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ARTICLE

Reactive Surfactants for Polymeric Nanocapsules via Interfacially Confined Miniemulsion ATRP

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ABSTRACT: Stable hollow polymeric nanocapsules with a cross-linked shell were prepared through an interfacially confined copolymerization of a monovinyl monomer and divinyl cross-linker via an activator generated by electron transfer atom transfer radical polymerization (AGET ATRP) in a miniemulsion system. An amphiphilic block copolymer poly(ethylene oxide)-*b*-poly(*n*-butyl methacrylate) (PEO−PBMA−Cl) was used as a stabilizer/macroinitiator. The amphiphilic nature of the macroinitiator ensures that the polymerization starts from the aqueous/monomer droplet interface with polymer chains slowly growing inward in a controlled manner by an AGET initiated ATRP. Characterization of the resulting particles by TEM, Cryo-SEM, and AFM provided direct evidence that nanoparticles with a hollow structure were successfully prepared. Introduction of cross-linking units to the shell of the particles improved the stability of the particles, which could be easily redispersed in some common organic solvents.

Introduction

Considerable effort has been expended over the past decade on the fabrication of hollow polymeric nanocapsules due to their potential application in catalysis, cosmetics or pharmaceutics.[1−4] The majority of these applications rely on the preservation of a large fraction of void space within the hollow structure of the nanocapsule, which can encapsulate and control the release of large quantities of active substances, such as drugs, enzymes, dyes and cosmetics.[4] In order to successfully store the guest molecules and deliver them to the targeted area, hollow polymer spheres, or polymeric nanocapsules, with well controlled tunable structural features such as shell thickness, composition, functionalities and good stability are required. Several techniques have been developed to achieve this goal. One of the commonly used methods for the preparation of particles with a hollow structure is hard templating against sacrificial solid particles.[5−13] Silica particles[5−7] are frequently employed because of their availability in wide range of size and narrow size distribution. Typical examples include layer-by-layer deposition techniques[3,8−10] or *in situ* polymerization from particle surfaces.[5,7,14] However, there are some practical limitations on the use of hard templates, such as the tedious procedures required for the synthesis of well-defined core/shell particles and the subsequent removal of the hard template by dissolution or thermolysis, and also the difficulty of refilling the guest molecules into the hollow interior of the particle.[4]

Recently, soft templates, such as (micro)emulsion droplets[15−18] or vesicles,[19,20] were successfully used for the preparation of polymeric nanocapsules. The use of soft templates can partially overcome the limitations of the hard template due to the easier removal of the liquid core by evaporation, as well as facile and efficient incorporation of functional species into the liquid core. However, stabilization of emulsions or formation of vesicles usually requires the use of a large amount of surfactant, which remains part of the system or has to be removed in a laborious manner. In dilute solution, it is also difficult to scale up the process. Miniemulsion polymerization[21,22] overcomes these limitations and has attracted increased attention for the preparation of nanocapsules.[23,24] This environmental friendly system is easy to scale up. Direct encapsulation of liquid organic molecules[25−29] and inorganic particles[30−32] was also successful in miniemulsion systems. For instance, Luo et al.[33−35] prepared nanocapsules with uniform structures by conducting an interfacially confined reversible addition−fragmentation chain transfer (RAFT)[36] miniemulsion polymerization with an amphiphilic block copolymer as a macro-RAFT agent.

The stability of the hollow particles/nanocapsules is an important issue that should receive more attention, particularly, since the shell may be sensitive to a variety of environmental parameters including temperature, pH, salt concentration, and the efficiency of encapsulation is affected by these parameters. One strategy to construct polymeric nanocapsules with a more stable and robust structure is to cross-link the polymer shell.[37−41] Wooley et al.[2] reported the generation of reinforced, nanoscale cage like structures by the removal of the core from shell cross-linked polymer assemblies.

