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Pickering Emulsion Templated Interfacial Atom Transfer Radical Polymerization for Microencapsulation

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This Article describes a new microencapsulation method based on a Pickering emulsion templated interfacial atom transfer radical polymerization (PETI-ATRP). Cationic LUDOX CL nanoparticles were coated electrostatically with an anionic polymeric ATRP initiator, poly(sodium styrene sulfonate-*co*-2-(2-bromoisobutyryloxy)ethyl methacrylate) (PSB), prepared by radical copolymerization of sodium styrene sulfonate and 2-(2-bromoisobutyryloxy)ethyl methacrylate (BIEM). The resulting PSB-modified CL particles were surface active and could be used to stabilize oil-in-water Pickering emulsions. ATRP of water-soluble cross-linking monomers, confined to the oil–water interface by the surface-bound PSB, then led to nanoparticle/polymer composite shells. This method allowed encapsulation of core solvents (xylene, hexadecane, perfluoroheptane) with different solubility parameters. The microcapsule (MC) wall chemistry could accommodate different monomers, demonstrating the versatility of this method. Double-walled MCs were formed by sequentially carrying out PETI-ATRP and in situ polymerization of encapsulated monomers. The double-walled structure was verified by both transmission electron microscopy (TEM) and scanning transmission X-ray microscopy (STXM).

Introduction

Polymeric microcapsules (MCs) are of great importance in industrial applications such as pesticide delivery,¹ food science,² imaging materials,³ catalyst design,⁴ and self-healing materials.⁵ Many microencapsulation processes including in situ radical polymerization,⁶ interfacial polycondensation,⁷ polymer phase separation,⁸ and coacervation⁹ rely on emulsions as templates to form capsular structures. Developments in controlled radical polymerization¹⁰ make it possible to achieve a high level of control of the site of polymerization, making it ideal for designing microencapsulation processes.¹¹

Recently, there has been an increasing interest in using emulsion-templated radical polymerization (ETRP) for preparing MCs because of the good compatibility of radical chemistry with

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most functional groups and the availability of a vast number of vinyl monomer, allowing for encapsulation of a wide range of core materials. Dispersion radical polymerizations (DRPs) where polymerization is confined to the dispersed phase, have led to MC shell formation through in situ phase separation. In Okubo's selfassembly of phase-separated polymer (SaPSeP) method,¹² a homopolymer forming in the dispersed phase phase-separates toward the interface to form a capsule shell. Similarly, copolymerization of hydrophilic with hydrophobic monomers in a dispersed phase can lead to amphiphilic copolymers that migrate to the oil/water interface and cross-link to form a permanently networked shell at the interface.¹³ While capable of forming MCs, these methods tend to require restrictive matching of core liquids and monomers. In this regard, interfacial radical polymerization (IRP) is advantageous because polymerization and cross-linking can only occur at the oil/water interface to produce polymers that automatically serve as MC walls. This approach is also much less dependent on the properties of monomers and core materials, making it possible to encapsulate a wider range of materials and to design functional MCs by taking advantage of the diversity of vinyl monomers available.

The key to IRP then is to confine radical polymerization at oil/ water interfaces, which can be realized by employing amphiphilic radical initiators or chain transfer reagents that could restrict the growing polymer to the interface. It is equally important to crosslink the growing polymer at the interface to form networked MC walls regardless of the polarity of the monomers. IRP has been implemented in oil-in-water mini-emulsion polymerizations using amphiphilic RAFT agents as reactive surfactants to confine polymerization of styrene at oil/water interfaces to form oil-filled polystyrene nanocapsules.¹⁴ This approach was extended to

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water-in-oil mini-emulsions to prepare water-filled poly(N-isopropylacrylamide) nanocapsules.¹⁵ Similarly, Matyjaszewski used an amphiphilic block copolymer both as a mini-emulsion stabilizer and as an ATRP macroinitiator for an oil-in-water mini-emulsion polymerization of butyl methacrylate. Cross-linking was incorporated to strengthen the shells, and the resulting nanocapsules could be well-dispersed in different solvents.¹⁶ Although the above methods could produce nanocapsules with different compositions, the formation of MCs requires interfacial initiators less prone to micelle formation, which could dominate particle generation. Additionally, in these methods, monomers are present in the dispersed phase, and their polymerizations in the organic phase could potentially interfere with the core materials. After polymerization, unreacted monomers may remain in the core and act as impurities, which would have a proportionally greater impact in the case of the much larger MCs.

In addition to using reactive molecular surfactants to confine radical polymerization at the interface, IRP can also be achieved using reactive Pickering emulsifiers. Pickering emulsions are particle stabilized emulsions¹⁷ that in comparison with surfactantstabilized emulsions often show high stability and less foaming, making them popular candidates for templating MC formation. By modifying the surface of Pickering emulsifiers with radical initiators or chain transfer agents, we can localize radical polymerizations on the particle surface or at the oil/water interface. In the presence of cross-linking, particulate emulsifiers can be locked-in at the interface to produce colloidosomes or composite MCs. The absence of micellization in Pickering emulsions prevents competition from micellar nucleations. As a result, polymerizations can be exclusively confined to the MC interface, which makes Pickering emulsions a promising base for templating IRP in microemulsion systems to produce MCs. Wang et al.¹⁹ reported the use of ATRP initiator-modified silica nanoparticles as Pickering emulsifiers in a paraffin-in-water emulsion system to confine the ATRP of 2-hydroxyethyl methacrylate (HEMA) at the interface. They covalently attached an ATRP initiator to silica nanoparticles by stepwise reactions.¹⁹ Slight in situ cross-linking between the polyHEMA chains was observed during polymerization and led to the formation of crosslinked MC shells. Wang's approach involved polymerization of the water-soluble monomer, HEMA, on the aqueous side of the interface, avoiding interference with core materials. However, this approach used a multistep synthesis to functionalize covalently the silica nanoparticles with an ATRP initiator. The degree of functionalization had to be carefully controlled to make appropriate Pickering emulsifiers, and the encapsulation was limited to very specific solvents.

