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ORIGINAL CONTRIBUTION

Synthesis of cross-linked poly (*N*-isopropylacrylamide) microparticles in supercritical carbon dioxide

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Abstract Herein, we report a new method that has been developed to prepare thermoresponsive polymers. The white, dry, fine powders were obtained directly from cross-linking polymerization of *N*-isopropylacrylamide in supercritical carbon dioxide ($scCO_2$) with *N*,*N*-methylenebisacrylamide as a cross-linker. The effects of the reaction pressure and time as well as the initial concentrations of the initiator, cross-linker, and monomer on the yield and morphology of the resulting polymer were investigated systematically. The polymer yield was increased with the concentrations of the cross-linker, monomer, and reaction time. Under the condition of using higher cross-linker concentrations, the cross-linked poly (*N*-isopropylacrylamide) microparticles with diameters of 50 nm were generated in $scCO_2$ in high-yield and short reaction times. These results suggest that the synthetic method using $scCO_2$ can be used to prepare biomedical materials such as the controlled drug-release system.

Keywords *N*-Isopropylacrylamide · Thermoresponsive · Supercritical carbon dioxide · Cross-linked microgels

Introduction

Intelligent or smart materials exhibit large property changes in response to small physical or chemical stimuli. Stimuli-responsive polymers have been studied as smart materials for various applications in biomedical fields or chemo-mechanical devices. Representatives of the stimuli-sensitive polymers include poly (*N*-isopropylacrylamide; PNIPA) and its copolymers, in which a coil-globule transition based on hydration–dehydration behavior is induced in response to temperature [1]. Temperature-sensitive hydrogel is the most investigated because these signals are easily controlled and have a wide-ranging applicability in the fields of biotechnology, chemical processing, and medicine [2, 3].

Cross-linked PNIPA microgels create systems that respond to external stimuli. The conjugation of drugs or proteins to microgels generates thermoresponsive entities that can be addressed through external stimuli. This could eventually be used to confer bioadhesive property. These many applications require the PNIPA materials to be very pure and free from residual solvent. However, PNIPA is usually produced by homogeneous radical polymerization in aqueous solutions or several conventional organic solvents [4–7]. Such product prepared by the above solution method needs to be precipitated into organic solvents such as diethyl ether and then rinsed thoroughly with distilled water, which generates large quantities of wastewater and requires substantial quantities of energy to dry the polymer product.

Recently, the use of supercritical carbon dioxide ($scCO_2$) as an alternative to traditional aqueous and organic solvents has attracted much attention in the fields of extraction, polymer synthesis, and materials processing [8–10]. Carbon dioxide is inexpensive, nontoxic, and nonflammable, and it has an easily accessible critical temperature of 31.1 °C and critical pressure of 73.8 bar [11]. $scCO_2$ can exhibit the best features of two worlds: gaslike diffusivities and liquidlike densities. In the vicinity of the fluid's critical point, its density is highly sensitive to modest changes in pressure or temperature. Higher $scCO_2$ diffusivities have important

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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 thermodynamic and transport properties of $scCO_2$ can be easily tuned by adjusting pressure or temperature. Produced polymers can be isolated from reaction mixtures by simple depressurization, which results in a clean, dry product. Therefore, this method eliminates the necessity for energy-intensive drying procedures often required in manufacturing polymers. The overall aim is to highlight areas where the unique properties of supercritical fluids can be exploited to generate polymers and process that would be difficult or inconvenient to obtain by other routes [12].

Many polar or hydrophilic molecules, such as water, proteins, amides, ionic species, sugars, etc., exhibit very poor solubility in CO_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 [13, 14], emulsion polymerization of *N*-ethylacrylamide [15], and dispersion copolymerization of *N*,*N*-dimethylacrylamide [16].

Special CO_2-soluble stabilizers have been developed and used in various dispersion and emulsion polymerization of monomers because of the low solubility of the majority of polymers in $scCO_2$. However, the presence of stabilizers that cannot be easily removed from the polymer becomes a serious problem for some applications. Precipitation polymerization is an alternative approach that produces stabilizer-free polymers [17]. In a precipitation polymerization, an initially homogeneous mixture of a monomer, initiator, and solvent becomes heterogeneous during the reaction process as insoluble polymer chains aggregate to form a separate polymer phase.

The objectives of the study herein are to find a new route towards materials that can be applied in biomedicine. In this work, the influences of initial concentrations of the initiator, cross-linker, and monomer as well as reaction pressure and time on synthesis of PNIPA microgel have been investigated.

