Atom Transfer Radical Dispersion Polymerization of Styrene in Ethanol

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ABSTRACT: An atom transfer radical dispersion polymerization of styrene in ethanol was successfully carried out with the formation of uniform sized particles. This was accomplished by using a "two-stage" polymerization technique, in which the first stage involves a standard free radical polymerization and the second a controlled/living radical polymerization. The required nucleation stage was completed in a relatively short period, and therefore particles with uniform size were achieved. The particles contained polymers with molecular weight ~20 000 g/mol and relatively low polydispersity (M_w/M_n = 1.4−1.8, compared with M_w/M_n = 4−5 from conventional dispersion polymerization), indicating a high fraction of retained chain-end functionality which can be readily employed for further modification of the particles. Monodisperse cross-linked polystyrene particles were also synthesized using the same technique; these particles were successfully chain-extended with 2-hydroxyethyl methacrylate, thereby modifying the surface properties of the particles.

Introduction

Monosized polymer beads with diameters between 0.1 and 10 μm are finding an ever-increasing number of applications in coatings, electronics, microelectronics, biomedical, and information technology.[1−4] Particle size control and narrow size distribution are key parameters for most of these applications. Several routes have been used to synthesize monodisperse polymeric particles. One method is seeded suspension polymerization which uses uniform particles as seeds that are swollen with monomers prior to conducting polymerization.[5,6] The other method is dispersion polymerization, which is generally recognized as a type of precipitation polymerization conducted in the presence of a suitable polymeric stabilizer that is soluble in the reaction medium. Under favorable circumstances the polymerization, in a batch step process, results in the preparation of polymeric particles of 0.1−15 μm in diameter, often monodisperse particles. Dispersion polymerization was initially developed in a hydrocarbon medium in the 1970s;[7] however, it was an extension of the procedure to polar solvents, such as ethanol or methanol, that greatly expanded the utility of this polymerization procedure.[8−11]

Living anionic dispersion polymerization has been achieved in hydrocarbon solvents.[12] In recent years, controlled/living radical polymerization (CRP) techniques have also been examined. Living radical dispersion polymerization, which encompasses a wide range of monomers and reaction media, is a promising way to expand both the design and scope of functional polymer colloids. Combining dispersion polymerization and CRP offers several benefits in addition to the preparation of uniform micron-sized particles. First of all, these particles contain polymers with predetermined chain-end functionality. Therefore, they are suitable materials for postpolymerization modification forming materials that would be suitable in a spectrum of applications. Since the particles obtained from a CRP can be designed to contain low molecular weight polymers that can be swollen in solvents or additional monomers, they are ideal materials for use as seeds for a seeded polymerization.[13]

In principle, when CRP is applied to a dispersion polymerization, all chains are quickly initiated and grow simultaneously. Uniform particle growth and good control over particle size were anticipated from a controlled/living dispersion polymerization, but problems were encountered when using nitroxide-mediated polymerization (NMP),[14,15] degenerative transfer polymerization,[13] and reversible addition−fragmentation chain transfer (RAFT) polymerization[16] as the CRP processes. While controlled molecular weight and sufficient chain-end functionality have generally been obtained, particle size distribution has been very broad. Furthermore, it was discovered that particle size uniformity, as well as the colloidal stability, declined as more controlled radical regulators (e.g., TEMPO or RAFT agents) were added to the system.[16,17]

Recently a "two-stage" polymerization technique was developed by Song and Winnik et al.[13,18,19] to solve the problem of size control in dispersion polymerization in the presence of degenerative chain transfer agents or RAFT agents. This method was successfully employed in the present study which resulted in successful atom transfer radical dispersion polymerization and the preparation of uniformly sized polymeric particles.

