

## Microcapsules Prepared from a Polycondensate-Based Cement Dispersant via Layer-by-Layer Self-Assembly on Melamine-Formaldehyde Core Templates

Thomas Pavlitschek, Markus Gretz, Johann Plank

Institute for Inorganic Chemistry, Technische Universität München, Lichtenbergstr. 4, Garching 85747, Germany

Correspondence to: J. Plank (E-mail: sekretariat@bauchemie.ch.tum.de)

**ABSTRACT:** Novel microcapsules were prepared from colloidal core-shell particles by acid dissolution of the organic core. Weakly crosslinked, monodisperse and spherical melamine-formaldehyde polycondensate particles (diameter  $\sim 1 \mu\text{m}$ ) were synthesized as core template and coated with multilayers of an anionic polyelectrolyte via layer-by-layer deposition technique. As polyelectrolytes, an anionic naphthalenesulfonate formaldehyde polycondensate that is a common concrete superplasticizer and thus industrially available, and cationic poly(allylamine hydrochloride) were used. Core removal was achieved by soaking the core-shell particles in aqueous hydrochloric acid at pH 1.6, resulting in hollow microcapsules consisting of the polyelectrolytes. Characterization of the template, the core-shell particles, and the microcapsules plus tracking of the layer-by-layer polyelectrolyte deposition was performed by means of zeta potential measurement and scanning electron microscopy. The microcapsules might be useful as microcontainers for cement additives. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** layer-by-layer; microcapsules; self-assembly; superplasticizer; melamine-formaldehyde polycondensate particles

Received 22 December 2011; accepted 29 April 2012; published online

DOI: 10.1002/app.37981

### INTRODUCTION

The enhancement of cementitious building materials such as concrete or mortar by the addition of superplasticizers is well known. The main purpose in the application of superplasticizers (dispersants) is the improvement in workability or pumpability of such systems. Polycondensates represent one kind of frequently used superplasticizers. Among them are sulfonated naphthalene formaldehyde (BNS), melamine-formaldehyde sulfite (MFS), and acetone formaldehyde sulfite (AFS) resins.<sup>1</sup> These polycondensates are negatively charged polyelectrolytes, which disperse cement particles by adsorption onto the positively charged surfaces of certain cement hydrates such as ettringite or monosulfoaluminate.<sup>2</sup> This way, the binder particles attain a highly negative charge, which results in electrostatic repulsion between the cement grains. Through this mechanism, dispersion of the solids is achieved.<sup>3</sup>

In a previous work, we have shown that AFS and MFS superplasticizers can be used successfully in the fabrication of multilayers on styrene/*n*-butyl acrylate latex core templates via the layer-by-layer (LbL) deposition technique.<sup>4</sup> Such core-shell particles represent valuable admixtures for construction materials

because they provide a controlled time release of two different functional molecules: At first, because of the high pH of the cement pore solution, the superplasticizer is released from the multilayer shell and provides a dispersing effect on cement over a period of  $\sim 1$  h. Subsequently, once the superplasticizer shell has disappeared, the latex particles now are set free and can form a polymer film within the cementitious matrix. Through this mechanism, the cement-based building material first is dispersed and exhibits better workability whereas later, the latex films improve tensile strength and reduce the brittleness of hardened concrete. Opposite to this, we now introduce an acid soluble melamine-formaldehyde (MF) polycondensate as a facile core template coated with BNS and poly(allylamine hydrochloride) (PAH).

The layer-by-layer assembly of polyelectrolyte multilayers on charged substrates was first described by Decher.<sup>5</sup> Other authors have extensively investigated the preparation of thin polymer coatings using this method.<sup>6</sup> The LbL technique comprises an alternating deposition of oppositely charged molecules, mostly polyelectrolytes, onto charged templates. Application of this versatile method for the coating of colloidal templates was extensively studied by Möhwald et al.<sup>7–9</sup> A great variety of colloidal

© 2012 Wiley Periodicals, Inc.

templates has been utilized for preparation of core-shell particles. Examples are surfactant free polystyrene lattices, silica spheres, calcium carbonate spherules, organic and inorganic crystals, or biological templates.<sup>10–15</sup> An interesting new application of LbL self-assembly can be found in core-shell structured smart materials. For example, these materials can improve the behavior on magnetorheological properties of optical finishes used in the automotive industry.<sup>16</sup>

An important application of the LbL self-assembly technique is the fabrication of hollow polyelectrolyte microcapsules and nanocapsules.<sup>7,9,17–19</sup> In these literatures, mainly weakly cross-linked MF polycondensate particles obtained from a commercial source were used as colloidal templates. Nowadays, polymeric capsule systems are used in the pharmaceutical, food, textile, adhesive, and agricultural industries.<sup>18</sup> Consequently, a facile fabrication of microcapsules that can be used as nanocontainers for drug delivery, immobilization of tumor cells, flavoring agents, and industrial admixtures is of great interest with respect to various potential applications.<sup>20,21</sup>