Experimental

Materials

The monomer NIPA was purchased from Acros (99%) and was used as received. *N*-isopropylmethylacrylamide (NIPMA) was purchased from Aldrich (98%) and was recrystallized from hexane. 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. Carbon dioxide gas was purchased from Guangzhou Gas Factory with a purity greater than 99.9%. High-pressure reactions were carried out in a 300-ml 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 0–600 bar. The temperature of the reactor was measured with a platinum resistance thermometer (model WMZK-01, Shanghai medical instruments factory). A magnetic stirrer was used for mixing the reaction system. Safety warning: It should be used with mirrors for the viewing of high-pressure windows instead of looking directly into the window.

Precipitation polymerization

The synthetic procedure used to conduct the polymerization is shown in Fig. 1. In a polymerization reaction, solid monomer, the free-radical initiator AIBN and cross-linker BIS, were loaded to the autoclave. The autoclave was then sealed. Next, the autoclave immersed in an ice bath was first purged with a flow of CO_2 to remove air from the vessel and then filled with liquid CO_2 to the desired amount (i.e., 250 g). After charging, the system was isolated, and

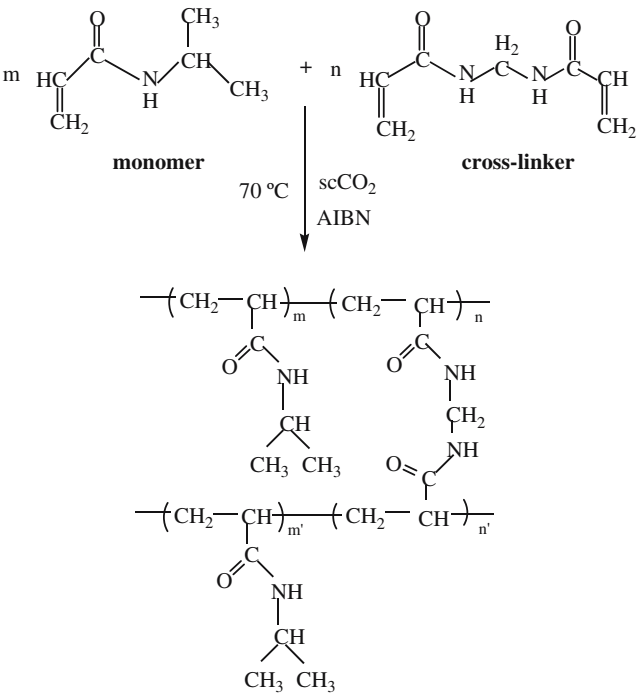

Fig. 1 Schematic illustration for synthesis of cross-linked PNIPA in $scCO_2$

Table 1 Effect of initiator concentration on the polymerization of NIPA in $scCO_2$

Entry	Initiator concentration per percent w/w w.r.t. monomer	Initiator concentration per percent w/w w.r.t. solvent	Yield/ %	Polymer morphology[a]
1	3.125	0.012	0	Glassy solid
2	6.25	0.024	64	Aggregate
3	12.5	0.047	69	Aggregate
4[b]	12.5	0.047	95	Dry powder
5	18.75	0.071	63	Aggregate

Reaction condition, 23 MPa (212 g CO_2); 0.8 g NIPA; 0.025 g BIS; 70 °C; 8 h
[a] Appearance of the polymer after venting
[b] 0.08 g BIS

the autoclave was gradually heated to 70 °C, and the pressure was increased to approximately 400 bar. Because of heating, the reaction system was mixed with a stick-shaped stir bar at a stirring rate of 1,000 rpm. To make reagents fully soluble in $scCO_2$ fluid, the heating rate was controlled; on average, it took approximately 120 min to heat the reaction system from room temperature to 70 °C (during the heating process, the system rapidly arrived in a supercritical state within 5 min), at which the reaction should be continued to the desired 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, and the products were treated with subcritical carbon dioxide by high pressure Soxhlet extractor to remove the unreacted monomers and initiator residues. The yield of products was calculated according to the mass of the final products and added monomer.

