Synthesis of PNIPA/PDMS-*g*-PAA Core-Shell Composites in Supercritical Carbon Dioxide

Li-Qin Cao,[1] Liu-Ping Chen,[2] Peng-Yuan Cui,[3] Ji-De Wang[1]

[1]Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education, Xinjiang University, Urumqi 830046, People's Republic of China
[2]School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China
[3]The Xinjiang Technical Institute of Physics and Chemistry, CAS, Urumqi, Xinjiang 830011, People's Republic of China

ABSTRACT: Herein we report a means that has been developed to prepare smart polymeric microgels consisting of thermosensitive cores with pH-sensitive shells. The microgels were obtained directly from seed polymerization of *N*-isopropylacrylamide in supercritical carbon dioxide (scCO$_2$). The effects of initial amounts of crosslinker, and Poly (dimethylsiloxane)-graft-polyacrylates (PDMS-*g*-PAA) on the yield and morphology of the resulting polymer were investigated. PDMS-*g*-PAA and crosslinker worked effectively as surfactant. PNIPA/PDMS-*g*-PAA particles with diameters in 50 nm were produced in scCO$_2$, in high yield and in short reaction times. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3843–3850, 2008

Key words: core-shell polymers; *N*-isopropylacrylamide; polysiloxanes; stimuli-sensitive polymers; supercritical fluids

INTRODUCTION

Supercritical fluids (SCFs) can exhibit the best features of two worlds: gas-like diffusivities and liquid-like densities. In the vicinity of the fluid's critical point, its density is highly sensitive to modest changes in pressure or temperature. Higher SCF diffusivities have important implications in polymerization kinetics and in polymer processing (i.e., diminishing the "cage effect" associated to the initiator decomposition in free radical polymerization processes). The resulting polymer can be isolated from the reaction medium by simple depressurization, resulting in a dry, solvent-free product. This technique eliminates drying procedures required in polymer manufacturing, offering a cost-effective, and very attractive technology. The thermodynamic and transport properties of SCFs can be easily tuned by adjusting the pressure or temperature. Supercritical carbon dioxide (scCO$_2$) has near-zero surface tension and large diffusion coefficient. Therefore, it can be used to impregnate polymer matrix with different organic molecules. The green properties of carbon dioxide have provided the driving force for the development of a number of new applications.[1–11]

Because of the insolubility of most of the polymers in scCO$_2$ (unless fluoropolymers or silicon-based polymers), polymerizations conducted in scCO$_2$ proceed in heterogeneous conditions. Many polar or hydrophilic molecules, such as water, proteins, amides, ionic species, sugars, etc., exhibit very poor solubility in scCO$_2$. So far, Limited research efforts have been made on the polymerization of water-soluble vinylic monomers containing amides in carbon dioxide, including inverse emulsion polymerization of acrylamide,[12] emulsion polymerization of *N*-ethylacrylamide,[13] and dispersion copolymerization of *N,N*-dimethylacrylamide.[14]

Environmental stimuli-responsive polymeric hydrogels attract increasing attention in numerous fields for their potential applications.[15–23] The representatives of the stimuli-responsive polymers include P (*N*-isopropylacrylamide) (PNIPA) and its copolymers. Temperature-and pH-sensitive hydrogels are the most investigated, because these signals are easily controlled and have wide-ranging applicability in the fields of biotechnology, chemical processing, and medicine.[24] Generally, the free radical emulsion polymerization technique is limited to the use of a pH-responsive vinylic monomer. The amount of pH-sensitive comonomer greatly affects the volume phase transition temperature (VPTT) of the microgels. To address this limitation, we recently have developed

a green route for synthesis of biomedical materials, in which the precipitation polymerization of N-isopropylacrylamide (NIPA) is carried out either in the absence of a crosslinker, or with a modified natural biopolymer as the surfactant, presents a new and simple method for preparing smart polymeric microgels that consist of temperature-sensitive cores with pH-sensitive shells.[25,26]

Here, we describe a one-step seed polymerization using $scCO_2$ medium to produce novel nano-sized core-shell stimuli-responsive polymers directly from a pH-sensitive siloxane polymer, poly (dimethylsiloxane)-graft-polyacrylates (PDMS-g-PAA). In this case the assistance of a synthetic graft copolymer surfactant allows to run the process as a dispersion polymerization in the early stage and to provide the final product with additional functionality. Hence their responsiveness to pH and temperature can be manipulated individually. Polysiloxanes have high chain flexibility ($T_g \approx 127°C$ for poly (dimethyl siloxane), PDMS) and thermal stability, hydrophobicity and biocompatibility.[27] Polydimethylsiloxane (PDMS)-based elastomers have a number of properties, including oxygen permeability, transparency, and mechanical properties, which make them useful in biomedical.[28]

Conjugation of drugs or proteins to PDMS-g-PAA/PNIPA generates thermoand pH-responsive entities that can be addressed through external stimuli. It could eventually be used to confer bioadhesive properties; pH-sensitive micelles might be applied in the drug delivery to tumors, inflamed tissues, or endosomal compartments, where the pH lower than that in normal tissue is found.

