

Facile synthesis of tunable core-shell particles via one-step copolymerization

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Abstract A type of tunable particles consisting of a soft poly(N-isopropylacrylamide) (PNIPAM) core and a solid shell were directly synthesized in toluene via a facile one-pot copolymerization of N-isopropylacrylamide (NIPAM), (3-Methacryloyloxypropyl)methyldiethoxysilane (MADS), and N,N'-methylenebis(2-propenamide) (MBA). Of particular concern is the shells' potential to burst due to the swelling and expansion of the PNIPAM core after soaking in water, resulting in an outflow of the core. The toughness of the particle shells could be tuned by altering the feed ratio of MADS or MBA relative to NIPAM, resulting in a series of morphologies that varied from resembling a broken egg to being deformed core-shell spheres. The morphologies could be further modulated by dispersing the particles in different solvents.

Keywords Tunable core-shell particles · Deformable particles with flowable core · Responsive hybrid particles with egg structure · Tunable morphology

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Introduction

Core-shell structure has attracted much attention due to their advantage in performing various functions, e.g., providing protection for the core material [1–4], exchanging substances through a permeable shell [5, 6], or controlling the release of the core substance [7, 8] resulting in their wide application in many fields, e.g., catalysis [9], biology [10], and drug delivery [11, 12]. Core-shell particles with responsive polymer cores have been reported in the literature [8, 13, 14] and exhibit attractive functionalities and potential applications for catalysis [15] or biotechnology [16], including drug delivery [17] or controlled release [18].

Most of the reported core-shell particles with responsive polymer possessed a soft polymer shell, e.g., particles with an inorganic core and a responsive polymer shell [19–21], or a core-shell polymer with polymer shell and polymer core [22], which exhibited self-assembly behavior [23]. Core-shell hybrid particles with a solid shell provide the opportunity to demonstrate many of the advantages of a core-shell structure not realized with a soft shell, such as the ability to maintain particle morphology, prepare hollow spheres [24–26], or load cargos [27].

The responsive particles with inorganic shell reported here were fabricated with a template method [28–30] via a sol-gel process similar to the preparation of most core-shell particles [31] that used a soft core or a hard core as a template, e.g., P(NIPAM-co-AA)/silica particles [28], poly(N-isopropyl acrylamide-co-styrene)/SiO₂ [29], and poly(N-isopropylacrylamide-3-(trimethoxysilyl)propylmethacrylate)/silica particles [30] in which a functional group (e.g., carboxyl group, or silane groups) is usually needed. Particles with surface-inserted inorganic nanoparticles (SiO₂) were also prepared by Pickering emulsion polymerization [32, 33], resulting in a raspberry-like particle with silica nanoparticles on surface. The Pickering

method usually requires a complicated process, e.g., pre-preparation of the particles. In this study, we report a facile one-step copolymerization method to prepare a type of biomimetic particle with a tunable shell and a soft core of responsive polymer that exhibits changeable shapes; in which the shell with inorganic composition was formed directly in polymerization, resulting in core-shell particles with polymer core. The method provides a new route of producing core-shell particles and potentially preparing hollow spheres.

Experimental section

Materials

The monomers, N-isopropylacrylamide (NIPAM, 99%) and (3-Methacryloyloxypropyl) methyl-diethoxysilane (MADS, 98%), were respectively purchased from J&K Scientific Ltd. and Tokyo Chemical Industry Co. Ltd. The crosslinker, i.e., N,N'-methylene bisacrylamide (MBA, 98%), and the initiator, i.e., 2,2'-azodiisobutyronitrile (AIBN, 98%), were from Tianjin Fuchen Chemical Regents Factory. Toluene (99.7%) and 95% ethanol were respectively, purchased from Beijing Chemical Works and Beijing Tongguang Fine Chemicals Company. All of the chemical reagents were used without any purification after purchase.