Experimental Section

Materials. All chemicals, including ethyl α-bromoisobutyrate (EBiB, 98%), 2,2′-bipyridyl (bpy, ≥99%), poly(*N*-vinylpyrrolidone) (PVP, average M_w ~ 55 000), Triton X-305 (octylphenol ethoxylate, 70%), and 2-hydroxyethyl methacrylate (HEMA, 98%), were purchased from Aldrich and were used as received unless otherwise stated. Styrene (99%) and divinylbenzene (DVB, 80%) were purified by passing through a column filled with basic aluminum oxide to remove inhibitor and/or antioxidant and was stored at −5 °C. 2,2′-Azobisisobutylronitrile (AIBN) was recrystallized in ethanol. Tripyridinemethyleneamine (TPMA) was synthesized according to the published procedures.[20,21]

Conventional Radical Dispersion Polymerization. A 50 mL Schlenk flask was charged with ethanol, styrene (and DVB, if preparing cross-linked particles), stabilizer PVP, costabilizer Triton X-305, and initiator AIBN. Detailed recipes are listed in Table 1. The resulting homogeneous solution was deoxygenated by bubbling with nitrogen at room temperature for 30 min. The flask was then placed in a 70 °C oil bath and stirred with a magnetic stirrer at

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Table 1. Recipe for the Dispersion Polymerizations of Styrene in Ethanol[a]

		first stage	second stage
run	initiation	St_1:AIBN:ethanol$_1$:$CuBr_2$/TPMA (g)	St_2:ethanol$_2$:$CuBr_2$/TPMA (g)
1	FRP	3.28:0.021:11:0	
2	one-batch direct ATRP	3.28:0:0.026(Cu^I)/0.052 (0.023 g of EBiB)	
3	one-batch reverse ATRP	3.28:0.021:11:0.04/0.052	
4	two-stage ATRP	1.64:0.021:5.5 :0	1.64:5.5:0.066/0.086
5	two-stage ATRP	1.64:0.034:5.5:0	1.64:5.5:0.105/0.137
6	two-stage ATRP	1.64:0.013:5.5:0	1.64:5.5:0.04/ 0.052
7	two-stage FRP	1.64:0.013:6.3:0	1.64:6.3:0 (0.03 g of DVB)
8	two-stage ATRP	1.64:0.013:6.3:0	1.64:6.3:0.04/ 0.052 (0.03 g of DVB)

[a] PVP: 0.49 g; Triton X-305: 0.13 g; polymerization temperature: 70 °C.

~100 rpm. The polymerization was stopped after 24 h by cooling the flask to room temperature.

Atom Transfer Radical Dispersion Polymerization. The detailed recipes are listed in Table 1. The one-batch reactions were performed using the same procedure employed for the conventional radical dispersion polymerization; the only difference was addition of the components required for the ATRP together with the monomer and solvents. In the two-stage experiments, all of the stabilizer (PVP), the costabilizer (Triton X-305), and initiator (AIBN) and half of the monomer and ethanol were charged to a 50 mL Schlenk flask. The formed homogeneous solution was deoxygenated by bubbling nitrogen through the mixture at room temperature for 30 min. The flask was then placed in a 70 °C oil bath under magnetic stirring, ~100 rpm. $CuBr_2$ and TPMA were dissolved in a mixture of the remaining styrene and ethanol at 70 °C under nitrogen. This solution was added to the reaction after the polymerization had run for 45 min. Aliquots were withdrawn from the reaction at different time intervals to determine conversion by gravimetry. The samples were dried and dissolved in THF before being subjected to gel permeation chromatography (GPC) for molecular weight analysis. The polymerizations were stopped by exposing the catalysts to air.

Chain Extension of Cross-Linked Polystyrene Particles Prepared by ATRP Dispersion with HEMA. A direct ATRP of HEMA was carried out with cross-linked polystyrene particles as macroinitiators in DMF at 35 °C. The halide exchange technique, i.e., a combination of a bromo-based initiator and a chloro-based catalyst, was used in the present experiment.[22] The cross-linked polystyrene particles were synthesized in a two-stage atom transfer radical dispersion copolymerization and were separated from the ethanol suspension medium by centrifugation (5000 rpm, 20 min). They were washed with THF to remove any remaining monomer and dried under vacuum. A dispersion of the particles (0.2 g) in DMF (3.6 mL) was mixed with HEMA monomer (1.44 mL) and bpy (0.0185 g), and then the mixture was subjected to five cycles of freeze−pump−thaw to remove oxygen. The reaction flask was then backfilled with nitrogen, and CuCl (0.0056 g) and $CuCl_2$ (0.0004 g) were added to the frozen mixture. The flask was sealed again and subject to vacuum followed by backfilling with nitrogen. The reaction flask was then placed in a 45 °C oil bath to conduct the polymerization. The polymerization was stopped after 40 h by exposing the reaction mixture to air. The products were separated by centrifugation (5000 rpm, 20 min) and washed by methanol for several times.

