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SHORT COMMUNICATION

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Characterization of Fe_3O_4/poly(styrene-*co*-*N*-isopropylacrylamide) magnetic particles with temperature sensitivity

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Abstract The average diameter, diameter distribution and surface morphology of Fe_3O_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_3O_4 entrapped in the particles was determined by atomic absorption spectrometry. A coarse structure was observed on the surface of the Fe_3O_4/P(St-NIPAM) particles. The hydrodynamic diameter of the Fe_3O_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_3O_4/P(St-NIPAM) an advantage of exploited magnetic separation.

Key words 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_3O_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_3O_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

Fe_3O_4/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 Fe_3O_4 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 quanties 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 Fe_3O_4.

Characterization

The average diameter, diameter distribution and surface morphology of the Fe_3O_4/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 Fe_3O_4/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-IE, 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.

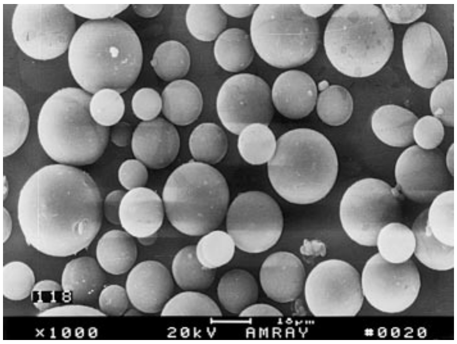
The content of nitrogen in the particles was determined with an element analyzer (1106, Cario Erba) and the content of PNIPAM was calculated from the nitrogen data. The content of Fe_3O_4 entrapped in Fe_3O_4/P(St-NIPAM) was obtained by determining the content of Fe using atomic absorption spectrometry (4100zl, PE).

The magnetic responsiveness of the Fe_3O_4/P(St-NIPAM) particles was determined as follows: Fe_3O_4/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).

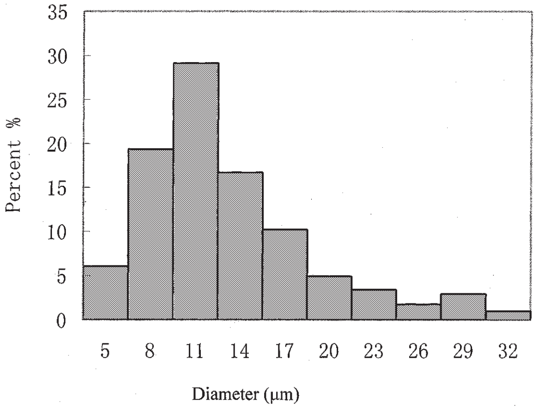
All the samples used for characterization were dried at 65 °C for 24 h under vacuum before the determinations.

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 Fe_3O_4/PSt and Fe_3O_4/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 Fe_3O_4/PSt and Fe_3O_4/P(St-NIPAM). A coarse structure is observed in the surface of Fe_3O_4/P(St-NIPAM) particles, but the surface of Fe_3O_4/PSt is smooth. This phenomenon is attributed to the existence of a PNIPAM hydrophilic layer on the surface of Fe_3O_4/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].



