Characterization of Fe$_3$O$_4$/poly(styrene-co-N-isopropylacrylamide) magnetic particles with temperature sensitivity

Abstract  The average diameter, diameter distribution and surface morphology of Fe$_3$O$_4$/poly(styrene-co-N-isopropylacrylamide)[P(St-NIPAM)] particles were characterized by scanning electron microscopy. The copolymer structure was confirmed by IR spectroscopy, differential scanning calorimetry and elemental analysis. The content of Fe$_3$O$_4$ entrapped in the particles was determined by atomic absorption spectrometry. A coarse structure was observed on the surface of the Fe$_3$O$_4$/P(St-NIPAM) particles. The hydrodynamic diameter of the Fe$_3$O$_4$/P(St-NIPAM) particles was found to exhibit about a 15% decrease in diameter on changing the temperature from 25 to 40 °C. The results also showed that Fe$_3$O$_4$/P(St-NIPAM) an advantage of exploited magnetic separation.

Keywords  Thermosensitive · Magnetic · Particle · Characterization

Introduction

There are many potential applications of “intelligent” polymers with critical phenomena in biomedical or biological fields. Critical phenomena, for example, phase transitions, can be induced by external stimuli such as temperature, pH, solvent, ionic composition, electric field, light, etc [1]. Most of the polymers studied previously are responsive to only one kind of stimulus, but for some applications, responsiveness to several stimuli may be required, and polymer with multiresponsiveness would provide more widely useful applications.

Poly(N-isopropylacrylamide) (PNIPAM) exhibits a lower critical solution temperature (LCST) and collapses and shrinks above the LCST, around 32–33 °C, and swells and expands below the LCST. This reversible thermosensitivity is considered to be useful in some fields, such as enzyme immobilization, drug delivery systems and separation of proteins [2–4]. Recently, copolymers of NIPAM and some functional monomers exhibiting multiresponsiveness have been studied. Chan and Hoffman [5] synthesized graft copolymers composed of side-chains of a temperature-sensitive polymer (NIPAM) grafted onto a pH-sensitive backbone polymer [poly(acrylic acid)]: the polymer undergoes marked solubility changes in water in response to temperature and/or pH changes. Gels containing NIPAM and the light-sensitive chromophore trisodium salt of copper chlorophyllin have been reported by Suzuki and Tanaka [6].

In our previous studies [7], multifunctional Fe$_3$O$_4$/poly(styrene-NIPAM)[P(St-NIPAM)] particles exhibiting thermosensitive and magnetic responsiveness were synthesized by copolymerization of NIPAM and St in the presence of Fe$_3$O$_4$ magnetic fluid. The properties of the particles mentioned above were characterized by several methods in this study.

Experimental

Materials

St was treated with 10% sodium hydrate solution to remove the inhibitor and was stored at 4 °C. NIPAM (Aldrich) was purified by
recrystallization from a mixture of 1/1 toluene and hexane. All other materials used in this study were of analytical grade and were used without further purification. Water was double-distilled.

Synthesis

Fe₃O₄/P(St-NIPAM) particles were prepared by copolymerization of NIPAM and St using potassium persulfate as initiator in an ethanol/water medium and in the presence of Fe₃O₄ magnetic fluid with an average diameter of 50 nm, which prepared by a precipitation-oxidation method as mentioned in our previous work [7]. Polymerization was carried out in a 250-ml four-necked flask equipped with a stirrer, an inlet of nitrogen and a condenser. The required quantities of the ingredients were placed into the flask and the reaction was allowed to proceed for 24 h at 70 °C under stirring. The resulting particles were dialyzed and purified by repetitive magnetic separation and decantation, and this purification procedure was repeated after the particles had been immersed in a 1 M HCl solution for 48 h in order to remove the nonencapsulated Fe₃O₄.

Characterization

The average diameter, diameter distribution and surface morphology of the Fe₃O₄/P(St-NIPAM) particles were obtained by scanning electron microscopy (AMRAY-1000), followed by statistical treatment with a computer system. The sample was sputtered with gold before viewing under the scanning electron microscope, and the hydrodynamic diameter of the Fe₃O₄/P(St-NIPAM) particles in water was determined at different temperatures using a laser diffraction particle size analyzer (SALD-2001, Shimadzu).

The copolymer structure was confirmed by IR spectroscopy (MX-1E, PE) with KBr pellets.

The glass-transition temperature (T_g) of the particles was obtained by differential scanning calorimetry (DSC) (DSC-7, PE) with a scanning rate of 10 °C/min under high nitrogen atmospheres.

The content of nitrogen in the particles was determined with an element analyzer (1106, Cario Erba) and the content of PNIPAM was calculated from the nitrogen data. The content of Fe₃O₄ entrapped in Fe₃O₄/P(St-NIPAM) was obtained by determining the content of Fe using atomic absorption spectrometry (4100zl, PE).

The magnetic responsiveness of the Fe₃O₄/P(St-NIPAM) particles was determined as follows: Fe₃O₄/P(St-NIPAM) particles were suspended in water solution and the transmittance (580 nm) of the suspension was determined with a spectrometer (721) at a certain time after the particles had been separated by an additional magnetic field (0.42 T).

All the samples used for characterization were dried at 65 °C for 24 h under vacuum before the determinations.

Results and discussion

The average diameter, diameter distribution and the surface morphology of the final particles were obtained by scanning electron microscopy. The results are shown in Fig. 1. The average diameter of the particles shown in Fig. 1a is about 11.5 μm. Our experimental results showed that particles with average sizes ranging from 5 to 100 μm could be prepared by changing the polymerization conditions. The particles were found to be polydisperse as shown in Fig. 1b. The detailed surface morphologies of Fe₃O₄/PSt and Fe₃O₄/P(St-NIPAM) are shown in Fig. 2 in the scanning electron microscope photographs taken with higher magnifications. As seen in Fig. 2, an appreciable difference is observed in the surface of morphology between Fe₃O₄/PSt and Fe₃O₄/P(St-NIPAM). A coarse structure is observed in the surface of Fe₃O₄/P(St-NIPAM) particles, but the surface of Fe₃O₄/PSt is smooth. This phenomenon is attributed to the existence of a PNIPAM hydrophilic layer on the surface of Fe₃O₄/P(St-NIPAM) particles. Particles with hydrophobic core/hydrophilic shell have been reported to be formed in several copolymerizations of hydrophobic and hydrophilic monomers in hydrophilic media [8].

The copolymer of St and NIPAM was confirmed by IR spectroscopy. The results are shown in Fig. 3b. Double bands at 1647 and 1541 cm⁻¹ appear due to the groups of amide(I) and amide(II) of PNIPAM, respectively, and the adsorption bands at 1388 and 1365 cm⁻¹ are related to isopropyl groups. The adsorption bands in