Here we present a robust and general method to immobilize ATRP initiators on Pickering emulsifiers, which can be utilized to template IRP to form MCs with a broad range of sizes and properties. This method involves the electrostatic deposition of a polyanionic ATRP initiator on cationic nanoparticle surfaces. The resulting modified nanoparticles are shown to be good Pickering emulsifiers, and the resulting Pickering emulsions can template interfacial ATRP of different monomers for encapsulating core materials with different polarities.

Experimental Section

Materials. Diethyl ether, dimethyl sulfoxide (DMSO), dichloromethane (DCM), and xylenes (a mixture of *para-*, *meta-*, and *ortho-*xylene) were purchased from Caledon Laboratories. Perfluoroheptane (mixed isomers) was acquired from PCR Research Chemicals. Sodium styrene sulfonate (SSS, > 80%) was supplied by Fluka. Other chemicals were obtained from Aldrich. All chemicals were used as received.

Synthesis of 2-(2-Bromoisobutyryloxy)ethyl Methacrylate. We prepared 2-(2-bromoisobutyryloxy)ethyl methacrylate (BIEM) using a procedure similar to that described by Venkatesh.²⁰ HEMA (8.8 g, 67.7 mmol), triethylamine (TEA, 13.7 g, 135.6 mmol), and dichloromethane (DCM, 86 g) were added to a 250 mL threeneck round-bottomed flask. The mixture was cooled to 0 °C in an ice bath, and 2-bromoisobutyryl bromide (18.7 g, 81.3 mmol) was introduced to the flask under stirring over 1 h through an addition funnel. The reaction mixture was stirred for another 4 h at 0 °C and then filtered to remove salts. The filtrate was extracted with deionized water (100 mL \times 2), 0.5 M aqueous Na₂CO₃ (100 mL \times 2), and saturated NaCl solution (100 mL \times 1). The resulting solution was dried over Na₂SO₄, and DCM was removed on a rotary evaporator. The crude product was further dried under vacuum for 24 h to afford a brown liquid 15.7 g (83% yield). ¹H NMR $(CDCl_3): \delta = 6.124 (1H), 5.582 (1H), 4.406 (4H), 1.917 (9H).$

Synthesis of Poly(sodium styrene sulfonate-*co*-2-(2-bromoisobutyryloxy)ethyl methacrylate) (PSB). SSS (7.0 g, 34.1 mmol), BIEM (3.23 g, 11.6 mmol), DMSO (91 g), and AIBN (99.1 mg, 0.60 mmol) were added to a 125 mL HDPP bottle. After dissolution, the mixture was bubbled with N₂ for 0.5 h. Polymerization was carried out at 70 °C for 24 h in an HB-1000 hybridizer at 15 rpm rotation. The polymer was precipitated in 1000 mL of diethyl ether, washed on a vacuum filter with diethyl ether (100 mL × 3), and dissolved in 250 mL of water. The solution was dialyzed against continuously running deionized water for 3 days in a MEMBRA-CEL dialysis tubing (molecular weight cutoff 7 kDa) and freeze-dried to give 4.22 g white product (41.3% yield). The ¹H NMR spectrum of the final product is shown in the Supporting Information.

Preparation of Particle/PSB Suspensions. We prepared the PSB-modified CL particle suspensions by mixing 4 wt % CL particle suspensions with equal amounts of PSB solutions with a range of PSB concentrations. The resulting suspensions were immediately manually shaken for 30 s and allowed to settle for 1 week before photographs were taken.

Determination of Free PSB in CL Particle Suspensions. We ultracentrifuged 2.0 wt % CL particle suspensions with different PSB/CL ratios for 40 min at 50 000 rpm at 25 °C using a Beckman L7-55 Preparative Ultracentrifuge. The depletion of PSB in the supernatants was measured by UV–vis spectroscopy using the peak at ~296 nm.

Mobility Tests. Electrophoretic mobilities of CL particles and MCs were measured on a ZetaPlus ζ -potential analyzer (Brookhaven Instruments). The mobilities of 2.0 wt % CL particles with different PSB/CL ratios were tested directly without the addition of extra electrolytes. The error bars of the electrophoretic mobilities represent the standard error of the mean value of 10 runs (15 cycles per run). We measured the mobilities of MCs by suspending clean MCs in 2.5 mM KCl. The error bars stand for the standard error of the mean value of the runs (15 cycles per run).

Preparation of Emulsions. To prepare an emulsion, we added 0.75 mL of CL particle suspension to a 3 mL glass vial containing 0.75 mL of xylenes. The mixture was homogenized using a Dremel Moto-Tool equipped with a tungsten carbide

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cutter (catalog no. 9905) at \sim 16 000 rpm for 2 min. Optical micrographs of the emulsions were taken from a drop of the emulsions deposited on a glass slide without dilution. Photographs of the emulsions were taken 7 days after their preparations. We obtained the mean size of the emulsion droplets by averaging the sizes of over 200 emulsion droplets that were manually measured using the optical microscope.