Herein we report the fabrication of stable polymeric nanocapsules through an interfacially confined atom transfer radical polymerization (ATRP)[42−46] in miniemulsion using an amphiphilic block copolymer, poly(ethylene oxide)-*b*-poly(*n*-butyl methacrylate) (PEO−PBMA−Cl), as a stabilizer and macroinitiator[47,48] (Scheme 1). The approach utilizes the specific solubility properties of the amphiphilic block copolymer that assemble at the interface of monomer droplets formed through ultrasonication. Initiation of the (co)polymerization of monovinyl monomer and/or divinyl cross-linker by an activator generated electron transfer atom transfer radical polymerization (AGET ATRP)[49,50] is constrained to the wall formed by the PEO−PBMA−Cl macroinitiator with well preserved halogen chain end functionalities. Therefore, an interfacially confined controlled polymerization, with the polymer chains extending inward, is expected. After reaching a certain monomer conversion, a stable cross-linked polymer network would form at the surface of the

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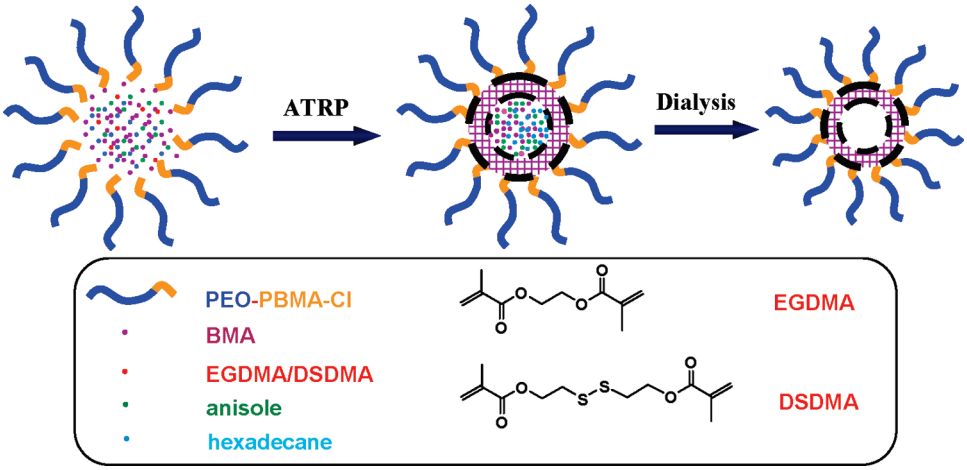
Scheme 1. Preparation of Polymeric Nanocapsules with Cross-Linked Shells by Surfactant Initiated Miniemulsion Polymerization



monomer droplets. Then the remaining monomer, cross-linker and solvent can be removed by dialysis and hollow polymeric nanocapsules with cross-linked shells can be obtained.

Experimental Section

Materials. *n*-Butyl methacrylate (BMA, 99%) and ethylene glycol dimethacrylate (EGDMA, 98%) were purchased from Aldrich and purified by passing through a column filled with basic alumina to remove the inhibitor and/or antioxidant then stored at −5 °C. Bis(2-pyridylmethyl)octadecylamine (BPMODA)[51] and bis(2-methacryloyloxyethyl) disulfide (DSDMA)[52] cross-linker were synthesized according to the previously published procedures. All other reagents, $CuBr_2$ (98%), hexadecane (99%), L-ascorbic acid (>99%), 2,2′-bipyridine (bpy, 99+%), tri(*n*-butyl)phosphine, and solvents, were purchased from Aldrich and used as received.

PEO-Br macroinitiator was prepared by esterification of poly(ethylene glycol) methyl ether (PEO−OH) (molecular weight: 5000 g/mol) with 2-bromoisobutyryl bromide (Aldrich, 98%) in the presence of triethylamine in methylene chloride, then chain extended with BMA by ATRP to synthesize a PEO−PBMA−Cl block copolymer using CuCl/bpy as catalyst, (PEO−PBMA−Cl, M_n = 12 000 g/mol, PDI = 1.15).