Here, we present the preparation of microcapsules via layer-by-layer adsorption of a polycondensate-type superplasticizer onto colloidal MF templates and subsequent core removal. First, weakly crosslinked, monodisperse, and spherical MF polycondensate particles were prepared following a newly developed, facile synthesis. They were coated with alternating layers of an anionic polycondensate-type superplasticizer (BNS) and cationic PAH. Multifilm formation on the core templates was tracked via zeta potential measurement. MF core template removal was facilitated at pH = 1.6 using aqueous hydrochloric acid. The coated MF core-shell particles were immobilized on glass plates and the hollow polyelectrolyte microcapsules were visualized by scanning electron microscopy (SEM).

## MATERIALS AND METHODS

### Materials

PAH ( $M_w \sim 70,000 \text{ g mol}^{-1}$ ) as well as melamine (99%) were purchased from Aldrich, Hannover, Germany. Formaldehyde (30 wt % aqueous solution) was obtained from Degussa, Rhöm, Darmstadt, Germany. Melcret<sup>®</sup> 500 F (BNS,  $M_w \sim 120,000 \text{ g mol}^{-1}$ ) was supplied by BASF SE, Ludwigshafen, Germany. All chemicals were utilized without further purification. Ultrapure water (resistivity > 18 M $\Omega$  cm) was used for all experiments.

### Preparation of Weakly Crosslinked Melamine-Formaldehyde Core Particles

Weakly crosslinked MF particles serving as soluble core templates were prepared as follows: In a typical synthesis, a 250-mL three-necked glass flask equipped with reflux condenser, stirrer, temperature controller, and dosing unit was charged with 100 mL of aqueous formaldehyde solution (0.75 wt.-%; 27 mmol) and 1.05 g (8.3 mmol) of melamine and then was heated up to 80°C. Upon complete dissolution of melamine, the pH was adjusted to 4 by addition of 0.4 mL of a 0.375M sulfuric acid (2 wt.-%). Gradual occurrence of turbidity of the liquid indicates the progressing formation and growth of the MF particles. After 15 min, the reaction was quenched with ice water. The suspension of MF particles was centrifuged (8 min, 10,000 $\times$ g) and the supernatant was discarded. Particles were redispersed in ultrapure water using

an ultrasonic bath, and centrifugation was repeated. This procedure was carried out for three times. The dispersion of MF particles obtained ( $c = 0.1 \text{ wt.-%}$ ) was stored at 4°C.

### Layer-by-Layer Deposition of Polyelectrolytes and Core Removal

Multilayers were fabricated in aqueous solution via layer-by-layer adsorption of the charged superplasticizer polyelectrolyte onto the colloidal MF templates. First, 1.5 mL of the MF particle suspension were centrifuged and subsequently dispersed in 0.5 mL aqueous NaCl solution (0.5 mol L<sup>-1</sup>). Multilayers were deposited by alternating addition of 1 mL of individual aqueous superplasticizer and PAH solutions ( $c = 10 \text{ mg mL}^{-1}$ ) to the core particle suspension. As anionic polyelectrolyte, BNS was used, whereas the cationic polyelectrolyte was PAH. The mixture was gently shaken for 6 min to allow sufficient interaction between the template particles and the polyelectrolyte. After deposition of each layer, excess polyelectrolyte was removed by three washing cycles. Each step consisted of centrifugation (8 min at 8500 rpm) and redispersion of the coated particles in 1.5 mL ultrapure water.

Microcapsules were prepared by immobilization of coated MF particles on glass plates. The MF core was dissolved by transferring the glass plates for 40 min into diluted hydrochloric acid (pH = 1.6). Before characterization by SEM imaging, the glass squares holding the microcapsules were rinsed four times with ultrapure water and dried slowly at 35°C.

### Analytical Instruments

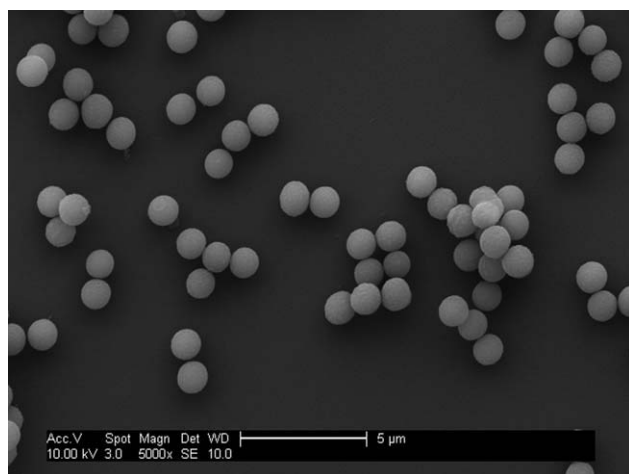
Electric surface charge characterization of the colloidal particles and tracking of polyelectrolyte layer-by-layer adsorption was conducted by measuring electrophoretic mobility on a Malvern Zetasizer Nano ZS (Malvern Instruments, Worcestershire, UK). Mobility was converted into a value for zeta potential by using the Smoluchowski relation. Before all measurements, coated and uncoated particles were dispersed in ultrapure water by ultrasonication.