Synthesis of particles

The polymerization was carried out in toluene using a 100-mL three-neck flask equipped with a magnetic stirrer, in which NIPAM and MADS were used as monomers while MBA served as the crosslinker. Typically, NIPAM, MBA, MADS, and AIBN were dissolved into 50 mL toluene with a feed molar ratio of 100: 10: 5: 1. After deoxygenation with nitrogen for 30 min, the polymerization was carried out at 70 °C for 4 h. The resulting product was collected by centrifugation and washed with toluene. A transparent gel-like particle was obtained. In the absence of MADS, pure poly(N-isopropylacrylamide) (PNIPAM) particles are obtained in polymerization.

Characterization

The morphology of the particles was investigated by scanning electron microscopy (SEM, JEOL7600). SEM samples were prepared as follows: particles were ultrasonically dispersed in various solvents (distilled water, 95% ethanol or toluene), followed by dripping the solutions onto silicon and air-drying. The SEM sample was sputtered with platinum before observation.

The structure of the particles was characterized with transmission electron microscopy (TEM). Samples were prepared

by dripping the dispersion of particles onto a carbon-coated copper grid, followed by air-drying. TEM micrographs were obtained with a JEM-2200FS instrument.

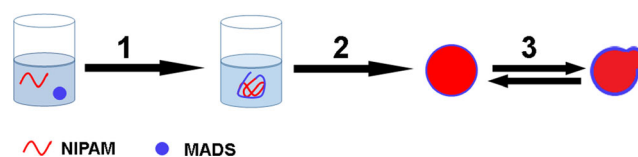
The composition of the particles was investigated by thermal gravimetric analysis (TGA), which was carried out in nitrogen using a Netzsch TG209F1 instrument. In order to remove the water in the sample, the following temperature program was carried out: Particles were first heated to 100 °C at a rate of 10 °C/min; the temperature was then kept at 100 °C for 15 min and finally, the temperature increased to 600 °C at a heating rate of 10 °C/min.

Fourier transform infrared spectroscopy (FT-IR) measurement of the particles was carried out on a FTIR spectrometer (Bruke TENSOR 27).

Results and discussion

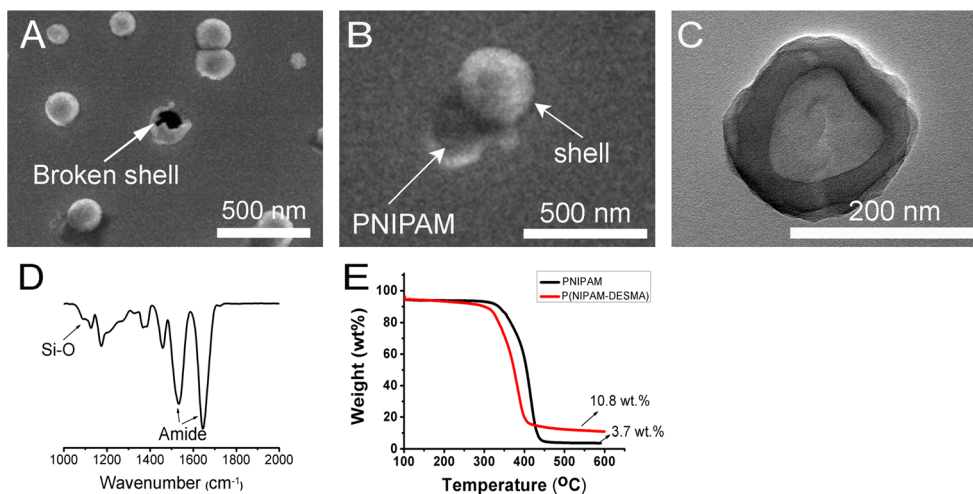
Novel soft core/solid shell particles were synthesized in a one-pot precipitation polymerization via phase separation. Most PNIPAM particles are prepared via aqueous polymerization; however, we found that the polymerization could be carried out in organic solvent, indicating the possibility to prepare a wide range of copolymers with NIPAM. The copolymerization was performed in toluene without any surfactant. Since different solubility and reactivity ratios exist between the two monomers in toluene, the PNIPAM chains would precipitate and form a core, resulting in a phase separation between the polymer chains and silicon. Scheme 1 shows how the core-shell particles were synthesized. Typically, N-isopropylacrylamide (NIPAM) and 3-Methacryloyloxypropyl)methyl-diethoxysilane (MADS) were used as monomers while MBA was used as a crosslinking agent. The polymer particles were synthesized in toluene at 70 °C using MADS and MBA feed molar ratios relative to NIPAM (i.e., the S/N and M/N ratio, respectively) of 5 and 10 mol%, respectively. The particles were collected after being washed with toluene. These particles were then re-dispersed into different solvents before checking their morphology with SEM.

