Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 5797–5803 **5797**
DOI: 10.1021/ma1008012

Hairy Hollow Microspheres of Fluorescent Shell and Temperature-Responsive Brushes via Combined Distillation-Precipitation Polymerization and Thiol−ene Click Chemistry

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Received April 13, 2010; Revised Manuscript Received June 8, 2010

ABSTRACT: Nearly monodispersed silica core−poly(*N*-vinylcarbazole) shell (SiO_2@PVK) microspheres of 226, 235, and 244 nm in average diameters were first synthesized by surface-initiated distillation-precipitation polymerization of *N*-vinylcarbazole, in the presence of divinylbenzene, from the 197 nm silica template microspheres prepared by the sol−gel reaction of tetraethyl orthosilicate (TEOS) and 3-(trimethoxysilyl)propyl methacrylate (MPS). The SiO_2@PVK−PNIPAM core−shell hairy microspheres (PNIPAM = poly(*N*-isopropylacrylamide)) were subsequently prepared by grafting the PNIPAM chains (M_n = 11 600 g/mol, polydispersity index = 1.32), prepared a priori by reversible addition−fragmentation chain transfer (RAFT) polymerization, to the SiO_2@PVK microspheres via the thiol−ene click chemistry. The grafting density of PNIPAM brushes on the SiO_2@PVK microspheres was about 0.1 chains/nm^2. Hairy hollow microspheres with a fluorescent and cross-linked PVK shell and temperature-responsive PNIPAM brushes were finally obtained, after selective removal of the inorganic silica core from the SiO_2@PVK−PNIPAM microspheres by HF etching. The air@PVK−PNIPAM hairy hollow microspheres were characterized by field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), fluorescence spectroscopy, and dynamic laser scattering (DLS).

1. Introduction

Hollow micro- and nanostructures have attracted considerable interest because of their potential applications in drug delivery and catalysis, and as anode materials for lithium ion batteries.[1−6] Moreover, hollow polymer microspheres with tailored morphology and physicochemical properties have been prepared to broaden their applications.[7−10] Various approaches, including dynamic swelling method,[11] layer-by-layer deposition[12] and self-assembly of block copolymers and dendrimers[13−16] have been developed for the fabrication of functional hollow polymer structures. Poly(*N*-vinylcarbazole) (PVK) is a well-studied electroactive material for optoelectronic applications.[17−19] Accordingly, it would be interesting to fabricate hollow PVK micro- or nanospheres with tailored surface properties via, for example, grafting of functional molecular brushes, and explore their applications in nonlinear optics and waveguides, photocatalysis, and chemical and optical sensors.[20]

The thiol−ene chemistry, which involves the hydrothiolation of a C═C bond, has recently attracted considerable research interest in polymer synthesis because of its characteristic "click chemistry".[21,22] The thiol−ene click reaction does not require additional transition metal catalysts, has good tolerance for many solvents, and is generally fast (in a matter of seconds) even at ambient temperature and pressure.[23,24] Thiol−ene click chemistry has been explored for the preparation of ploy((mercaptopropyl)methylsiloxane) (PMMS) stamps and microarrays,[25,26] modification of glass surfaces,[27] and synthesis of macrocyclic polymers[28] and branched carbosilane-thioether dendrimers.[29] On the other hand, distillation−precipitation polymerization, in combination with sol−gel chemistry, has been explored for the fabrication of core−shell and hollow polymer micro- and nanospheres with controllable morphology and tailored functionality.[30−32] A combination of different chemical synthesis approaches has also been used for the design and synthesis of novel macromolecular structures and functional materials.[33−35]

Herein, we report an approach to the preparation of narrowly distributed hairy hollow polymer microspheres with a cross-linked poly(*N*-vinylcarbazole) (PVK) shell and poly(*N*-isopropylacrylamide) (PNIPAM) brushes via combined sol−gel reaction, distillation-precipitation polymerization and thiol−ene click chemistry. Combination of the robust thiol−ene click chemistry with the traditional sol−gel reaction and radical polymerization technique has provided a novel strategy for the preparation of inorganic-polymer core−shell hybrids and hollow polymer microstructures with tailored surface functionalities.

2. Experimental Section

2.1. Materials. Tetraethyl orthosilicate (TEOS, 98%), 3-(trimethoxysilyl)propyl methacrylate (MPS, 98%), *N*-vinylcarbazole (VCz, 97%), and *N*-isopropylacrylamide (NIPAM, 97%) were received from Sigma-Aldrich Chemical Co. and used without further purification. Divinylbenzene (DVB55, containing 55% divinylbenzene isomers, Sigma-Aldrich) was washed with 5% aqueous sodium hydroxide and water, and then dried over anhydrous magnesium sulfate prior to use. 2,2′-Azobis(isobutyronitrile) (AIBN, Sigma-Aldrich) was recrystallized in methanol. 2-Dodecylsulfanylthiocarbonylsulfanyl-2-methyl propionic acid (DMP) was synthesized according to the literature.[36] 2,2′-Azobis(4-methoxy-2,4-dimethyl valeronitrile) (V70, Wako, 96%), hydrofluoric acid (HF, Riedel-de Haën, 48%), ammonia (Merck, 25%), and acetonitrile (Merck, HPLC grade) were used as received. The Spectra-Por dialysis membranes were obtained from