Measurement and characterization

Scanning electron microscopy (SEM) images were obtained using a JSM-6330 FE SEM (JEOL, Japan). The volume phase transition temperatures (VPTTs) of the microgels were determined by measuring the light transmittance (at 500 nm) of a microgel dispersion from 20 to 42 °C using CARY 300 UV-Vis spectrophotometer (Varian, USA) equipped with a circulating water bath. For the equilibrium swelling ratio study, a 0.100-g dried sample (W_d) was immersed in 20.0 ml of distilled water for 3 weeks; until the swelling equilibrium was attained, the weight of the wet sample (W_s) was determined after the surface water was removed by blotting with filter paper. The equilibrium swelling ratio (SR) was calculated from the following formula:

$$\mathrm{SR} = \frac{W_s - W_d}{W_d}$$

Results and discussion

Phase behavior of the reaction mixture

The phase behavior of the CO_2/monomer system was investigated by the coupling of the visual observation 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 mixtures adopted in this work, all of which were composed of a single phase under the operating conditions adopted to perform the polymerization. For example, during polymerization of NIPA at very low monomer concentrations (0.8 g NIPA), the polymerization mixture was initially all clear and homogeneous (25 °C, 85 bar). The solution was gradually heated (to 70 °C, 400 bar), and after reaching the experimental *p-T* parameters for 30–45 min, an orange/red color was observed because of the scattering of transmitted light by the growing polymer particles (namely, the Tyndall effect). After a relatively short time (around 0.5 h), the growing polymer could be seen precipitating out of solution

Table 2 Effect of cross-linker concentration on the polymerization of NIPA in $scCO_2$

Entry	Cross-linker concentration per percent w/w w.r.t. monomer	Yield/%	Morphology of the final product[a]
6	0	41	Yellow, sticky solid
25	2.5	57	Aggregated particles
7	4	69	Lightly aggregated particles
8	8	81	Dry, white, flow powder
9	10	97	Dry, white, flow powder
26	20	96	Dry, white, flow powder

Reaction condition, 40 MPa (250 g CO_2); 1.0 g NIPA; 0.1 g AIBN; 70 °C; 12 h
[a] Appearance of the polymer after venting

and coalescing on the cell window. Therefore, it would appear that under these conditions, the nature of the reaction is a precipitation polymerization.

Effect of initiator concentration

The polymerizations were conducted at four different concentrations of the initiator, as shown in Table 1. When the polymerization was conducted at the lowest initiator concentration (3.125 wt%), there was no homogeneous white powder, except a little coagulated solid monomer was obtained (entry 1). However, at a higher initiator concentration (6.25 wt%), the polymer yield reaches to 64% (entry 2). This increasing trend of yield is attributed to the creation of more numbers of reaction sites arising from an increase in the concentration of AIBN in the reaction system (300 ml), where rather high initiator concentrations seemed necessary to achieve good yields in $scCO_2$ [18]. Further increasing the initiator concentration from 6.25 to 18.75 wt %, there was a slight increase in the polymer yields ranging from 64 to 69% (entry 3), and then, it decrease to 63% (entry 5). These data indicate that adding much quantity of initiator does not accelerate the reaction further (i.e., there exists an optimal value of initial concentration that maximizes the polymerization rate).

The effect of cross-linker ratio

In the absence of a cross-linker, the precipitation polymerization of NIPA in $scCO_2$ resulted in poor yield (Table 2, entry 6). This result was different from Liu's [19] report that the cross-linker decreased the monomer conversion in synthesis of cross-linked poly (acrylic acid; PAA). The experimental result from the literature suggested that the solubility of AA is much larger than that of NIPA under similar conditions; it is mainly due to the difference in their vapor pressures (p=0.0881 Torr for NIPA, p=3.42 Torr for AA, at 25 °C). In their work, AA monomer conversion decreased with cross-linker as the cross-linker decreased the rate of polymerization [19]. In contrast, in our experiments,