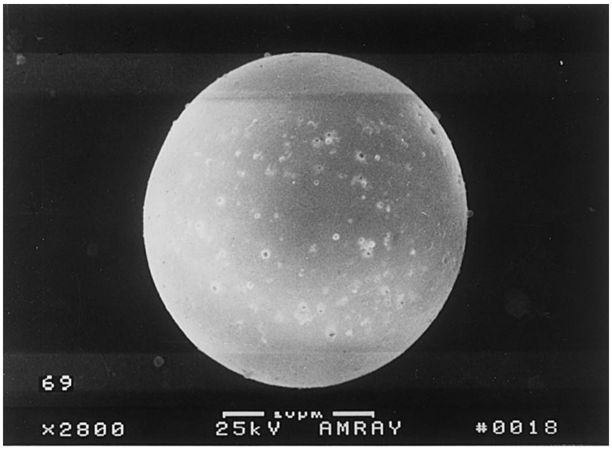
a: SEM



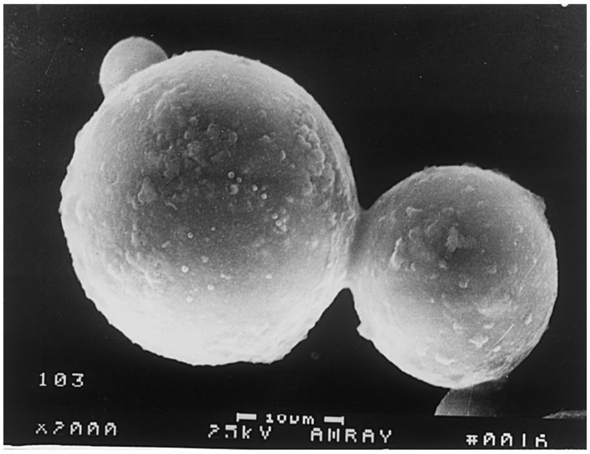
b: Histogram

Fig. 1 **a** Scanning electron micrograph (*SEM*) and **b** histogram of Fe_3O_4/poly(styrene-*co*-*N*-isopropylacrylamide)[*P*(*St-NIPAM*)] particles. Polymerization conditions: 4.92 wt% poly(ethylene glycol) (*PEG*) 3.00 wt% potassium persulfate (*KPS*) (based on monomer), 8.20 wt% Fe_3O_4 magnetic fluid, NIPAM/St(wt/wt) = 3/12, ethanol/H_2O(v/v) = 1.35

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



Fe_3O_4/PSt



Fe_3O_4/P(St-NIPAM)

Fig. 2 Surface morphology of **a** Fe_3O_4/PSt and **b** Fe_3O_4/P(St-NIPAM) particles. Polymerization conditions of Fe_3O_4/P(St-NIPAM): 4.92 wt% PEG, 3.00 wt% KPS (based on monomer), 8.20 wt% Fe_3O_4 magnetic fluid, NIPAM/St(wt/wt) = 4/11, ethanol/H_2O(v/v) = 1.35; polymerization conditions of Fe_3O_4/PSt: 4.92 wt% PEG, 3.00 wt% KPS (based on monomer), 8.20 wt% Fe_3O_4 magnetic fluid, 12.5 wt% St, ethanol/H_2O(v/v) = 1.35

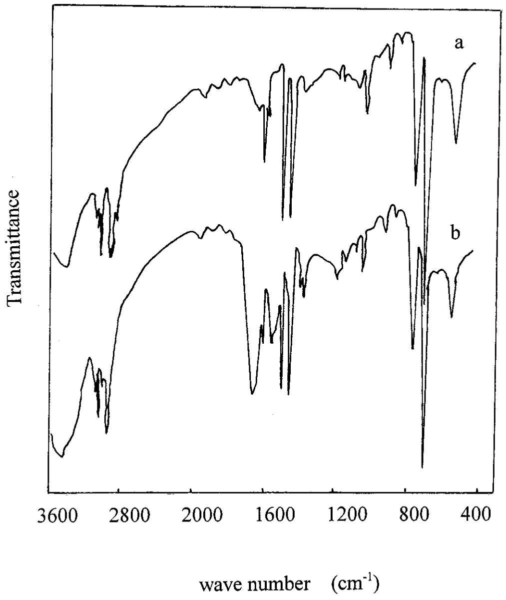


Fig. 3 IR spectrum of Fe_3O_4/PSt (*a*) and Fe_3O_4/P(St-NIPAM) (*b*) particles

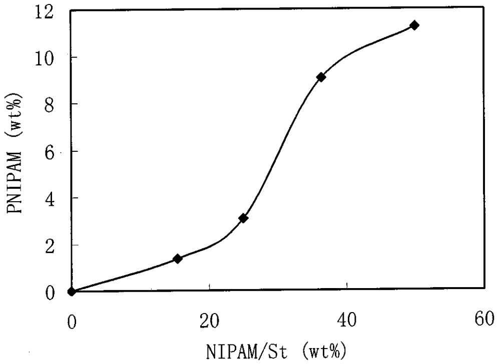


Fig. 4 Content of PNIPAM (based on total) in Fe_3O_4/P(St-NIPAM) particles. Polymerization conditions: 4.92 wt% PEG, 3.00 wt% KPS (based on monomer), 8.20 wt% Fe_3O_4 magnetic fluid, ethanol/H_2O(v/v) = 1.35

the region 2000–1668 cm^{-1} and the double peaks at 760 and 690 cm^{-1} are the characteristic bands of PSt.

