A New Route to the Formation of Nanoporous Capsules using Block Copolymer Thin Films and Colloids

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ABSTRACT

Polymeric micellar multilayers are deposited onto spherical colloidal particles of weakly cross-linked melamine formaldehyde (MF), via the so-called layer-by-layer approach (LbL). The MF particles were coated sequentially with layers of oppositely charged diblock copolymer micelles formed from either $PDMA_{96}$-$PDEA_{26}$ or $PDEA_{50}$-$PMAA_{50}$ [PDMA: *poly(2-dimethylamino)ethyl-methacrylate*, PDEA: *poly(diethylamino)ethylmethacrylate,* PMAA: *poly(methacrylic acid)*]. To provide additional stability, the outermost layer can then be cross-linked using BIEE; the effects of this were investigated here. To form capsules, the *core* MF is removed by dissolution. In a variation to this approach, alternative coatings can also be produced by replacing one or more layers with polymer coated Au nanoparticles, which can provide us with a range of different properties of what is a hollow particle. This paper focuses solely on the polymer encapsulated MF and its core dissolution and results on the incorporated with Au coatings are to be presented elsewhere.

Keywords: MF, diblock copolymers, BIEE, LbL, nanocapsules

1 INTRODUCTION

Nanosciences and nanotechnologies provide a revolutionary approach in the way of conceptualizing and producing new materials by moving from "the small to the large" rather than the more conventional reverse approach. Nanotechnology is truly multidisciplinary and it opens the way towards new production routes, new structures and towards more efficient, better performing and intelligent materials. The properties of nanomaterials fundamentally differ from those of the macroscale ones, brought about by the size reduction and by new properties only apparent at the nanoscale. Nanotechnology, alongside the growth in research on soft materials brought about the new era of "soft nanotechnology". Exploitation of the self-organization of soft materials can be used to create a myriad of nanostructures for a number of diverse applications, such as the preparation of nanoparticles.

The objective of our research are ultimately to prepare novel porous nanocapsules; idealized examples of which are shown in Figure 1. To achieve this, spherical colloidal particles, such as weakly cross-linked melamine formaldehyde (MF), are sequentially coated with block copolymer micelles, via the so-called layer-by-layer approach (LbL). [3], [4] Different coating sequences allow the design of coatings with different properties. Diblock copolymers of $PDMA_{96}$-$PDEA_{26}$ and $PDEA_{50}$-$PMAA_{50}$, are used to create these complex multilayers on MF particles. The corona of the outermost micelle layer can be cross-linked with 1,2-bis(2-iodoethoxy)ethane (BIEE) and the MF dissolved. The production of these novel hollow capsules can then be investigated, the morphology of which is studied experimentally via the use of a range of analytical techniques and instrumentation such as Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), light scattering, ζ-potential and UV-VIS. This novel type of hollow shells can have a variety of potential applications; in the field of drug delivery, as well as in separation media (chromatography columns with well defined, adsorbent beads), coatings, catalysis, even in photonics and a range of other technologies that rely on porous particles.

Figure 1: Schematic of porous hollow shells [1]

2 EXPERIMENTAL SECTION

2.1 Materials

Diblock copolymers of tertiary amine methacrylates PDMA-PDEA having various block ratios, quaternisation degrees and molecular weights are available. In this study, we primarily used a $PDMA_{96}$-$PDEA_{26}$ diblock [where subscripts denote the degree of polymerization] at a 0q or 100q [where Xq denotes the percentage of quaternisation of the PDMA residues]. This polymer was synthesized by group transfer polymerization (GTP) and forms cationic micelles at high solution pH. The zwitterionic diblock copolymer, $PDEA_{50}$-$PMAA_{50}$ was used here to provide anionic copolymer micelles. [2] The chemical structures of the two diblock copolymers samples are shown in Figure 2.

Acid-soluble, monodisperse, weakly cross-linked melamine formaldehyde resin particles were purchased from Microparticles GmbH in Berlin, Germany. These particles have a size of 1.98±0.2µm, a density of 1.51g/cm^3 and decompose at a temperature above 300°C. They have a storage temperature of approximately 4°C and their solubility lifetime is up to 4 weeks.

10mM KNO_3 was used as a background electrolyte in all experiments carried out. A range of different concentrations of KOH, HNO_3 were used for adjustment of the pH.

BIEE [1,2-bis(2-iodoethoxy)ethane], a bifunctional quaternizing agent, was purchased from Sigma-Aldrich and used as a chemical cross-linker for the amine residues in the copolymer micelles.