Preparation of Poly(N,N'-methylene bisacrylamide) (PMBAAm) MCs with Different Fills. In an Aldrich hands-inbag polyethylene bag filled with N2, a CL particle suspension containing 0.8 wt % CL particles and 0.2 wt % PSB (PSB/CL = 0.25) was added to a 3 mL glass vial containing 0.75 mL of core solvent. The mixture was then emulsified using the Dremel Moto-Tool at $\sim 16\,000$ rpm for 2 min. Four batches of such emulsion were prepared and combined. Separately, 10 mL of aqueous solution containing 0.20 g MBAAm (1.297 mmol) and 6.4 mg hexamethyltriethylenetetraamine (HMTETA, 0.046 mmol) was bubbled with N2 for 30 min in a 20 mL glass vial and then transferred to the handsin-bag. CuBr (3 mg, 0.046 mmol) was then added to this solution, followed by the addition of the pre-prepared emulsion. The reaction mixture was sealed and placed on a set of horizontal rollers at room temperature or heated to 65 $^{\circ}\mathrm{C}$ and rotated for different amounts of time. After polymerization, the formed MCs were allowed to cream in a 50 mL centrifuge tube, and the supernatant was removed from the bottom using a syringe. Deionized water (40 mL) was added to dilute the MC suspension, and this separation was repeated three times to remove unreacted monomer, catalyst, and ligand. Optical micrographs of the MCs were taken from a drop of the MC suspension deposited on a glass slide. We obtained the mean size of MCs by averaging the sizes of 100 MCs. Different core solvents including xylenes, hexadecane, and perfluoroheptane were encapsulated using the same procedure. Dry hexadecane-filled poly-MBAAm MCs were sputter-coated with a layer of gold before scanning electron microscope measurements.

Preparation of Poly(sodium methacrylate-co-N,N'methylene bisacrylamide) (poly(SM-MBAAm) MCs with a Xylene Core. An aqueous solution containing 287.0 mg methacrylic acid (MA), 138.4 mg NaOH, 192.4 mg MBAAm, and 9.39 mL of H₂O was passed through a 10 cm long column (inner diameter ~ 6 mm) packed with inhibitor remover (Aldrich). After treatment, 5 g of such solution was mixed with 3.0 mg HMTETA in a 20 mL glass vial, and the pH of this solution was adjusted to 9.5 by the addition of 0.1 N HCl solution. The solution was then bubbled with N2 for 30 min before being transferred to a N₂-filled hands-in-bag and mixed with 3 mg CuBr. The emulsion preparation was the same as that of polyMBAAm MCs aforementioned. Two batches of freshly prepared xylene-in-water emulsion were added to the above-mentioned solution. The resulting solution was then sealed in a vial and placed in the roller reactor at 65 °C for 1 h. After polymerization, MCs were purified using a procedure similar to that used for PMBAAm MCs.

Preparation of Poly([3-(methacrylamino)propyl]trimethylammonium chloride-co-N,N'-methylene biscrylamide) (poly-(MAPTAC-MBAAm)) MCs with a Xylene Core. We mixed 575.8 mg 3-(methacrylamino)propyl]trimethylammonium chloride (MAPTAC) solution (50 wt %), 190.2 mg MBAAm, and 9.24 mL of H₂O, and the resulting solution was passed through a 10 cm column (inner diameter ~ 6 mm) packed with inhibitor remover particles. After treatment, 5 g of such solution was mixed with 3.7 mg HMTETA in a 20 mL glass vial, and the pH of this solution was adjusted to 9.6 by the addition of 0.1 N NaOH solution. The solution was then bubbled with N_2 for 30 min before being transferred to a N₂-filled hands-in-bag. Two batches of freshly prepared xylenein-water emulsion were then mixed with the solution. The resulting solution was then sealed in a vial and put in the roller reactor at 65 °C for 1 h. After polymerization, MCs were purified using a procedure similar to that used for polyMBAAm MCs.

Preparation of Double-Walled MCs. An aqueous phase containing 16 mg CuBr, 25.7 mg HMTETA, and 330 mg MBAAm

in 18.2 g water was bubbled with N₂ in a 20 mL vial for 30 min and then transferred to a N₂-filled hands-in-a-bag. In the same handsin-a-bag, 0.75 mL of organic phase containing 10 wt % styrene and 0.1 wt % AIBN in hexadecane was emulsified with 0.75 mL of PSB-modified CL particle suspension (0.8 wt % CL particles and 0.2 wt % PSB) at ~13 000 rpm for 2 min. The freshly prepared emulsion was then mixed with the aqueous solution in the vial. The vial was promptly sealed and placed on a rotator (Glas-Col) at a rate ~60 rpm for 5 h at room temperature. The vial was then transferred to the roller reactor and rotated there at 60 °C for 22 h. After polymerization, MCs were purified using a procedure similar to that used for PMBAAm MCs.

MC Wall Permeability Tests. The permeability tests were based on xylene-filled polyMBAAm MCs that were prepared using polymerization at 65 °C for 1 h. The aqueous MC suspension was placed on a rotary evaporator under vacuum at 60 °C for 30 min to replace the xylene fill with aqueous phase. We then mixed 0.2 mL of the resulting water-filled MC suspension with 0.2 mL 0.1 wt % fluorescein-labeled dextran solutions with different molecular weights. After incubation for 72 h, one drop of MC suspension was placed on a microscope glass slide and covered with a glass coverslip to flatten and seal the top and bottom surfaces of the MCs, which permitted the observation of dextran-*f* in the capsules by fluorescence microscopy.