Since $scCO_2$ behaves a lot of advantages as green medium mentioned above, it can be used to impregnate polymer matrix with different organic molecules. Polymeric particle coating finds wide applications in various important industries: pharmaceutical, food, fertilizer, cosmetics, electronic, and biomedical, just to name a few. It is often a crucial industrial process in particle handling to enhance compatibility, flowability, wettability, and dispersibility, or to serve as a barrier for controlled release or masking. Conventional polymeric particle coating usually prepared in aqueous or organic solutions and the use of a large amount of organic solvents may raise serious air and water pollution concerns. Therefore, effective and clean coating methods are of strong interest. This idea gives further understanding to the one-step seed polymerization of smart hydrogels in $scCO_2$.

The objectives of the study are (i) to show that PDMS-g-PAA can simultaneously as stabilizer for seed polymerizations and a functional portion of the composite particles, and (ii) to find a new route towards materials that can be applied in biomedicine. The effects of crosslinker and PDMS-g-PAA dose on the resulting polymers were explored.

EXPERIMENTAL

Materials

The monomer NIPA was purchased from Acros (99%) and was used as received. PDMS-g-PAA was purchased from Sigma-Aldrich (Mn ~ 26,000, dimethylsiloxane, ~ 80 wt %). 2,2′-Azobis (isobutyronitrile) (AIBN) was supplied by Shanghai Chemical Agent fourth Factory and was recrystallized twice from methanol. N,N-methylenebisacrylamide (Bis) was analytical reagent grade and supplied by Tianjin Chemical Reagent Company. Carbon dioxide gas was purchased from Guangzhou Gas Factory with > 99.95% purity. High-pressure reactions were carried out in a 300-mL columniform stainless steel reactor equipped with sapphire windows used for observation of the phase behavior during the reaction process. The pressure in the reactor was measured using a pressure gauge in the range of 0–400 bar. The temperature of the reactor was measured with a platinum resistance thermometer (model WMZK-01, produced by Shanghai medical instruments Factory). A magnetic stirrer was used to mixing the reaction system.

Preparation of PNIPA/PDMS-g-PAA composites

In a typical experiment, the known amounts of PDMS-g-PAA, solid monomer, the free-radical initiator AIBN and crosslinker Bis were loaded to the reaction vessel. Next, the reactor immersed in an ice bath was first purged with a flow of CO_2 to remove any entrapped air from the vessel and then filled with liquid CO_2 to desired amount (210 g), after charging, the system was isolated and the reactor was heated to 70°C and the pressure was increased to ~ 260 bar, with a stick-shaped stir bar agitated the mixture. The reaction conditions were maintained at 70°C, 260 bar during the reaction time. At the end of the reaction, the system was then cooled to room temperature, and CO_2 was slowly vented. The physical form and the overall appearance of the polymer were noted. The yield of the polymer product was determined gravimetrically.

Characterization

The VPTTs of the microgels were determined by measuring the light transmittance (at 500 nm) of a microgel dispersion between 20 and 50°C using CARY 300 UV–vis Spectrophotometer (Varian, USA), equipped with a circulating water bath. Scanning electron microscopy (SEM) images were obtained using a Quanta 400 FEG (FEI Company, USA). The core-shell nanostructures of the microgels were observed using a transmission electron microscope (JEM-2010HR, JEOL, Japan) at an accelerating voltage of 200 kV after ultrasonic dispersing in ethanol.
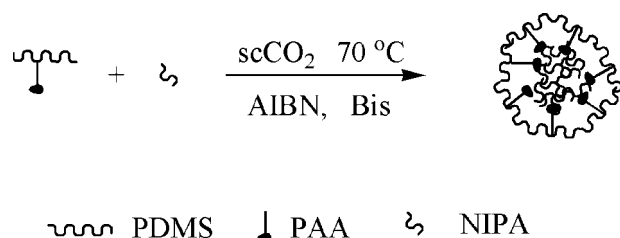
Scheme 1 Presentation of the formation of core-shell PNIPA/PDMS-*g*-PAA in scCO$_2$.