As shown in Fig. 1a, b, particles with a size of approximately 200 nm were observed after the formed particles were dispersed into water. Many of the particles were broken, with the soft polymer escaping the shell, such as a broken egg. Additional particles can be seen in Fig. S1. The “broken egg”



Scheme 1 Schematic illustration for one-step polymerization of tunable core-shell particles. (1) Copolymerization of NIPAM and MADS in organic solvent with the help of MBA (2) the formation of a core-shell structure through a phase separation of the different polymer chains, and (3) the change of particle shapes in different solvents

Fig. 1 The as-prepared particle with a flowable core. **a** SEM image of particles. **b** the magnified image of a broken particle with a flowing core. **c** TEM image of particles. **d** IR spectra of the as-prepared P(NIPAM-MADS). **e** TGA curves of P(NIPAM-MADS) and the pure PNIPAM particles. Particles were prepared with a S/N ratio of 5 mol% and an M/N ratio of 10 mol%



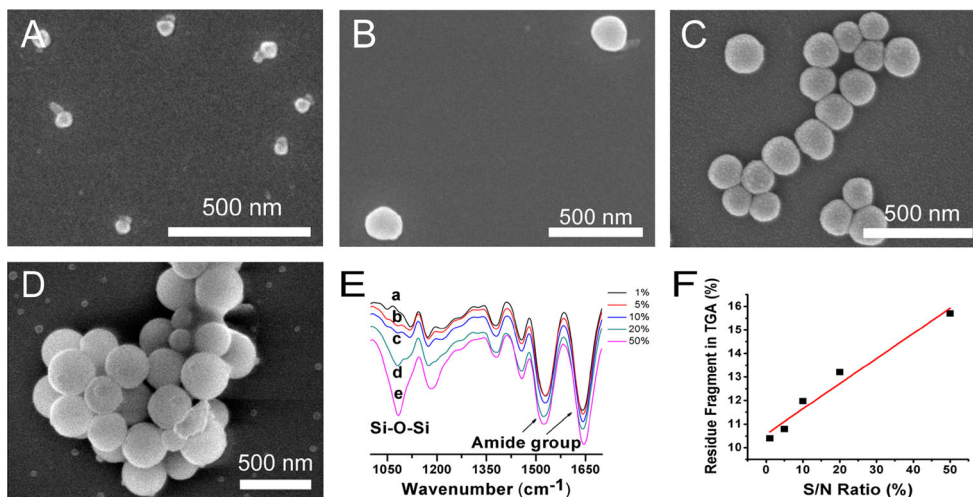
result could be attributed to the swelling of the polymer chains that occurred after soaking in water, rupturing the shell. This phenomenon indicated that the inner core of the particles consisted mainly of the soft polymer, PNIPAM, while the solid shell contained silicon. The experiment also confirmed that MADS hydrolyzed in water and became hard due to the formation of Si–O–Si bonds, while the wet PNIPAM exhibited extendibility of the polymer chains, as shown in Fig. 1b. In short, the particles possessed a solid shell and a soft core of PNIPAM. As shown in Fig. 1c, the TEM images clearly show that the particles have a core-shell structure, confirming that novel core-shell particles were created via polymerization. Since this polymerization was performed in an organic solvent, this process could be applied using numerous other comonomers to prepare core-shell particles with different shells.