Preparation of Dry MC Wall Fragments. We diluted 3 mL of concentrated MC suspension in 40 mL of ethanol. The MCs were allowed to sediment, and the supernatant was decanted. This washing procedure was repeated another three times to ensure complete removal of water and the core solvent. The final sedimented MCs were then dried under vacuum for 48 h to yield powder-like MC wall fragments.

Thermogravimetric Analysis of MC Walls. Thermogravimetric analysis (TGA) of MC fragments was performed using a NETZSCH STA 409 PC/PG apparatus. We carried out TGA measurements by heating 20–30 mg of dry MC wall fragments at a rate of 5.00 °C/min until 800 °C in the air. The percentage of polymer ($P_{polymer}$) in the MC walls was calculated by the measured weight loss from 200 to 800 °C. The remaining percentage was assigned to CL particles (P_{CL}). The percentage of PSB was estimated to be $^{1}/_{4}$ that of P_{CL} . Therefore, polyMBAAm/CL ratios were determined by the following equation: $r_{polyMBAAm/CL} = (P_{polymer} - ^{1}/_{4}P_{CL})/P_{CL}$. The conversion of MBAAm (C_{MBAAm}) was calculated using the following equation: $C_{MBAAm} = (m_{CL} \times r_{polyMBAAm/CL}/m_{MBAAm}) \times 100\%$, where m_{MBAAm} is the total mass of MBAAm added.

Fourier Transform Infrared. Fourier transform infrared (FTIR) analyses were carried out on a Bio-Rad infrared spectrometer (FTS-40) in transmission mode.

Transmission and Scanning Electron Microscopy. Dry MC wall fragments were embedded in an epoxy resin prepared by mixing trimethylolpropane triglycidyl ether and 4,4'-methylenebis-(2-methylcyclohexylamine) in a 1:1 weight ratio and curing at 70 °C for 3 days. Thin sections were cut using a Leica Ultracut UCT ultramicrotome and deposited onto Formvar-coated Cu grids. Transmission electron microscopy (TEM) images were recorded using a JEOL JEM 1200 EX TEMSCAN transmission electron microscopy images were obtained using a TESCAN VEGA 3 XM SEM.

Characterization. ¹H NMR was recorded using a Bruker 200 MHz NMR spectrometer. The carbon and hydrogen content in PSB was determined by combustion analysis using an EA 1108 CHN analyzer. The bromide content of PSB was determined by oxygen flask combustion method and analyzed using the ion chromatography technique. Photographs of particle suspension and emulsions were taken using a Canon PowerShot S5 IS digital camera. UV measurements were carried out on a Cary 50 UV/vis spectrophotometer. The spin rates of the Dremel Moto-Tool for emulsification were determined using an AMETEK model 1726

Scheme 1. Illustration of the Microencapsulation Process Using PETI-ATRP^a



^a Note: particles and capsules are not drawn to scale.

dual function digital tachometer. The optical micrographs of emulsions and MCs were obtained using an Olympus BX51 optical microscope fitted with a Q-Imaging Retiga EXi digital camera, ImagePro software, and fluorescence optics for fluorescein and rhodamine. Scanning transmission X-ray microscopy (STXM) measurements on ultramicrotomed cross-section samples of the double-walled MCs were performed at the polymer STXM beamline 5.3.2 of the Advanced Light Source (ALS).²¹

Results and Discussion

Recently, we and others have shown that the surface of charged inorganic particles can be easily modified by electrostatic interaction using oppositely charged organic electrolytes, turning these hydrophilic particles into Pickering emulsifiers for oil-in-water emulsions.²² The modification decreases the charge density on the particle surface and introduces hydrophobic groups, which both help make the particle surface active. This method of particle modification seems quite general and has been used to turn various types of particles into effective Pickering emulsifiers.²² We recently showed that nanoparticles coated electrostatically with polyelectrolytes can be used to form Pickering emulsions that are less sensitive to pH changes and capable of forming multilayer shells by further layer-by-layer deposition of polyelectrolytes and charged nanoparticles.²³

In the present work, a polyanion containing ATRP initiator groups, PSB, was used as a surface modifier to make LUDOX CL particles surface active. These positively charged nanoparticles are narrow-disperse and have been previously studied as emulsifier precursors.²⁴ Their small size makes it possible to produce small emulsion sizes and, in turn, relatively small-sized MCs. The SSS unit in PSB can bind to the positively charged CL particle surface between pH 2.0 and 8.5, whereas the BIEM unit was designed to function as an ATRP initiator to confine radical polymerization at the oil/water interface, promoting the formation of MCs (Scheme 1).

PSB was prepared by copolymerization of SSS with BIEM in DMSO using AIBN as the radical initiator (Scheme 2). The SSS-to-BIEM ratio in the copolymer was determined to be 68:32 by ¹H NMR (shown in the Supporting Information), close to the comonomer feed ratio of 70:30, in agreement with the tendency of such comonomers to form random copolymers with a slight

Scheme 2. Synthesis of Poly(sodium styrene sulfonate-co-2-(2-bromoisobutyryloxy)ethyl methacrylate) (PSB)



tendency toward alternation.²⁵ In contrast, elemental analysis for bromine gave an SSS-to-BIEM ratio of 86:14. The discrepancy between the NMR and elemental analysis results is attributed to partial loss of bromine from the tertiary site during dialysis. The syntheses of similar polyelectrolyte macroinitiators bearing 2-bromoisobutyrate moieties through ATRP and postesterification have recently been reported by Armes' group.²⁶ Our copolymerization approach is shorter but may lead to more hydrolysis during workup.