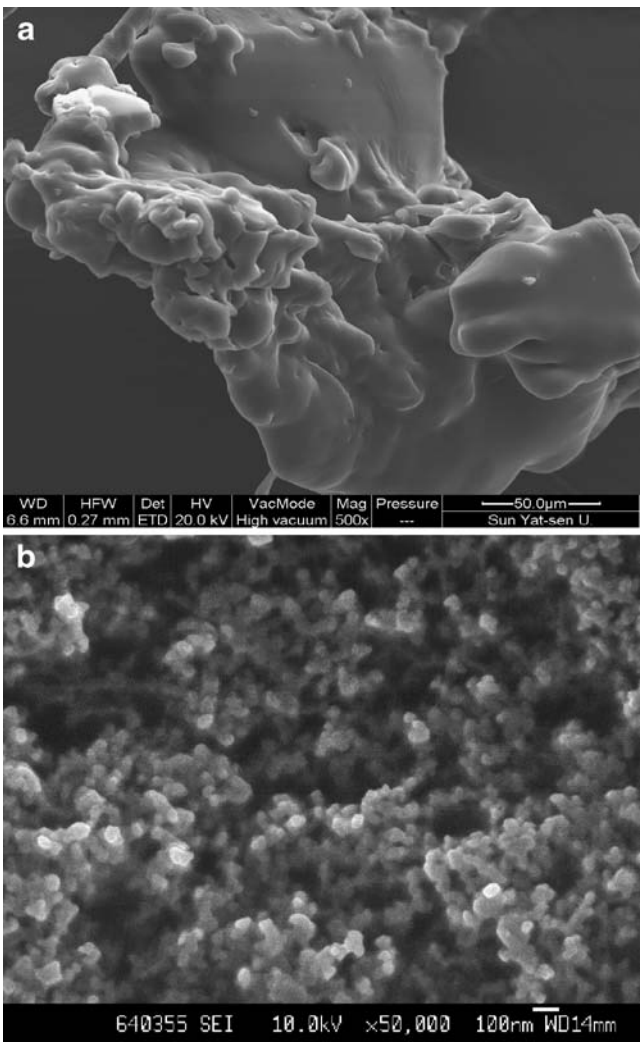

Fig. 2 Effect of the amount of cross-linker on polymerization of NIPA in $scCO_2$. **a** 0 and **b** 0.08 g BIS

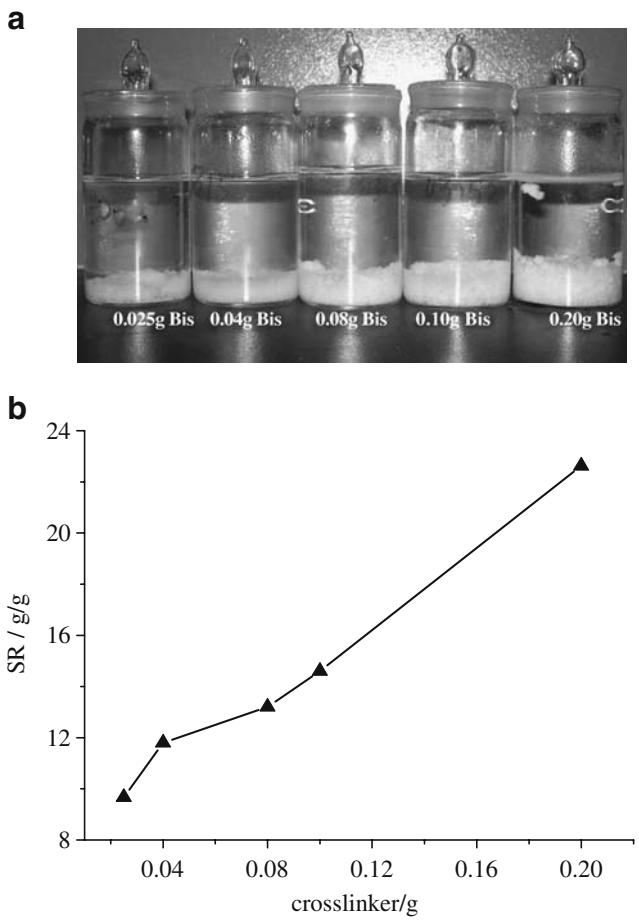

Fig. 3 **a** Visual inspection of equilibrium swollen for cross-linked PNIPA. **b** Swelling ratio as a function of cross-linker dose