The composition of these particles was characterized with infrared spectroscopy (IR) (Fig. 1d). The strong absorbance at 1647 and 1502 cm^{-1} was assigned to the amide group, indicating that the particles mainly consisted of NIPAM polymer. The absorbance at 1080 cm^{-1} indicated the existence of silicon. Their thermal stability was investigated with TGA. The

onset value of particle decomposition was approximately 331 $^{\circ}\text{C}$ (Fig. 1e). The particle residue was 10.8 wt.% for the P(NIPAM-MADS) particles, which is considerably higher than that of the pure PNIPAM particles (3.7 wt.%), confirming the introduction of silicon into the particles.

A series of particles was synthesized with different S/N ratios while the M/N ratio was fixed at 10 mol%. As shown in Fig. 2a, the as-prepared particles with S/N ratio of 1 mol% exhibited a bi-compartmental structure in water due to the outflow of PNIPAM as a result of too thin shells (Fig. 2a). The particles were very small, approximately 100 nm, and the size of the biggest particles was less than 200 nm (Fig. S2a). Increasing the S/N ratio to 5 mol% resulted in the typical size of the particles increasing to close to 200 nm. The shell of the particles became hard, giving rise to a propensity to crack due to the swelling of the polymer core when placed in water, as shown in Fig. 1. When the S/N ratio was further increased to 10 or 20 mol%, the diameter of the particles became greater than 200 nm. The strength of the particle shells also improved such that most of particles remained unbroken even if they were ultrasonicated in water. Outflow of the polymer core was not typically observed for these larger particles

Fig. 2 SEM images of particles prepared with different S/N ratios. **a** 1 mol%. **b** 10 mol%. **c** 20 mol%. **d** 50 mol%. **e** IR spectra of particles prepared with different S/N ratios. **f** TGA residue fragment of particles as a function of the S/N ratio. The polymerization was carried out at 70 $^{\circ}\text{C}$ while the M/N ratio was fixed at 10 mol%



(Fig. 2c). However, their shape often became non-spherical due to the expanding core, as shown in Fig. 2b, c. Supplementary images of the particles can be found in Fig. S2b, c. When the S/N ratio reached 50 mol%, particles became very large with a diameter of approximately 300 nm. Moreover, the morphology of particles became spherical (Fig. 2d). In addition, some small particles were observed near the large particles, which could possibly be silica particles produced after the MADS was exhausted. In sum, the strength of particles' shells could be increased and their shape in water evolved from a broken egg shape to deformed particles to spheres by increasing the feed ratio of MADS. This result further confirmed that the shell formation primarily resulted from the MADS. In addition, the particle sizes also gradually became larger with the increase in the MADS feed.

The composition of the particles was characterized with IR spectroscopy (Fig. 2e). The absorbance assigned to Si–O at 1080 cm^{-1} was gradually enhanced with an increase in the S/N feed ratio. The amide group peaks at 1539 and 1647 cm^{-1} indicated an increasing content of silica in particles.

TGA and DTG curves are shown in Fig. S3. The residue fragment at $650\text{ }^\circ\text{C}$ gradually increased from 10.4 to 15.7 wt.% as the feed ratio of MADS increased from 10 to 50 mol%. The residue results from TGA are shown in Fig. 2f as a function of S/N ratio and clearly exhibit a linearly increasing residue dependent on the feed ratio of MADS. All of the DTG curves also show a shoulder peak approximately $280\text{ }^\circ\text{C}$ in addition to the main decomposition peak at approximately $370\text{ }^\circ\text{C}$ (Fig. S3b), confirming the presence of two different phases in the particles.

