Abstract

Stimuli-responsive (stimuli-sensitive, intelligent, or smart) polymers are polymer materials which, after small external stimuli, evidently change their physical or chemical properties. Smart polymers can be classified according stimuli they respond to such as: temperature changes, mechanical stress, light irradiation, ultrasonic treatment, application of external magnetic as well as electric field, changes of pH, ionic strength, addition of the chemical agents and presence of biomolecules and bioactive molecules. Stimuli-responsive synthetic polymer systems has attracted considerable attention due to wide range of applications, i.e. controlled drug delivery and release systems, diagnostics, tissue engineering and 'smart' optical systems, as well as biosensors, microelectromechanical systems, coatings, and textiles. Among the types of stimuli for this dissertation temperature, pH and reactive oxygen species (ROS) responsive polymer systems were studied. In case of thermoresponsive polymers, when polymer chains are molecularly dissolved in a good solvent, changes (increasing or decreasing) of temperature result in insolubility (globular nanoparticles formation) of polymer chains, called temperature induced phase-separation. pH responsive polymers change properties such as: solubility, volume (gels), chain conformation as well as which bonds can cleavage upon changes in pH of environment. The ROS responsivity results in changes in solubility, hydrolysis, phase transition, and/or degradation of polymer chains.

In this work ^{1}H NMR spectroscopy was applied for structure and temperature induced phase transition characterization (during gradual heating and/or cooling) of various thermoresponsive polymer systems based on: poly(2-ethyl-2-oxazoline), poly(*N*-isopropylacrylamide), poly(vinyl methyl ether), as well as for study of the: interactions between the reaction mixture components, behavior of reaction mixture during the cooling processes (to freezing) and for following the course of polymerization reaction *in situ* in poly(*N*-isopropylacrylamide)/Laponite XLS cryogels. Moreover ^{1}H (and/or ^{13}C) NMR were used for polymer structure and degradation products characterization of novel MPEO-PCL diblock copolymers with acid labile ketal group as a block linkage (pH responsive), pinacol-type boronic ester self-immolative and biodegradable polyoxalate prodrug based on the anticancer chemotherapeutic hormone analog diethylstilbestrol (ROS-degradable). For thermoresponsive polymers ^{1}H spin-spin relaxation times (temperature and time dependences) were measured to follow the changes in interactions and molecular motions of polymer, water and/or additive in solution. Additionally, in case of copolymers for characterization of conformational changes of polymer chains 2D NOESY spectra were recorded.

Keywords: stimuli-responsive, phase transition, temperature, pH, ROS, copolymers, cryogel, PNIPAm, PEO, PVME, PEOx, PCL, ^{1}H NMR, ^{1}H spin-spin relaxation times, 2D NOESY