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Table 1. Size, Size Distribution, and Shell Thickness of the SiO_2@PVK Core−Shell Microspheres

sample	D_n[a] (nm)	D_w[a] (nm)	PDI[a]	shell thickness[b] (nm)	CV[c] (%)
SiO_2−MPS core	197	203	1.03		9
SiO_2@PVK core−shell-1[d]	226	229	1.01	14	6
SiO_2@PVK core−shell-2[d]	235	240	1.02	19	5
SiO_2@PVK core−shell-3[d]	244	249	1.02	23	8

[a] D_n is the number-average diameter, D_w is the weight-average diameter, and PDI is the polydispersity index. [b] The shell thickness of the core−shell was measured from the FESEM images. [c] CV is the coefficient of variation or the ratio of standard deviation to the mean. [d] The SiO_2@PVK (PVK = poly(*N*-vinylcarbazole)) core−shell microspheres were prepared via surface-initiated distillation-precipitation polymerization of *N*-vinylcarbazole (VCz, monomer) and divinylbenzene (DVB, cross-linker) in acetonitrile. Different thickness of the polymer shell on silica core was achieved by varying the weight ratio of (VCz + DVB) to SiO_2−MPS (MPS = 3-(trimethoxysilyl)propyl methacrylate) from 3 to 3.5 and 4. The 2,2′-azobis(isobutyronitrile) (AIBN, initiator) was kept at 2 wt % of (VCz + DVB), and the weight ratio of VCz to DVB was 1:1.

Spectrum Laboratories, Inc. (molecular weight cutoff: 12 000−14 000).

2.2. Preparation of Silica Core−Poly(*N*-vinylcarbazole) Shell (SiO_2@PVK) Microspheres. MPS-modified silica template microspheres were prepared according to modified Stöber method.[37,38] About 9 mL of TEOS was added to a mixture of 150 mL of ethanol, 15 mL of deionized water, and 3 mL of ammonia. The mixture was stirred vigorously at room temperature for 2 h. Then, 2 mL of MPS was added to the silica sol over a period of 24 h. After the reaction, the MPS modified silica microspheres (SiO_2−MPS) were purified by three redispersion/centrifugation cycles in a 1:1 ethanol:deionized water mixture (100 mL:100 mL).

The fluorescent SiO_2@PVK core−shell microspheres were prepared by distillation-precipitation polymerization of VCz, with DVB as the cross-linker and AIBN as the initiator, in acetonitrile.[30] Briefly, about 0.1 g of the SiO_2−MPS seed microspheres were dispersed in 20 mL of acetonitrile with the aid of sonification for 30 min. A mixture of VCz (0.15 g, 0.78 mmol), DVB (0.15 mL, 1 mmol) and AIBN (6 mg, 0.036 mmol) was then added to the flask to initiate the polymerization. The polymerization reaction was allowed to proceed for 3 h under reflux conditions. The resultant SiO_2@PVK microspheres were dispersed in 30 mL of THF, followed by reprecipitation in 10 mL of *n*-hexane under centrifugation (8,000 rpm), and then in 30 mL of acetone and 30 mL of ethanol to remove the unreacted monomers and oligomers. The SiO_2@PVK microspheres were dried in a vacuum oven at 50 °C until a constant weight was obtained. PVK shells of 14, 19, and 23 nm in thickness were tuned by using VCz feed concentrations of 0.04, 0.045, and 0.05 M, respectively. Finally, SiO_2@PVK microspheres with diameters of 226, 235, and 244 nm were obtained (Table 1).

2.3. Synthesis of Thiol-Terminated Poly(*N*-isopropylacrylamide) (PNIPAM−SH) via RAFT Polymerization. The thiol-terminated PNIPAM (PNIPAM−SH) chains were synthesized via reversible addition−fragmentation chain transfer (RAFT) polymerization of NIPAM and subsequent thiol-modification.[39] The NIPAM monomer (2.26 g, 0.02 mol), V-70 initiator (3.3 mg, 0.01 mmol) and DMP chain transfer agent (CTA, 31.5 mg, 0.08 mmol) were introduced into 2 mL of THF in a dry flask. The solution was degassed with argon for 20 min. The reaction tube was then sealed and stirred at 65 °C for 3 h. The reaction mixture was diluted with THF, and poured into an excess volume (200 mL) of diethyl ether to precipitate the polymer product. The as-prepared polymers chains (PNIPAM−CTA) were further purified by three cycles of dispersion and precipitation in THF and diethyl ether, respectively. About 1.5 g of light-yellow powder was obtained after drying the sample in a vacuum oven at room temperature overnight (Gel permeation chromatography measurements: M_n = 11 600 g/mol, polydispersity index or PDI = 1.32).

