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Unusual swelling behavior of core-shell microgels built from polymers exhibiting lower critical solubility temperature

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ABSTRACT

Using a combination of two LCST-type polymers a set of new core-shell microgels was obtained. Interestingly, the swelling behavior of obtained core-shell microgels was characteristic for the polymeric gels that possess both UCST-type and LCST-type properties. The cores were based on cross-linked poly(*N*-isopropylacrylamide-sodium acrylate) and were obtained by employing the precipitation polymerization. Then, the shells, based on cross-linked poly(*N*-isopropylacrylamide-sodium acrylate), were built over the cores via the seed polymerization. The swelling behaviors of the microgels were investigated by doing DLS experiments in a temperature range of 20–50 °C. This microgel appeared to be the first relatively simple system that can exist in the swollen state only in a narrow temperature range. The swelling of the microgels took place at temperature below the volume phase transition temperature (VPTT). The maximum value of radius appeared at VPTT of the core. This phenomenon was observed for various compositions of the core and the shell and in a wide range of pH. Differential scanning calorimetry measurements showed that the swelling process occurring at a temperature below VPTT is endothermic. The reported particle properties may open new possibilities in application of such materials in the fields of controlled release of various molecules, construction of sensors and chemical separations.

1. Introduction

Microgels are small cross-linked particulate polymeric systems, colloidal in size and swollen in a suitable solvent. Microgels have similar properties to polymers and bulk gels but microgels are discrete particles. Microgels, similarly to bulk hydrogels, possess high water content and an interior network that is responsible for storing the mechanical energy and providing desired mechanical properties. Microgels based on intelligent polymers are environmentally sensitive; they are able to switch their properties in response to an external stimulus. They can exist in two different states: swollen and collapsed. The transition from one state to another is called the volume phase transition (VPT). The reversible transition occurs as a response to changes in temperature, pH, redox potential, pressure, presence of particular ions, solvent composition, and electromagnetic radiation [1–4]. Stimuli-sensitive microgels attract increasing attention due to their applications in such fields as sensors, catalysis, optics, enzyme immobilization and controlled drug delivery [5–7]. In recent years, a novel architecture of the microgels was proposed. Two different polymers were used to form a core and a shell around the core. These core-shell microgels have already attracted some attention because they revealed extra properties not possessed by the individual components [8].

Much attention has been given to thermo-sensitive microgels [9–11]. Thermoresponsive polymers can be classified into two

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groups. One possesses the lower critical solution temperature (LCST) and exhibits, in a given solvent, a soluble-to-insoluble reversible phase transition when temperature becomes higher than the LCST. The second one is characterized by upper critical solution temperature (UCST) and undergoes the opposite, insoluble-to-soluble reversible phase transition when temperature becomes higher than the UCST. The phase behavior of a linear-polymer solution directly influences the swelling behavior of cross-linked polymer networks. The cross-linked polymers with a LCST-type thermal behavior, swollen in a given solvent, undergo a reversible shrinking process (volume phase transition) stimulated by an increase in temperature. In the case of cross-linked UCST polymers an increase in temperature leads to a transition from the shrunken- to the swollen state.

In most of the cases, the shrinking process, affected by an increase in temperature above the LCST, is caused by breaking of hydrogens bonds between the solvent molecules and the polymer chains and the following domination of interactions between the hydrophobic groups. There are many examples of LCST-type thermal-behavior hydrogels; the gels based on cross-linked poly(*N*-isopropylacrylamide) are such and are most frequently investigated [12,13]. In contrast to a rather large number of LCST-type cases only a few examples of UCST-type polymer network were reported [14–16]. Generally, the UCST-type behavior is based on breaking of intra- and inter- chain hydrogen bonding and electrostatic attractions caused by an increase in temperature [17].

Lyon and co-workers studied LCST-type core-shell (CS) microgels synthesized by a two-stage precipitation polymerization. Core particles, composed of cross-linked poly(*N*-isopropylacrylamide) (pNIPA) or poly(*N*-isopropylacrylamide-acrylic acid) (p(NIPA-AAc)), were synthesized first and then were used as the nuclei for subsequent polymerization of p(NIPA-AAc) and pNIPA, respectively [18–20]. Richtering et al. presented core-shell microgels consisting of two different-temperature responsive polymers, pNIPA and pNIPMA - poly(*N*-isopropylmethacrylamide), with a difference between their LCSTs of circa 10 °C. Zeiser et al. reported on core-shell microgels based on pNNPA - poly(*N*-n-propylacrylamide) and pNIPMA, which due to a large LCST gap exhibited a linear swelling behavior in a temperature range from circa 21 °C to 44 °C [21].