Characterizations. Monomer conversion was measured gravimetrically. Molecular weight and molecular weight distribution (M_w/M_n) were determined by GPC equipped with an autosampler (Waters, 717 plus), HPLC pump with THF as eluate at 1 mL/min (Waters, 515), and four columns (guard, 10^5 Å, 10^3 Å, and 100 Å; Polymer Standards Services) in series. Toluene was used as an internal standard. A calibration curve based on linear polystyrene standards was used in conjunction with a differential refractometer (Waters, 2410). Particle sizes and particle size distributions were examined by scanning electron microscopy (SEM, Hitachi S-2460N). SEM samples were prepared by drying a drop of diluted suspension on a clean microscope cover glass. The average particle size was based on measurement of 300 individual particles in the SEM images.

Results and Discussion

Dispersion polymerization is defined as a type of precipitation polymerization in which the monomer and all other reactants (including polymeric stabilizers) are initially soluble in the reaction medium, but the polymer is insoluble. Dispersion polymerization starts as a homogeneous solution polymerization reaction, but as polymer (or oligomer) chains grow in size they eventually reach a molecular weight higher than a certain critical value and precipitate from solution and aggregate to form colloidally unstable precursor particles. These particles coalesce and adsorb stabilizers from the reaction medium onto their surface until they become colloidally stable. At this point, the total number of particles in the system is fixed, and the nucleation stage ceases. Subsequent polymerization, also termed the particle growth stage, occurs either inside the swollen nuclei or in the reaction medium depending on the polymer−solvent interactions. However, the newly formed polymers should not form additional nuclei but should be captured by existing particles.[23]

It has been widely accepted that the key issue for preparation of uniformly sized colloidal particles is a short nucleation stage.[24] The particle number and particle number distribution are determined during the nucleation stage, and no secondary particles or coagulum should be formed during the particle growth stage. A prolonged nucleation stage usually results in a broad particle size distribution. Furthermore, the nucleation stage in dispersion polymerization is very sensitive to variations in reaction components or conditions. It has been found that incorporation of functional monomers[25] or cross-linking agents[18] in dispersion polymerization is much more difficult than that in other heterogeneous polymerizations such as emulsion polymerization.

The sensitivity of the nucleation process to reaction components was also reflected when combining atom transfer radical polymerization (ATRP)[26−32] and dispersion polymerization. Monodisperse particles could not be achieved in a single batch mode. When a direct ATRP was used, i.e., Cu(I) species were added as the activators, nucleation (turbidity of the reaction system) was observed ~15 min after injection of initiators. This is visibly later than that in a conventional radical dispersion polymerization, in which nucleation occurred after ~5 min under the similar reaction conditions. When a reverse ATRP was used, i.e., ATRP deactivators Cu(II) species were added together with a conventional radical initiator,[33,34] such as AIBN, the observed nucleation was postponed even more. The SEM images of polystyrene particles prepared in one-batch dispersion polymerization using free radical polymerization (FRP), direct ATRP, and reverse ATRP are shown in Figure 1. Comparing Figure 1A with Figure1B,C, it is clear that particle size distribution