FTIR spectra of crosslinked PNIPA, PDMS-*g*-PAA and composites samples were taken in KBr pellets using a Bruker/VECTOR 22 FTIR spectrophotometer (Bruker Optics, Germany). The pH sensitivity was measured by swelling ratios in different pH buffers. Copolymer particles were immersed in the buffers of various pH values from 4.6 to 9 for 2 weeks.

RESULTS AND DISCUSSION

Phase behavior of the reaction mixture

The phase of the CO$_2$/monomers/PDMS-*g*-PAA system was investigated by coupling visual observations of the mixture to the recording of the pressure trend inside the fixed-volume view autoclave as a function of the temperature during the slow heating of the reaction system. At room temperature, all the investigated systems were composed of two fluid phases, which merged into a single phase during the heating cycle. This simple static synthetic method was repeated for all initial feed compositions of the reaction mixture adopted in this work, all of which were initially composed of a single phase under the operating conditions adopted to perform the polymerization. The clear solution developed a white opaque appearance after 3 h, and precipitate formation was observed after 4 h.

Synthesis of core-shell microgels

In heterogeneous processes, two polymerization loci may contribute to the polymer production: the CO$_2$-rich continuous phase and the polymer-rich dispersed phase. The mass transport of reactants between phases is the key factor in determining the relative importance of each polymerization locus. Generally, the surfactant sterically stabilizes the dispersion of solid particles or water droplets in the scCO$_2$ phase. Surfactants for use in CO$_2$ are amphiphilic molecules containing both a CO$_2$-phobic and a CO$_2$-philic portion. The CO$_2$-phobic portion displays poor solubility in CO$_2$ and therefore prefers to reside away from the continuous phase; the CO$_2$-philic tail has good solubility in CO$_2$ and extends out into the bulk solvent. The surfactants are typified by micelles

or more complex aggregates in which the lyophobic segments form a core surrounded by a shell of the highly solvated lyophilic segments that extend into the continuous phase. The core regions of such micelles are technologically useful, as they are capable of emulsifying otherwise insoluble materials into a microphase-separated environment within a preferred continuous solvent phase.[29]

The approach of synthesis of core-shell polymeric particles in scCO$_2$ is shown in Scheme 1. Primary radicals are formed from thermally promoted fragmentation of the initiator AIBN, which then initiated polymerization of NIPA concurrently in the presence of a crosslinker, *N*,*N*-methylenebisacrylamide. At the beginning, the only active locus is the continuous phase, where the first polymer chains are produced. Thus the PNIPA became "CO$_2$-phobic" and phase-separated during the polymerization. It was postulated that PDMS-*g*-PAA was effective amphiphatic stabilizer because it contained a lipophilic backbone that could anchor onto the acrylamide surface of growing polymer particles. The CO$_2$-philic PDMS chain could trajectory into the continuous phases and give rise to steric stabilization and preventing particle flocculation. From this point on, the polymerization proceeds in two phases, namely, the
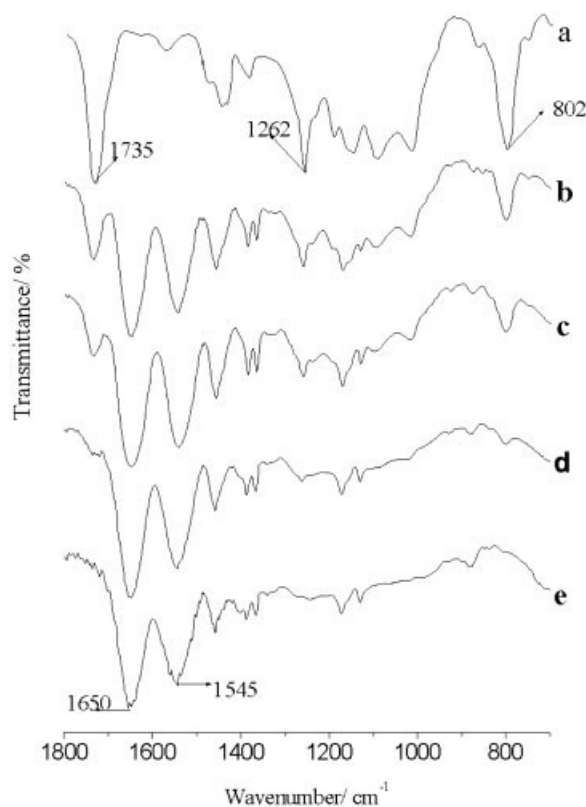

Figure 1 FTIR spectra of (a) PDMS-*g*-PAA, (b) PDMS-*g*-PAA/PNIPA (2.5/8/w/w), (c) PDMS-*g*-PAA/PNIPA (1.5/8/w/w), (d) PDMS-*g*-PAA/PNIPA (0.5/8/w/w), and (e) crosslinked PNIPA.

