OPTICAL ROTATORY DISPERSION FOR POLYMERS*

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The poly(ethylene oxide) derivatives are – in design – synthetic analogues of coiled-coil-forming peptides. The dependence of the specific rotation on wavelength offers valuable information about the conformational and the configurational changes in the polymer structure. The optical rotatory dispersion is also useful in the analysis of the chiroptical behaviour of polymers in different solvents. In this paper some results regarding the optical rotatory dispersion of some poly(ethylene oxide) derivatives are discussed.

Key words: specific rotation, chiroptical behaviour, poly(ethylene oxide) derivatives.

INTRODUCTION

Nowadays, polymers represent a class of materials widely used in all fields of our daily life. Beside the optical properties which are intensely studied (reflection, refraction, absorption, transmission), optical activity of polymers presents a great interest. Therefore, the synthesis and characterization of optically active polymers have been receiving a special attention. These materials have found interesting applications because of their specific properties and they are used as a stationary phase in chromatographic methods for enantiomeric separations [1, 2] or as key materials for various optical devices, for example, lenses, optical disks, and functional films for liquid crystal displays, due to their ease of processing, light weight, high transparency, and low cost [3].

Optical properties of polymers are not so different from others substances with a similarly structure, excepting those properties which are related to the dimension and the structure of the macromolecular chain or to the conformational changes [4]. In the case of polymers one can distinguish two kind of optical properties:

– optical properties which result from the macromolecular mean properties
– optical properties which are caused by local fluctuations in the optical characteristics of the polymer.

Optical activity of polymers is given by the asymmetry of their chemical structures, such as:
– asymmetrical carbon atoms
– atropoisomere sequences
– chains with spiral conformation.

First two types of structures are located in the structural unit and they are characterized by its configuration. The third type of structure is correlated to the second structure of the macromolecule – the conformation – which depends on the structural unit composition and on the nature of the intermolecular interaction forces, respectively. If a macromolecule is composed by several types of chiralic structures, their contribution to the optical activity must be summated.

In order to evidence the optical activity, we 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:

$$[\alpha] = \frac{\alpha \cdot 100}{l \cdot c} \tag{1}$$

where α 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).

Frequently, there is also used the molecular rotation $[\alpha]$:

$$[\Phi] = \frac{[\alpha] \cdot M}{100} \tag{2}$$

where M represents the molecular weight of the structural unit.

For liquid solutions of substances dissolved in optically inactive solvents [5], the rotation angle of the polarization plane can be expressed as follows:

$$\alpha = [\alpha_c] \cdot c \cdot L \tag{3}$$

where $[\alpha_c]$ is the specific rotation of the solution.

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 dependence of the specific rotation on the wavelength is important because it offers valuable information concerning the conformational changes and Cotton effect. If the macromolecule presents a spiral conformation, (for example

polypeptides) the optical rotation curves mathematically can be described by Moffit's relationship:

$$[M] \cdot \frac{3}{n^2 + 2} = \frac{a_0 \lambda_0^2}{\lambda^2 - \lambda_0^2} + \frac{b_0 \lambda_0^2}{(\lambda^2 - \lambda_0^2)^2} \qquad (4)$$

where n is the refractive index of the solvent, a_0 and b_0 are constants which characterize the structural unit and the chain conformation contribution to the optical activity of the polymer.

Optical activity is strongly dependent on the conformational equilibrium [6], and therefore, circular dichroism and optical rotatory dispersion spectroscopy are two techniques that can give valuable information about the spatial arrangement of molecules in solution. Changes in the conformational states are strongly reflected by the modification of the polymer solutions optical activity.

The optical rotatory dispersion is also useful in the analysis of the chiroptical behaviour of polymers in different solvents. In this paper some results regarding the optical rotatory dispersion of some poly(ethylene oxide) derivatives are discussed.

EXPERIMENTAL SETUP

The poly(ethylene oxide)-based synthetic polymers **1-3** shown in Fig. 1 are designed to form coiled-coil superstructures on the basis of hydrophobic interactions. Their primary structure is a repeat unit of polar ethylene oxide units, addressing the repeat of polar and apolar units in coiled – coil – forming peptides. The isobutyl and methyl side-chains in **1-3** are placed not only in a regioregular fashion, but also in a stereoregular fashion, mimicking the chirality in peptides.
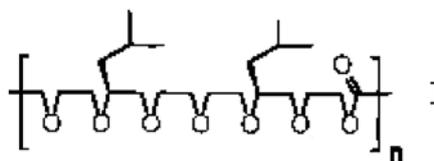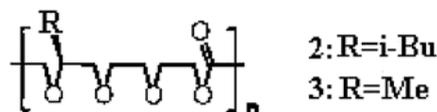

Fig. 1 – Poly(ethylene oxide)-based polymers **1-3** analogues – in primary structure – of coiled-coil-forming peptides.

2: R = i-Bu
3: R = Me

The chirality of the macromolecules **1-3** is used to investigate the optical activity of these samples. In order to determine the specific rotation of the

studied polymers, the solutions must be sufficiently concentrated, homogeneous, transparent and not macroscopically ordered. We have analysed the chiroptical behaviour of **1-3** in tetrahydrofuran (THF) and THF/water mixture at 25°C. The solutions concentrations were of 2.5 (mg/mL).