AGET ATRP of BMA in Miniemulsion with PEO−PBMA−Cl as Macroinitiator and Stabilizer. The PEO−PBMA−Cl block copolymer was used as stabilizer and macroinitiator for AGET ATRP of BMA in a miniemulsion polymerization. Typically, $CuBr_2$ (0.0012 g, 0.005 mmol) and BPMODA (0.0024 g, 0.005 mmol) are dissolved in a mixture of BMA (0.35 mL, 2.2 mmol) and anisole (0.10 mL) in a round-bottom flask by stirring at 60 °C for ∼1 h to form homogeneous organic solution. The resulting solution was then cooled to room temperature and hexadecane (0.13 mL) was added. Meanwhile, PEO−PBMA−Cl surfactant/initiator (0.12 g, 0.01 mmol initiating sites) was dispersed in 10 mL of water. Then the aqueous PEO−PBMA−Cl solution was added to the organic solution. The resulting mixture was subjected to sonication in an ice bath (Heat Systems Ultrasonics W-385 sonicator; output control set at 8 and duty cycle at 70% for 5 min). The resulting stable miniemulsion was transferred to a Schlenk flask and purged with nitrogen for 30 min before being immersed in an oil bath thermostated at 65 °C. 0.2 mL of a deoxygenated aqueous solution of ascorbic acid, containing 0.0015 mmol of ascorbic acid, was injected into the miniemulsion to activate the catalyst and start the polymerization. Samples were taken at timed intervals to measure the conversion gravimetrically and to determine the molecular weight by GPC.

Hollow polymeric nanocapsules with a cross-linked shell were synthesized using similar procedures. The only difference is the addition of some cross-linkers (either permanent or degradable) to the formed organic solution together with the hexadecane. The polymerization was stopped after a certain time and the product was dialyzed against water and THF to remove the unreacted monomer, cross-linker, solvent, hexadecane costabilizer and any unincorporated PEO−PBMA−Cl macroinitiator.

Characterization. The molecular weight and polydispersity index (M_w/M_n) of each sample were measured by GPC (Polymer Standards Services (PSS) columns (guard, 10^5, 10^3, and 10^2 Å), with THF eluent at 35 °C, flow rate = 1.00 mL/min and differential refractive index (RI) detector (Waters, 2410)). The apparent molecular weights and polydispersity index were determined with a calibration based on linear polyMMA standards using WinGPC 6.0 software from PSS. Latex particle size and size distribution were measured by dynamic light scattering (DLS) on a high-performance particle sizer, model HP5001 from Malvern Instruments, Ltd. Transmission Electron Microscopy (TEM) analysis was conducted using an Hitachi H-7100 TEM (Hitachi High Technologies America) operating at 50 kV. Scanning Electron Microscopy (SEM) was performed with a FESEM HITACHI S-4800 instrument in a cryo mode with the aid of an Alto 2500 cryo-transfer system (GATAN). The material was fixed on a holder and was rapidly frozen with liquid nitrogen. It was then transferred to the high vacuum cryo-chamber. Atomic force microscopy (AFM) studies were conducted using a Nanoscope IIIa from Digital Instruments operating in the tapping mode. Standard silicon cantilevers were used (PPP-NCH from Nanosensors) with a spring constant $k \approx 42$ N/m and an oscillation frequency ≈ 330 kHz. Height and phase images were recorded simultaneously at a scan rate of 1 Hz. The samples were cast onto freshly cleaved mica by spin coating at a rotation speed of 2000 rpm.

Results and Discussion

Evaluation of PEO−PBMA−Cl as the Reactive Stabilizer for Miniemulsion ATRP of BMA. Miniemulsion polymerization, which starts with stabilized oil droplets with average diameter between 50 and 500 nm and narrow size distribution dispersed in water, is one of the most commonly used methods for the preparation of polymeric nanoparticles. Miniemulsion polymerization has also been proven to be one of the best aqueous dispersed media procedures for conducting an ATRP, because all components necessary for an ATRP process, including the initiator, catalyst and monomers, are initially located within the stabilized monomer droplets, or the "mini-reactor". Particle nucleation occurs in the monomer droplets and ideally each droplet turns into a polymeric particle after polymerization, since mass transport through aqueous dispersed media is limited.[22,50]