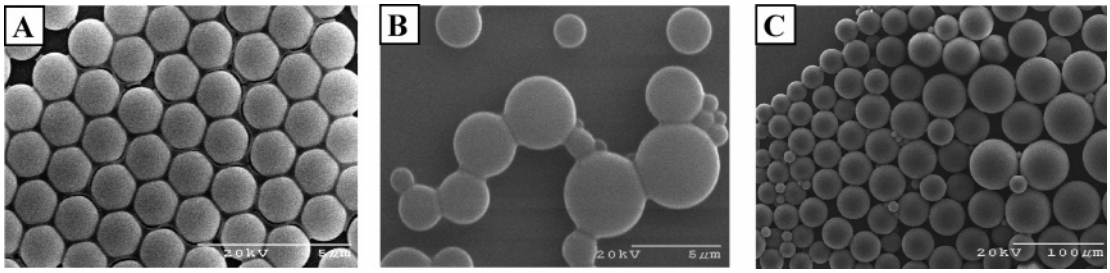

Figure 1. SEM images of polystyrene particles prepared by conventional dispersion polymerization (A), one-batch direct ATRP (B), and one-batch reverse ATRP (C). The scale bars represent (A) 5, (B) 5, and (C) 100 μm. Polymerization conditions: Table 1, runs 1, 2, and 3.

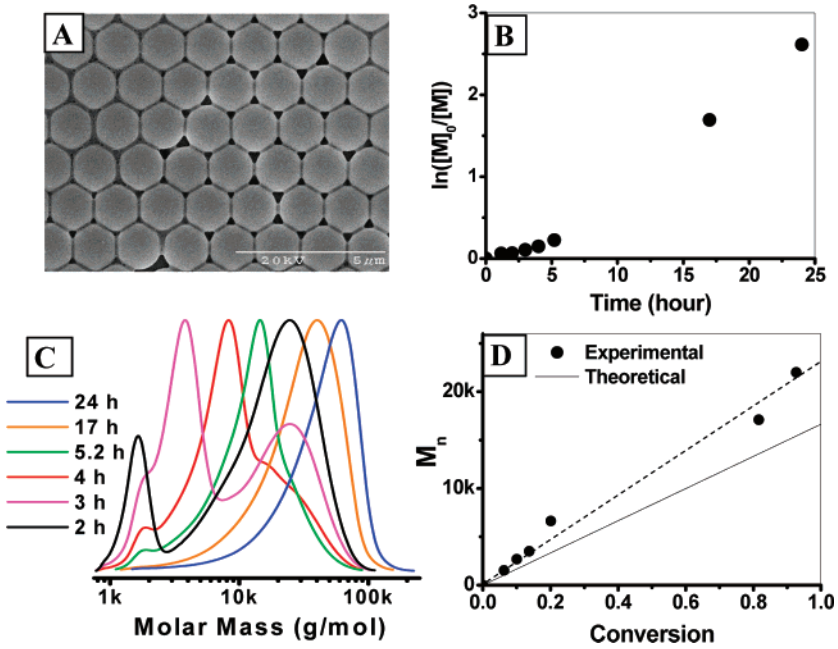

Figure 2. SEM images of the polystyrene particle (A), polymerization kinetics (B), GPC traces of the obtained polymers during the polymerization (C), and molecular weight evolution with monomer conversion (D). Polymerization conditions: Table 1, run 3. The scale bar represents 5 μm.

broadened to a significant degree with the involvement of the components of an ATRP in the reaction media, regardless of using direct or reverse initiation of the ATRP. The presence of small and exceptionally large sized particles indicates both an extended nucleation stage and secondary nucleation (nuclei formed after the first nucleation stage).

In a CRP, because all chains grow at the same rate, the time required for the preparation of high molecular weight polymer, with a molecular weight above the critical molecular weight, is significantly longer than that in FRP. This slower controlled polymerization process directly influences, most likely extends, the nucleation stage in a dispersion polymerization. This is supported by recent research from Choe et al.,[35] in which improved particle size control was obtained by adding camphorsulfonic acid to a NMP because camphorsulfonic acid accelerates the rate of polymerization by reducing the concentration of the persistent radical, TEMPO. While this idea has merit, it cannot be easily extended to other systems. On the other hand, the procedure reported by Song and Winnik et al.,[13] named a "two-stage" dispersion polymerization, can be applied to a number of systems.[17] In this technique, the first stage is a FRP and all other control reagents, such as chain transfer agents, cross-linking agents, are added during the second stage, i.e., particle growth stage.[13,18] The delayed addition of the "problematic reagents" proved to be beneficial for improving particle size polydispersity.