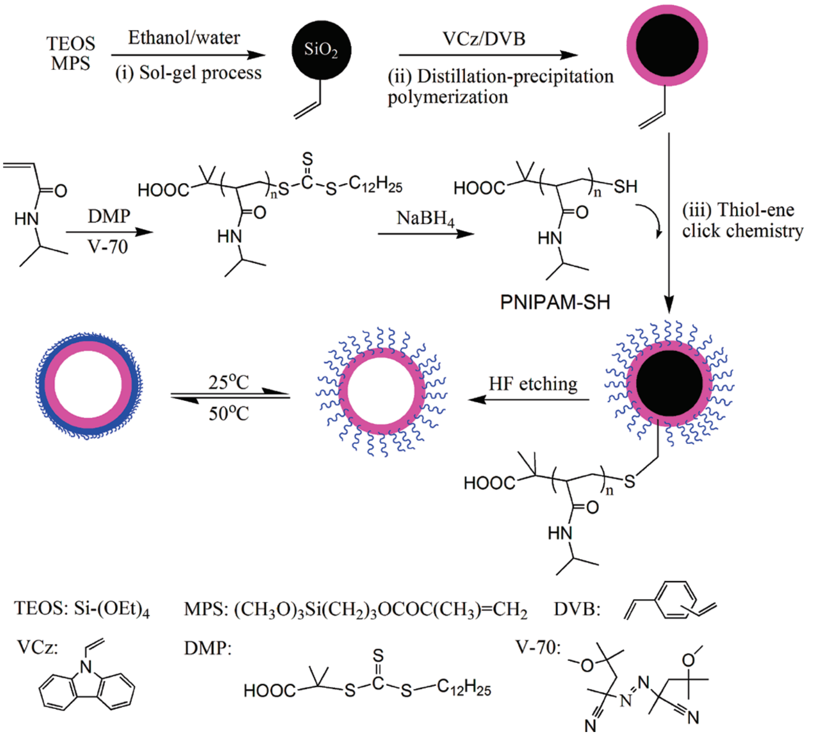
About 0.4 g of the so-obtained PNIPAM−CTA was dispersed in 50 mL of methanol. Then, about 1 mL of $NaBH_4$ in methanol solution (1 M) was added to the polymer solution under vigorous stirring. The reaction mixture was stirred at room temperature for 48 h under an argon atmosphere to ensure complete reduction of the dithioester terminal groups to thiol groups. During this period, the originally light-yellow solution turned colorless. The resultant thiol-terminated PNIPAM (PNIPAM−SH) was dialyzed against deionized water for 72 h and the solvent was removed by rotary evaporation. Finally, about 0.35 g of PNIPAM−SH was obtained as a white powder.

2.4. Preparation of the SiO_2@PVK−PNIPAM Hairy Core−Shell Microspheres by Thiol−Ene Click Reaction. About 0.075 g of the SiO_2@PVK microspheres (SiO_2@PVK core−shell-2 of Table 1) and 0.15 g of PNIPAM−SH was introduced into 10 mL of acetonitrile in a reaction flask under vigorous stirring. Then, about 0.02 g of AIBN initiator was added into the reaction mixture after degassing by argon for 15 min. The flask was sealed and the reaction was allowed to proceed at 70 °C for 18 h. The resultant hairy SiO_2@PVK−PNIPAM hybrid core−shell microspheres were purified using procedures similar to those for the SiO_2@PVK core−shell microspheres.

2.5. Preparation of the PVK−PNIPAM Hairy Hollow Microspheres (air@PVK−PNIPAM Microspheres). The hairy hollow air@PVK−PNIPAM microspheres were prepared by removal of the inorganic SiO_2 core from the SiO_2@PVK−PNIPAM hairy microspheres by HF etching. About 50 mg of the SiO_2-@PVK−PNIPAM microspheres was stirred in 10 mL of 20% HF at room temperature for 24 h to ensure the complete dissolution of the silica shell. (**Caution!** HF is hazardous and very corrosive. Goggles and gloves must be worn during the operation.) The excess HF and SiF_4 were removed from the air@PVK−PNIPAM hairy hollow microspheres by dialysis in deionized water for 1 week. Finally the hairy hollow microspheres were freeze-dried. To investigate the mechanical stability of the hollow microspheres, the as-synthesized hairy PVK−PNIPAM hollow microspheres were immersed in HCl solution of pH 2 for 24 h and then NaOH solution of pH 12 for 24 h. Finally, the hairy hollow microspheres were collected by centrifugation at 10,000 rpm in an Eppendorf 5801 centrifuge.

2.6. Characterization. Field-emission scanning electron microscopy (FESEM) and energy-dispersive X-ray (EDX) were carried out on a JEOL JSM-6700 scanning electron microscope. Transmission electron microscopy (TEM) images were obtained on a JEOL TEM-2010 transmission electron microscope. Fourier transform infrared spectra (FT-IR) analysis was carried out on a Bio-Rad FTS 135 Fourier transform infrared spectra spectrophotometer, and the diffuse reflectance spectra were scanned over the wavenumber range of 4000−400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos AXIS Ultra HSA spectrometer equipped with a monochromatized Al Kα X-ray source (1468.6 eV photons). The dynamic laser scattering (DLS) measurements were performed on a Brookhaven 90 plus laser light scattering spectrometer at the scattering angle $\theta = 90°$. The hydrodynamic diameter of microspheres was obtained by averaging the values from five measurements. The UV−visible absorption spectra in the wavelength range of 200 to 800 nm were obtained on a Shimadzu UV-3101PC spectrophotometer. The fluorescence spectra were measured on a Shimadzu RF-5031 spectrophotometer, with an excitation wavelength of 295 nm. The polydispersity index (PDI) of the

