Abstract

Temperature-sensitive polymers or "smart" polymers are materials that undergo phase separation initiated by temperature change. Some of these polymers possess phase separation temperatures close to human body temperature (37 °C), thus offering a wide range of potential applications in controlled drug release or gene delivery systems, bioseparations, tissue engineering, etc. Of the polymers with a phase separation temperature close to 37 °C, poly(N-isopropylacrylamide) (PNIPAM) and poly(vinyl methyl ether) (PVME) are perhaps the most important and were selected as the subjects of this study. In this work, these two polymers have been examined in the presence of low molecular weight additives, and their colloidal stability evaluated using ^{1}H NMR (nuclear magnetic resonance) and time-resolved ^{1}H NMR spin-spin relaxation time T_2 experiments. An improved model of the two exchangeable states was applied for a more detailed characterization of the phase separation process. The main focus of this study was to determine the influence of additives on the phase separation behavior of the polymers (phase separation temperature, width of transition, maximum number of polymer chains participating in phase separation), reversibility of the phase separation, dynamics of solvent molecules (water and additive), interactions between solvent molecules, additives and polymer chains. Another objective of this thesis was to perform a thorough characterisation of temperature-sensitive porphyrin-PNIPAM conjugates by a variety of physico-chemical methods. Thermodynamic parameters associated with the phase separation phenomenon were obtained by NMR spectroscopy and compared with data obtained by differential scanning calorimetry. Phase diagrams based on Flory-Huggins theory were constructed and the influence of the concentration and length of the polymer chain on phase separation was evaluated. Small angle X-ray scattering (SAXS) provided information about the internal structure of aggregated, phase-separated, and protonated structures of the conjugates. Protonation occurring in the porphyrin-PNIPAM conjugates was studied by UV-Vis spectrophotometry, SAXS, NMR, and dynamic light scattering (DLS). During the protonation process, the colour of the conjugate solutions changes from red to green, accompanied by a change in geometry of the porphyrin core. The colour change is fully reversible and can be used as a visual indicator for sensing applications. Additionally, a co-nonsolvency effect was observed for the conjugates and was studied by NMR, DLS and optical microscope.