In order to shorten the nucleation stage, and provide monodisperse polymeric particles, this "two-stage" technique was employed in the present ATRP system. The initiation system was still a reverse ATRP. The slight difference between the initiation systems applied in this research from that of a classic reverse ATRP is that the deactivator is added to the reaction at a certain time (45 min, with monomer conversion ~3%) after the polymerization was initiated. In this way, the first stage of the polymerization only involved a standard FRP forming high molecular weight polymer, which should result in a short and clean nucleation stage, and improved uniformity in the size of the particles. The second stage should be an ATRP, during which time the polymers produced should exhibit the characteristics of a living and controlled polymerization process.

This in-situ two-stage polymerization strategy efficiently resolved the problem of particle size uniformity. As seen in Figure 2A, the particles had very narrow size distribution. In addition, comparing Figure 1A and Figure 2A, it can be seen that the particles prepared from free radical dispersion polymerization and the new "two-stage" atom transfer radical dispersion polymerization have very similar particle size (1.50 ± 0.05 and 1.54 ± 0.05 μm, respectively). This can be considered as proof that the nucleation stage was complete before addition of ATRP deactivators.

The rate of atom transfer radical dispersion polymerization was considerably slower than a conventional radical dispersion polymerization because of the addition of ATRP deactivators during the second stage. The molecular weight steadily shifted toward higher value, demonstrating the retention of chain-end functionality during the polymerization. The weight fraction of

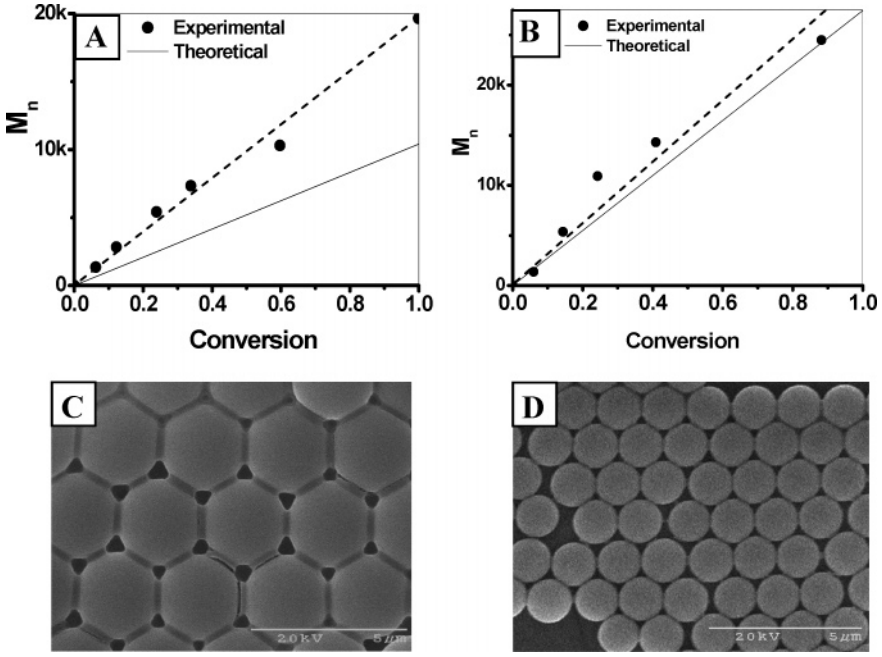

Figure 3. Molecular weight evolutions (A, B) and SEM images of polystyrene particles (C, D) from two-stage atom transfer radical dispersion polymerization. The scale bars represent 5 μm. Polymerization conditions: Table 1, runs 5 and 6.

polymers formed during the first stage, nucleation process, became insignificant in the final polymers, as evidenced by the inconsequential fraction of the FRP polymer peak in the final GPC trace (Figure 2C). The GPC trace of the final polymer had tailing toward the low-MW area, which can be attributed to the slow continuous decomposition of AIBN. The obtained polymer was with molecular weight ~21 400 g/mol and relatively narrow polydispersity ($M_w/M_n = 1.6$), compared with $M_w/M_n = 4-5$ from conventional dispersion polymerization.

