ALIPHATIC MONOMER INVOLVEMENT IN OPTICAL PERFORMANCE OF SOME POLYIMIDES FOR FLAT PANEL DISPLAY MANUFACTURING

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Abstract: *Several imidic polymers were proposed in this study to analyze the impact of aliphatic diamine configuration on the optical performance of corresponding polyimide. The manner in which suggested structures are able to interact with electromagnetic radiation was investigated. Two theoretical approaches were used to evaluate the refractive index, leading to similar variations of this parameter in regard with chemical structure. The potential energy of interaction with a nematic molecule was determined, revealing that all samples are interacting favorable with the considered liquid crystal. The reported data are important in fabrication of flat panel displays, where polyimides are used for orientation of nematics.*

Keywords: *polyimide, refractive index, liquid crystal*

1. Introduction

Polymers with imidic structure, known as polyimides (PIs), are widely investigated owing their practical implications in numerous industrial sectors [Mathews, 2008]. Their optical properties are intensively exploited in manufacturing of flat panel displays [O'Mara, 2013]. Such devices are based on liquid crystal cells, which consist in two polyimide films between which is injected a thin layer of nematic molecules. The uniform orientation of the liquid crystal determines the performance of the device and this is ensured by optical and surface properties of the polyimide [Stoica, 2013]. The latter is used as an alignment layer and its surface must have anisotropic features.

Classical polyimides have some limitations derived from their aromatic structure that causes absorption of visible light [Ghosh, 1996]. Given the fact that for such applications good transparency in visible range and low refractive index are mandatory, many efforts have been made to optimize these features. One of the most feasible methodologies relies on utilization of aliphatic monomers in synthesis of imidic polymers [Mathews, 2008].

In this work, some polyimides are subjected to molecular modeling to verify the implications of aliphatic monomers configuration on improvement of interactions with electromagnetic radiations and nematic liquid crystals. The refractive index is assessed based on two theoretical approaches, namely group contribution theory and connective indices approach. These results are discussed in relation with the sample structure and its architecture. The latter is obtained through simulation procedures using a method for geometry optimization that accounts for complex chemical composition of the samples. The interaction potential of polyimides with a nematic, used in display manufacturing, is determined. These data are important for selecting the proper materials as liquid crystal alignment layers (LCAls) for display devices.

2. Experimental

2.1 Materials

The polymers used in this study are represented by polyimides with fully aliphatic

structures. All samples are derived from the same alicyclic dianhydride monomer, namely 5-(2,5-dioxotetrahydro-furyl) -3-methyl-3-cyclohexenyl -1,2-dicarboxylic anhydride. This monomer is combined with the following four aliphatic diamines: 1,4-diaminocyclohexane (PI1), 1,4-bis (aminomethyl)cyclohexane (*cis*- and *trans*-mixture) (PI2), 4,4'-methylenebis (cyclohexylamine) (mixture of isomers) (PI3) and 4,4'- hexafluoroisopropylidene bis (cyclohexylamine) (PI4), respectively.

Certain of them contain methylene or fluorinated groups, which are meant to enhance the flexibility of the polyimide main chain. The monomers used to construct the samples are mainly of commercial nature. Deeper knowledge on these reactants can be found in literature [Hulubei, 2007; Banerjee, 2015]. The monomers were selected in such manner to allow analysis of the impact of diamine moiety configuration on the optical performance of the final polymer. The monomer structures and acronym of each studied polyimide is presented in **Figure 1**.

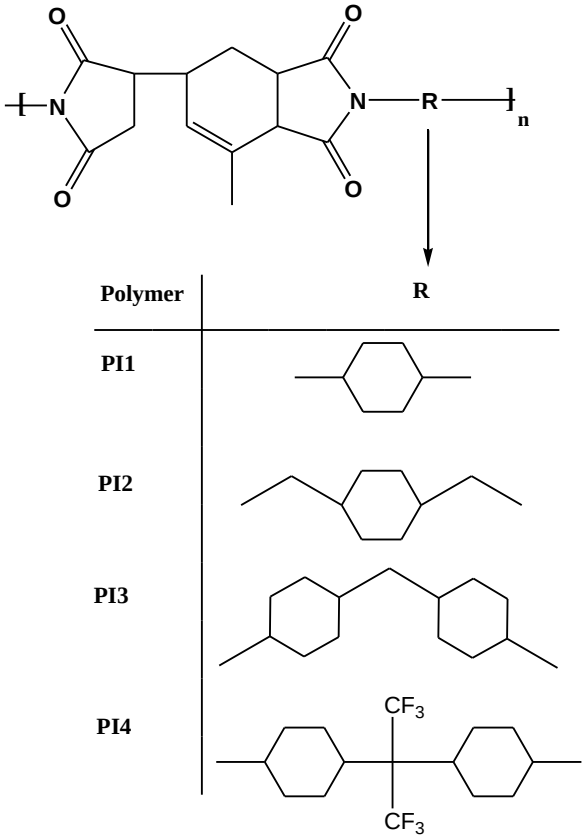

Figure 1: *The chemical structures and acronyms of the cycloaliphatic polyimides.*