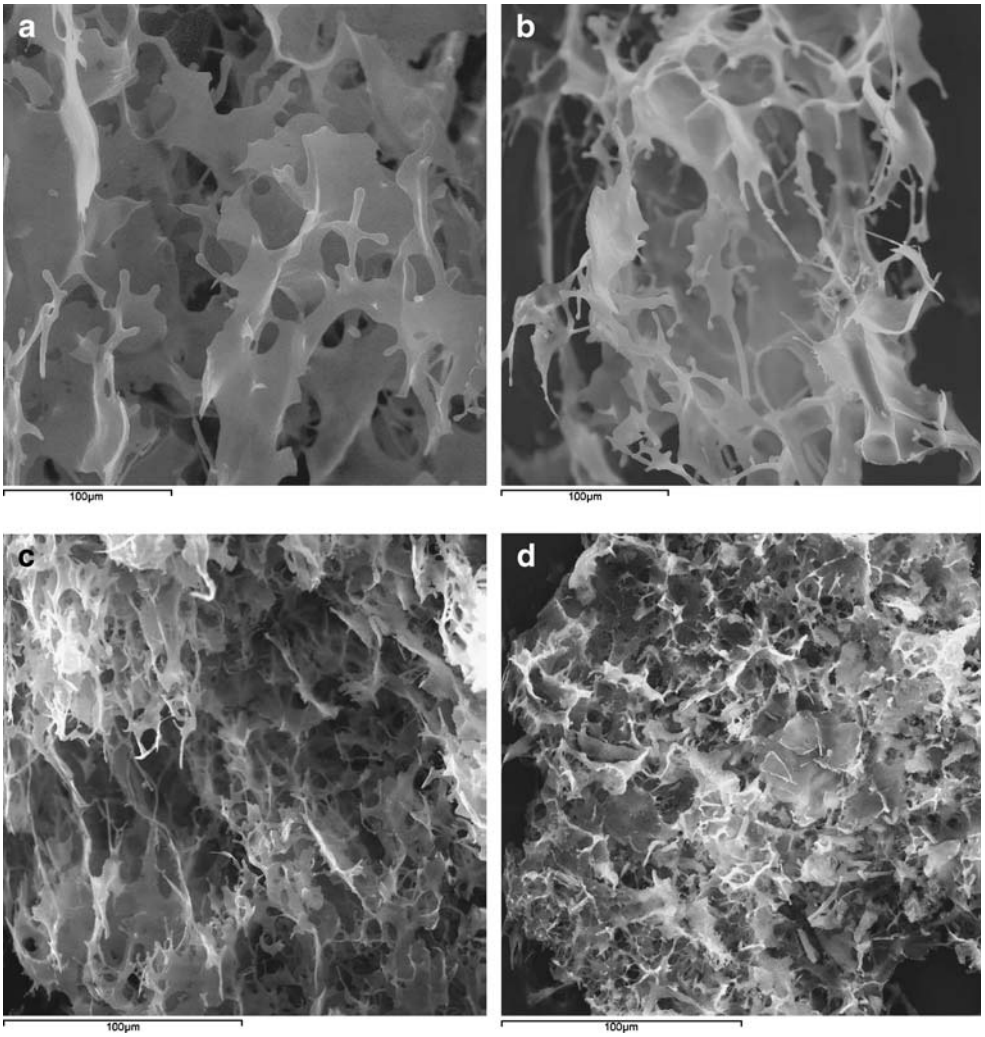

Fig. 4 SEM micrographs of cross-linked PNIPA microgels. **a** 0.025, **b** 0.04, **c** 0.10, and **d** 0.20 g BIS

the rate of NIPA homopolymerization in $scCO_2$ is slower and yield less than 42%. However, for cross-linking polymerization of NIPA in the presence of BIS, the formation of branched and cross-linked polymer molecules that promote the generation of larger molecules are done in less time. The higher the amount of the cross-linker in the system, the faster the polymerization will proceed and the sooner the gelation point will be reached. Finally, the polymer yield is increased with the cross-linker. As from reference, in copolymerization with the cross-linking of vinyl/divinyl monomers in $scCO_2$, the autoacceleration effect is more pronounced; the polymerization rate is much faster when the gelation molecule occurs, particles precipitating out from CO_2 fluid phase.

The effect of the amount of the cross-linker on the morphology of the polymer was shown in Fig. 2. The cross-linking structure reduced the solubility of PNIPA chains in $scCO_2$, so that the polymers with a higher degree of cross-linking precipitated out from the CO_2 fluid phase faster. Therefore, the increase in the concentration of the cross-linker could lead to generate more nuclei in the reaction

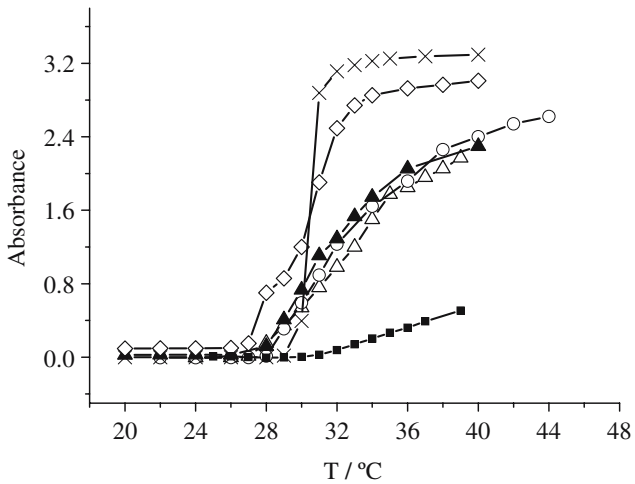

Fig. 5 Light absorbency as a function of temperature (λ=500 nm). Gram (g) NIPA; the *letter X* indicates 0 g BIS; *diamonds* indicate 0.025 g BIS; *open circles* indicate 0.04 g BIS; *filled triangles* indicate 0.08 g BIS; *open triangles* indicate 0.10 g BIS; and *filled squares* indicate 0.20 g BIS

