EVALUATION OF DIANHYDRIDE MOIETIES IMPLICATIONS ON OPTICAL AND ELECTRICAL PROPERTIES OF IMIDIC COMPOUNDS

Raluca Marinica Albu[1], Andreea Irina Barzic[1]

[1] *"Petru Poni" Institute of Macromolecular Chemistry, Iasi, 700487, Romania, e-mail: alburaluca@yahoo.com*

Abstract: *The paper is focused on some imidic polymers which are based on the same aromatic diamine and several aliphatic dianhydrides with distinct features. The sample chain flexibility and polarizability has a great influence on its optical and electrical properties. The refractive index and dielectric constant were decreased by enhancing the free volume. All specimens present high volume resistivity, particularly those having low chain packing efficiency. The reported data are important in developing a proper structure-property relation that would help to adequate selection of monomers that would render to the final polymer the pursued features.*

Keywords: *polymer, molecular polarization, refractive index, dipole moment*

1. Introduction

Macromolecular compounds containing imidic groups have been widely investigated because of their outstanding physical properties [Ghosh, 1996]. Such polymers have several advantages that make them easier to be applied in this domain, including good processability and facile modeling of their architecture through synthetic or processing procedures [Hulubei, 2007]. These materials are used as interlayer dielectrics in integrated circuit fabrication. For this purpose there is a great need to reduce the dielectric constant in order to minimize cross talk and maximize signal propagation speed in devices [Heaney, 1999]. Therefore, many efforts have been focused on reduction of the dielectric constant by lowering chain crystalline character, the intermolecular charge-transfer and the electronic polarization interactions. All these strategies involved incorporation of specific monomers that minimize backbone polarizability or impart a high degree of free volume.

In the past years, it was revealed that partially aliphatic imidic polymers present lower probability to form inter- or intramolecular charge-transfer complexes, thus reducing the magnitude of dielectric constant. In this context, bulky and aliphatic monomers are designed for diminishing the molecular density [Mathews, 2008]. This procedure created polymers with micro-/nano-scale porosity and implicitly a low dielectric constant [Matsumoto, 2001].
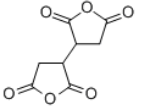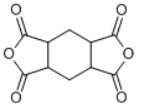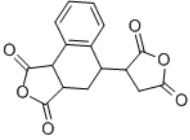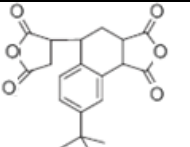
In this paper, a series of imidic compounds derived from the same aromatic diamine containing ether linkages combined with different types of aliphatic dianhydrides was investigated in regard with some basic physical properties. Group contribution theory was applied to assess molar volume and molar refraction, which are the main parameters used for evaluation of the refractive index. The latter was further used to calculate the dielectric constant. The obtained results were discussed in correlation with the chemical structure of the samples highlighting the implications of the dianhydride moieties on studied physical characteristics. These data are useful in pre-establishing some features of the polymers (before starting the synthesis

reactions) that are essential for electronic applications.

2. Materials

The investigation is based on imidic polymers that are built from the same aromatic diamine and several cycloaliphatic dianhydrides. The aromatic monomer, namely 4,4'-ethylenedianiline, contains flexible ethylene groups. The dianhydrides used in this investigation present distinct size and flexibility. Most of them are commercially available or the synthesis was reported in literature [Guo, 2013; Banerjee, 2015]. Their nomenclatures and the acronyms corresponding to each polyimide are listed in **Table 1**.

Table 1: The chemical structures and acronyms of the dianhydride monomers constituting the investigated polyimides

Sample	Dianhydride structure	Nomenclature
PI I		meso-butane-1,2,3,4-tetracarboxylic dianhydride
PI II		1,2,4,5-cyclohexane-tetracarboxylic dianhydride
PI III		4-(2,5-dioxo-tetrahydrofuran-3-yl)-1,2,3,4-tetrahydro-naphthalene-1,2-dicarboxylic anhydride
PI IV		3,4-dicarboxy-1,2,3,4-tetrahydro-6-tert-butyl-1-naphthalene succinic dianhydride

The main objective of the paper is to predict certain physical characteristics before starting the synthesis procedure. The implications of the dianhydride residues on the final polymer properties could be an important clue that could help designing products with the desired features.