2.2 Molecular modeling

The molecular conformation of the designed polyimides was determined using HyperChem 8.0 professional program (Demo Version). The approximation method was based on molecular mechanics force field, which allows structure building and energy minimization for achieving the optimization of macromolecular geometry. For the latter, the termination condition was set to take place at 5000 cycles. Some basic properties, like the polarizability and the volume (considering Van der Waals surface), were also computed using QSAR approach.

2.3 Theoretical background

Basic polymer features can be theoretically estimated starting from its chemical structure. Among the approaches found in the literature, one can mention the group contribution approach [Groh, 1991] and connectivity indices procedure [Bicerano, 1996]. The first methodology relies on assessing a property (P) by adding the contribution of the sub-structures (p_i) that constitute the macromolecule.

$$P=\sum p_i . \quad (1)$$

This can be applied for determining the molar refraction and molar volume of the samples. These were further inserted in the Clausius–Mossotti relation to evaluate refractive index.

$$\frac{n^2-1}{n^2+2}=\frac{4\pi N}{3}\alpha . \quad (2)$$

where n is the refractive index, N is number of molecules per unit volume, and α is the mean polarizability.

The second theoretical methodology used in this study takes into consideration a series of indices as atomic and bond descriptors of the polymer structure. The resulted scheme of correlation also allowed calculating the refractive index.

$$n = 1.885312 + 0.024\frac{17^{0}\chi^{\upsilon} - 20^{0}\chi}{N} - 0.024\frac{12^{1}\chi^{\upsilon} - 9N_{r}}{N}. \quad (3)$$

where ${}^{0}\chi$ and ${}^{0}\chi^{\upsilon}$ are zero-order connectivity indices, is first-order connectivity index, N_r is a term which shows the backbone degree of freedom and N is the number on non-hydrogen atoms.

3. Results and discussion

The refractive index is an important optical parameter that must be accounted in manufacturing of flat panel displays. This parameter reveals information on interaction of the material with electromagnetic radiation. In case of polymers, the refractive index is affected by the polarizability and adopted chain conformation. A low refractive index is indispensable to ensure faster travelling of the radiations through the polymer medium.

In the first stage of this study, the spatial arrangement of the proposed polyimides was computed for four structural units. The obtained data indicated that the type of used diamine determines a distinct macromolecular architecture. **Figure 2** shows the spatial molecular conformations of samples.

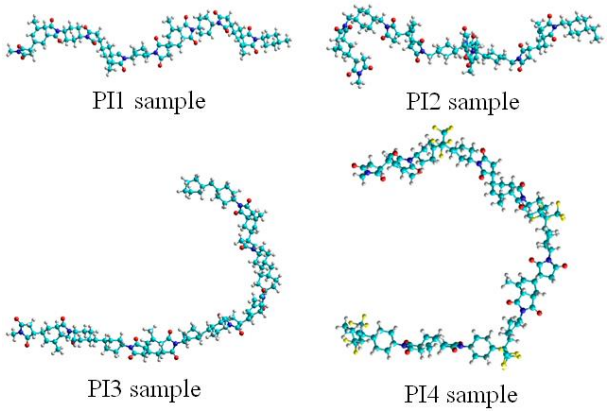

Figure 2: *The spatial molecular conformations of the analyzed cycloaliphatic polyimides obtained for four structural units.*

The computed QSAR properties are displayed in **Table 1**. The diamine residues render to the final polyimide different backbone polarizability. Also, the volume occupied by each sample is changed depending on the flexibility induced by the diamine part.

Table 1: The mean polarizability and volume (obtained by considering Van der Waals surface) of the studied cycloaliphatic polyimides

Polymer	α (Å^3)	V (Å^3)
PI1	35.40	311.59
PI2	39.07	344.72
PI3	47.47	419.33
PI4	50.68	467.43

The results concerning the refractive index are displayed in **Table 2**. The values of this parameter are ranging in the same manner for each sample, regardless the applied theoretical approach. However, there are some differences between the data provided by both employed methods of calculation.