TABLE I
Effect of PDMS-g-PAA:NIPA ratio on Polymerization in scCO$_2$[a]

Entry	PDMS-g-PAA: NIPA /(w/w)	Conversion (%)	Polymer morphology[b]
1	0.5/8	68	Aggregate
2	1.5/8	91	White flow powder
3	2.5/8	100	White flow powder
4	3.5/8	100	White flow powder
5	5.0/8	100	White flow powder

[a] Reaction condition: 0.8 g NIPA, 0.08 g Bis, 0.05 g AIBN, 260 bar(210 g CO$_2$), 70°C, 10 h.
[b] Appearance of the polymer after venting.

polymer-rich phase and the CO$_2$-rich phase. However, as soon as crosslinked PNIPA microgels are formed, monomer, initiator and active species are partitioned between the continuous and polymer phases and both loci are effective. Under stable conditions of anchor-to-soluble balance, the microgels very rapidly become the dominant locus. The polymerization continues only in the polymer-rich phase, which is swollen with monomers (NIPA and Bis) and CO$_2$. Then the core portion of the hybrid particles was formed. During this stage, diffusion-controlled phenomena become very important. Therefore, the smart particles of PNIPA/PDMS-g-PAA were mainly stabilized by the PDMS shell that prevents the coagulation of the growing chains and enables the formation of a stable composites structure. The same mechanism was used to synthesize PS/PMMA core-shell materials.[30]

FTIR spectroscopic

The FTIR spectra of crosslinked PNIPA, PDMS-g-PAA and PNIPA/PDMS-AA as shown in Figure 1, confirm the presence of both PDMS-AA and PNIPA in the composites formed. The bands due to —C=O stretching and NH-bending for secondary amides at 1650 and 1540 cm^{-1}, respectively, and a double band for isopropyl group at 1385 and 1370 cm^{-1} are characteristic absorptions of PNIPA. Furthermore, the clear increases in the relative intensity of the characteristic bands due to Si(CH$_3$)$_2$ (1262 and 802 cm^{-1}) and Si—O (1110–1000 cm^{-1}) indicate an increase of the siloxane units of PDMS along with the PDMS-g-PAA content (by weight) in the composites.

Effect of the PDMS-g-PAA/PNIPA weight ratio

The Polymerization at four different doses (0.05, 0.15, 0.25, and 0.35 g PDMS-g-PAA) were conducted in 260 bar CO$_2$ at 70°C (Table I). In all four cases, the contents of NIPA, Bis, and AIBN were kept constant at 0.8 (0.38% ~ w/v), 0.08, and 0.05 g,[30] respectively.

