“Nanoparticles in complex fluids”
Abstract of a dissertation by Ewelina Kalwarczyk

A modern, twenty-first-century chemistry, not only continues the research conducted in previous centuries, but also brings together various branches of science and technology. The goal of this approach is usually to create new materials characterized by an interesting combination of physicochemical properties. In my studies, I followed this trend and applied nanotechnology in the soft matter science. I investigated combination of nanoparticles, i.e., particles whose size is one billionth of a meter, with liquids having complex internal structure, referred to as complex fluids. In the present dissertation, I employed complex fluids being solutions of surfactants and polymers. One of the key achievements of the research presented in the dissertation is development of a new method that allows fabrication of nanostructured materials consisting of nanoparticles enclosed in a soft or solid template of a prescribed internal structure.

The results obtained are divided into three parts and presented in subsequent sections. In the first section, a new method to induce phase separation in solutions of ionic surfactants is described. In this method, the phase separation is obtained either by addition of polyelectrolytes or nonionic polymers along with inorganic salt. As a result, the system separates into polymer-rich and surfactant-rich phase. Four types of the mixtures are investigated: (i) anionic surfactants and anionic polyelectrolytes, (ii) cationic surfactants and cationic polyelectrolytes, (iii) cationic surfactants and nonionic polymers, and (iv) anionic surfactants and nonionic polymers. Surprisingly, I found that the addition of polyelectrolyte with the charge of the same sign as that of surfactant can induce the phase separation in a wide range of surfactant concentrations. The phase separation process is accompanied by the ordering of the surfactant molecules inside the surfactant-rich phase. I named this separation/ordering phenomenon the polymer-induced phase separation (PIPS). In the second section, I demonstrated that PIPS offers a facile method to fabricate novel nanostructured materials. In particular, I showed that PIPS may be used to incorporate charged nanoparticles into different types of ordered phases (lyotropic liquid crystals) formed by ionic or nonionic surfactants. Additionally, I succeed to transform this kind of soft nanocomposites into solid forms. In the third section, I described the results of studies on the dispersion of nanoparticles in fluids with a low degree of complexity, that is, in micellar solutions of surfactants. I demonstrated that nonionic surfactants adsorb at the surface of the nanoparticles functionalized with carboxylic acid groups to form a double-layered shell. In the case of semiconductor quantum dots functionalized with COOH groups, the adsorption of the surfactant molecules leads to the quenching of fluorescence. Fluorescence spectroscopy studies revealed that the formation of the surfactant coating is adsorption process following the first-order kinetics.