Scheme 1. Schematic Illustration of the Fabrication of air@PVK−PNIPAM Hairy Hollow Microspheres by Combined Sol−Gel Reaction, Distillation−Precipitation Polymerization, and Thiol−Ene Click Chemistry (PVK = Poly(*N*-vinylcarbazole); PNIPAM = Poly(*N*-isopropylacrylamide))



microspheres was calculated from the following statistical formulas:[44]

$$\mathrm{PDI} = D_{\mathrm{w}}/D_{\mathrm{n}} \quad D_n = \sum_{i=1}^{k} n_i D_i \Big/ \sum_{i=1}^{k} n_i \quad D_{\mathrm{w}} = \sum_{i=1}^{k} n_i D_i^{\,4} \Big/ \sum_{i=1}^{k} n_i D_i^{\,3}$$

where PDI is the polydispersity index, D_{n} is the number-average diameter, D_{w} is the weight-average diameter, D_i is the diameter of the microspheres, and n is the number of microspheres. In each case, about 50−100 microspheres in the FESEM image were used for the analysis. Coefficient of variation (CV), defined as the ratio of the standard of deviation to the mean, was used to estimate the error in microsphere size, D_{n}, determination. The molecular weight and molecular weight distribution of PNIPAM prepared from RAFT polymerization and the corresponding thiol-terminated PNIPAM were characterized by gel permeation chromatography (GPC). GPC measurements were carried out using *N*,*N*-dimethylformamide (DMF) as the eluent at a flow rate of 1.0 mL min^{-1}. The calibration curve was generated using polystyrene standards with molecular weights of 1660, 5000, 10050, 28500, and 65500 g/mol.

3. Results and Discussion

Procedures for the synthesis of poly(*N*-vinylcarbazole)-poly(*N*-isopropylacrylamide) hairy hollow microspheres (air@PVK−PNIPAM microspheres) with a fluorescent PVK shell and temperature-responsive PNIPAM brushes are illustrated in Scheme 1. Initially, the silica-3-(trimethoxysilyl)propyl methacrylate (SiO_2−MPS) template microspheres with an average diameter of about 200 nm were synthesized via the modified Stöber process.[37,38] The field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images of the SiO_2−MPS seed microspheres are shown in Figure 1, parts a and b, respectively. The images reveal that the SiO_2−MPS template microspheres are narrowly distributed with a smooth surface. The FT-IR spectrum of the SiO_2−MPS microspheres is shown in Figure 2a. The absorption peak at 1098 cm^{-1} is assigned to the asymmetric stretching vibration of the Si−O−Si bonds. The absorption peak at 1631 cm^{-1} is attributable to the stretching vibration of vinyl groups on the SiO_2−MPS surfaces.[30] These carbon−carbon double bonds will serve as initiation and anchoring sites for the subsequent surface-initiated radical polymerization for the preparation of SiO_2@PVK core−shell microspheres.

Narrowly dispersed SiO_2@PVK microspheres were synthesized by distillation-precipitation polymerization of *N*-vinylcarbazole (VCz), in the presence of divinylbenzene (a cross-linking agent), from the SiO_2−MPS template microspheres. TEM images of the so-obtained SiO_2@PVK microspheres with two different PVK shell thicknesses of about 14 and 19 nm are shown in Figure 1, parts c and d, respectively. A uniform polymeric shell of lower image contrast surrounding the inorganic silica core is readily discernible. The cross-linked PVK shells of different thickness can be obtained via adjustment of the initial VCz monomer concentration during distillation-precipitation polymerization. The size, size distribution and shell thickness of the resultant SiO_2@PVK microspheres are summarized in Table 1. The X-ray photoelectron spectroscopy (XPS) wide-scan spectra of the SiO_2−MPS template microspheres and the SiO_2@PVK core−shell-2 microspheres of Table 1 are shown in Figure 3, parts a and b, respectively. The photoelectron lines at the binding energies (BE) of about 102 and 154 eV are associated with the Si 2p and Si 2s species from the SiO_2−MPS template microspheres. The Si 2p and Si 2s signals are barely discernible in the XPS wide-scan spectrum of the SiO_2@PVK microspheres (Figure 3b), consistent with the fact that the grafted PVK shell thickness (~19 nm) is greater than the probing depth of the XPS technique (~8 nm in an organic matrix[40]).

Parts a and b of Figure 4 show the UV−visible absorption spectra of the SiO_2−MPS microspheres before and after surface grafting of a cross-linked PVK shell. For the SiO_2@PVK core−shell microspheres, the absorption peak at 295 nm, which