The above particles were synthesized with a fixed M/N ratio at 10%. When the feed ratio of MADS was fixed in polymerization, e.g., a 5 mol% S/N ratio, the morphologies and compositions of particles could further be tuned by changing the M/N ratio, i.e., changing the feed ratio of the crosslinking agent MBA. When the M/N ratio was reduced to 5 mol%, the outer shell burst (Fig. 3a) and the particles were destroyed. Additional images of particles with disintegrated shells can be seen in Fig. S4. The disintegration of the shell could be attributed to a low degree of crosslinking, resulting in fragile shells easily destroyed during the expansion of the swollen PNIPAM chains in water. This result again confirmed that the shell formation resulted from the MADS, which hydrolyzed in water and became stiff and brittle. Moreover, if particles were synthesized with a 5 mol% M/N

ratio, the shells of most of the particles disintegrated in water, regardless of whether there was a low or high concentration of MADS in polymerization.

Fixing the S/N ratio at 5 mol% while raising the M/N ratio to 10 mol% resulted in as-prepared particles with stiff shells that merely broke in half (Fig. 1) instead of disintegrating into pieces. By further increasing the M/N ratio to 20 mol%, the strength of particles shells significantly increased and it was difficult to find broken shells; however, it was still possible for the PNIPAM soft core to flow out of the shell from a crack (Fig. 3b, S5A), and some non-spherical particles still existed. If the M/N ratio was increased to 30 mol% during polymerization, the morphology of the particles became stably spherical and no broken shells were observed, as shown in Figs. 3c and S5B. The change in morphology could mainly be attributed to the high toughness of the shells when the feed ratio of the crosslinking agent was very high. In addition, the reduced swelling of PNIPAM with increasing MBA might also be helpful for maintaining a spherical shape; however, the reduction in swelling is likely to be less important because the as-prepared particles synthesized using low concentrations of MADS were also broken even when the feed ratio of MBA was very high. Nonetheless, the crosslinking agent is very important for maintaining the integrity of particles' morphology.

The shapes of the above particles could be controlled by dispersing them into different solvents (Fig. S6). In general, the particles were spherical in organic solvents and became non-spherical or broken in water. For example, for the particles prepared with M/N and S/N ratios each at 10 mol%, if the SEM sample was prepared directly in toluene, they usually had good spherical morphology (Fig. S6a). However, if they were dispersed into 95% ethanol, the particles were less spherical (Fig. S6b), and if they were dispersed in water, we obtained deformed particles with a vertex (Fig. S6c). These results also indicated that the shell was permeable, which can further be proven by TEM characterization after particles absorbed metal ions (Fig. S7), and this is necessary for applications in biologic medicine or catalysis.

Conclusions

We synthesized tunable particles with a core-shell structure via a facile one-pot method, which is potentially suitable to

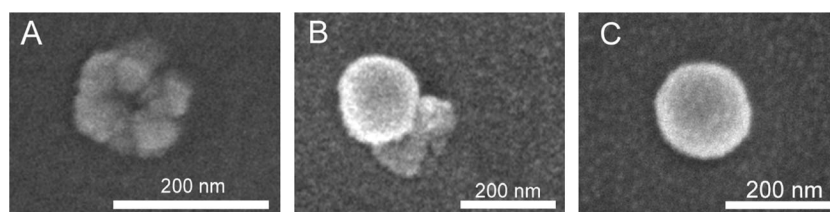


Fig. 3 SEM images showing the morphology of the particles as a function of M/N ratios. **a** 5 mol%. **b** 20 mol%. **c** 30 mol%. The S/N ratio was fixed at 5 mol% during polymerization

prepare particles on a large scale. The compositions of the as-prepared particles with a PNIPAM core could be tuned conveniently by adjusting the S/N and the M/N feed ratio, resulting in a series of different particle morphologies. These “egg structure” particles have wide potential application in drug delivery, catalysis, or microelectronics.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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