Two general trends were obtained. First, the composites were similar in morphology to that of formed by polymerization of other monomers (MMA or St) in scCO$_2$ in the presence of surfactant. Free flowing powders were obtained in all cases. At the higher ratio investigated, PDMS-g-PAA/NIPA = 2.5/8 (run 3), partially aggregated microspheres were obtained with diameters mostly in 50 nm [Fig. 2(a)]. In the absence of PDMS-g-PAA, larger, agglomerated structures were observed [Fig. 2(b), entry 10]. The second
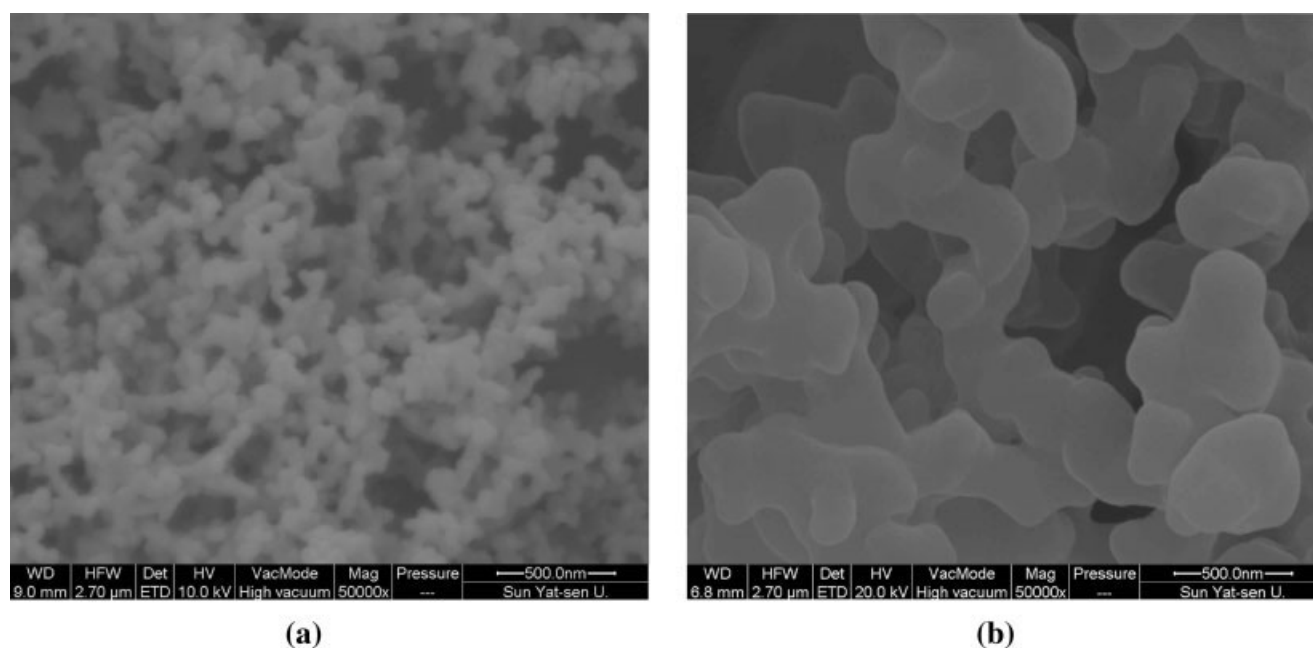

Figure 2 SEM images of composites produced using (a) 0.25 g PDMS-g-PAA and (b) 0 g PDMS-g-PAA. Reaction condition: 0.8 g NIPA, 0.08 g Bis, 0.05 g AIBN, 70°C, 260 bar, 10 h.

TABLE II
Effect of Crosslinker Ratio on Polymerization in scCO$_2$[a]

Entry	Crosslinker (g)	Conversion (%)	Polymer morphology[b]
6	0	–	Little yellow solid
7	0.008	77.8	Aggregate
8[c]	0.008	–	Liquid monomer
9	0.016	87.4	White flow powder
10[c]	0.016	53.5	Aggregate

[a] Reaction condition: 0.8 g NIPA, 0.25 g PDMS-g-PAA, 0.05 g AIBN, 260 bar (210 g CO$_2$), 70°C, 10 h.
[b] Appearance of the polymer after venting.
[c] 0 g PDMS-g-PAA.

notable trend was a strong dependence of conversion on PDMS-g-PAA amount (Table I). At the lowest ratio investigated, PDMS-g-PAA/NIPA = 0.5/8 (run 1), the monomer conversion was 68%, quite lower than that obtained at higher PDMS-g-PAA/NIPA ratios.

We next investigated the effect of PDMS-g-PAA amount on the polymerization at lower contents of crosslinker. First, a series of polymers was prepared at lowest crosslinker contents (Bis = 0.008 g) (Table II, entries 7 and 8).The resulting polymer was found to accumulate as dry powders at the bottom of the reactor with yields of 77.8% (PDMS-g-PAA = 0.25 g) and a little liquid (without PDMS-g-PAA), respectively. Another series of polymers was prepared at lower crosslinker contents (Bis = 0.016 g) (Table II, entries 9 and 10). Accordingly, the yields of the resulting polymer were 87.4 and 53.5%, respectively. It appears that the increase in the PDMS-g-PAA dose increased the monomer conversion of polymerization. This may be attributed to the fact that, in a polymerization, the number of polymer particles formed is associated with the surfactant concentration. In our investigated systems, PDMS-g-PAA was necessary to enable effective emulsification of the system to stabilize the water soluble and CO$_2$-insoluble PNIPA in CO$_2$. With more surfactant PDMS-g-PAA molecules, the number of reaction sites increases, thus resulting in an increase in conversions. Besides, the PDMS-g-PAA behaved as a surfactant, preventing polymer particles from coagulation, thereby decreasing the particle diameter and increasing the particle number. This is consistent with previous studies.[14,31–33]

The dry polymer particles (entry 2) were observed by TEM, after ultrasonic dispersing of the particles, the nanostructures of the microgels were revealed with TEM micrographs. Figure 3 shows that the microgels are approximately spherical and have well-defined core-shell morphologies where PNIPA cores are coated with PDMS-g-PAA shells.