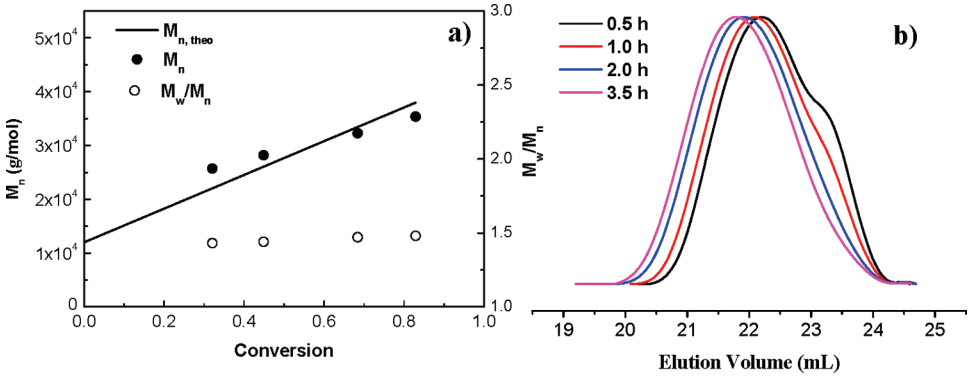


Figure 1. (a) Dependence of number-average molecular weights M_n on BMA conversions and (b) GPC traces during the polymerization of BMA by ATRP. Polymerization conditions: [BMA]:[PEO−PBMA−Cl]:[$CuBr_2$/BPMODA]:[ascorbic acid] = 220:1:0.5:0.15, [hexadecane] = 25 wt % based on monomer and anisole, 30 vol% of anisole compared to BMA, 3 wt % of BMA compared to water, 65 °C.

Careful selection of the surfactant/stabilizer, which can stabilize the latexes and control the particle size, is very important in order to successfully conduct an ATRP in miniemulsion. Recently, a reactive amphiphilic block copolymer has been successfully used as the stabilizer for the miniemulsion polymerization of various monomers by AGET ATRP.[47,48] The amphiphilic block copolymer acts as both stabilizer and initiator for the miniemulsion polymerization, which initially emulsified the monomer phase and then was chain extended with another monomer. Stable polymer latexes with controlled size were obtained, and due to the covalent linking of the stabilizer to polymer chains, no free surfactant was left in the reaction system and the stability of the polymer latexes was improved. Since the majority of the block copolymers were anchored at the interface, the polymer chains would grow inward, which provided a facile way for the preparation of polymeric nanocapsules.

In the present approach, an amphiphilic block copolymer, PEO−PBMA−Cl, was used as a reactive surfactant for the preparation of polymeric nanocapsules in miniemulsion. This reactive stabilizer initiated the copolymerization of BMA and EGDMA or DSDMA by ATRP from the water/monomer droplet interface, resulting in the formation of nanocapsules with cross-linked shells.

The performance of PEO−PBMA−Cl as a reactive stabilizer for miniemulsion ATRP was first evaluated by conducting a homopolymerization of BMA. The targeted degree of polymerization (DP) was set at 220 and monomer conversion reached ca. 85% after 3.5 h. Molecular weight increased smoothly as the conversion increased during the polymerization. However, at the beginning of the polymerization, a small shoulder was observed in the GPC traces which indicated a slow initiation process. The slow initiation may result from a difference in the activation rate between the macroinitiator with Cl end functionalities and the formed polymers containing Br chain ends, since the former one had a lower activation rate constant. As the polymerization continued, more macroinitiators were consumed, indicated by the clean shift of the GPC traces toward higher molecular weight as the monomer conversion increased. The number average molecular weights, M_n, finally closely matched the theoretical values (Figure 1). Nevertheless the molecular weight distribution was broad ($M_w/M_n \approx 1.5$), which can be caused by the slow initiation process. The miniemulsion polymerizations resulted in polymer latexes that displayed good stability and the average diameter of formed polymer latexes was around 200 nm with relatively narrow size distribution (coefficient of variation < 0.10) as determined by DLS, indicating that the majority of the amphiphilic copolymers were anchored at the interfaces and worked well as reactive stabilizers for the system.