The theoretical number-average molecular weight ($M_{n(theo)}$) was calculated on the basis of the equation $M_{n(theo)} = (\Delta[M]/2f[AIBN]_0)M_m$, in which f is the initiation efficiency of AIBN, which was assumed to be 75%, and M_m refers to the molecular weight of the monomer. The initiation efficiency of this system is reflected in the ratio of experimental molecular weight to theoretical molecular weight. It was calculated to be ~70% (Figure 2D). The incomplete initiation efficiency is due to (1) overestimated decomposition efficiency of AIBN and (2) coupling of oligomers in the initial stage of polymerization, which reduces the number of living chains.

A lower concentration of initiator should assist in attaining higher initiation efficiency, as indicated by the experiment targeting a higher degree of polymerization (DP_{target}). Figure 3A,B shows evolution of molecular weight of the two systems with DP_{target} of 100 and 260. It can be seen in the latter case that the initiation efficiency was very close to 100% while the lower DP_{target}, of 100, resulted in initiation efficiency as low as ~53%. As the DP_{target} decreased, i.e., the initiator concentration increased, it became obvious that the particle size increased (Figure 3C,D). This is a consequence of the higher initiator concentration which results in a higher concentration of growing oligomers and a rate of the polymerization which was faster than the adsorption rate of the stabilizer. Therefore, the oligomers tended to aggregate and form larger nuclei before sufficient stabilizers were able to adsorb onto the particles to stabilize them. Therefore, a larger particle size was obtained.

As addressed in the Introduction, it is a significant challenge to prepare uniform cross-linked particles by dispersion polymerization because of the sensitivity of the nucleation stage to the presence of cross-linking agents. This "two-stage" technique offers a resolution to the difficulties of preparing cross-linked particles, since it provides a method to avoid any negative effects from the presence of cross-linking agents in the nucleation stage. Song and Winnik et al. reported success using the two-stage technique to incorporate cross-linking agents into the polystyrene particles in a conventional radical dispersion polymerization.[18] However, the report also pointed out that when DVB was used as the cross-linking agent, the rapid consumption of DVB into the cross-linked system resulted in a low swelling ability of the growing particles/nuclei with monomers and therefore irregular-shaped particles, and particle coagulation was observed when the concentration of DVB is higher than a critical value even when using the two-stage technique. A dispersion polymerization in the presence of 1 wt % DVB resulted in severe coagulation after 2−3 h. This phenomenon was also observed in our study. It is necessary to add fractions of the required amount of DVB multiple times to resolve these stability problems.[18]

In fact, using CRP can be beneficial for incorporation of higher concentration of cross-linking agents into the cross-linked system because the lifetime of a radical is significantly longer in a CRP and the polymer chains have more time to relax during their dormant period, resulting in a more uniform cross-linked structure. Particles with a uniform cross-linked structure should swell more efficiently in monomer/solvent, and therefore they should have less stability problems. In our study, cross-linked polystyrene particles were successfully prepared by using a two-stage atom transfer radical dispersion polymerization, in which 1 wt % DVB was added together with the second fraction of monomers and solvents. The particles remained stable after 24 h, with monomer conversion ~95%.

It is worth noting that the un-cross-linked polystyrene particles can only be clearly observed in SEM when the monomer conversion was higher than 50−60%. At low conversion the particles are excessively swollen with monomer and solvent. They form a film on the glass substrate, and a very soft SEM image would be anticipated. However, as Figure 4A shows, even at the low monomer conversion (26%), the cross-linked particles

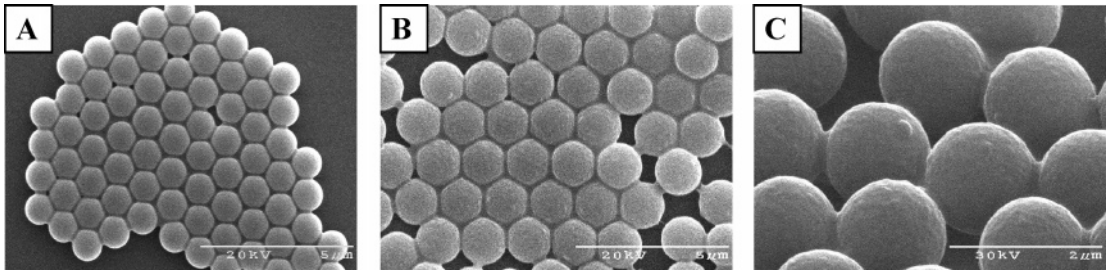

Figure 4. SEM images of cross-linked PS particles prepared by two-stage atom transfer radical dispersion polymerization at 8 h with monomer conversion 26% (A) and 24 h with monomer conversion 95% (B, C). The scale bars represent (A) 5, (B) 5, and (C) 2 μm. Polymerization conditions: Table 1, run 8.