CL Particle Surface Modifications Using PSB. We coated CL particles by mixing 4.0 wt % CL particle suspensions with equal volumes of PSB solutions of different concentrations. CL particles are positively charged at pH values below 8.5 due to a thin alumina layer on their outer surface.²⁷ Negatively charged PSB will thus electrostatically bind the particle surfaces and render the CL particles surface-active. Electrophoretic mobility tests (Figure 1) showed that the direction of motion, and hence the surface charge, reverses with increasing PSB/CL ratio used in the coating process, with a minimum near a PSB/CL ratio of about 0.2 indicating the isoelectric point. Beyond a PSB/CL ratio of ~0.4, the mobility levels off again, presumably reflecting surface saturation with PSB. The negative charge on CL particle surfaces at PSB/CL ratios above 0.25 is attributed to the free tails and loops of excess PSB chains bound to the particle surface.

The residual amounts of PSB present in the supernatants following CL particle coating with different PSB/CL ratios were determined by UV/vis. Figure 2 shows that for PSB/CL ratios up to and including 0.25, all PSB added was adsorbed onto the particles, whereas above that value the amount of free PSB in the supernatant increased linearly with increasing PSB/CL ratio,

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Figure 1. Electrophoretic mobility of PSB-modified CL particles in suspensions as a function of PSB/CL ratio. The line is drawn to guide the eye.



Figure 2. Plot of weight concentration of free PSB in supernatant versus PSB/CL ratio. The line is drawn to guide the eye.



Figure 3. Photographs of (a) CL particle suspensions with different levels of PSB modification and (b) attempted xylene-in-water Pickering emulsions made with corresponding particle suspensions from part a.

indicating that the surfaces of CL particles are saturated with PSB.

The visual appearance of CL particle suspensions modified with different PSB/CL ratios is shown in Figure 3a. The concentration of CL particles was set to 2 wt % in all suspensions. The CL particle suspension without PSB addition is almost clear with a bluish tint. The addition of PSB caused immediate cloudiness and increased viscosity due to particle flocculation, which then led to precipitation with time. The volume of precipitate showed a maximum at the PSB/CL ratio of 0.25, which is attributed to charge neutralization at the CL particle surface at this PSB/CL ratio, indicated by the minimum in mobility shown in Figure 1. At higher PSB/CL ratios, CL particles carry net negative charges, increasing their colloidal stability.

Xylene-in-Water Emulsions Made by PSB-Modified CL Particle Suspensions. CL particle suspensions with different



Figure 4. Optical micrographs of Pickering emulsions (a,b) and polyMBAAm MCs (c,d) in both wet (a,c) and dry (b,d) states. The scale bars are 50 μ m.

PS/CL ratios were used to emulsify xylenes in a 1/1 v/v ratio (Figure 3b). CL particles without PSB are unable to stabilize these emulsions and within seconds reform two layers. In contrast, CL particles modified with PSB formed stable xylene-in-water emulsions at PSB/CL ratios from 0.125 to 1.000. In particular, emulsions prepared with a PSB/CL ratio of 0.250 combine excellent resistance against coalescence and creaming and a high loading of initiator groups, with an absence of free PSB in the continuous phase. Emulsions from higher PSB/CL ratios could also be used for ATRP coating following the removal of excess free PSB in the supernatant to prevent solution initiation.

Preparation of Xylene-Filled Poly(N,N'-methylenebisacrylamide) MCs. Xylene-in-water emulsions with a PSB/CL ratio of 0.250 were used as a template for the interfacial atom transfer radical polymerization of methylenebisacrylamide (MBAAm). MBAAm was chosen because it has sufficient solubility in water to restrict the polymerization to the aqueous side of the capsules. As a divinyl monomer, it further has the ability to form a cross-linked network, which is required to form a stable shell. Emulsions made using 2.0 wt % CL particle suspension showed a large number of free particles in the supernatant of the emulsion. These PSB-coated, free CL particles could initiate polymerization of MBAAm in the supernatant, competing with the interfacial polymerization for MC wall formation and causing bulk precipitation of polyMBAAm. To minimize the polymerization in the supernatant, we reduced the CL particle loading to 0.8 wt %, where the emulsions showed nearly no free particles in the emulsions. The optical micrographs of the resulting Pickering emulsion are shown in Figure 4a,b (wet and dry, respectively). The emulsion showed a fairly wide size distribution with an average diameter of \sim 44 μ m. When allowed to dry on a glass slide, the membrane at the xylene/water interface ruptured instantly to release xylene from the core, resulting in shattered fragments on the glass slide (Figure 4b).

The Pickering emulsion was then exposed to an aqueous solution containing MBAAm, HMTETA, and CuBr to carry out the interfacial ATRP. HMTETA was selected as the ligand because it provides tetradentate coordination to Cu(I), which could suppress the disproportionation of Cu(I) and provide sufficient catalytic activity.²⁸ Because of the hydrophilic nature of HMTETA, its complexes with Cu(I) and Cu(II) reside primarily in the aqueous phase. As a result, the polymerization happened

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Figure 5. TGA plots of polyMBAAm MCs synthesized using different reaction conditions.