Preparation of Polymeric Nanocapsules in a Miniemulsion System. Since PEO−PBMA−Cl was an efficient stabilizer for the miniemulsion polymerization of BMA, the reactive stabilizer was then used for the preparation of polymeric nanocapsules with a cross-linked shell through the introduction of a cross-linker to the system. The reagent ratio was set at [PEO−PBMA−Cl]:[BMA]:[EGDMA] = 1:220:20. All the other conditions were the same as for BMA homopolymerization. In this case, the monomer droplets formed through ultrasonication should contain BMA monomer, EGDMA cross-linker, anisole as the solvent, hexadecane as the costabilizer, and the higher oxidation state copper complexes as the catalyst precursor. When polymerization started after the reduction of Cu(II) species with ascorbic acid, the PEO−PBMA−Cl initiated the copolymerization of BMA and EGDMA, and a polymer network started to form on the outer shell of the droplet and thicken as the polymerization continued. The polymerization was stopped after 2 h. On the basis of the kinetic data from the homopolymerization of BMA in miniemulsion conducted under similar conditions, the monomer conversion at this point should be around 60−70%. After the product was purified through dialysis against water and/or THF to remove unreacted monomer, cross-linker and solvent, polymeric nanocapsules with a cross-linked shell were obtained. The content of cross-linked nanocapsules in the final product was essentially 100% (determined gravimetrically) due to the high level of cross-linker used, and no free polymer chains were detected in the final product by GPC. Due to the incorporation of the divinyl cross-linker and formation of covalently cross-linked polymer shell, the stability of the hollow spheres was improved. The average diameter of the cross-linked particles by DLS analysis was around 200 nm in water and 250 nm in THF. The particles could be easily redispersed in various common organic solvents, such as THF, DMF, CH_2Cl_2, $CHCl_3$, methanol, and other good solvents for PEO or PBMA.

The morphology of the resulting polymer particles were characterized by cryo-SEM, TEM, and AFM. Figure 2 shows the cryo-SEM and TEM images of the formed nanocapsules. In the cryo-SEM images, the diameter of most polymer particles was within the range of 150−300 nm, which was in agreement with the particle size determined by DLS. Under higher magnification (Figure 2b), the presence of small indentations in the toroidal particles provide evidence that the initial particles had a hollow structure and

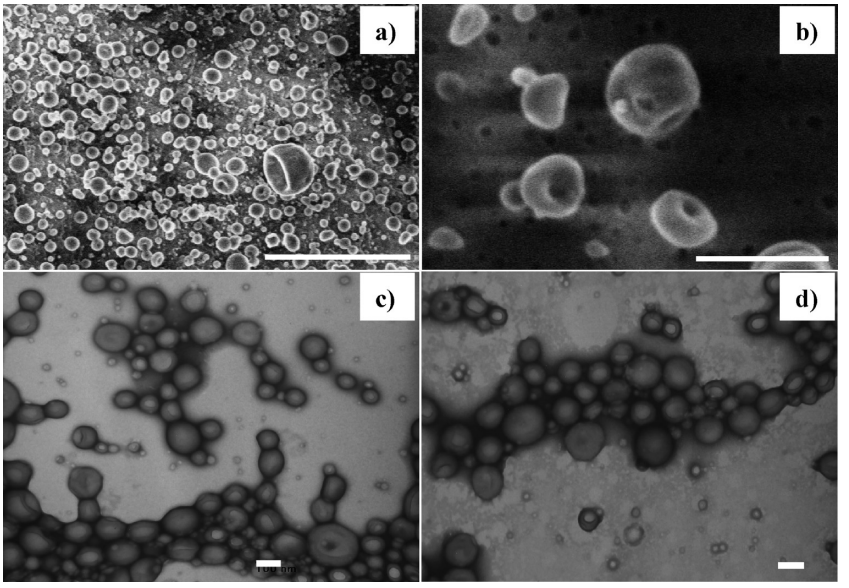


Figure 2. Cryo-SEM (a, b) and TEM (c, d) images of nanocapsules prepared via miniemulsion ATRP of BMA and EGDMA using PEO−PBMA−Cl as reactive stabilizer. The scale bars in the images represent 2 μm, 500 nm, 100 nm, and 100 nm, respectively.