pH-dependent electrokinetic surface properties of all polyelectrolytes were determined by means of streaming potential using a PCD 03 pH particle charge detector (PCD; Müttek BTG, Herrsching, Germany). For each measurement, 13 mL of a 0.0018-mmol L<sup>-1</sup> polyelectrolyte solution was used. The pH was adjusted by addition of 0.01 mol L<sup>-1</sup> aqueous NaOH or 0.01 mol L<sup>-1</sup> aqueous HCl, respectively.

SEM images were obtained from an XL-30 FEG microscope (FEI, Eindhoven, The Netherlands). Before the analysis, all samples were coated with gold in a ScanCoat Six (BOC Edwards, Crawley, UK).

Thermal analysis was carried out with a STA 409 PC TA system, equipped utilizing a QMS 403 C mass spectrometer (Netzsch Gerätebau, Selb, Germany). The sample was placed in a corundum crucible and heated at a constant rate of 10 K min<sup>-1</sup> in a constant flow of synthetic air.

Infrared spectra were recorded with an attenuated total reflectance Fourier transform spectrophotometer (attenuated total reflectance-Fourier transform infrared spectroscopy [ATR-FTIR]) (Vertex 70 from Bruker Optics, Karlsruhe Süd, Ettlingen, Germany). The measurements were performed on KBr tablets. Each spectrum was acquired in transmittance mode by accumulation of 64 scans with a resolution of 4 cm<sup>-1</sup> and a spectral range of 4000–350 cm<sup>-1</sup>.



**Figure 1.** SEM micrograph of the synthesized monodisperse melamine-formaldehyde core templates (magnification 5 000 $\times$ ).

## RESULTS AND DISCUSSION

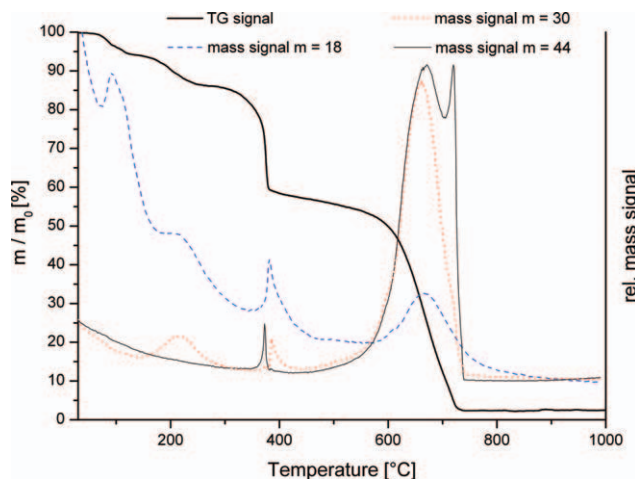
### Synthesis of the Melamine-Formaldehyde Core Templates

To begin with, we developed a facile synthesis for the weakly crosslinked MF core templates because in all previous works (e.g. in Ref. 7), commercial MF particles were used, and hence no information on their fabrication was provided.

The weakly crosslinked, monodisperse, and acid soluble MF templates were synthesized by condensation of methylol melamine under acidic conditions. First, methylation of melamine was performed by dissolution of melamine in an aqueous formaldehyde solution at a molar ratio of  $\sim 1 : 3$  at a temperature of  $80^\circ\text{C}$ . Next, the pH was set to 4 by addition of sulfuric acid. Gradual occurrence of turbidity of the solution indicated formation and growth of the MF particles. The condensation reaction was quenched with ice after 15 min. By using this process, spherical MF particles possessing a particle size of  $1.1\ \mu\text{m}$  and a zeta potential of  $+12\ \text{mV}$  were obtained. The particles are monodisperse. Figure 1 shows the morphology of the synthesized MF particles.