Table 3 Effect of monomer concentration on the polymerization of NIPA in $scCO_2$

Entry	Monomer concentration per percent w/w w.r.t. solvent	Initiator/ monomer ratio per percent	Yield/ %	Morphology of the final product[a]
10	0.18	25	58	Aggregate
11	0.27	16.7	81	Lightly aggregate
12	0.36	12.5	85	Free flow dry powder
13	0.45	10	95	Free flow dry powder
14	0.54	8.33	100	Free flow dry powder

Reaction condition, 28 MPa (220 g CO_2); 0.08 g BIS; 0.1 g AIBN; 70 °C; 12 h

[a] Appearance of the polymer after venting

system and then reduce the particle diameter. In addition, it was assumed that the particle formation and growth mechanisms were similar to those of dispersion polymerization, except that the particles were stabilized against coagulation by their rigid, cross-linked surfaces rather than by added stabilizers [20]. The homogeneous polymerization of NIPA without adding a cross-linker was also studied, only a little yellow solid particle was obtained (Fig. 2a). Its morphology was very different from cross-linked polymers. The fact that the lightly cross-linked polymers did not form microparticles (entry 7) is consistent with this idea. The polymer formed from higher concentrations of the cross-linker were significantly less agglomerated than those formed from lower concentrations of the cross-linker, perhaps because the highly cross-linked microgels were more rigid and therefore less prone to aggregation. Such similar phenomena were also found in an early work [21].

As shown from Fig. 3, the swelling ratio of PNIPA microgel increased with the amount of the cross-linker. This abnormal result may be explained that the lower the amount of the cross-linker present in the system, the lower the polymer yield, and there may be formation of branched polymer and oligomers with lower molecular weight, which are not a completely cross-linked network. Therefore, only when all the studied sample yields are high, the swelling ratios of PNIPA microgels will decrease with the cross-linker as usually described.

The interior morphology of these microgels was studied by using an SEM, and the morphologies were shown in Fig. 4. The structure of microgels (0.2 g BIS) was compact with many small pores; in contrast, the samples with a lower degree of cross-linking presented bigger pores and a heterogeneously distributed matrix.

The VPTTs of the samples in water were examined by measuring the transmittance of the microgels dispersion as a function of temperature. Figure 5 demonstrated the variation in absorbance of the PNIPA homopolymer and cross-linked PNIPA microgel as a function of temperature. For the PNIPA homopolymer, a sharp variation in absorbance occurred at 31 °C, i.e., LCST. However, the microgels with a lower degree of cross-linking (BIS=0.025–0.10 g)

Table 4 Effect of reaction pressure on the polymerization of NIPA in $scCO_2$

Entry	Pressure/MPa	Yield/%	Polymer morphology[a]
15	15	92	Dry, white, pieces
16	25	99	Dry, white, fine powder
17	31	85	Dry, white, fine powder
18	35	89	Dry, white, fine powder