 Table 1. Influences of Reaction Temperature and Time on the Composition of MC Walls

| run | temperature/°C | time/h | polyMBAAm/CL | conversion/% |
|-----|----------------|--------|--------------|--------------|
| 1 | 20 | 1 | 1.21 | 14.5 |
| 2 | 65 | 0.5 | 2.49 | 29.9 |
| 3 | 65 | 1 | 2.97 | 35.7 |
| 4 | 65 | 24 | 2.98 | 35.7 |
| | | | | |

^{*a*} Calculations are based on TGA results. Only the polymers in the MC walls were considered for calculation. The conversion of MBAAm to free polymer in solution was considered negligible.

mainly on the aqueous side of interface, having minimum impact on the core materials.

Figure 4c,d shows the polyMBAAm MCs after polymerization at 60 °C for 1 h. The MCs were well-dispersed in the suspension. These MCs showed an average diameter of 33μ m, slightly smaller than that of the primary emulsion. Bulk precipitation of polymers was not observed in the MC suspension, indicating that polymerization mainly occurred at the xylene/water interface. These MCs rapidly lost xylene and collapsed when dried on a glass slide, reflecting their permeable shell. Compared with the primary Pickering emulsion, the MC wall showed improved resistance to rupture as almost intact MC walls remained after loss of the core, indicating that the CL particles at the interface had been interconnected by polyMBAAm to form a coherent MC shell.

MC walls made with different polymerization times and temperature were subjected to TGA (Figure 5). The conversion of MBAAm in each run was calculated on the basis of the TGA results and is given in Table 1. The weight loss from room temperature to 200 °C was attributed to loss of moisture and other low-molecular-weight substances in the MC walls. The thermal degradation of polymers was observed from 230 to 650 °C, with weight remaining above 650 °C assigned to the inorganic CL particles. As shown in Table 1, MBAAm conversion increased with temperature and with reaction time up to 1 h. The relatively low conversion of the monomer in all runs can be attributed to the disproportionation of CuBr to form Cu and CuBr₂ and to the slow oxidation of CuBr to CuBr₂ during polymerization.

The composition of the PSB-modified CL particles and the resulting MC walls was studied using FTIR. The FTIR spectrum of CL particles (Figure 6b) shows the typical IR adsorption signal



Figure 6. Transmission FTIR spectra of (a) PSB, (b) CL particles, (c) PSB-modified CL particles (PSB/CL = 0.25), and (d) poly-MBAAm MC walls (65 °C, 1 h).

from silica at wavenumbers of 798.8 and 1110.6 cm⁻¹, which are assigned to the symmetrical and asymmetrical stretching vibrations of Si–O–Si bonds. The PSB modification led to a small peak at 1734.1 cm⁻¹ (Figure 6c) attributed to the C=O stretching vibration of PSB. The FTIR spectrum of the MC wall (Figure 6d) is similar to that of SiO₂/polyMBAAm core–shell composite materials reported by Yang et al.²⁹ In addition to a strong silica signature at 1110.6 cm⁻¹, the spectrum shows strong absorptions at 1525.0 cm⁻¹ and 1661.8 cm⁻¹, which are characteristic of an amide group. This confirms that the MC wall was a composite of polyMBAAm and CL particles. The absorption of vinyl group was not observed in the spectrum of polyMBAAm MC walls,

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Figure 7. TEM micrographs of wall cross sections of polyMBAAm MCs with different magnifications. Part b shows the boxed area in part a, and part c shows the boxed area in part b.



Figure 8. Fluorescence microscope images (a-d) and the corresponding optical microscope images (e-h) of polyMBAAm MCs incubated with dextran-*f* of different molecular weights (70, 150, 250, and 500 kDa) for 72 h. The scale bars are 50 μ m.

 Table 2. Some Physical Properties of Selected Solvents for

 Microencapsulation

| solvent | perfluoroheptane | hexadecane | xylene |
|---|------------------|--------------|------------------|
| solubility parameter/ δ (MPa ^{1/2}) ³³ | 12.5 | 16.4 | 18 |
| density $(g/mL)^{34}$ boiling point (°C) ³⁴ | 1.745 82-84 | 0.773 287 | 0.868 137-140 |



Figure 9. Optical micrographs of perfluoroheptane-filled (a,b) and hexadecane-filled (c) MCs in both wet (a,c) and dry (b) states. (d) SEM image of hexadecane-filled MCs in a dry state. The scale bars are $100 \,\mu$ m.

which, we believe, could be hidden in the broad peak at 1661.8 cm^{-1} .



Figure 10. Optical micrographs of poly(SM-MBAAm) MCs (a,b) and poly(MAPTAC-MBAAm) MCs (c,d) in both wet (a,c) and dry (b,d) states. The scale bars are 50 μ m.

| Table 3. | Electrophoretic | Mobilities | of Different | MCs |
|----------|------------------------|------------|--------------|-----|
|----------|------------------------|------------|--------------|-----|

| MCs | polyMBAAm | poly(SM-co- MBAAm) | poly(MAPTAC- co-MBAAm) |
|---|----------------|-----------------------|---------------------------|
| mobility $(10^{-8} \text{ m}^2/(\text{V s}))$ | -0.58 ± 0.25 | -2.50 ± 0.25 | $+2.51\pm0.09$ |

Cross sections of the wall of polyMBAAm MCs were studied by TEM. Dry polyMBAAm MCs from run 3 in Table 1 were embedded in an epoxy resin consisting of trimethylolpropane triglycidyl ether and 4,4'-methylenebis(2-methylcyclohexylamine), an embedding resin we developed that has proven to be



very radiation resistant because of the absence of ester and polyether groups.³⁰ Figure 7 shows that the MC walls contained an \sim 80 nm thick layer of CL nanoparticle aggregates that were likely originally formed during PSB modification of the CL nanoparticles. After serving as Pickering emulsifiers and initiators for interfacial ATRP, these nanoparticle aggregates are now covalently interconnected at the xylene/water interface to form an MC wall. The polyMBAAm in the MC walls was not visible in these TEM micrographs, likely because of its low contrast relative to the embedding resin.