The thermo gravimetric (TG) curve presented in Figure 2 shows a first mass loss of 6 wt.-%, which occurs from RT to  $150^\circ\text{C}$ . This is followed by a second one (36 wt.-%) from  $150$  to  $380^\circ\text{C}$  and a third one from  $380$  to  $750^\circ\text{C}$  (56 wt.-%). The first mass loss can be ascribed to loss of physisorbed water in the sample. This is evidenced on the mass spectrometer by a peak for the mass signal of  $\text{H}_2\text{O}$  (mass 18). The second mass loss starting at  $150^\circ\text{C}$  is assigned to the removal of accessible amine groups present on the surface of the particle which releases water and nitric oxide, as demonstrated by the peaks for  $\text{H}_2\text{O}$  (mass signal 18) and  $\text{NO}$  (mass signal 30). At  $380^\circ\text{C}$ , a rapid loss of mass was detected which can be ascribed to beginning decomposition of the cross-linked MF polymer. In addition, a minor amount of carbon dioxide is released, thus confirming breakdown of the molecular framework. Decomposition of the macromolecules is complete at  $\sim 750^\circ\text{C}$  where a total mass loss of 98 wt.-% was observed.

The IR spectrum of the MF template is shown in Figure 3. There, all characteristic absorption bands as known from the literature<sup>22</sup> are observed while no impurities seem to be present.

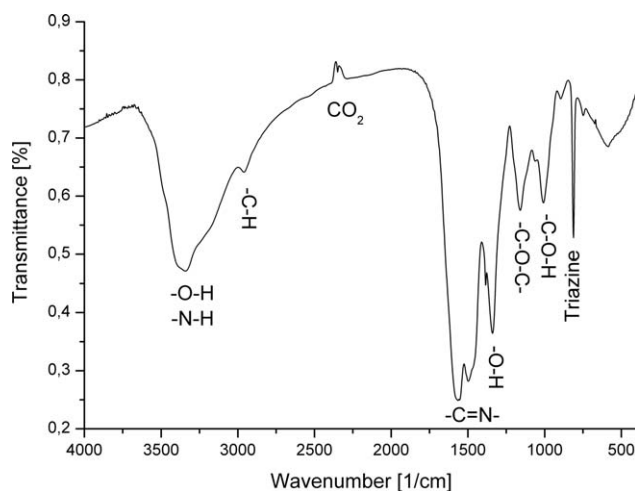


**Figure 2.** Thermo gravimetric and mass loss curves for the synthesized MF template. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

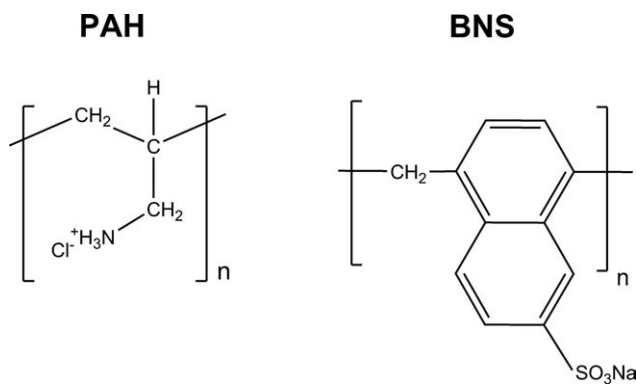
The synthesized MF templates are readily soluble in hydrochloric acid at a pH of 1.6. After this treatment, no polymeric residues were detected by SEM. Careful control of the reaction conditions as described in the experimental section is crucial to ensure completeness of dissolution of the MF templates in the acid and later to obtain immaculate microcapsules. In the condensation reaction, two different crosslinking mechanisms can be distinguished according to Möhwald et al.<sup>23</sup> Condensation of adjacent methylol functionalities results into ether bridges ( $\text{R}_2\text{N}-\text{CH}_2-\text{O}-\text{CH}_2-\text{NR}_2$ ), whereas reaction of methylol groups with amino groups, which are present due to incomplete methylation of melamine, results in methylene bridging ( $-\text{NH}-\text{CH}_2-\text{NH}-$ ) between the triazine rings.

Therefore, weak crosslinking of the MF particles is achieved by incomplete methylation and a low degree of condensation that stems from pH, temperature, and condensation time.

For complete particle dissolution in HCl, precise pH control is necessary. It was found that for the synthesized MF particles, a



