Centre of Molecular and Macromolecular Studies Polish Academy of Sciences
Adam Michalski
„Supramolecular structures of linear and star-shape polylactide via end groups interactions and stereocomplexation.”

Abstract in English

The presented dissertation consists of three main threads and an appendix, for which the mutual feature are the synthesis of linear and star-shaped polylactides (PLAs) functionalized with hydroxyl (-OH) and carboxyl (-COOH) end groups and their macromolecules interactions in different solvents. To acquire this goal, the series of linear and star-shaped PLAs end-capped with –OH and –COOH were synthesized, as described in the first part of the dissertation. The modification of PLA hydroxyl end-groups into carboxyl end groups was carried out by applying the reaction with succinic anhydride in a controlled and stoichiometric manner. For this purpose, the relevant number of amine catalysts was tested and the most efficient one was selected. Subsequently, the viscosity of the obtained linear and star-shaped PLAs with different functional groups polymers in N-methylpyrrolidone (NMP) was compared. The difference in their viscosity was attributed to the intramolecular interactions of end groups in star-shaped PLAs, which was related to their architecture and end groups functionality. Additionally, the obtained PLAs were able to form reversible, supramolecular gels in NMP. In the second part, the stereocomplexed gels were prepared from obtained star-shaped PLAs by simply mixing the equimolar amount of enantiomeric PLLA and PDLA in NMP. The formation of PLA stereocomplex was confirmed by FT-IR spectroscopy, both for the wet-gel and dry-gel. In addition, the thermal stability of the gels was examined. The unique properties of obtained gels were ascribed to the dominance of intermolecular over intramolecular interactions in stereocomplexed macromolecules, in comparison to enantiomeric macromolecules. In the third part of the work, the linear and star-shaped PLAs were used for the preparation of stereocomplexed nano- and micro-particles in 1,4-dioxane and tetrahydrofurane (THF). After mixing enantiomeric components in a proper solvent, the particles precipitate spontaneously in the form of stereocomplexed particles. However, their morphology differs with the applied solvent, functionality, and architecture of macromolecules. For instance, regular microspheres are formed in THF from stereocomplex PLAs with -OH end groups, whereas spherical stereocomplexed nanoparticles with diameters of about 400 nm are formed from PLAs with carboxylic and ionic end groups.

The appendix part the work focuses on the description of the synthesis of linear and star-shaped PLAs with high molecular mass and the comparison of their thermal stability. The thermogravimetric (TGA) analysis of obtained products allowed for the determination of their thermal decomposition at the PLA processing temperature. The pre-purification of PLA by precipitation did not influence the thermal degradation, however, the addition of a stabilizer such as Irganox inhibits PLA degradation during processing.