The content of PNIPAM in the particles was obtained by calculation from the nitrogen data determined by elemental analysis. The results are shown in Fig. 4.

It was found that the content of PNIPAM in the final particles increases with increasing ratio of NIPAM/St, but the final ratios of PNIPAM/PSt of the particles are not equal to the ratio of NIPAM/St monomer. The reason is that the reactivity of NIPAM is higher than that of St and some PNIPAM homopolymer would be formed during the polymerization and remain in the medium [9].

Several DSC curves of final particles containing different amounts of PNIPAM are shown in Fig. 5, and the T_g data obtained from DSC are listed in Table 1. Each curve exhibited only one absorption peak, which indicates the polymers are not a blended composite of two homopolymers of PSt and PNIPAM, but a copolymer of P(St-NIPAM). The value of T_g obtained by DSC increased as the content of PNIPAM increased, and the T_g data obtained by experiment are approximated to the value of T_g obtained by calculation from Eq. (1).

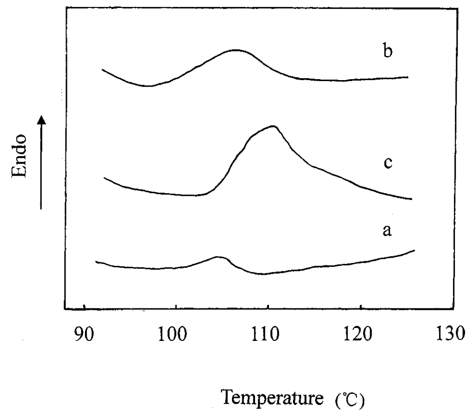


Fig. 5 Differential scanning calorimetry curves of Fe_3O_4/PSt and Fe_3O_4/P(St-NIPAM) particles. Polymerization conditions of Fe_3O_4/P(St-NIPAM): 4.92 wt% PEG, 3.00 wt% KPS (based on monomer), 8.20 wt% Fe_3O_4 magnetic fluid, ethanol/H_2O(v/v) = 1.35; content of PNIPAM in particles (based on total) *a* 0.00 wt%, *b* 3.07 wt%, *c* 11.24 wt%

Table 1 Glass-transition temperatures (T_g) of Fe_3O_4/poly(styrene-*co-N*-isopropylacrylamide)[*P*(*St-NIPAM*)] particles. T_g of the homopolymer of PNIPAM is 134.00 °C [10]

PNIPAM (wt%)	0.00	3.07	11.24
T_g/°C (Experimental)	105.00	105.81	109.57
T_g/°C (Calculated)	105.03	105.83	108.05

$$1/T_g = W_a/T_{ga} + W_b/T_{gb} \ , \qquad (1)$$

where T_g, T_{ga} and T_{gb} are the glass-transition temperatures of copolymer, polymer a and polymer b, respectively, and W_a and W_b are the weight percent of polymer a and polymer b, respectively.

The content of Fe_3O_4 in the Fe_3O_4/P(St-NIPAM) particles was obtained from the content of Fe determined from atomic adsorption spectrometry. The content of Fe_3O_4 entrapped in the Fe_3O_4/P(St-NIPAM) particles after being immersed in 1 M HCl solution at different times is shown in Fig. 6. The result shows that the content of Fe_3O_4 decreased rapidly within the first 48 h because the Fe_3O_4 which was not entrapped dissolved rapidly in the HCl solution. Our experimental results showed that 20–200 mg/g Fe_3O_4 could be entrapped tightly by copolymer under different polymerization conditions.

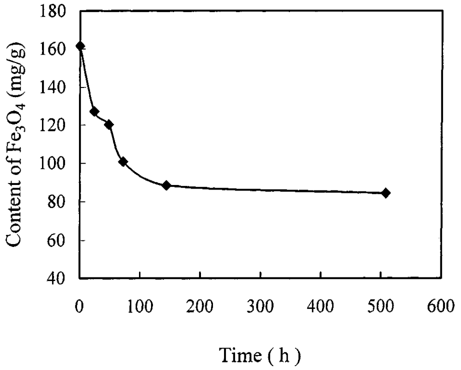


Fig. 6 Content of Fe_3O_4 in Fe_3O_4/P(St-NIPAM) particles at a certain time after immersion in 1 mol/l HCl solution. Polymerization conditions: 4.92 wt% PEG, 3.00 wt% KPS (based on monomer), 8.20 wt% Fe_3O_4 magnetic fluid, ethanol/H_2O(v/v) = 1.35