**Figure 3.** Infrared (IR) spectrum (KBr) of the synthesized MF template.

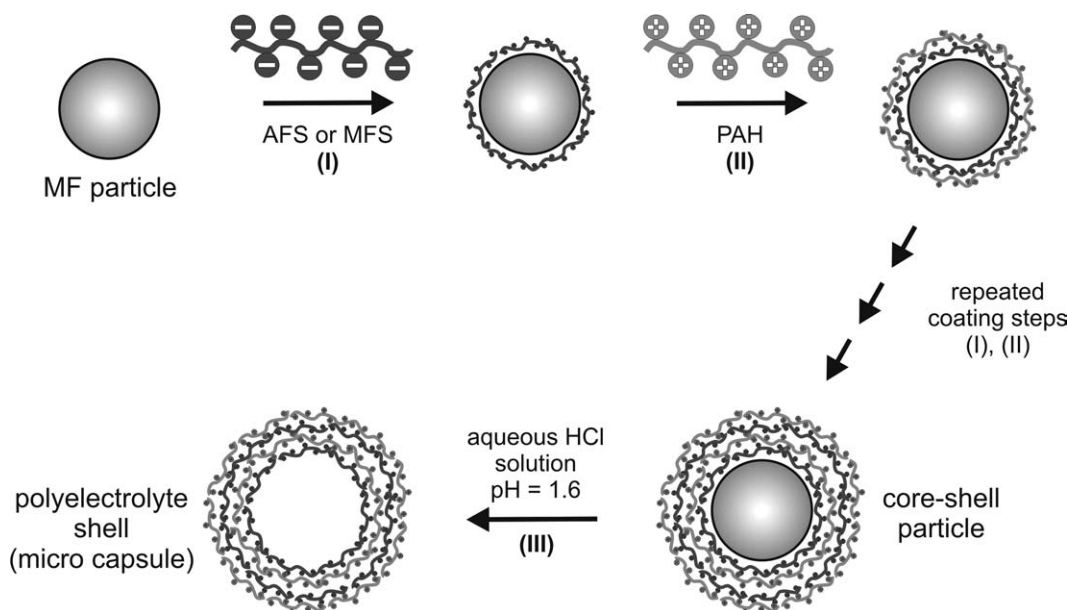


**Figure 4.** Chemical structures of the polyelectrolytes PAH and BNS used for fabrication of the multilayer films.

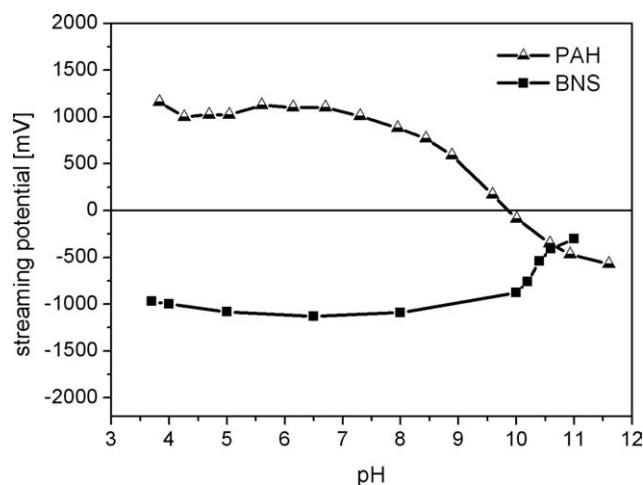
$\text{pH} \leq 1.6$  has to be adjusted to ensure complete particle dissolution. This can be ascribed to several potential reactions occurring during ether cleavage under acidic conditions. Only at  $\text{pH} \leq 1.6$ , soluble MF fragments are being formed ( $\text{R}_2\text{N}-\text{CH}_2-\text{OH}$ ) whereas at  $\text{pH} \geq 1.6$ , further condensation occurs, which leads to insoluble particles possessing only methylene bridges.<sup>24</sup>

#### Anionic Polyelectrolyte Used for LbL Deposition

Generally, numerous polyelectrolytes can be used for multilayer film assembly on core templates. However, at least 50% of the monomer units present in the polyelectrolyte should carry a charge.<sup>25</sup> Among the polyelectrolytes that are most commonly used in LbL assembly of multilayer formation are sodium poly(styrene sulfonate, sodium salt), PAH, or poly(diallyl dimethyl ammonium chloride) (polyDADMAC).<sup>9</sup> Meanwhile, a great number of diverse shell materials ranging from natural polyelectrolytes to inorganic materials has been utilized in the synthesis of multilayers.<sup>18</sup>



**Scheme 1.** Preparation of core-shell particles through layer-by-layer assembly of negatively (BNS) and positively (PAH) charged polyelectrolytes onto MF templates (steps I and II) and subsequent core removal in aqueous hydrochloric acid at  $\text{pH} 1.6$  (step III).

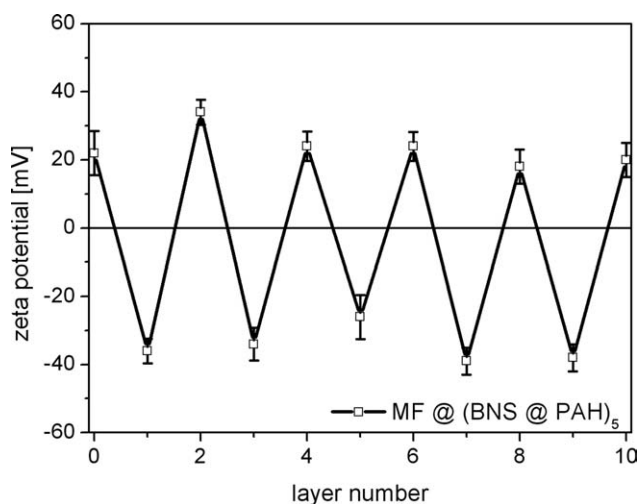


**Figure 5.** pH-dependent streaming potential of PAH and of the BNS superplasticizer respectively ( $c = 0.0018 \text{ mmol L}^{-1}$ ), determined by means of a particle charge detector.