3. Results and discussion

The group contribution theory is a facile procedure that provides relatively accurate results on various physical properties of polymers. The concept of additivity can be applied to molar refraction and molar volume [Groh, 1991], which further inserted in Lorentz-Lorenz formula, can lead to the value of the refractive index. This is basic optical property of polymers, which is directly related to their mean polarizability and chain packing efficiency. The results concerning molar refraction, molar volume and refractive index of the specimens are presented in **Table 2**.

Table 2: The molar refraction, molar volume and refractive index for the studied polyimides containing cycloaliphatic units

Polymer	R (cm^3/g)	V (cm^3)	n
PI I	89.20	228.17	1.71
PI II	105.03	275.40	1.69
PI III	130.27	341.31	1.68
PI IV	149.50	403.35	1.66

For all samples the refractive index ranges particularly at the second and the third decimal. Analyzing the data, one may observe the following inequality for refractive index: PI IV < PI III < PI II < PI I. The imidic polymers based on meso-butane-1,2,3,4-tetracarboxylic dianhydride moieties (PI I) or 1,2,4,5-cyclohexane-tetracarboxylic dianhydride (PI II) present the highest refractive index. This can be explained by considering the small size of the dianhydride monomer that determines a higher density of polar imide groups along the chains. Specimen PI III contains an aromatic ring in the dianhydride sequences that maintains a level of chain conjugation, which is reflected in a high refractive index. Moreover, PI IV sample exhibits the lowest values for this parameter. This could be indicative of low chain packing density, which is a factor known to reduce the refractive index [Cosutchi, 2008; Ramani, 2015; Long, 2003].

Introducing the results from **Table 2** in Maxwell relation one can determine the dielectric constant. The dependence of this

parameter on molar polarization is illustrated in **Figure 1**. It can be noticed that the dielectric constant decreases with increasing the molar polarization. The unexpected result shows that permittivity is less affected by the mean chain polarizability and more impacted by the polymer chain packing ability, which in case of studied samples is determined by the distinct features of the dianhydride moieties.
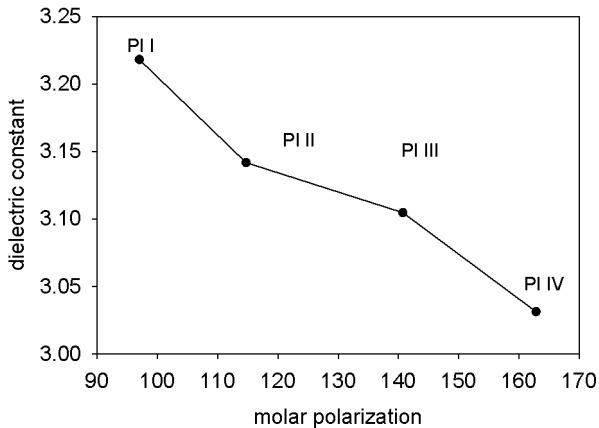

Figure 1: *The dependence of the dielectric constant on the molar polarization of studied samples.*

Figure 2 displays the variation of the dielectric constant with the chain packing density of analyzed imidic polymers.
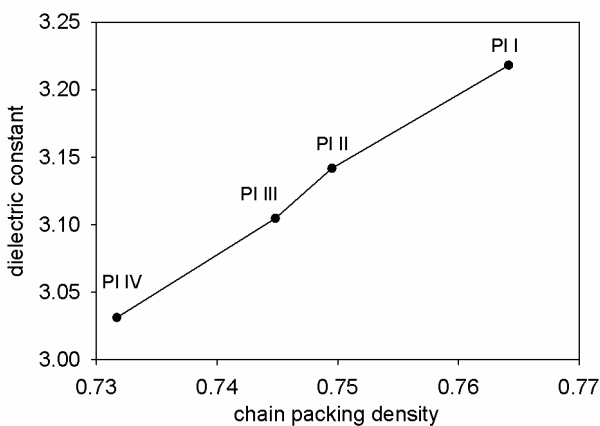

Figure 2: *The dependence of the dielectric constant on chain packing density of studied samples.*

Material PI I, which is derived from the dianhydride moieties with smallest size, presents the highest chain packing ability. Addition of bulky lateral groups favors a

loosened character of chains and thus a less dense material. This is reflected in a lower dielectric constant as observed especially for PI III and PI IV specimens, which have higher free volume.