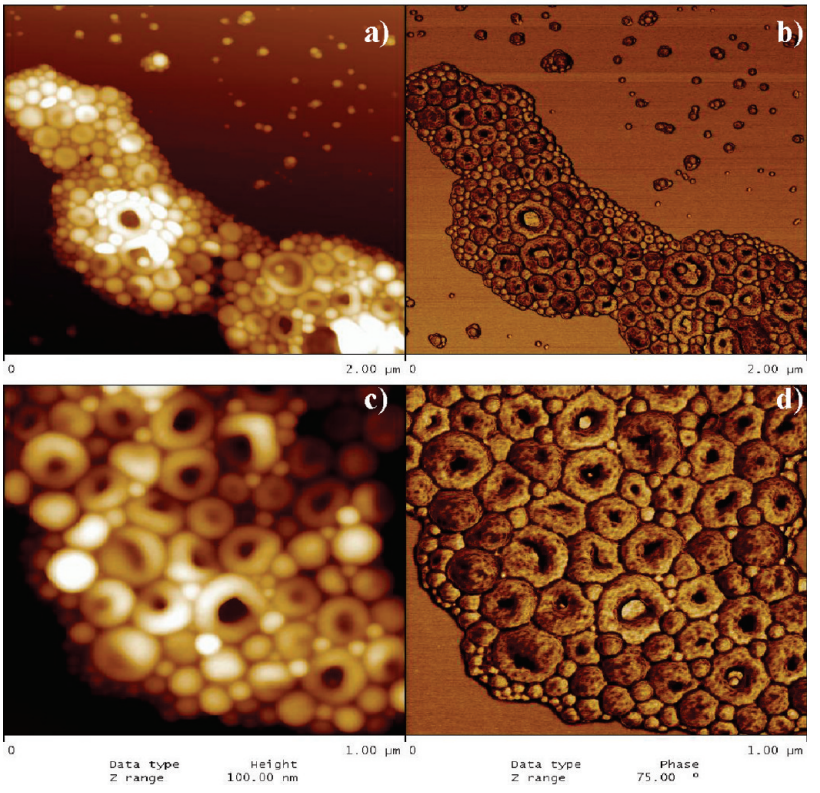


Figure 3. AFM images of nanocapsules obtained via miniemulsion ATRP of BMA and EGDMA using PEO−PBMA−Cl as reactive stabilizer (height images, a and c; phase images, b and d).

the structure collapsed during the isolation procedures and subsequent drying. TEM images provide further evidence of the hollow architecture of the capsule particles, in Figure 2c, d, polymer particles with a dense shell can be found in most of the particles. Furthermore, deformed or indented structures could also be observed in some of the particles, which indicate that nanocapsules with liquid cores were obtained. Based on the TEM images, the size of polymer particles was around or below 100 nm, which is smaller than the size determined by DLS and cryo-SEM. This can be attributed to the sample preparation process, the polymer chains would shrink significantly when they were dried on the TEM grid, while the particles were in the swollen state for DLS measurements and in frozen state for cryo-SEM.

The morphology of the formed nanocapsules was also visualized using tapping mode AFM. As shown in Figure 3, large indentations can be clearly observed in the larger polymer particles in both height images (a, c) and corresponding phase images (b, d). This provides further evidence for the formation of a hollow structure and the presence of a

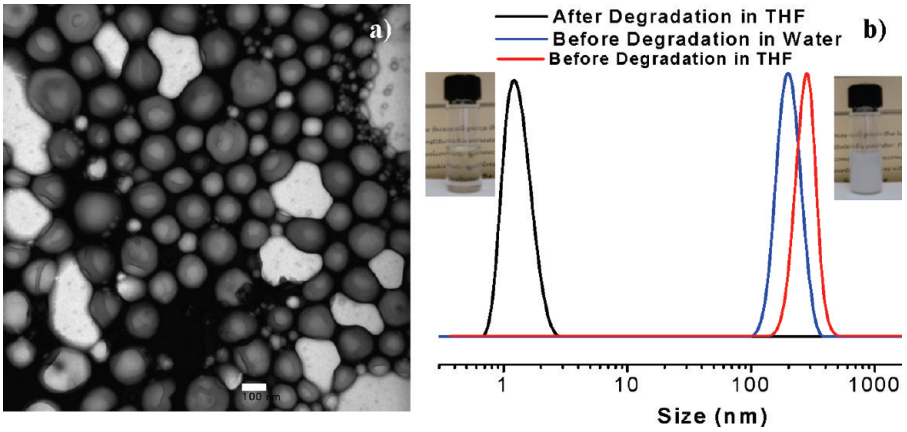


Figure 4. (a) TEM image of nanocapsules prepared via miniemulsion ATRP of BMA and DSDMA using PEO−PBMA−Cl as reactive stabilizer (the scale bar in the image represents 100 nm) and (b) DLS plots and images of the nanocapsules and corresponding degraded polymers in THF solutions. Degradation conditions: 0.02 g of polymeric nanocapsules in 1 mL of 0.16 M Bu_3P THF solution at room temperature for 24 h.

