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ORIGINAL ARTICLE

Stability of poly(N-isopropylacrylamide-co-acrylic acid) polymer microgels under various conditions of temperature, pH and salt concentration

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Abstract This research article describes the colloidal stability of poly(N-isopropylacrylamide-co-acrylic acid) [P(NIPAM-co-AAc)] polymer microgels with different acrylic acid contents in aqueous medium under various conditions of temperature, pH and sodium chloride concentrations. Three samples of multi-responsive P(NIPAM-co-AAc) polymer microgels were synthesized using different amounts of acrylic acid by free radical emulsion polymerization. Dynamic laser light scattering was used to investigate the responsive behavior and stability of the prepared microgels under various conditions of pH, temperature and ionic strength. The microgels were found to be stable at all pH values above the pK_a value of acrylic acid moiety in the temperature range from 15 to 60 °C in the presence and absence of sodium chloride. Increase in temperature, salt concentration and decrease in pH causes aggregation and decreases the stability of microgels due to the decrease in hydrophilicity.

1. Introduction

Microgels have rapidly gained importance in field of materials science owing to their potential applications in drug delivery (Murthy et al., 2003), pollution control (Morris et al., 1997), enhanced oil recovery (Sun et al., 2011), sensors (Retama et al., 2003), catalysis (Lee et al., 2008), fabrication of photonic crystals (Jones and Lyon, 2000), template-based synthesis of inorganic nanoparticles (Zhang et al., 2004) and chemical separation (Nilsson and Hansson, 2005). A large number of applications of microgels arises from their ability to undergo reversible volume phase transitions in response to external stimuli such as a change in pH (Nisato et al., 1999), temperature (Dowding et al., 2000) and ionic strength of the surrounding medium (López-León et al., 2007). Poly(N-isopropylacrylamide) [P(NIPAM)] is a widely studied temperature responsive

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polymer microgel (Jones and Lyon, 2000). From application point of view, microgels would be much favorable if they could respond to several stimuli simultaneously. Therefore N-isopropylacrylamide (NIPAM) is copolymerized with ionic monomers to get multiresponsive microgels. For example copolymerization of NIPAM with ionic monomer containing carboxylic acid groups form a pH sensitive microgel in addition to the temperature responsive particles. The combination of acrylic acid (AAc) (Naeem et al., 2012) and NIPAM is largely used to prepare pH responsive polymer microgels, because AAc is hydrophilic and can increase the volume phase transition temperature (VPTT). Microgels with tunable VPTT have a potential to be used for biomedical applications (Farooqi et al., 2011a,b). They assigned a photoresponsive drug delivery system based upon gold (Au) nanorods and P(NIPAM-co-AAc) hybrid material (Gorelikov et al., 2004). Jones and his coworkers prepared poly(N-isopropylacrylamide-co-acrylic acid) [P(NIPAM-co-AAc)] core–shell microgel and studied its functioning for physiological applications. They studied its working at pH 3.5 and 6.5 under 0–0.8 M saline solutions (Jones and Lyon, 2003). Kim also synthesized microspheres of NIPAM and AAc and investigated its thermosensitivity within 25–48 °C range at pH 3.0 and 6.5 (Kim et al., 2004). They synthesized P(NIPAM-co-AAc) microgels and investigated their pH and temperature responsive bahaviour in aqueous medium (Debord and Lyon, 2003). Zhang et al. designed a glucose sensor by the chemical reaction of P(NIPAM-co-AAc) microgels with phenylboronic acid in the presence of *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDC) catalyst (Zhang et al., 2006). Mohan et al. used P(NIPAM-co-AAc) microgels as microreactor to synthesize Ag nanoparticles. They were able to tune optical properties of nanoparticles by the variation of pH and temperature of the surrounding medium (Mohan et al., 2010).

It is important to investigate the range of stability of P(NIPAM-co-AAc) microgels under various conditions of temperature, pH and salt concentrations for all the above applications. To the best of our knowledge, no one has reported stability of P(NIPAM-co-AAc) microgels under such conditions in a systematic way in the previous studies.

Herein we prepared P(NIPAM-co-AAc) microgels with different feeding contents of AAc and NIPAM, and investigated their responsive behavior in the presence of various stimuli like pH, temperature and NaCl concentration using Dynamic Light Scattering (DLS). We reported the stability of microgels under various conditions and determined the range of temperature, pH and ionic strength in which microgel is stable. The aggregation behavior of the microgels has been explained on the basis of proposed theories.

2. Experimental

2.1. Materials

NIPAM and AAc were purchased from Sigma–Aldrich while N,N-methylenebis(acrylamide) (BIS) was obtained from ACROS. NIPAM was purified by recrystallization from n-hexane and dried in an oven, prior to use. AAc was purified by distillation under reduced pressure. Ammonium persulfate (APS), sodium dodecylsulfate (SDS) and BIS were used as received. Water used for all reactions, solutions preparation and polymer purification was distilled and deionized. The pH values were measured on a WTW Inolab pH 720 pH meter.

2.2. Synthesis of P(NIPAM-co-AAc) microgels

For synthesis of sample G1, 0.01237 mol of NIPAM, 0.000214 mol of BIS, 0.000197 mol of SDS and 0.000721 mol of AAc were dissolved in 100 mL of deionized water in a three necked round bottom flask which was equipped with a condenser and nitrogen inlet. The reaction mixture was heated at 70 °C under a gentle stream of nitrogen. After 1 h, polymerization was started with the addition of 5 mL APS solution (0.06 M). The resulting microgels were purified by dialysis for 1–2 weeks using Spectra/Por molecular porous membrane tubing (cutoff 12,000–14,000) against very frequently changed water at room temperature, and followed by centrifugation. Samples G2 and G3 were prepared and purified using the same method. The compositions of all the microgel samples are given in the Table 1.

2.3. Characterization

DLS was used to investigate the responsive behavior of microgels. Before taking measurement, all the solutions of microgel were filtered through a Millipore millex filter (0.45 μm) into the scattering cell (cuvette) whose outer surface was cleaned with a special type of cleaning paper. The dynamic light scattering experiment was carried out on a commercial LLS spectrometer BI-200SM motor-driven goniometer equipped with BI-9000AT digital autocorrelator and a cylindrical 22 mW uni-phase He–Ne laser (wavelength = 637 nm) at different temperatures (15–60 °C) and pH (2–9) under different concentrations of NaCl at a scattering angle of 90°.

3. Results

3.1. Fourier transforms infrared (FTIR) spectroscopy

The absorption peaks which were recorded in the spectra of three microgels samples are given in the Table 2. FTIR spectrum of G1 in Fig. 1 lacked peak of the carbon–carbon double bond, which confirmed that polymerization occurred at this point since NIPAM and AAc, both monomers have C=C groups. The peaks of all the remaining functional groups of monomers are recovered in the spectrum of microgels, confirming that polymerization has successfully occurred.

3.2. Effect of temperature

The hydrodynamic radius (R_h) of dilute dispersion of sample G3 as a function of temperature at various pH values is shown in Fig. 2. Microgel dispersion was found to be stable in the pH range of 3.80–8.65 at 15–60 °C but it is unstable at pH = 2.25 at a temperature greater than the volume phase transition of microgels at this pH value. The increase in temperature and decrease in pH cause hydrophobicity in the system. Under such conditions, microgel particles combine with each other and aggregation takes place. That is why the R_h value suddenly increases at pH 2.25 and temperature of 32 °C. Increase in pH increases the stability of microgel dispersion but eliminates