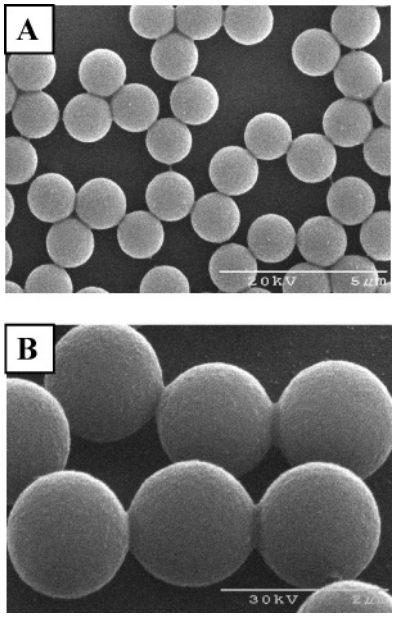

Figure 5. SEM images pf pHEMA-modified cross-linked polystyrebe particles. The scale bas represent (A) 5 and (B) 2 μm.

were already clearly imaged, indicating DVB has been incorporated into the particles. The surface morphology of the particles was rather smooth at low monomer conversion (Figure 4A), but noticeably rougher when the conversion was higher (Figure 4B), which can be clearly seen with a high magnification in Figure 4C. This increase in surface roughness has been also observed when conventional dispersion polymerization was carried out in the presence of cross-linking agents.[18,36] In the present study, the particles remained spherical and monodisperse until the end of polymerization. The cross-linked particles can be easily dispersed in THF.

One advantage of carrying out ATRP for the preparation of cross-linked particles is that the retained chain-end functionalities can be directly used for further chain-extension and particle surface modification.[37,38] When using the particles from conventional radical polymerization, the initiators have to be further introduced to the surface,[39−42] while this step can be avoided when using particles prepared directly by ATRP.

In the present study, these polystyrene particles were used as macroinitiators for chain-extension polymerization with 2-hydroxyethyl methacrylate (HEMA). The halide exchange technique was applied in this study because the cross-propagation rate from polystyrene macroinitiators to methacrylate monomer is slower than the subsequent propagation rate of methacrylate monomers.[43] After polymerization of HEMA, the particles can be dispersed in methanol, which indicates that the surface of the particles have been modified by successful chain extension with polyHEMA, because bare polystyrene particles cannot be dispersed in methanol. On the basis of gravimetrical measurement, the obtained particles contained 1.4 wt % polyHEMA. It can be seen from the SEM images (Figure 5) that the surface of the modified polystyrene particles became smoother after polyHEMA modification.

Conclusions

Atom transfer radical dispersion polymerization of styrene in ethanol was successfully carried out using a "two-stage" polymerization technique, in which the first stage involves a FRP and the second an ATRP. Polystyrene particles with particle size 1.5−2.5 μm were obtained. The particles prepared using ATRP displayed a narrow size distribution, containing polymers with molecular weight ~20 000 g/mol and relatively narrow polydispersity ($M_w/M_n = 1.4-1.8$, compared with M_n ~110 000 g/mol and $M_w/M_n = 4.5$ from conventional dispersion polymerization). This technique also facilitated the preparation of uniform cross-linked polystyrene particles by two-stage atom transfer radical dispersion polymerization. As a consequence of the involvement of ATRP, the incorporation of the cross-linking agent was better controlled and uniform cross-linked particles were formed. In addition, these cross-linked particles were successfully chain-extended with HEMA, indicating well-retained chain-end functionality in the particles for further modification of particle surfaces.

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