Effect of crosslinker dose

In the absence of crosslinker, the polymerization of NIPA in scCO$_2$ resulted in poor yield (Table II, entry 6). Figure 4 shows the effect of the amount of the crosslinker on the morphology of the polymer particles.

We also think that the formation of microspheres in our samples also attributes to the rigidity of the polymers. In addition to stabilization of PDMS-g-PAA, the Bis not only behave as a crosslinker for preparation microgel, but also to stabilize the composites. Since the homopolymerization of NIPA without crosslinker was also studied, little yellow free flow solid particles were obtained. The morphology is very different from above samples. The fact that the lightly crosslinked polymers did not form microspheres (entry 6) is consistent with this idea.
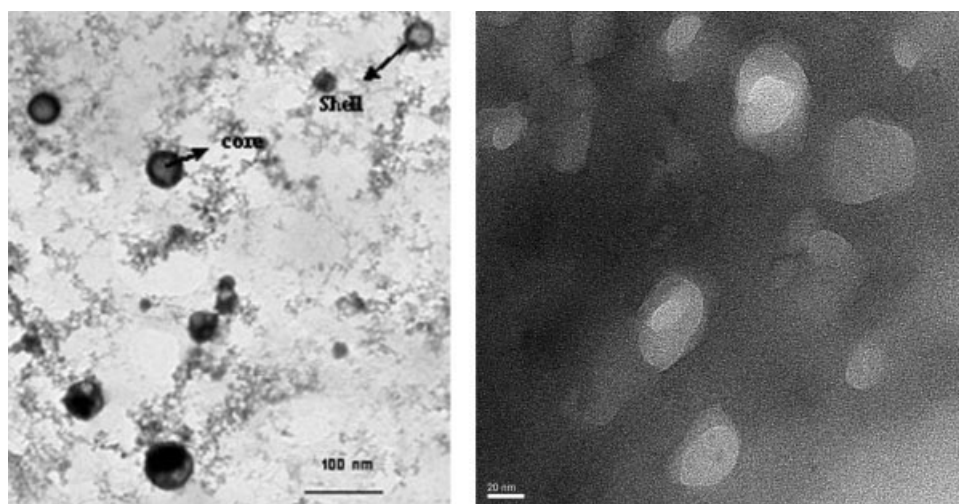

Figure 3 TEM images of PNIPA/PDMS-g-PAA composites from the reactions (a) 0.08 g Bis; 0.8 g NIPA; 0.25 g PDMS-g-PAA; 0.05 g AIBN; 70°C; 260 bar; 10 h.
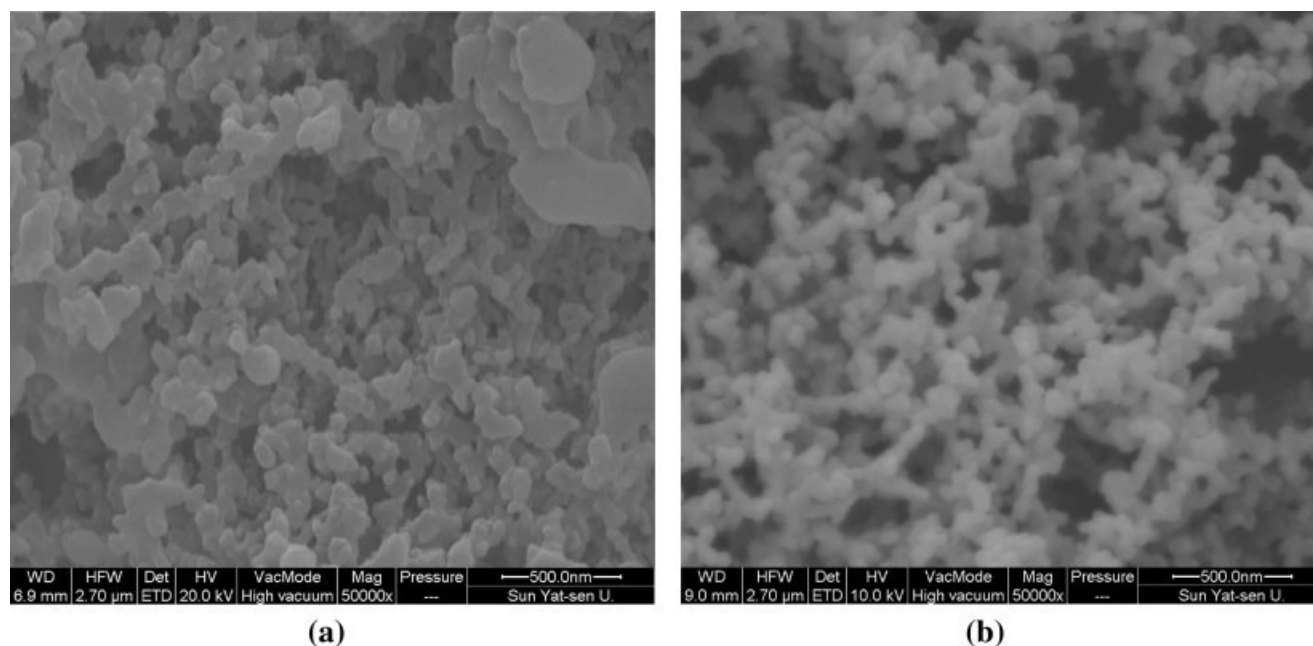
Figure 4 SEM images of composites produced using (a) 0.008 g Bis and (b) 0.08 g Bis. Reaction condition: 0.8 g NIPA, 0.25 g PDMS-*g*-PAA, 0.05 g AIBN, 70°C, 260 bar, 10 h.