Table 2: The refractive index determined by group contribution method (n_{group}) and connective indices approach (n_{ci}) for the studied cycloaliphatic polyimides

Polymer	n_{group}	n_{ci}
PI1	1.59	1.66
PI2	1.57	1.65
PI3	1.54	1.64
PI4	1.48	1.59

The distinct values can be explained by considering the fact that each methodology starts from dissimilar assumptions. The group contribution theory involves the concept of additivity, while the connectivity indices formalism describes the conformational properties through specialized topological parameters. This is why the second method leads to results that are closer to the ones provided by experiments [Ioan, 2007; Albu, 2012].

The ratio between mean molecular polarizability and the volume of the repeating unit seems to influence the resulted refractive index, as seen in **Figure 3**.

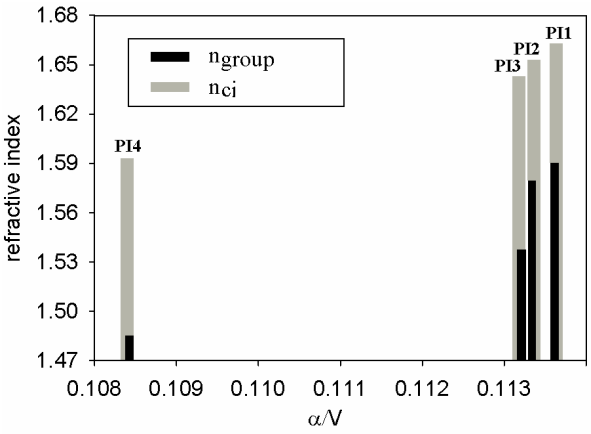

Figure 3: *The influence of the ratio between mean molecular polarizability and the volume of the structural unit on the refractive index values for the studied polyimides.*

It can be noticed that the presence of methylene or trifluoromethyl groups in the vicinity of cyclohexane into the diamine monomer structure led to lower number of polarizable groups per unit of volume and implicitly to smaller refractive index from PI1 to PI4 sample. Therefore, the latter cycloaliphatic polyimide, here under analysis, it is presumed to allow faster travelling of electromagnetic radiations comparatively to the other specimens.

Another important aspect relies on the interaction of the polyimide with nematic liquid crystals, like N-4`-methoxybenzylidine-4-n-butylaniline (MBBA). Some molecular parameters of this compound were previously reported [Rashad, 2012]. The potential energy of interaction between reported polymers and MBBA was assessed (**Figure 4**).

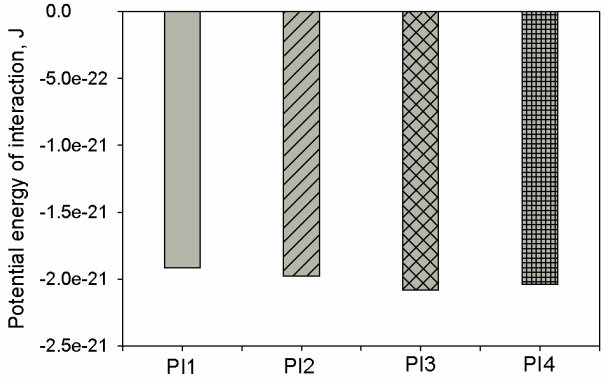

Figure 4: *The potential energy of interaction between studied imidic polymers and MBBA.*

Results were achieved by considering the distance between the two dipolar materials of 15 Å. The predicted data are displayed in Figure 4. In this context, it may be presumed that these all polyimides interact favorable with MBBA being adequate for construction of display devices based on liquid crystal cells.

4. Conclusions

This work was focused on a series of four imidic polymers with distinct conformations induced by the configuration of the diamine moiety. The refractive index is monotone function with respect to the ratio between polarizability and volume of the structural unit. As the latter decreases, the refractive index is smaller (see sample PI4). The potential energy of interaction of investigated polyimides with MBBA nematic was also influenced by the type of diamine moieties. It was observed that these polymers are able to interact with the liquid crystal molecules. This is a favorable aspect in manufacturing flat panel displays, where the phenomena at alignment layer/nematic interface determine the reliability of such devices. Considering their optical properties one can recommend samples PI4 and even PI3 as being suitable as alignment layers for liquid crystal display devices.

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