Abstract

This thesis is devoted to the theoretical and experimental studies of polymer composites containing spiropyranes. The research concerns two spiropyrans placed in three popular polymer matrices: polyvinyl alcohol (PVA), polystyrene (PS) and poly (methyl methacrylate) (PMMA). The thesis aims to determine correlations between nonlinear-optical properties of composite materials and applied polymeric matrix by the research of experimental studies and quantum-chemical calculations performed with the DFT method with a few different functionals.

The implementation of the experimental part includes the preparation of the polymer foils by the drop cast and solution cast methods using solvents differing in polarities, and then: 1) carrying out a series of studies providing insight into the morphology and structure of a given material, 2) determining their thermal stability, 3) verifying the existence of photochromism phenomenon for the solid-state and 4) finding the dependencies between the generated nonlinear-optical effects and the form of the spiropyran photoisomer. For this purpose, the absorption and oscillation spectra were recorded, the measurements of DSC, SEM, the second and third harmonics generation were performed.

As part of the computational part, quantum-chemical calculations were made for molecules surrounded by the polymers treated as solvents for two models: SCRF and ONIOM models. For this purpose, several DFT functionals were tested - including long-range functionals and functionals containing dispersion corrections – as well as two basis sets differing in size. Both forms of a given spiropyran were tested, and the influence of the symmetry group on the obtained results was also investigated. The calculations for the free molecules and the SCRF model were used as preliminary tests – the conclusions were used to perform calculations with the ONIOM model. In total, almost 2700 calculations were performed, including around 1700 calculations for the SCRF model.

The culmination of the thesis is a comparison of the calculations and empirical results. In this part, the relationships between the obtained results and (I) type of polymer, (II) relative substrates concentrations and (III) influence of the used solvent (polar / non-polar) were determined. In addition, a method (and a basis set) was selected that gives the best compliance with empirical data, both in terms of structural data and the empirically observed properties of the tested chemical compounds. In the case of the analysis of calculation method effectiveness, the revision of the proper dominant form of spiropyran in a given medium is the novelty aspect of the studies.

The innovative nature of the work is related to comprehensive theoretical research using models of different computational complexity, which aim is to try to reproduce the results obtained through empirical research to the greatest possible extent. It should be noted that in the literature there are no reports concerning calculations for molecules in polymer matrices, and it is difficult to find complex studies comparing both solvent models in terms of their compatibility with experimental results. Thus, the obtained results broaden the knowledge about the effectiveness of the computational methods depending on the used solvent model, provide additional information on the properties of spiropyranes and their polymer composites, and verify the efficiency of reproducing specific molar ratios of reagents in quantum-chemical studies.

Keywords: spiropyran polymer composite DFT NLO SCRF ONIOM

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