The electrical volume resistivity of samples is dependent on the dielectric behavior. The estimated values are presented in **Table 3**. One may observe that all imidic polymers exhibit prevalently insulating character, which is favorable for their utilization as dielectric layers or alignment supports for nematics [Stoica, 2013]. This is sustained by the magnitude of the resistivity, namely 10^{19} Ohm cm. The ability to prevent electric current travelling is higher for the samples that have low dielectric constant.

Table 3: The values of volume resistivity and dipolar moment for the studied polyimides

Polymer	Resistivity (Ohm cm)	Dipolar moment (D)
PI I	6.05e+19	0.62
PI II	7.22e+19	0.68
PI III	7.86e+19	0.71
PI IV	9.31e+19	0.80

The dipolar moment was also determined for all examined polyimides. This parameter is dependent on the molar refraction and polarization mechanisms.

It results that there is a synergism between the polarizability and polymer chain packing that must be considered when designing new polymers for microelectronics. For instance, the structure of the polymer PI IV even if exhibits the highest molar polarity (of the backbone and implicitly dianhydride moieties) it does not lead to the highest dielectric constant and lowest volume resistivity comparatively with the other samples.

4. Conclusions

The paper is devoted to the theoretical assessment of the dianhydride residues influence on some basic physical properties of imidic polymers, which are essential in electronic applications. For this purpose we proposed for analysis a series of imidic

compounds that were made from the same aromatic diamine and different dianhydride with aliphatic sequences.

One may conclude that backbone polarizability reported to the molar volume and polymer chain packing ability must be considered when designing new polymers for microelectronics. Among all investigated samples, the polyimide PI IV is the most suited for manufacturing dielectric components for electronic devices.

References

1. Ghosh, M.K. and Mittal, K.L., *Polyimides: fundamentals and applications*, Marker Dekker, New York, 1996.
2. Hulubei, C., Hamciuc, E. and Bruma, M., *New polyimides based on epiclon*, Rev. Roum. Chim., 52, 1063, 2007.
3. Heaney, M.B., *Electrical conductivity and resistivity*, in The measurement, instrumentation, and sensors: Handbook, 43-1-43-14, Boca Raton, Florida, CRC Press, 1999.
4. Mathews, A.S., Kim, D., Kim, Y., Kim, I. and Ha, C.S., *Synthesis and characterization of soluble polyimides functionalized with carbazole moieties.*, J. Polym. Sci. Part A, 46, 8117, 2008.
5. Matsumoto, T., *Colorless full-alicyclic polyimides with low dielectric constant*, J. Photopolym. Sci. Technol., 14, 725, 2001.
6. Guo, Y.Z., Shen, D.X., Ni, H.J., Liu, J.G. and Yang, S.Y., *Organosoluble semi-alicyclic polyimides derived from 3,4-dicarboxy-1,2,3,4-tetrahydro-6-tert-butyl-1-naphthalene succinic dianhydride and aromatic diamines: Synthesis, characterization and thermal degradation investigation*, Progr. Org. Coatings, 76, 768, 2013.
7. Banerjee, S., *Handbook of specialty fluorinated polymers- preparation, properties, and applications*, Elsevier, Amsterdam, 2015.
8. Groh, W. and Zimmermann, A., *What is the lowest refractive index of an organic polymer?,* Macromolecules, 24, 6660, 1991.
9. Cosutchi, A.I., Hulubei, C., Stoica, I., Dobromir, M. and Ioan, S., *Structural and dielectric properties of some epiclon-based polyimide films*, e-Polymers, 8, 778, 2008.
10. Ramani, R., Ramachandran, R., Amarendra, G. and Alam, S., *Direct correlation between free volume and dielectric constant in a fluorine-containing polyimide blend*, J. Phys.: Conference Series, 618, 012025, 2015.
11. Long, T.M. and Swager, T.M., *Molecular design of free volume as a route to low-kappa dielectric materials*, J. Am. Chem. Soc., 125, 14113, 2003.
12. Stoica, I., Barzic. A.I. and Hulubei, C., *The impact of rubbing fabric type on surface roughness and tribological properties of some semi-alicyclic polyimides evaluated from atomic force measurements*, Appl. Surf. Sci., 268, 442, 2013.