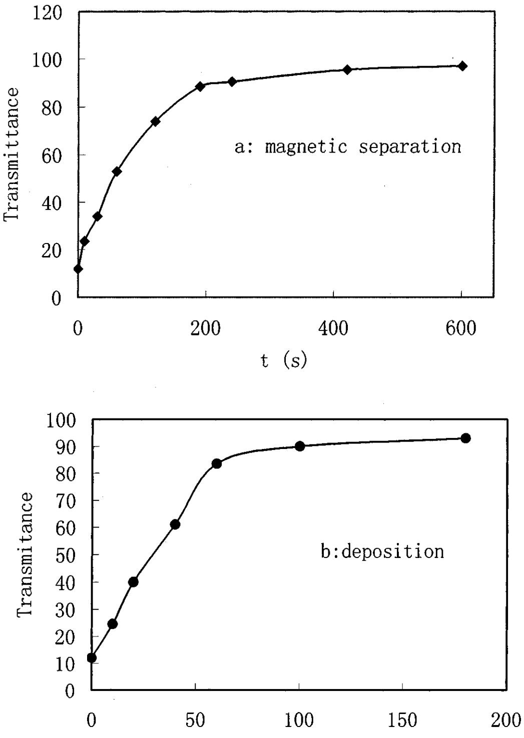


Fig. 7a, b Transmittance–time curves of the solution containing thermosensitive magnetic particles. Polymerization conditions: 4.92 wt% PEG, 3.00 wt% KPS (based on monomer), 8.20 wt% Fe_3O_4 magnetic fluid, NIPAM/St(wt/wt) = 4/11, ethanol/H_2O(v/v) = 1.35

The magnetic separation properties were measured by determining the transmittance of the particle suspension at a certain time after the particles had been separated by a 0.42 T magnetic field. The results are shown in Fig. 7. Our experiment showed Fe_3O_4/P(St-NIPAM) particles exploited an advantage of magnetic separation, such as rapid and easy operation. The transmittance of the suspension reached about 95% within 5 min with magnetic separation, while in separation by deposition, it took at least 2 h for the transmittance to reach about 90%.

The various curves of the hydrodynamic diameter of Fe_3O_4/P(St-NIPAM) particles and Fe_3O_4/PSt particles at different temperatures are shown in Fig. 8. As the

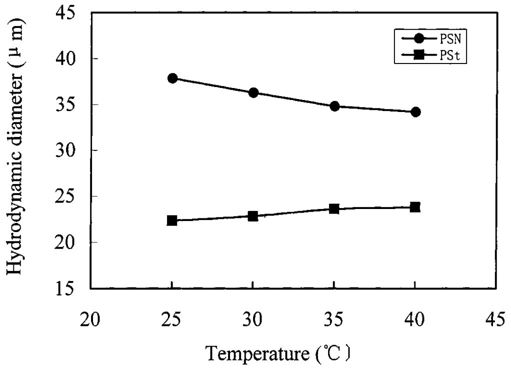


Fig. 8 Particle hydrodynamic size in double-distilled water at different temperature *PSN*: Fe_3O_4/P(St-NIPAM) particles; *PS*: Fe_3O_4/PST. Polymerization conditions: PSN, 4.92 wt% PEG, 3.00 wt% KPS (based on monomer), 8.20 wt% Fe_3O_4 magnetic fluid, NIPAM/St(wt/wt) = 4/11, ethanol/H_2O(v/v) = 1.35

temperature increased from 25 to 40 °C, the hydrodynamic size of the Fe_3O_4/P(St-NIPAM) particles decreased from 35.9 to 30.4 μm, exhibiting about 15% shrinkage. In contrast, the Fe_3O_4/PSt particles did not display similar behaviour under the same conditions; they became slightly bigger because of thermal expansion.

The previously mentioned response of Fe_3O_4/P(St-NIPAM) particles to the temperature change and magnetic field could provide some useful applications, such as enzyme immobilization, protein purification, recovery of enzymes, etc. We have investigated the interactions between Fe_3O_4/P(St-NIPAM) particles and protein (human serum albumin) and some of the results have been discussed in another article [11].

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