The permeability of polyMBAAm MC walls was studied using fluorescently labeled dextran. An MC suspension from run 3 in Table 1 was placed on a rotary evaporator under vacuum at 60 °C for 30 min to replace the xylene fill of MCs with water. Some MC aggregation was observed during this process. The resulting water-filled MCs were mixed with dextran-*f* solutions having molecular weights ranging from 70 to 500 kDa. After incubation for 72 h, fluorescence microscopy was used to test for the presence of dextran-*f* within the MC interior. As shown in Figure 8, the 70 kDa dextran-*f* entered the majority of MCs. The fraction of permeable MCs decreased with increasing molecular weight of dextran-*f*, such that 500 kDa dextran-*f* was unable to diffuse into any MCs.

Preparation of PolyMBAAm MCs with Different Core Solvents. Polyelectrolyte-coated nanoparticles can serve as Pickering emulsifiers for a wide range of core solvents.²³ Therefore, the PETI-ATRP described here was also used to encapsulate the more hydrophobic solvents, hexadecane and perfluoroheptane. Table 2 shows the solubility parameters, densities, and boiling points of perfluoroheptane, hexadecane, and xylene. Microencapsulated perfluorocarbons may be used as blood substitutes.³¹ However, encapsulation of perfluorocarbons has proven to be challenging for traditional microencapsulation methods because of their nonpolar character. Perfluoroheptane-in-water emulsions were successfully prepared using PSB-modified CL particles (PSB/CL = 0.25) and were used as the template for interfacial ATRP of MBAAm. Figure 9a, b shows the optical micrographs of perfluoroheptane containing MCs in both wet and dry states. These MCs resemble the xylene-filled MCs (Figure 4c), with dimpled surfaces. Upon drying, the MCs completely collapsed by losing the perfluoroheptane core, leaving behind ruptured MC walls. This fast rupture of the MC walls is similar to what we observed for xylene cored MCs, which could be attributed to the capillary forces during drying and the thin MC walls.³²

The analogous hexadecane-filled MCs stayed inflated upon drying, likely because the high-boiling hexadecane did not evaporate at a significant rate from their surfaces (Figure 9d). MCs containing hexadecane and other hydrocarbons are of interest as



Figure 11. Optical micrographs (a,b) of double-walled MCs and TEM micrographs (c,d) of the wall cross-section of a double-walled MC. The scale bars in a–d are 100 μ m, 100 μ m, 4 μ m, and 200 nm, respectively.

thermal storage materials.³⁵ Traditional methods for preparing hexadecane-filled MCs include in situ polymerization,³⁶ polymer phase separation,^{9a} coacervation,³⁷ and interfacial polycondensation.³⁸ The current method supplements these existing methods by providing a higher core-to-shell ratio and minimum interference with the core by both the encapsulation process and wall-forming materials.

Preparation of Xylene Core MCs with Different Wall Materials. An advantage of interfacially confined polymerization is its decreased dependence on the polarity of wall-forming materials, making it possible to prepare MC walls with an array of different functionalities. To demonstrate this, both positively and negatively charged vinyl monomers were used as comonomers with MBAAm to form charged MC walls. In both cases, a feed ratio of ionic monomer to MBAAm of 7:3 was used to ensure sufficient cross-linking in the formed MC walls. Sodium methacrylate (SM) and [3-(methacrylamino)-propyl]trimethylammonium chloride (MAPTAC) were chosen as the charged monomers. The resulting MCs are shown in Figure 10a,b,c,d. In the wet state, both MCs resembled the original polyMBAAm MCs. The poly(SM-MBAAm) MCs released xylene fill rapidly when they dried on a

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Figure 12. STXM analyses of the cross-section of a double-walled MC. (a) STXM optical density image recorded at 285.1 eV. (b) Individual component maps of epoxy resin, polystyrene, polyMBAAm, and residue. (c) Color-coded composite map of the three components. (d) Component profiles across the MC wall (dashed box in c). The scale bar in a denotes $10 \,\mu$ m, and the rest of the scale bars are $1 \,\mu$ m.

glass slide, similar to what we observed for polyMBAAm MCs. In contrast, a portion of the poly(MAPTAC-MBAAm) MCs retained their fill under the same conditions, apparently because of the lower swellability of the polycationic shells in xylene. The electrophoretic mobility measurements of the resulting MCs reveal the strongly negative and positive surface charges of these MCs (Table 3). The corresponding measurement of the original poly-MBAAm MCs indicate only slightly negative surface charges, attributed to the negatively charged PSB modifiers.

