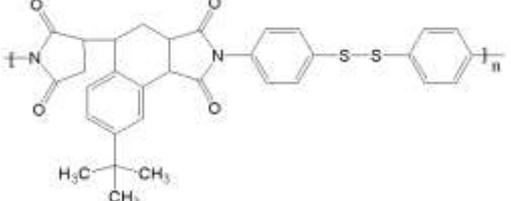
This work proposes for investigation a set of polyimides that are made of the same diamine monomer (i.e. 4-aminophenyl disulfide) and several dianhydrides having alicyclic structure. Based on group contribution approach, the refractive index (n) of each sample is determined and the impact of chemical structure on increasing the magnitude of the n parameter is analyzed. Optical losses, caused by reflection at the interface between each sample and TCO layer,

are evaluated and discussed in regard to the conversion efficiency of the photovoltaic device.

2. Materials and methods

Polyimides (PIs) are generally obtained by polycondensation reaction between a diamine and a dianhydride in solution, via soluble polymer precursors. The details of this chemical procedure are reported in the literature [Hulubei,2007]. All PIs, here under study, have a common segment derived from the diamine monomer, namely 4-aminophenyl disulfide. The chemical structures of each studied PI are presented in Table 1.

Table 1. Chemical structures and acronyms of the investigated PIs.

Sample structure	Code
	PI-1
	PI-2
	PI-3
	PI-4

The refractive index of all polymer samples was determined using the Lorentz-Lorenz formula:

$$R_u = V_u \left(n^2 - 1\right)/\left(n^2 + 2\right) \qquad (1)$$

where n is the refractive index, while R_u and V_u are the molar refraction and molar volume of the structural unit, respectively.

In order to evaluate R_u and V_u, the principles of the group contribution theory were applied [Groh,1991], as seen in equations (2) and (3):

$$R_u = \sum_i a_i \cdot R_i \qquad (2)$$

$$V_u = \sum_i a_i \cdot V_i \qquad (3)$$

where V_i and R_i represent the contributions of a certain chemical group, and a_i is the number of groups i present in the PI structural unit.

The increments of the substructures R_i and V_i found in the composition of the PIs presented in Table 1, are extracted from literature [Groh,1991].

3. Results and discussion

3.1 Refractive index

The molar refraction and molar volume corresponding to the structural unit of the semi-alicyclic PIs are determined using equations (2) and (3) and the resulted values are listed in Table 2.

Table 2. The values of the molar refraction and molar volume corresponding to the structural unit of the semi-alicyclic PIs.

Sample	R_u (cm^3/g)	V_u (cm^3)
PI-1	99.776	232.502
PI-2	108.784	263.558
PI-3	120.071	294.288
PI-4	135.508	346.315

The refractive index data, estimated based on the Lorentz-Lorenz formula, are displayed in Figure 1.
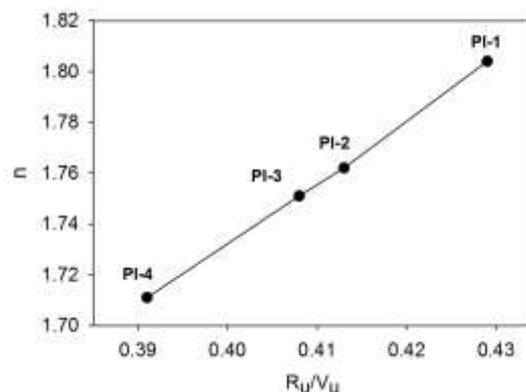

Figure 1: *The refractive index variation with the ratio between molar refraction and molar volume of the structural unit of the semi-alicyclic PIs.*

It can be noticed that the magnitude of the n parameter is higher as the R_u / V_u ratio is increasing. The presence of dithiol bridges in the polymer backbone increases the chain polarizability and implicitly the refractive index. Literature sustains the idea that PI containing aliphatic units have good transparency [Barzic,2018], whereas the PI that have chalcogen elements display an enhancement in the refractive index of polymers [Kim,2019]. The calculations show that sample PI-1 has the biggest refractive index of 1.804, while PI-4 has the lowest n value, i.e. 1.711, among the studied set of PI structures. Given the fact that all samples have a common diamine sequence, it can be noted that the type of the dianhydride moieties is influencing the refraction properties of the PI. The PI-1 structure is made of a rigid and small dianhydride, which enables a higher density of polar imide groups and a more dense chain packing, all favoring the increase of the refractive index. In the case of PI-2, the size of the dianhydride moiety is higher and slightly decreases the density of imide rings along the chains producing a slight reduction of n. When dealing with semi-flexible and bulky dianhydrides, like those from PI-3 and PI-4 samples, the macromolecular chains are loosened and the polarity is diminished and this is reflected in a lower refractive index value.

3.2 Band gap energy

The optical band gap energy (noted as Eg) is an important parameter depicting the minimum amount of energy imposed to excite the electron, so that it can assist in optical absorption processes. There are many theories that are relating Eg to the refractive index.