The particles formed from higher crosslinker agent samples [Fig. 4(b)] were significantly less agglomerated than those formed from lower crosslinker agent samples [Fig. 4(a)], perhaps because the highly crosslinked particles were more rigid, and therefore less prone to aggregation. Such similar phenomena are also found by other works.[34,35]

Temperature and pH sensitivities

The VPTT of the core-shell microgels in water were examined by measuring the transmittance of the microgels dispersion as a function of temperature.
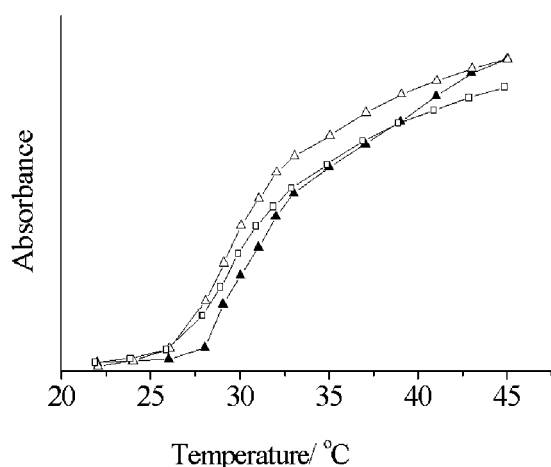

Figure 5 Effect of crosslink density on VPTT of PNIPA/PDMS-*g*-PAA core-shell microgels: (Δ) 0.008 g Bis; (□) 0.016 g Bis; (▲) 0.08 g Bis. Reaction conditions: 0.25 g PDMS-*g*-PAA, 0.8 g NIPA, 0.05 g AIBN, 70°C, 260 bar, 10 h.

The effect of crosslink density on VPTT of microgels was shown in Figure 5. As can be seen, the composites particles show a same volume transition temperature (32°C) although differ in crosslink density in the core. This observation is in agreement with the investigations of Liu et al.[36] And the result further indicates that in our investigated crosslinking degree (0.008, 0.016, and 0.08 g), crosslinker content do not affects the volume transition within the PNIPA network. This result may be attributed to the scCO$_2$ as a good plasticizing agent, which could mobilize the polymer chains of the morogels network. The effect of composite on VPTT of microgels was shown in Figure 6. A slight decrease in the VPTT of microgels was observed when the PDMS-*g*-PAA content was raised from 0.25 to 0.50 g; this is to be expected in general when the hydrophobic association of PDMS chain reinforce the composites' phase separates gradually from water at a lower temperature. Accordingly, the VPTT of these microgels were found to be in the range 29–33°C. The VPTT of the PNIPA/PDMS-*g*-PAA microgels (entry 2) at pH 5, 7, and 9 were almost the same (32°C) (Fig. 7). The result strongly suggests that the microgels have a well defined core-shell nanostructure. Hence the properties of core and shell can be altered independently without interfering with each other.