Synthesis and Characterization of Double-Walled MCs. Recently, double-walled MCs have attracted much attention because of their potential in designing multifunctional MCs. Common approaches for preparing this type of MCs include the sequential execution of two separate microencapsulation processes³⁹ and sequential polymerization of two monomers with different reactivities using the same mechanism.⁴⁰ In this study, we combined interfacial PETI-ATRP with a subsequent internal styrene-free radical polymerization to prepare double-walled MCs. PSB-modified CL particles (PSB/CL = 0.25) were used to stabilize an oil phase consisting of styrene, AIBN and hexadecane. We carried out the PETI-ATRP of MBAAm at room temperature for 5 h to form the outer layer composed of a polyMBAAm/CL particle composite shell. We then heated the MC suspension to 60 °C for 22 h to induce the polymerization of styrene in the oil phase. The resulting polystyrene precipitated from the nonsolvent hexadecane at the interface to form the second, interior shell layer, as illustrated in Scheme 3. The optical micrographs of the resulting double-walled MCs are shown in Figure 11a,b. These MCs were stable and retained their core after they were dried on a glass slide. The double-walled structure was verified by TEM imaging of shell cross sections. Figure 11c,d clearly shows a two-layer structure of the MC shell, consisting of an outer nanoparticle layer and an inner polymer layer.

The polyMBAAm formed in the first stage of the process should be associated with the nanoparticles in the outer layer but could not be resolved by TEM because of its low contrast against the embedding matrix. The dense inner layer is expected to consist of polystyrene formed in the second stage. We used STXM to identify positively and quantitatively map these shell components. STXM is a synchrotron-based X-ray spectromicroscopy technique that combines good spatial resolution with excellent spectral resolution, making it a very useful tool for mapping the composition of polymeric microspheres⁴¹ and MCs.⁴² Figure 12a shows an STXM optical density image of the cross-section of a doublewalled MC imaged at 285.1 eV, the energy of highest contrast of the MC wall against the embedding material. The white ribbon in the image is assigned to the polystyrene layer in the MC wall, which has a significant X-ray absorption at 285.1 eV because of the C 1s $\rightarrow \pi^*$ transition of phenyl rings. We further studied a small wall area on the bottom (yellow box in Figure 12a) by recording an image sequence at selected energies through the carbon 1s region between 280 and 315 eV. For quantitative analysis, near-edge X-ray absorption fine structure (NEXAFS) spectra for the embedding matrix, polystyrene, and polyMBAAm were obtained⁴³ and normalized at both 280 and 315 eV to a scale that is set by the known elemental composition and atomic absorption coefficients for 1 nm thick samples.⁴⁴ Figure 13 shows the normalized reference NEXAFS spectra of embedding matrix, polystyrene, and polyMBAAm. Polystyrene shows the strong C 1s $\rightarrow \pi^*_{C=C}$ absorption at 285.1 eV, whereas polyMBAAm has a strong peak at 288.2 eV due to the C 1s $\rightarrow \pi^*_{C=O}$ transition of the amide groups. The energy separation of 3.1 eV between the signals of these two polymers ensures accurate differentiation of

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Figure 13. NEXAFS reference spectra of the embedding matrix, polystyrene, and polyMBAAm that correspond to 1 nm thickness of each component.

polystyrene and polyMBAAm. The embedding matrix, which consists of aliphatic polyetheramines, has no sharp spectral features that could interfere with these two major components in the MC wall. It is noteworthy that the CL particles, which are primarily silica, do not have any spectral features in the C 1s region. The image sequence was then fitted with reference spectra using singular value decomposition to yield the component maps shown in Figure 12b. The grayscale of each map indicates the spatial distribution of the thickness of that component. The component maps show that the section has an average thickness of ~220 nm. The polystyrene layer has a thickness of \sim 350 nm and is fairly dense with little penetration of the embedding material. The polyMBAAm layer was identified using this polyMBAAm map to be fairly thin (150–250 nm thick) and either porous or swellable, allowing the embedding resin to diffuse into it during the embedding process, making its visualization in TEM more challenging. On the basis of these component maps, a rescaled color-coded composite map (Figure 12c) was then constructed to reflect the relative spatial arrangement of each component. Red, green, and blue were assigned to the embedding matrix, polystyrene, and polyMBAAm, respectively, in the map. This colorcoded map confirmed the double-walled structure with polystyrene in the inner wall and polyMBAAm in the outer wall. The swelling of the polyMBAAm layer by the aliphatic embedding resin reflects the apparent low cross-link density of the grafted layer and is in accordance with the high permeability seen, especially in the absence of the polystyrene inner shells. This suggests that in future studies STXM can be used to monitor layer porosity/swellability, a useful feature in the design of capsules containing fugitive fills.

Article

Conclusions

LUDOX CL particles were surface-modified with PSB by electrostatic interaction, and the modified, surface-active particles were used to stabilize xylene-in-water Pickering emulsions. The ratio of PSB/CL of 0.25 was found to result in stable emulsions with very little free PSB. Such Pickering emulsions were then used as templates to confine interfacial ATRP of MBAAm at the oil/ water interface to form composite polyMBAAm/CL MC walls. Studies of the MC walls using TEM and FTIR spectroscopy confirmed their composite nature, with a total wall thickness of \sim 80 nm. The permeability of the MC walls was investigated using fluorescently labeled dextran with different molecular weights, which suggested that the molecular weight cutoff for the MC walls was below 500 kDa.

The same method was successfully applied to encapsulate fills of different polarities and viscosities such as hexadecane and perfluoroheptane. The wall chemistry was also varied by incorporating monomers with different charges to tune the charge character of the MC walls.

Finally, we synthesized double-walled MCs by sequentially performing an interfacial ATRP of MBAAm to form the outer layer, followed by an internal free radical polymerization of encapsulated styrene to form the inner layer. The resulting double-walled shell structure was confirmed using both TEM and STXM.

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Supporting Information Available: ¹H NMR of PSB and more SEM images of hexadecane filled MCs. This material is available free of charge via the Internet at http://pubs.acs.org.