Reaction condition, 1.2 g NIPA; 0.1 g AIBN; 0.08 g BIS; 70 °C, 12 h

[a] Appearance of the polymer after venting

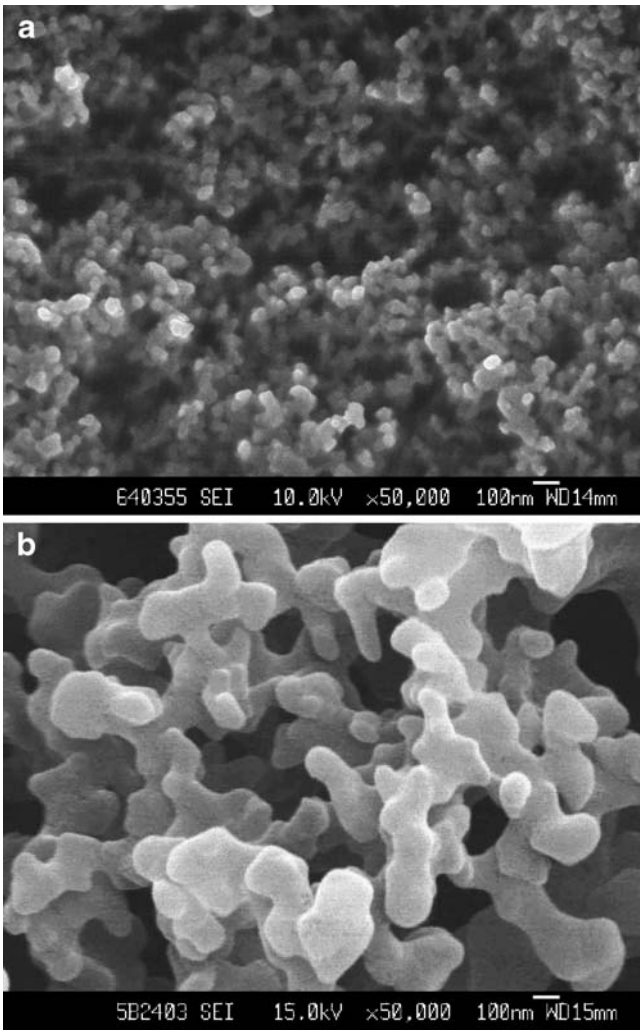

Fig. 6 Effect of reaction pressure on the polymerization of NIPA in $scCO_2$. **a** 260 and **b** 150 bar

presented a variation in absorbance when the temperature was above 28 °C and spanned over a broader range than that of the PNIPA homopolymer; in contrast, at a higher degree of cross-linking (BIS=0.20 g), no dramatic change in absorbance was observed for the PNIPA microgel. This suggests, although obtaining a high yield, the sample's swelling ratio may be limited by a tighter network; the existence of cross-linked network hinders the PNIPA chains from fully collapsing, and water is retained in the microgel.

Effect of monomer concentration

Precipitation polymerizations were conducted at five different monomer concentrations. As seen from Table 3, polymer yield increased with monomer concentration. The low yields at monomer concentrations of less than 0.27% w/w almost certainly reflect poor initiator efficiencies under those conditions [22], in which the primary particles were agglomerated to form larger structures [20], and still, little monomer residues are on the surface of the products. A further increasing monomer concentration, high yields, and white, dry, fine powders were obtained; although they changed slightly with initial monomer concentration (0.36–0.54%). On the other hand, in the case of the highest monomer concentration, the polymerization proceeded faster than that of the lower monomer concentration. This situation may have something to do with diffusion-controlled effects.

In addition, as shown from Table 3, when the monomer concentration increases, the initiator/monomer ratio is decreased gradually from 25–8.33%; the polymer yield will increase early and then decrease as discussed previously. From observations of the experimental result, such influence did not affect the overall trend of monomer conversion.

Effect of reaction pressure

A particular utility to supercritical fluids as a reaction medium is the ability to adjust the solvent properties through its easily tunable density by simple changes in the pressure or temperature. Moreover, for free-radical reactions, CO_2 offers no chain transfer to a solvent and high free-radical initiation efficiency with acceptable initiator decomposition kinetics [23]. The precipitation polymerizations of cross-linked PNIPA microgels in $scCO_2$ were carried out at four different pressures, and the results are collected in Table 4. In these experiments, the corresponding CO_2 densities were 0.508, 0.738, 0.796, and 0.823 $g \cdot ml^{-1}$, respectively. When the reaction pressure was varied from 150 to 350 bar, two abnormal trends were observed. As seen from Table 4, first, high yields occurred at 250 bar, indicating that the reaction could be carried out perfectly at this moderate pressure; secondly, there was a dramatic change in the final product morphology. This demonstrated that the polymerization of cross-linked PNIPA in $scCO_2$ was extremely sensitive to the density of

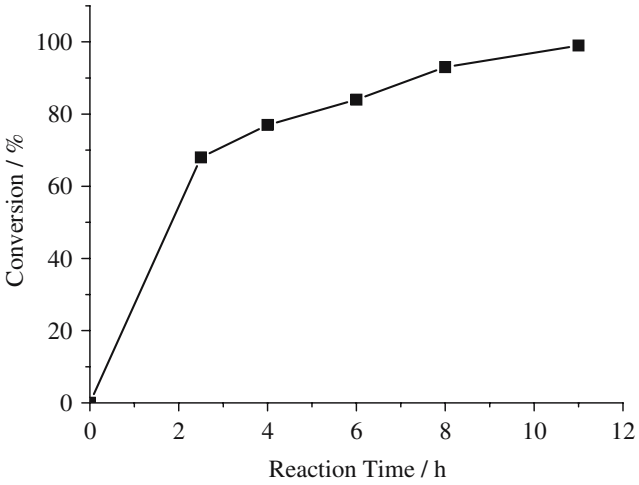

Fig. 7 Effect of reaction time on NIPA conversion

Table 5 Effect of reaction time on the polymerization of NIPA in $scCO_2$

Entry	Time/h	Yield/%	Morphology of the final product[a]
19	2.5	68	Aggregate
20	4	77	Aggregate
21	6	84	Dry, white, fine powder
22	8	93	Dry, white, fine powder
23	11	99	Dry, white, fine powder
24[b]	11	75	Aggregate