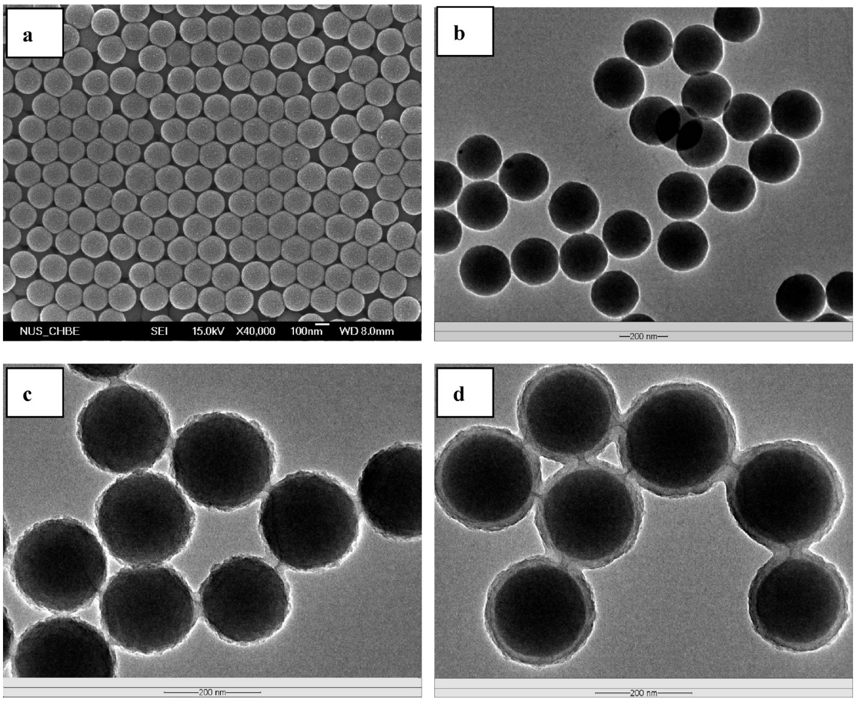


Figure 1. (a) FESEM and (b) TEM images of the SiO_2−MPS seed microspheres prepared by sol−gel process; TEM images of the (c) SiO_2@PVK core−shell-1 and (d) SiO_2@PVK core−shell-2 microspheres of Table 1 prepared by distillation-precipitation polymerization (MPS = 3-(trimethoxysilyl)propyl methacrylate; PVK = poly(*N*-vinylcarbazole)). The respective scale bars for parts a−d are 100, 200, 200, and 200 nm.

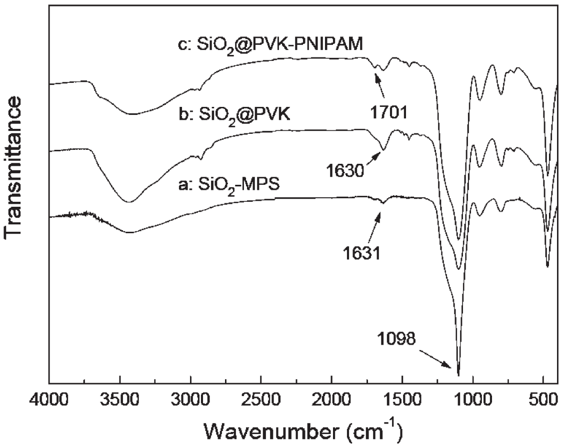


Figure 2. FT-IR spectra of the (a) SiO_2−MPS seed microspheres, (b) SiO_2@PVK core−shell-2 microspheres of Table 1, and (c) SiO_2-@PVK−PNIPAM hairy core−shell microspheres (MPS = 3-(trimethoxysilyl)propyl methacrylate; PVK = poly(*N*-vinylcarbazole); PNIPAM = poly(*N*-isopropylacrylamide)).

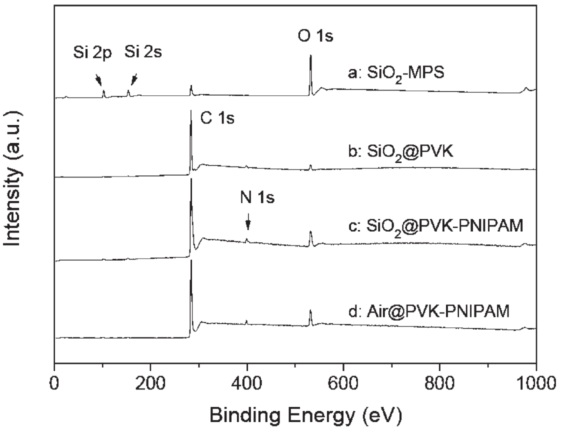


Figure 3. XPS wide-scan spectra of the (a) SiO_2−MPS seed microspheres, (b) SiO_2@PVK core−shell-2 microspheres of Table 1, (c) SiO_2@PVK−PNIPAM hairy core−shell microspheres, and (d) air@-PVK−PNIPAM hairy hollow microspheres (MPS = 3-(trimethoxysilyl)propyl methacrylate; PVK = poly(*N*-vinylcarbazole); PNIPAM = poly(*N*-isopropylacrylamide)).

is absent in the SiO_2−MPS precursor microspheres, is characteristic of PVK.[41] The fluorescence spectrum of the SiO_2@PVK microspheres dispersed in ethanol (0.5 mg/mL), measured at an excitation wavelength of 295 nm, is shown in Figure 5a. The two emission peaks at 349 and 365 nm are assigned to the excited monomer and the partially overlapped excimer of the carbazole moieties, respectively. The emission peak at 420 nm, associated with the sandwich-like excimer fluorescence of the totally eclipsed conformation, is of reduced intensity, consistent with the presence of a limited extent of totally eclipsed conformation (isotactic sequence) in a cross-linked PVK shell.[41,42]

For the synthesis of fluorescent SiO_2@PVK microspheres, DVB was selected as a cross-linking agent. Not only does it have the similar rigid molecular structure as that of PVK, the PDVB polymer also provides residual carbon−carbon double bonds on the surface of core−shell microspheres after distillation-precipitation polymerization.[43,44] The FT-IR absorption peak of the SiO_2@PVK microspheres at around 1630 cm^{-1} is attributable to the stretching vibration of double bonds from the DVB segments (Figure 2b).[45] These vinyl groups on the fluorescent SiO_2@PVK microspheres will allow subsequent grafting of the thiol-terminated poly(*N*-isopropylacrylamide) (PNIPAM−SH) chains, prepared a priori by reversible addition−fragmentation chain transfer (RAFT) polymerization, via the thiol−ene click reaction to produce the hairy core−shell microspheres (Scheme 1). The molecular weight and molecular weight distribution of the chain transfer agent-terminated PNIPAM chains from RAFT polymerization (PNIPAM−CTA) and the corresponding PNIPAM−SH chains