large liquid core inside the formed polymer particles. In addition to the large hollow particles, AFM images indicate the presence of some smaller particles without any visible indentations present in the particle. In the present system, a hollow structure can be expected only when the particle reached a certain size and the extended polymers remained on the outer shell of the droplet. However, due to the distribution of monomer droplets size, some smaller droplets could turn into particles with small cavities, which cannot be clearly visualized. Moreover, the formation of polymer particles with small or no cavities, might be also caused by the reactive stabilizer used in the system. Due to the amphiphilic nature of the stabilizers, the majority of the polymer chains should be anchored at the interface of the monomer droplets or formed polymer latexes. This was already proven by the formation of a stable miniemulsion throughout the reaction. However, it is expected that the dynamic exchanges of the amphiphilic macroinitiators among the monomer droplets take place, and a small percentage of the amphiphilic macroinitiators may form micellar structures in water. Then, secondary nucleation could occur in the system. Since hexadecane cannot transfer among the particles, these initiators can only initiate the copolymerization of monomer and divinyl cross-linker, resulting in the formation of particles with no or only small cavities.

Preparation of Degradable Polymeric Nanocapsules Using a Disulfide-Based Cross-Linker. The successful encapsulation of guest molecules inside the polymer particles is the first step required for potential delivery application of polymeric nanocapsules. The controlled release of the molecules to targeted area is the ultimate goal. Introduction of specific cleavable linkers to the shell of the nanocapsules should help control the delivery of the encapsulated substance. A cross-linker containing a disulfide group (DSDMA) was selected and introduced to this system for this purpose, since the disulfide group can be cleaved to the corresponding thiols in the presence of reducing agents, such as tri(*n*-butyl)phosphine (Bu_3P), dithiothreitol (DTT), and glutathione.[53]

The reaction conditions were exactly the same as when the permanent EGDMA cross-linker was used. Cross-linked polymer particles with average diameter around 200 nm in water and 290 nm in THF were obtained with DSDMA cross-linker. A typical TEM image of the formed product is shown in Figure 4a, polymeric nanocapsules with a dense shell were observed for most of the particles, indicating the successful preparation of a hollow structure. The polymeric nanocapsules were then cleaved in THF using an excess amount of Bu_3P as reducing agent. The cleaved product was analyzed by GPC. The number average molecular weight of cleaved polymers M_n is ca. 34 200 g/mol and polydispersity index PDI is 2.0; both of these values are slightly higher than those for the polymers obtained from the homopolymerization of BMA shown in Figure 1. The higher PDI of the polymers formed after degradation could be related to the thiol side groups or remaining branched polymers in the product. The successful cleavage of disulfide linkage by Bu_3P was further confirmed by the DLS results and the images of the nanocapsule solution before and after degradation (Figure 4b). The size of resulting degraded polymers in THF was less than 2 nm, indicating the formation of soluble polymers after reduction. The images show the turbid/cloudy nanocapsules solution before degradation and completely transparent THF solution of the soluble polymer chains after the disulfide cross-linkages were cleaved.

Conclusion

Successful preparation of hollow polymeric nanocapsules with a cross-linked shell was achieved via the interfacial miniemulsion copolymerization of BMA and EGDMA or DSDMA by AGET ATRP using a reactive PEO−PBMA−Cl block copolymer as a stabilizer and macroinitiator. The average diameter of the resulting nanocapsules was ca. 200 −300 nm. The particles were very stable and could be easily dispersed in some common organic solvents due to the introduction of cross-linking units into the shell. The use of a cross-linker containing a disulfide group allowed the preparation of degradable nanocapsules, which can be easily cleaved by reducing agents.

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