Moss developed a simple relation denoting that energy levels of electrons in solid materials are scaled by a factor $1/n^4$ [Moss,1950]:

$$n^4 = K / E_g, \text{ where } K = 95 eV \qquad (4)$$

Ravindra and collaborators indicated that the use of K = 108 eV is more suitable for obtaining a better curve-fit [Ravindra,1979]:
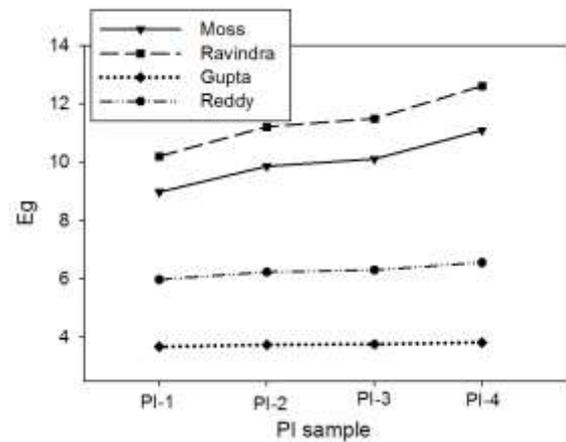
$$n^4 \cdot E_g = 108 \qquad (5)$$

Gupta proposed a linear relation between n and Eg, as shown in equation (6) [Gupta,1980]:

$$n = 4.084 - 0.62 \cdot E_g \qquad (6)$$

Reddy and co-workers formulated another equation describing an exponential behavior, as seen below [Reddy,1992]:

$$E_g \cdot e^n = 36.3 \qquad (7)$$

Figure 2 illustrates the variation of calculated Eg data with the PI structure, according

Figure 2: *The variation of optical band gap with the polyimide structure.*

Ravindra and Moss's relations lead to the highest values of Eg, whereas the Gupta and Reddy equations conduct to lower values, which are closer to those reported in the literature for transparent polymers [Jarzabek,2002]. Regardless of the used calculation formula, Eg increases with molar refraction for all PIs.

3.3 Optical losses and conversion efficiency

The superstrate configuration of a solar cell consists of the active zone, TCO material and protective cover. TCOs are used in such devices as contacts and they need to fulfill specific optical criteria in terms of transparency, refractivity and conductivity. High-efficiency photovoltaics are made by deposition of CdTe/CdS on a TCO-coated cover layer. Among the TCO materials,

literature mentions metal oxides like tin oxide (SnO_2), indium tin oxide (In_2O_3/SnO_2), and zinc oxide (ZnO) [Ikhmayies, 2017].

Tin oxide is a n-type semiconductor material, characterized by a high band gap energy (around 3.6 eV) and refractive index of 1.925 at 589 nm [Gong,2019]. The solar radiations that reach the junction of the photovoltaic system are forced to travel through several media of distinct refraction properties. For this reason, at air/cover and cover/TCO interfaces, the reflection losses are negatively affecting the conversion efficiency [Morawiec,2020]. The amount of transmitted light at the air/sample and sample/SnO_2 interface is determined and the results are presented in Table 3.

Table 3. The estimated transmitted light at air/sample and sample/SnO_2 interface.

Sample	$T_{SnO2-sample}$ (%)	$T_{air-sample}$ (%)
PI-1	99.895	91.778
PI-2	99.805	92.389
PI-3	99.776	92.548
PI-4	99.654	93.122

It can be remarked that when the values refractive index of each medium are close, the amount of transmitted light is higher. Conversely, when the differences between refractive indices of media are more pronounced, optical losses take place due to the reflection of the radiations in the incident medium. Light management in photovoltaics is essential for proper working of the device [Enrichi,2020; Haug,2015; Jacobs,2019]. Among the studied samples, PI-1 enables more light to propagate at its surface with TCO, while the losses at air interface are highest. Analyzing the obtained data, the most suitable sample as shielding layer would be PI-4 since it leads to the lowest reflection losses at the air interface, while those at SnO_2 interface are not varying very much in regard to the other samples. The fact that this polymer allows a larger amount of light to pass towards the active zone, will render a higher conversion efficiency of the solar cell, improving its performance. The reported data are of great significance for the future design of the shielding layers of photovoltaic devices with elevated efficiency.

4. Conclusions

The paper investigated a set of four polymers with an imidic structure. The combination of alicyclic segments and dithiol bridges in the main chain is beneficial for increasing the magnitude of the refractive index, while keeping good optical clarity. The estimated refractive index of samples is high, namely n is ranging between 1.711-1.804. The optical band gap, determined with the Gupta relation, is higher than 3 eV for all samples, indicating a low probability of absorption processes. The PI-4 shielding cover enables the highest amount of light to reach the solar cell junction, thus improving the device's conversion efficiency.

5. References

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