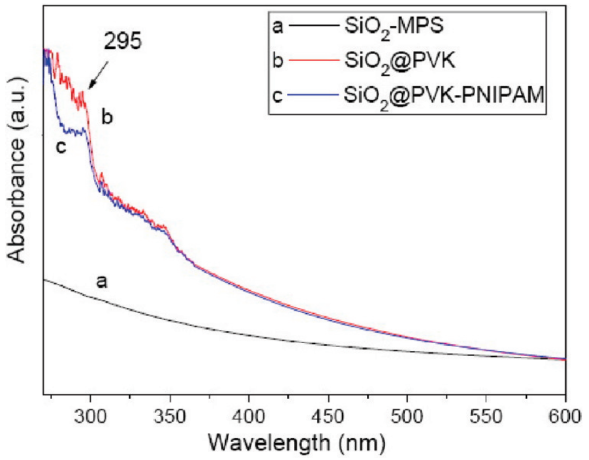


Figure 4. UV–visible absorption spectra of the (a) SiO_2–MPS seed microspheres, (b) SiO_2@PVK core–shell-2 microspheres of Table 1, and (c) SiO_2@PVK–PNIPAM hairy core–shell microspheres (MPS = 3-(trimethoxysilyl)propyl methacrylate; PVK = poly(*N*-vinylcarbazole); PNIPAM = poly(*N*-isopropylacrylamide)).

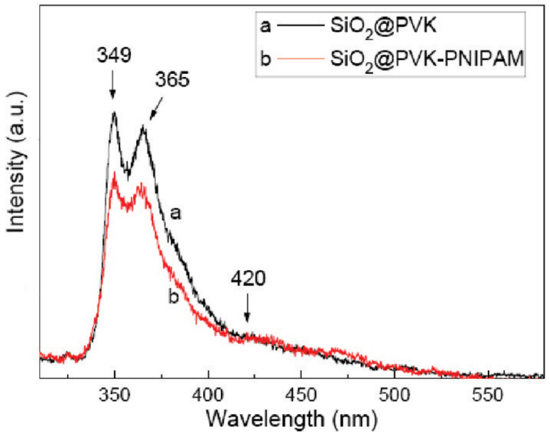


Figure 5. Fluorescence spectra of the (a) SiO_2@PVK core–shell-2 microspheres of Table 1 and (b) SiO_2@PVK–PNIPAM hairy core–shell microspheres (λ_{Ex} = 295 nm) (PVK = poly(*N*-vinylcarbazole); PNIPAM = poly(*N*-isopropylacrylamide)).

were characterized by gel permeation chromatography (Figure S1, Supporting Information). PNIPAM–CTA has a number-average molecular weight (M_n) of about 11 600 g/mol and a polydispersity index (PDI) of 1.32. The molecular weight and distribution of PNIPAM–SH remain practically the same as those of PNIPAM–CTA, albeit for the presence of a high molecular weight fraction in the elution curve of PNIPAM–SH, suggesting disulfide coupling some chains (about 30%, Figure S1, Supporting Information) has occurred during the reduction process. The chemical shift at about 2.9 ppm in the ^{1}H NMR spectrum of PNIPAM–CTA (Figure S2, Supporting Information) suggests the persistence of chain transfer agent at the polymer chain end after RAFT polymerization.

Figure 2c shows the FT-IR spectrum of SiO_2@PVK–PNIPAM microspheres from the thiol–ene click reaction of SiO_2@PVK microspheres with the PNIPAM–SH chains. The absorption peak at 1701 cm^{-1} is associated with the characteristic amide stretching vibration of the PNIPAM brushes.[46] The almost complete disappearance of C═C stretching vibration absorption at 1630 cm^{-1} indicates that most of the C═C bonds have been hydrothiolated. The residual C═C bonds are embedded in the cross-linked PVK shell, and are therefore inaccessible to the thiol–ene click reaction at the shell surface. The SiO_2@PVK–PNIPAM microspheres are hydrophilic and can be dispersed in deionized water at room temperature. The morphology of SiO_2@PVK–PNIPAM microspheres is revealed by the FESEM and TEM images of Figure 6, parts a and b, respectively. The FESEM image suggests that the well-defined spherical shape of the microspheres is retained after the thiol–ene click reaction. The hairy core–shell structure is suggested by the coarse surface structure of the SiO_2@PVK–PNIPAM microspheres in the TEM image under higher magnification (Figure 6b). The UV–visible absorption spectrum (Figure 4c) and fluorescence spectrum (Figure 5b) of the SiO_2@PVK–PNIPAM microspheres indicate that the optical properties of PVK shell are retained after grafting of the PNIPAM–SH brushes to the core–shell microspheres. The grafting density of PNIPAM brushes on the SiO_2@PVK microspheres was calculated from the weight loss of grafted PNIPAM chains in thermo-gravimetric analysis (TGA) to be about 0.1 chains/nm^2 (Supporting Information, Figure S3).

HF etching of the SiO_2@PVK–PNIPAM microspheres removes the SiO_2 template core and gives rise to the air@PVK–PNIPAM hairy hollow microspheres with a fluorescent shell and temperature-responsive brushes. The FESEM and TEM images of the air@PVK–PNIPAM hairy hollow microspheres are shown in Figure 6, parts c and d, respectively. The biconcave shape of the resultant air@PVK–PNIPAM hollow microspheres, similar to that of the red blood cells (RBCs) in human beings,[47] is readily discernible in the FESEM image. The TEM image in Figure 6d suggests that the silica core has been removed from the SiO_2@PVK–PNIPAM microspheres to produce the hollow polymer microspheres. The removal of silica core from the SiO_2@PVK–PNIPAM microspheres is further ascertained by energy-dispersive X-ray (EDX) analysis. In comparison with that of the EDX spectrum of SiO_2@PVK–PNIPAM microspheres in Figure 7a, the Si signal in the EDX spectrum of air@PVK–PNIPAM hollow microspheres (Figure 7b) is barely discernible.