The swelling ratio for PNIPA/PDMS-*g*-PAA in different pH solutions was shown in Figure 8. The increase of swelling ratios at pH values varied from 3 to 11 was induced by the ionization of carboxyl groups (COO—) at pH values above the pKa of PAA, in which the ionic electrostatic repulsion
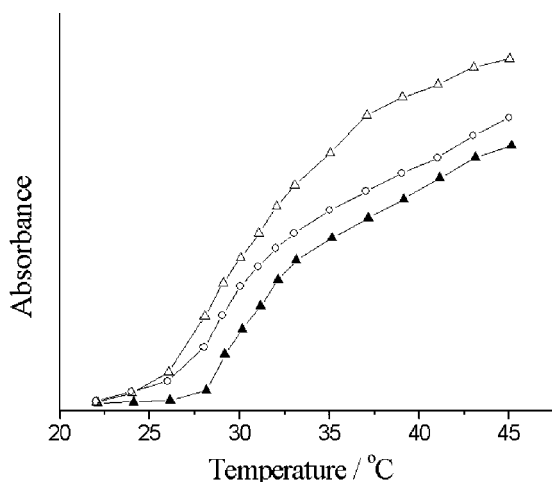
Figure 6 Effect of PDMS-g-PAA contents on VPTT of PNIPA/PDMS-g-PAA core-shell microgels: (Δ) 0.50 g (○) 0.35 g (▲) 0.25 g PDMS-g-PAA. Reaction conditions: 0.08 g Bis, 0.8 g NIPA, 0.05 g AIBN, 70°C, 260 bar, 10 h.

between COO— expands the polymer network. At pH values above 5, significantly higher swelling was observed in the microgels with higher PDMS-g-PAA contents. These results evidently demonstrate that PDMS-g-PAA shells are pH-sensitive, and the thickness of the shell can be easily altered with the change of pH of the dispersing medium.

Conclusions

It was demonstrated that core-shell PNIPA/PDMS-g-PAA microparticles can be produced in scCO$_2$ through a simple one-step seed polymerization method. PDMS-g-PAA and crosslinker worked effectively as surfactant in the stabilization of the PNIPA/PDMS-g-PAA microparticles. It is possible to obtain nano-sized spherical particles with narrow
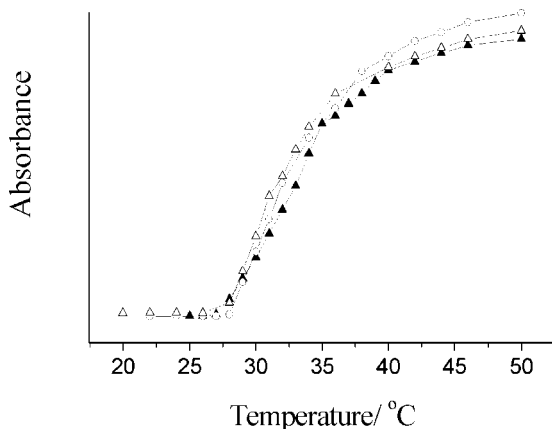

Figure 7 Effect of pH on VPTT of (a) PNIPA/PDMS-g-PAA core-shell microgels: (▲) pH 5; (○) pH 7; (Δ) pH 9. Reaction condition: 0.08 g Bis, 0.8 g NIPA, 0.25 g PDMS-g-PAA, 0.05 g AIBN, 70°C, 260 bar, 10 h.

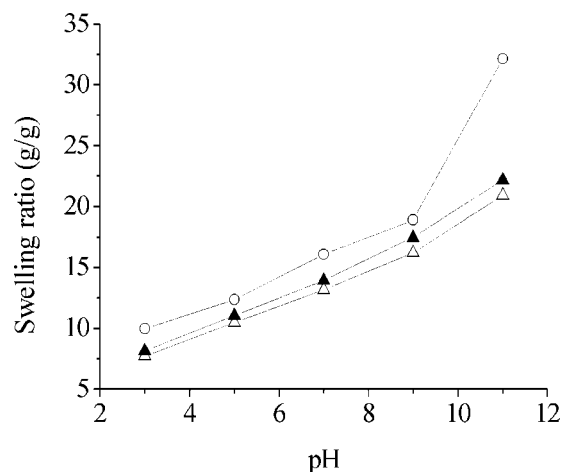**Figure 8** Effect of pH on swelling ratios. PDMS-g-PAA: (Δ) 0.15 g (▲) 0.25 g. (○) 0.50 g. Reaction condition: 0.8 g NIPA, 0.08 g Bis, 70°C, 260 bar, 10 h.

size distribution and in short reaction times, by changing the initial amounts of crosslinker and PDMS-g-PAA. The polymers were obtained in high yield as dry, fine, and free flowing material directly from the reaction vessel. No contamination of monomer was obtained in the final product by continuously washing the polymer at the end of the reaction with high-pressure CO$_2$. This technically and environmentally satisfying method using CO$_2$ as the solvent is applicable to many combinations of different materials and can lead to the production of a wide variety of new polymer composite microparticle materials.

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