Here, we use a specific polyelectrolyte, which is commonly used as superplasticizer in concrete for the synthesis of layer-by-layer deposited multilayers on MF core templates. The type of superplasticizer used in this study is a BNS condensate. Its chemical structure is shown in Figure 4. This kind of superplasticizer presents a highly effective cement dispersant and therefore is applied to improve the workability of concrete.<sup>1</sup> Various types and modifications of it are available from the industry and applied as concrete admixture. As BNS is a well-established superplasticizer for concrete, many studies on its properties have been published. Also, the interaction of BNS with cement has been investigated extensively, for example, in a recent report by Nakajima et al.<sup>26</sup>

The BNS used for this work is a commercially available industrial product and has an average  $M_w$  of  $\sim 120,000 \text{ g mol}^{-1}$ .





**Figure 6.** Zeta potential of MF particles coated with alternating layers of BNS/PAH (conductivity  $\sim 0.01 \text{ mS cm}^{-1}$ ; pH = 6.8).

Usually, BNS is prepared by sulfonation of naphthalene at temperatures of 120–150°C, followed by reaction with formaldehyde. Under elevated pressure (2–4 bar) the BNS polycondensate is then formed.<sup>27</sup>

The electrical charge of the polyelectrolytes varies with pH. Obviously, this effect will greatly impact their behavior during the layer-by-layer assembly on template surfaces and the stability of the resulting polyelectrolyte multilayers. Thus, pH-dependent electrokinetic properties of the polyelectrolytes were measured by means of a PCD. Figure 5 presents the streaming potentials of PAH and the BNS superplasticizer, respectively, as a function of pH (polyelectrolyte concentration:  $0.0018 \text{ mmol L}^{-1}$ ).

The streaming potential of PAH that possesses amino groups is strongly affected by pH. At pH  $\leq 10$ , the protonated amino groups produce a positive charge, whereas at highly alkaline pH, a negative charge results from deprotonation of the amino groups ( $\text{p}K_a$  of the amino group present in PAH  $\sim 8.5$ ).<sup>28</sup> The isoelectric point for PAH was to be found at pH  $\sim 9.8$ . In contrast to PAH, the surface charge of the anionic BNS polyelectrolyte is only slightly affected by pH. This behavior indicates that BNS is a much stronger polyelectrolyte than PAH. At pH 7, the

streaming potential of the superplasticizer reaches a negative maximum ( $\sim$  to 1,100 mV) whereas at pH  $> 10$ , the streaming potential becomes less negative because of an increased electrolyte content. This effect leads to compression of the electrochemical double layer and consequently to a less negative value of the streaming potential.

### Coating of the Core Templates

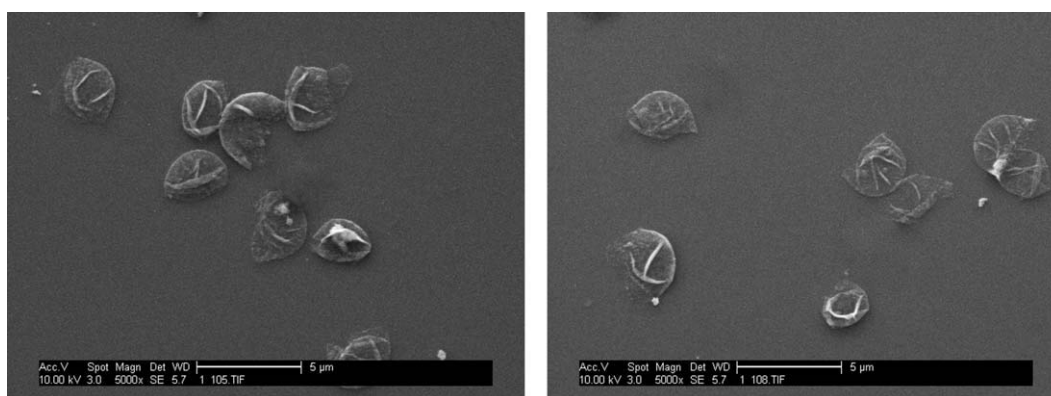
To prepare the core-shell particles, MF templates were coated with multilayers of polyelectrolytes using the layer-by-layer deposition technique. Subsequently, hollow polyelectrolyte capsules were obtained by removal of the MF cores in aqueous hydrochloric acid. The principle steps involved in the fabrication of the core-shell particles are shown in Scheme 1.