The so-obtained air@PVK–PNIPAM hollow microstructure is of great interest not only for its unique morphology, but also for its function. The grafted PNIPAM brushes have endowed the hollow microspheres with thermo-responsive properties. The hydrodynamic diameters (D_h) of the air@PVK–PNIPAM hairy hollow microspheres were characterized by dynamic laser scattering (DLS). As shown in Figure 8, the average hydrodynamic size of the air@PVK–PNIPAM microspheres decreases from about 354 nm to about 308 nm as the temperature of the aqueous medium increases from 25 to 50 °C. This change in particle sizes is consistent with the fact that the grafted PNIPAM brushes exhibit a lower critical solution temperature (LCST) behavior in aqueous media.[48,49] As the temperature of the medium is raised to above the LCST of about 32 °C, the grafted PNIPAM brushes in the hairy hollow microspheres associate hydrophobically on the PVK shell to decrease the effective hydrodynamic diameter of the hollow microspheres.

The mechanical stability of the air@PVK–PNIPAM hairy hollow microspheres is one of the most important criteria governing their practical applications. The hairy hollow structure the air@PVK–PNIPAM microspheres were retained, upon explosure to an acid medium (pH 2, t = 24 h), base solution (pH 12, t = 24 h) and high centrifugation force (10 000 rpm), as shown by the respective FESEM and TEM images of the stressed microspheres in Figure 9, parts a and b, respectively. No broken or fractured microspheres were observed. The stability of the hairy hollow microspheres is probably associated with the cross-linked nature of the PVK shell. Moreover, the as-synthesized hairy hollow air@PVK–PNIPAM microspheres can be dispersed in both organic solvents (such as ethanol, THF, and DMF) and aqueous medium at room temperature, due to the simultaneous presence of a hydrophobic PVK shell and hydrophilic PNIPAM

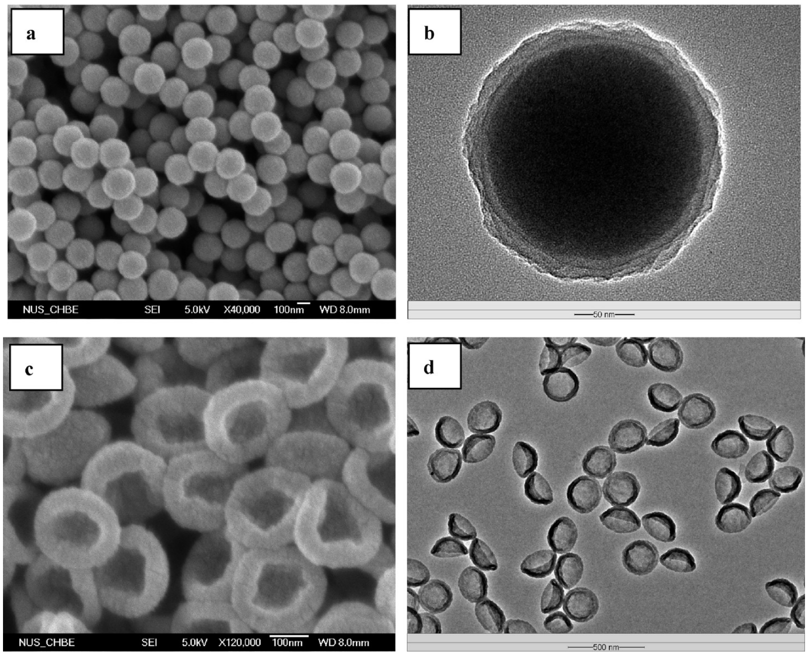


Figure 6. FESEM and TEM images of the (a and b) SiO_2@PVK−PNIPAM hairy core−shell microspheres and (c and d) air@PVK−PNIPAM hairy hollow microspheres after removal of the silica core by HF etching (PVK = poly(*N*-vinylcarbazole); PNIPAM = poly(*N*-isopropylacrylamide)). The respective scale bars for parts a−d are 100, 50, 100, and 500 nm.

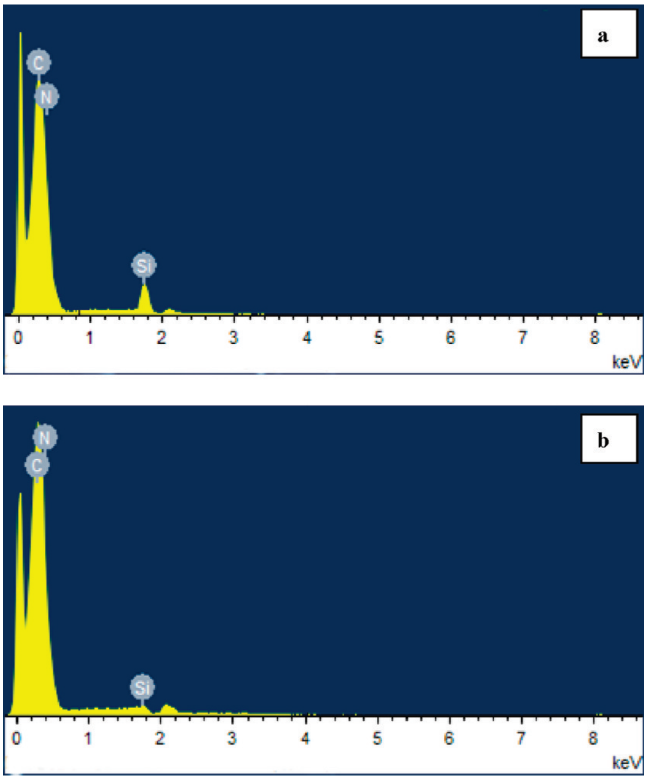


Figure 7. EDX analysis spectra of the (a) SiO_2@PVK−PNIPAM hairy core−shell microspheres, and (b) air@PVK−PNIPAM hairy hollow microspheres (PVK = poly(*N*-vinylcarbazole); PNIPAM = poly(*N*-isopropylacrylamide)).