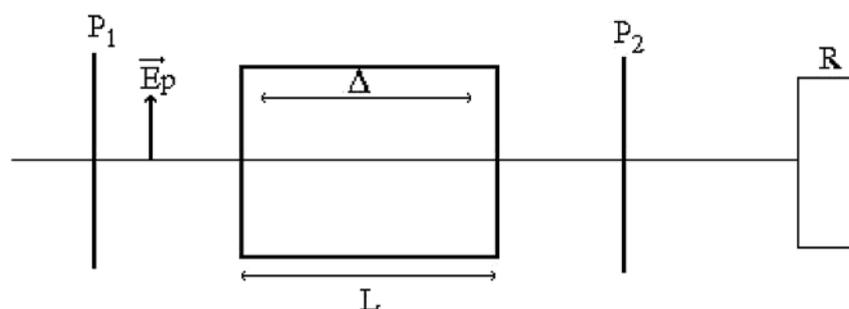The device used in the specific rotation determination is schematically drawn in Fig. 2.

Fig. 2 – The experimental device used to evaluate the specific rotation: P_1, P_2 – polarizers; Δ – the direction of the optical axis; L – the thickness of the recipient which contains the polymer solutions; R – radiation detector.

The monochromatic beam is linearly polarized with the help of polarizer P_1 and it passes through the polymer solution parallel to its optical axis. After the beam crossing through the substance layer of thickness L = 200 mm, it is analysed by a radiation detector (R).

RESULTS AND DISCUSSIONS

The specific rotation of the poly(ethylene oxide)-based polymers solutions in THF at 25°C were measured at different wavelengths. The optical rotatory dispersion revealed that all polymers displayed a negative specific rotation in THF, while in THF/water mixture sample **3** presents positive values. All polymers showed the same trend: increasing the polarity of solvent induced a less negative specific rotation. In particular for the polymer **1**, but also for polymer **2**, no dramatic changes in specific rotation could be induced by changing the polarity of the solvent, whereas – in contrast – polymer **3** displayed an inversion in optical rotation going from apolar to polar solvents. In Table 1 are given the specific rotation values of the studied samples.

In Fig. 3 the variation of the specific rotation against the wavelength for the poly(ethylene oxide)-based polymers **1-3** in THF is represented. One can see that the specific rotation displays a great dispersion.

Table 1

The specific rotation values of the poly(ethylene oxide)-based polymers **1-3** in THF and
THF/water at 25°C at different wavelengths and the specific rotation variation of the wavelength

| Sample	$[\alpha]_{THF}$	$\dfrac{d[\alpha]_{THF}}{d\lambda}$	$[\alpha]_{THF/water}$	$\dfrac{d[\alpha]_{THF/water}}{d\lambda}$	λ [nm]
1	–41.45	–0.145	–33.87	–0.135	450
	–34.21	–0.118	–28.12	–0.094	500
	–28.28	–0.198	–23.41	–0.099	550
	–24.76	–0.238	–18.42	–0.097	600
	–12.84	–0.237	–13.54	–0.083	650
2	–87.51	–0.600	–60.03	–0.221	350
	–57.50	–0.531	–48.96	–0.347	400
	–30.92	–0.236	–30.25	–0.107	450
	–26.64	–0.137	–24.87	–0.121	500
	–19.75	0.138	–18.83	–0.019	550
3	–34.03	–0.138	0.61	0.002	400
	–27.12	–0.188	0.47	0.005	450
	–24.30	–0.184	0.18	–0.001	500
	–15.06	–0.301	0.19	0.002	550
	–14.76	–0.289	0.09	0.001	600
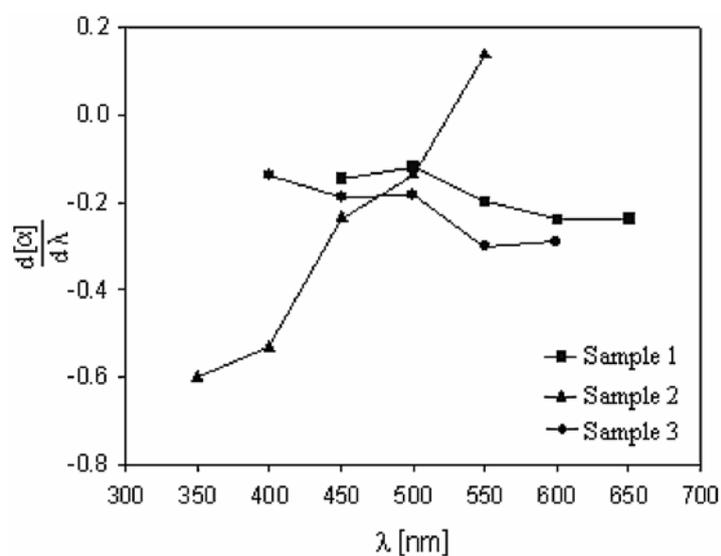
Fig. 3 – The ratio $\dfrac{d[\alpha]}{d\lambda}$ *versus* the wavelength for the poly(ethylene oxide)
derivatives **1-3** in THF.

Analyzing the data resulted from the optical rotatory dispersion one can assume that the inversion of optical rotation is caused by changes in the polymers conformation.

CONCLUSIONS

Measurements of the specific rotation offer information regarding the conformational changes. The specific rotation of the investigated polymers displays a great dependence on the wavelength. Assuming that an inversion of optical rotation in the studied examples of chiral ethylene oxides occurs, the systems suffer a transition from a random conformation to a helical conformation Thus, it is proposed that polymer **3** and possibly **1** and **2** adopt helical conformations in water.

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