

„Design, synthesis and study of properties of responsive polymers with thermo-release function”

mgr Magdalena Paluch

Abstract

Polymer materials in particular those being able to adapt to changes in environmental conditions are of increasing interest and application in biomedicine. The alteration in physical and chemical properties such polymeric systems, also known as “smart polymers”, is a response to the change in environmental parameters, like temperature, pH, or concentrations of certain chemical compounds.

The transformation in responsive polymers caused by an external trigger is usually a reversible process, and the system returns to its initial state when the stimulus has been removed. This dissertation is devoted to the synthesis and studies of properties of new polymeric materials with characteristic of the thermo-release feature, which is an irreversible thermo-sensitivity. The homopolymers and copolymers developed in the presented work undergo irreversible transformations, resulting in the release of a bicyclic model compound. The synthesis of these materials is based on newly designed monomers with a thermosensitive 2-pyridinyl function. Derivatives of this kind undergo temperature initiated intramolecular cyclization, which has been accepted as a mechanism of release of model bicyclic compounds for macromolecular systems. Development of new thermo-responsive materials is an important scientific task, as thermo- and pH-responsive polymers are often used in drug delivery systems or as carriers of biologically active substances.

In presented research, responsive homopolymers PMPyAEA, PBPyAEA, PMPyAPA, and a series of statistical copolymers PNIPAM-co-PMPyAEA, both reversible and irreversible thermo-sensitive, were obtained. For this purpose, the controlled radical polymerization with addition-fragmentation chain transfer (RAFT) together with universal RAFT reagent as a chain transfer agent, were optimized. Polymers of interest were obtained from designed monomers containing 2-pyridinyl group, allowing thermally controlled release of the bicyclic compound from the

macromolecular system. As a result of this process, the model thermo/pH-responsive polymer is transformed into an ionic system in which the pH-responsive poly(acrylic acid) chain is negatively charged, and the released bicyclic compound is bearing a positive charge. The chemical structure of homo- and copolymers was confirmed by spectroscopic methods (NMR, FT-IR). Additionally, molar mass and polydispersity were determined for each of the obtained products using size exclusion chromatography (GPC/SEC) and NMR spectroscopy.

The results of presented study indicate that the process of intramolecular cyclization, and thus the rate of release of the bicyclic compound, can be controlled by modifications in chemical structure of the monomer and the protonation of endogenous nitrogen in 2-pyridinyl moiety. The thermocyclization process can be monitored using UV-Vis spectroscopy, due to the absorption profile change. In addition, significant chemical structure transformations, i.e., the transition of the linear form of the side chain to the ionic form can be successfully monitored by ^1H NMR.

Results obtained in presented investigations are an excellent starting point for the design of polymer systems useful in delivery of biologically active substances and their controlled thermo-release through the process of intramolecular cyclization.