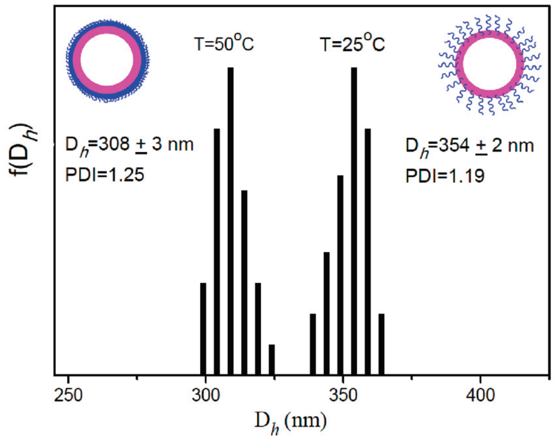


Figure 8. Hydrodynamic diameters (D_h) of the air@PVK−PNIPAM hairy hollow microspheres in the aqueous medium at two different temperature of 25 and 50 °C (PVK = poly(*N*-vinylcarbazole); PNIPAM = poly(*N*-isopropylacrylamide)).

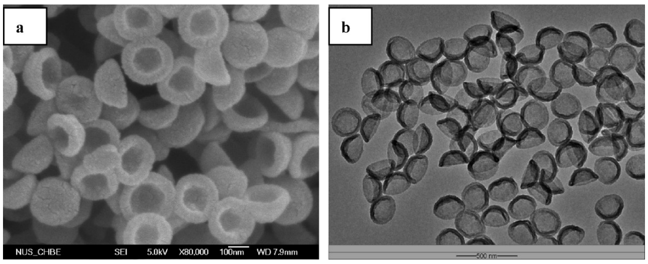


Figure 9. (a) FESEM and (b) TEM images of the air@PVK−PNIPAM hairy hollow microspheres, after explosure to acid (HCl, pH 2) for 24 h, base solution (NaOH, pH 12) for 24 h and high centrifugation force (10 000 rpm) (PVK = poly(*N*-vinylcarbazole); PNIPAM = poly(*N*-isopropylacrylamide)). The respective scale bars for parts a and b are 100 and 500 nm.

brushes. The good stability and dispersity in both organic solvents and aqueous media allow further device fabrication of these hairy hollow microspheres via solution-processing.

The cavity or void size of the air@PVK−PNIPAM hairy hollow microspheres can be controlled by varying the size of SiO_2 template microspheres during the sol−gel process. The thickness of PVK shell and the length of PNIPAM brushes can also be regulated through the simple adjustment of initial VCz monomer concentration and molecular-weight of the PNIPAM chains, respectively. Moreover, the SiO_2@PVK microspheres are produced by surface-initiated distillation-precipitation polymerization in a "grafting from" process. The grafting of PNIPAM−SH brushes to the surface of SiO_2@PVK microspheres via the thiol−ene click reaction, on the other hand, is a "grafting to" process. The present work has thus illustrated the versatility of combining the "grafting from" and "grafting to" processes in the construction of multifunctional hollow polymer microstructures.

4. Conclusions

Narrowly distributed and well-defined hairy hollow microspheres, with a fluorescent poly(*N*-vinylcarbazole) (PVK) shell and temperature-responsive poly(*N*-isopropylacrylamide) (PNIPAM) brushes (air@PVK−PNIPAM microspheres), have been synthesized by removal of the SiO_2 core from the corresponding hairy SiO_2@PVK−PNIPAM core−shell microspheres. The SiO_2@PVK−PNIPAM hybrid microspheres were prepared via the (i) sol−gel process to produce the 3-(trimethoxysilyl)propyl methacrylate-modified silica (SiO_2−MPS) core templates, (ii) distillation-precipitation polymerization of *N*-vinylcarbazole from (or "grafting from") the SiO_2−MPS core template, in the presence of divinylbenzene cross-linker, and (iii) thiol−ene click reaction of the PNIPAM chains, prepared a priori from reversible addition−fragmentation transfer (RAFT) polymerization, to (or "grafting to") the PVK shell. In addition to the well-defined and stable hollow microstructure, the air@PVK−PNIPAM microspheres also exhibited fluorescent and thermo-responsive properties. The combined approach of distillation-precipitation polymerization ("grafting from" technique) and thiol−ene click chemistry ("grafting to" technique) has provided a versatile tool for the synthesis of multifunctional hollow polymer microstructures.

Supporting Information Available: Figures showing gel permeation chromatography (GPC) of the PNIPAM−CTA and PNIPAM−SH chains, ^{1}H NMR spectrum of the PNIPAM−CTA chains, TGA of the SiO_2@PVK core−shell-2 microspheres and SiO_2@PVK−PNIPAM hairy microspheres. This material is available free of charge via the Internet at http://pubs.acs.org.

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