Multilayer shell fabrication was accomplished by using the functional BNS polymer from the construction industry and reagent grade PAH. The self-synthesized MF templates were coated by alternating adsorption of polyanions (BNS) and polycations (PAH). Electrostatic attraction between cationic PAH and anionic BNS and entropic effects are the dominant driving forces in the LbL assembly process.<sup>29</sup> Multilayer deposition was conducted at pH  $\sim 6$  where PAH and BNS possess opposite electrical charges (Figure 5). Coating was conducted in aqueous NaCl solution ( $0.5 \text{ mol L}^{-1}$ ) under conditions of polyelectrolyte excess. Loading of the particles with polyelectrolyte was followed by repeated centrifugation and redispersion in ultrapure water before the next layer was adsorbed.

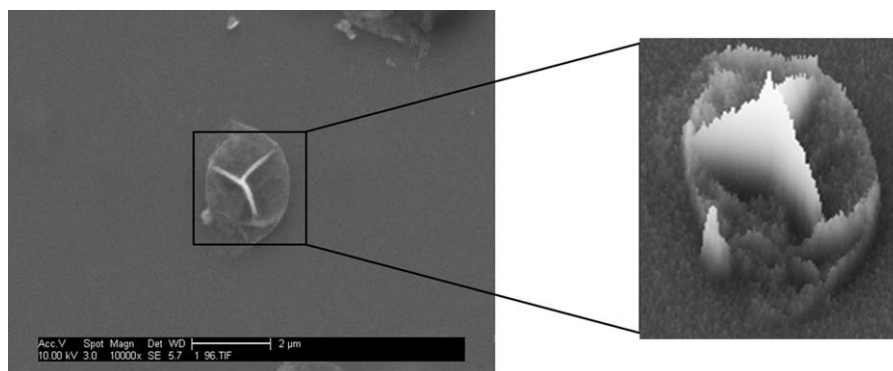
The zeta potential of the particles shows a change of sign after each layer deposition, indicating successful multilayer assembly on the MF templates (Figure 6). At first, anionic BNS was adsorbed onto the positively charged MF cores ( $\zeta = +22 \text{ mV}$ ). The zeta potential of the particles coated with the first BNS layer then becomes negative ( $\zeta = -36 \text{ mV}$ ). The zeta potentials for each individual positive or negative layer are almost the same.

### Preparation of BNS/PAH Microcapsules

To produce hollow microcapsules, the MF templates contained in the core-shell particles were then dissolved in HCl. Particles coated with PAH as the surface layer were immobilized on glass plates and submerged into HCl at pH 1.6. A change to transparency of the glass plates indicates MF core dissolution. An



**Figure 7.** SEM micrographs of BNS/PAH polyelectrolyte shells after MF core removal (magnification: 5,000 $\times$ ).



**Figure 8.** SEM micrograph (magnification: 10,000 $\times$ ) and three-dimensional altitude profile of BNS/PAH microcapsules after MF core removal.

exposure time of 20 min was found to be sufficient for complete MF core removal. Figures 7 and 8 show SEM images of the BNS/PAH microcapsules obtained from the monodisperse MF particles as core templates. Obviously, after exposure to aqueous HCl (pH = 1.6), the MF templates were completely decomposed and removed. Consequently, a collapsed shell structure can be observed.

For the hollow BNS/PAH microcapsules, a variety of folds was observed, thus indicating that the remaining structure represents a thin film (Figure 7). It is worth to note that the apparent diameter of the hollow capsules is of the same order as that of the original core templates.

## CONCLUSIONS

Polyelectrolyte microcapsules were prepared by coating monodisperse weakly crosslinked MF particles with a polycondensate-type cement dispersant using the layer-by-layer deposition technique. This method represents an easy way to fabricate hollow shells using commonly used concrete superplasticizers.

A facile synthesis procedure for the weakly crosslinked MF particles was developed. Soluble MF templates possessing a uniform particle-size distribution are accessible by quenching the condensation of dimethylol and trimethylol melamines at an initial state of the reaction. Complete solubility of the MF colloids under acidic conditions was proven by SEM and subsequent polyelectrolyte shell formation.

Coating of the MF cores was facilitated using a common concrete superplasticizer as anionic polyelectrolyte. Multiwall film formation was tracked via zeta potential measurement, which confirmed successful layer-by-layer deposition. Complete MF core removal was achieved at a pH of 1.6 in aqueous hydrochloric acid. SEM imaging demonstrated that BNS/PAH microcapsules have been accomplished.