Xiao et al. developed UCST type CS microgels based on poly(acrylamide-styrene) (p(AAM-St)) core and interpenetrating polymer network (IPN) shell of poly(acrylamide-acrylic acid) (p(AAM-AAc)) which were prepared using a three-step synthesis [22]. Yin et al. reported on core-shell microgels with both LCST and UCST properties [23]. The slightly cross-linked poly(2-vinylpyridine) (P2VP) was coated with pNIPA by doing the seed emulsion polymerization. In the presence of 2,6-naphthalenedisulfonate (2,6-NDS), that acted as an ionic cross-linker in the core, the UCST behavior (swelling) was initiated by the compromised electrostatic attractive interactions between the protonated core ($P2VPH^+$) and 2,6-NDS at elevated temperatures. The subsequent LCST transition (shrinking) was related to the shrinking of the pNIPA shell.

In this study, we report on a novel thermo-sensitive core-shell microgels of unusual properties. Both the core and the shell were composed of LCST-type thermal-behavior hydrogels based on cross-linked poly(*N*-isopropylacrylamide-sodium acrylate) (pNIPA-AANa) (it is known that polymers pNIPA-AANa exhibit LCST [24–26]). In our work sodium acrylate, compared to previous studies, was employed for the preparation of both core and shell. The addition of a shell was performed at a temperature above VPTT where the core was shrunken. That led to limitation of further swelling of the core (core compression effect). Additionally, the use of sodium acrylate led to the formation, in the core, of a thin carboxylic-group-rich outermost layer. The complex structure of the new CS microgels resulted in an unusual swelling behavior. The CS microgels possessing both UCST and LCST properties were obtained. We focused our attention on the investigation of the influence of temperature and pH on the swelling behavior and stability of the core-shell microgels synthesized with various amounts of the carboxylic groups in the core and in the shell.

2. Experimental

2.1. Chemicals

N-isopropylacrylamide (NIPA, 97%), *N,N′*-methylenebisacrylamide (BIS, 99%), ammonium persulfate (APS, 99.99%), uranyl acetate dihydrate (UO_2Ac_2, 98%) and sodium acrylate (AANa, 97%) were purchased from Aldrich. Sodium hydroxide (NaOH, 99%) and hydrochloric acid (HCl, 35–38%) were purchased from POCh.

The chemicals were not further purified except for NIPA, which was recrystallized twice from a 9:1 benzene/hexane mixture. All solutions were prepared from high-purity water obtained from a Hydrolab/HLP purification system (water conductivity: 0.056 μS cm^{-1}).

2.2. Synthesis of p(NIPA-AANa) core and p(NIPA-AANa)/p(NIPA-AANa) core-shell

2.2.1. p(NIPA-AANa) core

The core-shell microgel particles were prepared by two-step aqueous dispersion polymerization. p(NIPA-AANa) cores were obtained by precipitation polymerization [27]. The appropriate amounts of NIPA monomer, SDS (0.5 mM), BIS and AANa were dissolved in 195 mL of deionized water in a three-neck flask equipped with a magnetic stirrer (set at 250 rpm during the entire polymerization), reflux condenser, inlet and outlet of inert gas. The total concentration of NIPA, AANa and BIS was kept constant at 100 mM. The microgels were synthesized with the mole fraction of the AANa equal to $Y_{solution}$ in the pre-gel solution. In this study $Y_{solution}$ was set to 2, 5 and 7%. The mole fraction of BIS was kept constant at 1%. The monomer solution was purged with argon for 0.5 h to remove any dissolved oxygen and heated up to 70 °C in an oil bath. Then APS (96 mg dissolved in 5 mL of deionized and degassed water) was added to initiate the polymerization. The pH of the solution was ca. 8. The reaction continued for 5 h under an argon blanket. p(NIPA-AANa(2%)), p(NIPA-AANa(5%)) and p(NIPA-AANa(7%)) were obtained. Next the solution was cooled down to room temperature and the core particles were purified by dialysis. Microgels were placed in a dialysis tube with a 10,000 Da