THE SPECIFIC ROTATION DEPENDENCE ON WAVELENGTH FOR OPTICALLY ACTIVE POLYMERS

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Optical properties of polymers are not so different of other substances, excepting those characteristics related to the chain dimension and structure or conformational changes. Optically active polymers have found interesting applications because of their specific properties. The optical properties of these materials lie at the basis of many applications, for example in chromatographic methods for enantiomeric separations or creating complex optical devices. In this study are presented some aspects concerning the optical activity of polymers, especially the dependence of the specific rotation on wavelength. The dispersion of the specific rotation offers information regarding the conformational changes or Cotton effect.

1. INTRODUCTION

Nature provides us with an almost infinite number of well-defined, functioning, supramolecular systems [1] and therefore gives inspiration to scientists in their search for useful, new architectures. The construction of synthetic equivalents of structures found in nature is challenging and may eventually lead to new insights in the development of materials with unique and previously unattainable properties.

In the last decades there has been a considerable interest in the synthesis and characterization of optically active polymers. These materials have found interesting applications because of their specific properties [2]. One of the key features of organic polymers used in optical applications is the specific rotation. Lenses, optical waveguides, and non-linear optical devices are some examples where this material parameter plays a key role in the system design.

The optical properties of polymers depend on macromolecular chain structure and dimension or its conformational state [3]. Optical activity is a physical characteristic of chiralic materials, caused by conformational or configurational transitions and structures with no symmetry plane.

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Optically active polymers can be classified as follows:

- optically active polymers with configurational chirality: the optical activity is given by the presence of an asymmetric carbon atom in the backbone or in the side chain of the monomer;
- optically active polymers with conformational chirality: the optical activity is related to the conformational changes;
- optically active polymers with both configurational and conformational chirality: the optical activity is given by macromolecular asymmetry and by the presence of the asymmetrical centers.

2. MATERIALS AND METHODS

In order to evidence the optical activity, one must measure the rotation angle of the polarization plane at a constant wavelength.

Optically active polymers present a specific rotation $[\alpha]$, which is related to the rotation angle, as equation (1) shows:

$$[\alpha] = \frac{\alpha \cdot 100}{l \cdot c}$$

where $\alpha$ is the rotation angle of the polarization plane, $l$ represents the thickness of the polymer solution and $c$ is the concentration of the solution (g/ml).

The molecular rotation is also frequently used:

$$[\Phi] = \frac{[\alpha] \cdot M}{100}$$

where $M$ represents the molecular weight of the structural unit.

The specific rotation $[\alpha]$ is dependent on the modification of the wavelength. Optical rotatory dispersion curves can be normal (characterized by no minima or maxima) or abnormal (they present a minimum or a maximum or both). In the latter case, the polymer presents an absorption band in the investigated spectral range. The abnormal curves are also known as Cotton effect.

The study of the specific rotation or molecular rotation dependence on the wavelength is important because it offers information regarding the spatial arrangement of molecules in solution.

The investigated polymers are 1,2-cyclohexan dicarboxylic acid (compound 1), its methyl ester (compound 2) and its corresponding polyester with ethylene glycol (compound 3) in 2,2,2-t-fluorethanol.

The corresponding structures are presented in figure 1.
Fig. 1: The structures of 1,2-cyclohexan dicarboxylic acid (compound 1), its methylic diester (compound 2) and its corresponding polyester with ethylene glycol (compound 3) in 2,2,2-t-fluorethanol.

3. RESULTS AND DISCUSSION

In order to analyze the optical activity of the studied polymers, the solutions must be sufficiently concentrated, homogeneous, transparent and not macroscopically ordered. The recipient that contains the polymer solution is placed between a system containing two polarizers, which allows us to determine the molecular rotation (Table 1).

Table 1: Molecular rotation and its dispersion

<table>
<thead>
<tr>
<th>λ (μm)</th>
<th>[Φ] 10^-3 deg cm²/dmol</th>
<th>dΦ/dλ</th>
<th>[Φ] 10^-3 deg cm²/dmol</th>
<th>dΦ/dλ</th>
<th>[Φ] 10^-3 deg cm²/dmol</th>
<th>dΦ/dλ</th>
</tr>
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<tr>
<td>200</td>
<td>4.83</td>
<td>0.34</td>
<td>3.90</td>
<td>0.24</td>
<td>2.79</td>
<td>0.18</td>
</tr>
<tr>
<td>210</td>
<td>1.46</td>
<td>0.23</td>
<td>1.46</td>
<td>0.22</td>
<td>0.98</td>
<td>0.18</td>
</tr>
<tr>
<td>220</td>
<td>-0.90</td>
<td>0.82</td>
<td>-0.76</td>
<td>0.21</td>
<td>-0.85</td>
<td>-0.01</td>
</tr>
<tr>
<td>230</td>
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<td>-0.08</td>
<td>-1.35</td>
<td>-0.10</td>
<td>-0.77</td>
<td>-0.06</td>
</tr>
<tr>
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<td>0.41</td>
<td>-0.12</td>
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<tr>
<td>250</td>
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<td>-0.29</td>
<td>-0.09</td>
<td>-0.06</td>
<td>0.11</td>
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<tr>
<td>260</td>
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<td>0.01</td>
<td>-0.03</td>
<td>-0.01</td>
<td>0.18</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The variation of the molecular rotation against the wavelength for the studied samples in 2,2,2-t-fluorethanol is represented in figure 2.
Fig. 2: Molecular rotation of studied polymers versus the radiation wavelength.

It can be observed that optical rotatory dispersion curves present Cotton effect. Molecular rotation values show that the investigated polymers yield an optical activity that change with wavelength. The phenomenon presents a maximum in UV. Analyzing the data resulted from the optical rotatory dispersion one can assume that the inversion of optical rotation is caused by changes in the polymer’s conformation.

4. CONCLUSIONS

Though molecular rotation dependence on the wavelength offer valuable information concerning the spatial arrangement of molecules in solution. The molecular rotation of the investigated polymers displays a great dependence on the wavelength. Changes in the conformational states are strongly reflected by the modification of the polymer solutions optical activity.

REFERENCES