The successful preparation of microcapsules from concrete superplasticizers such as BNS or other polycondensates confirms the general usefulness of those highly versatile polyelectrolytes in the fabrication of multifilms and polymeric microcapsules. Through osmotic diffusion, these microcontainers or nanocontainers can be filled with other chemical admixtures useful in construction applications. In highly alkaline cement pore solution, the polyelectrolyte microcapsules will stepwise disintegrate

and then gradually release the admixture over time. This way, effectiveness over an extended period of time (a time-controlled slow release effect) is achievable at comparably low admixture dosages.

## REFERENCES

- Ramachandran, V. S.; Malhotra, V. M. In *Concrete Admixtures Handbook*; Ramachandran, V. S., Ed.; Noyes Publications: New Jersey, **1996**, pp 410–506.
- Plank, J.; Hirsch, C. *Cem. Concr. Res.* **2007**, *37*, 537.
- Kong, H. J.; Bike, S. G.; Li, V. C. *Cem. Concr. Res.* **2006**, *36*, 851.
- Gretz, M.; Plank, J. *Coll Surf A: Physicochem. Eng. Asp.* **2010**, *366*, 38.
- Decher, G. *Science* **1997**, *277*, 1232.
- Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. *Macromol. Rapid Commun.* **2000**, *21*, 319.
- Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S. A.; Möhwald, H. *Angew. Chem.* **1998**, *110*, 2323.
- Sukhorukov, G. B.; Donath, E.; Lichtenfeld, H.; Knippel, E.; Knippel, M.; Budde, A.; Möhwald, H. *Colloids Surf A: Physicochem. Eng. Asp.* **1998**, *137*, 253.
- Sukhorukov, G. B.; Donath, E.; Davis, S.; Lichtenfeld, H.; Caruso, F.; Popov, V. I.; Möhwald, H. *Polym. Adv. Technol.* **1998**, *9*, 759.
- Sukhorukov, G. B.; Volodkin, D. V.; Günther, A. M.; Petrov, A. I.; Shenoy, S. B.; Möhwald, H. *J. Mater. Chem.* **2004**, *14*, 2073.
- Caruso, F.; Yang, W.; Trau, D.; Renneberg, R. *Langmuir* **2000**, *16*, 8932.
- Petrov, A. I.; Gavryushkin, A. V.; Sukhorukov, G. B. *J. Phys. Chem. B* **2003**, *107*, 868.
- Diaspro, A.; Silvano, D.; Krol, S.; Cavalleri, O.; Gliozzi, A. *Langmuir* **2002**, *18*, 5047.
- Landfester, K.; Ramirez, L. *Condens. Matter* **2003**, *15*, 1345.
- Tiarks, F.; Landfester, K.; Antonietti, M. *Macromol. Chem. Phys.* **2001**, *202*, 51.
- Liu, Y. D.; Choi, H. J. *J. Appl. Phys.* **2012**, *111*, 07B502.

17. Möhwald, H. *Colloids Surf A: Physicochem. Eng. Asp.* **2000**, *171*, 25.
18. Peyratout, C. S.; Dähne, L. *Angew. Chem. Int. Ed.* **2004**, *43*, 3762.
19. Liu, W.; He, G.; He, Z. *J. Appl. Polym. Sci.* **2010**, *115*, 1630.
20. Nagashima, R.; Hirose, H.; Matsuyama, H. *J. Appl. Polym. Sci.* **2011**, *121*, 321.
21. Peng, C.; Zhang, Y.; Tong, W.; Gao, C. *J. Appl. Polym. Sci.* **2011**, *121*, 3710.
22. Gottwald, W.; Wachter, G. *IR-Spectroscopy for Applicators*; Wiley-VCH-Verlag: Weinheim, **1997**.
23. Gao, C.; Moya, S.; Lichtenfeld, H.; Casoli, A.; Fiedler, H.; Donath, E.; Möhwald, H. *Macromol. Mater. Eng.* **2001**, *286*, 355.
24. Gao, C.; Moya, S.; Donath, E.; Möhwald, H. *Macromol. Chem. Phys.* **2002**, *203*, 953.
25. Glinel, K.; Moussa, A.; Jonas, A. M.; Laschewsky, A. *Langmuir* **2002**, *18*, 1408.
26. Nakajima, Y.; Goto, T.; Yamada, K. *J. Am. Ceram. Soc.* **2005**, *88*, 850.
27. Hattori, K.; Yamakawa, T. Kao Soap Co., Ltd. US Patent 3,686,133, **1972**.
28. Bhatia, S. R.; Khattak, S. F.; Roberts, S. C. *Curr. Opin. Colloid Interface Sci.* **2005**, *10*, 45.
29. Sukhorukov, G. B.; Fery, A.; Brumen, M.; Möhwald, H. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4078.