Reaction condition, 28 MPa (220 g CO_2); 1.2 g (0.011 mol) NIPA; 0.1 g AIBN; 0.08 g BIS; 70 °C

[a] Appearance of the polymer after venting

[b] 1.2 g NIPMA

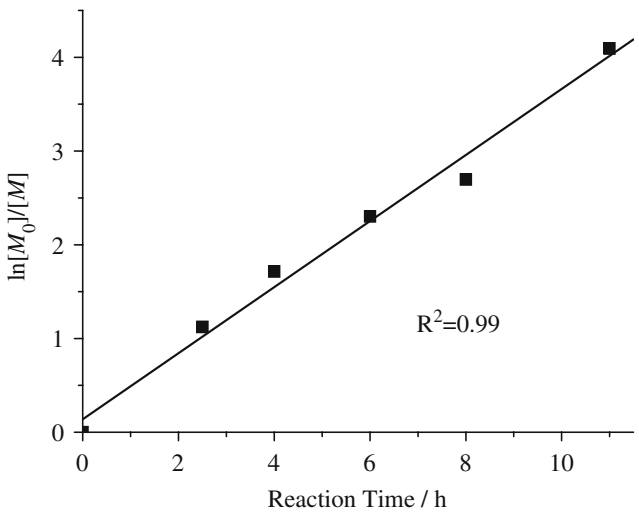

Fig. 8 First-order kinetic plot for the polymerization of NIPA in $scCO_2$. $[M_0]$ and $[M]$ are the initial concentration of NIPA and its concentration at time t, respectively

the continuous phase. In addition, the higher the pressure was, the more isolated particles were obtained. Furthermore, an interesting behavior was found during the synthesis of cross-linked polymers: when the pressure was 150 bar, the dry and soft polymers filled the whole reactor space instead of depositing only at the bottom of the view cell. However, at a pressure above 250 bar, white, dry, and fine powders were obtained at the bottom of the autoclave. Similar results were obtained in most batch experiments. As can be clearly seen by comparing Fig. 6a with Fig. 6b, the polymers produced at 250 bar are slightly aggregated, and the polymer particle size was about 50 nm, but those formed from the pressure at 150 bar are highly coagulated and larger in diameter size. A similar trend was found in other works [24, 25]. A possible explanation is that at lower pressure, the thermodynamics of mixing favors the expulsion of CO_2 and monomer from the polymer-rich phase [26], which resulted in a bulgy, soft, larger particle aggregates.

Effect of reaction time

The reaction time has a strong effect upon the yield and morphology of the resulting polymer. In an effort to gain insight into the reaction progress as a function of time, samples were obtained by stopping the reactions at various intervals. Table 5 and Figs. 7 and 8 depicted the results from this study. As shown from Fig. 7, the polymer yields increased with reaction time. When the reaction time was increased to 1.5 h, the formation of particles, although with larger aggregation, was observed. After 6 h, a white, dry, fine powder was obtained with yields around 90%. Figure 8 has shown the first-order kinetic plot for the polymerization reactions of NIPA and BIS. The plots are close to linear, indicating that the concentration in active centers remains constant throughout the polymerization. The apparent first-order rate constant for the reaction under these conditions is found to be $9.79\times10^{-5}s^{-1}$.

Synthesis of cross-linked PNIPMA

Based on the above discussion, a white, dry, fine powder was prepared in most cases; subsequent experiments were carried out for synthesis of cross-linked PNIPMA. The result was listed in Table 5 (entry 24). The resulting polymer product was formed in a low yield and more agglomerated than those obtained from the polymerization of NIPA under equivalent conditions. This was possibly due to the lower solubility of NIPMA in $scCO_2$ and the lower propagation rate constant for NIPMA than that for NIPA [27].

Conclusions

This study indicates that cross-linked PNIPA microparticles can be prepared in $scCO_2$. It is possible to obtain nanosized particles by changing the initial concentrations of the initiator, cross-linker, and pressure as well as reaction time. The polymers were obtained in high yield as dry, fine, and free-flowing materials directly from the reaction vessel; there was no contamination of monomer in the final product because of continuously washing the polymer at the end of the reaction with high-pressure carbon dioxide. As a series of work, our future study will focus on the impregnation of cross-linked PNIPA with water-insoluble drug in $scCO_2$ and on their adsorption behavior.

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