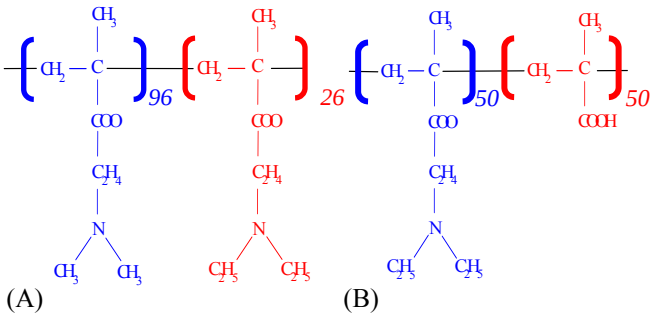

Figure 2: Molecular structures of the diblock copolymers (A) PDMA-PDEA and (B) PDEA-PMAA

2.2 LbL Multilayer preparation

Alternate adsorption of the cationic $PDMA_{96}$-$PDEA_{26}$ and the anionic $PDEA_{50}$-$PMAA_{50}$ diblocks onto spherical colloidal negatively charged MF particles, was carried out at pH 9. At this pH both polymers exist as micelles. Briefly, 20ml of a 0.01%wt MF solution at pH 9 is centrifuged, the supernatant is decanted and an equal volume of 500ppm $PDMA_{96}$-$PDEA_{26}$ cationic polymer is added at the same pH and left to stir for a few hours. Then, that solution is again centrifuged down and with the supernatant once again decanted; an equal volume of 500ppm $PDEA_{50}$-$PMAA_{50}$ anionic polymer is added and left to stir. The procedure is then repeated up until the point where five layers have been absorbed onto the MF particle.

2.3 Cross-linking procedure

Cross-linking of the outmost layer ($PDMA_{96}$-$PDEA_{26}$) of the coated MF resin was carried out in aqueous solution at pH 9, at room temperature (20°C). Shell cross-linking was achieved by addition of 1.6mg of the cross-linker (BIEE) per 5ml of 0.01%wt MF suspension and left stirring over a period of 24hrs, before core dissolution.

2.4 Instrumentation

TEM. TEM images were obtained with a Philips CM200 FEGTEM instrument. TEM cross-section images were obtained via the use of a Joel 1200ex TEM or a Philips CM10 TEM.

SEM. Samples were imaged under a Philips XL30 ESEM (Environmental Scanning Electron Microscope).

Mastersizer. Nanosize and ζ–potential measurements were performed using a Malvern instrument, Zetasizer, Nano series, Nano-ZS.

3 RESULTS AND DISCUSSION

The hydrodynamic diameter measured for the MF particles gave a size of 2.17µm, near to the manufacturers quoted size (for a dry sample). The ζ-potential was recorded at pH 9 and has a value of -30mV. The particles have an isoelectric point (iep) of 5.3 and at pH values lower than the iep they are positively charged (cationic). With decreasing pH the particle charges, coming from the protonation of triazine amino and/or imino groups, increase. At low pH values on the other hand further cross-linking of the polymer is triggered again, finally resulting in poorly soluble or insoluble beads.

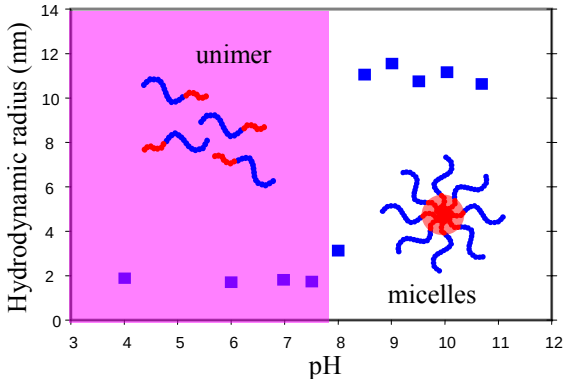

Figure 3: Reversible micellisation of $PDMA_{96}$-$PDEA_{26}$ diblocks in aqueous solution

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The $PDMA_{96}$-$PDEA_{26}$ copolymer, with a critical micellisation point of pH 8 (see Figure 3), has a positive ζ–potential at pH 9 with a value of +10mV, whereas the zwitterionic $PDEA_{50}$-$PMAA_{50}$, with a critical point of pH 7.9 (see Figure 4), has a negative ζ–potential of -35mV. A pH of 9 was therefore chosen as the condition for the formation of multilayers of block copolymer micelles, starting with the cationic micelle deposition.

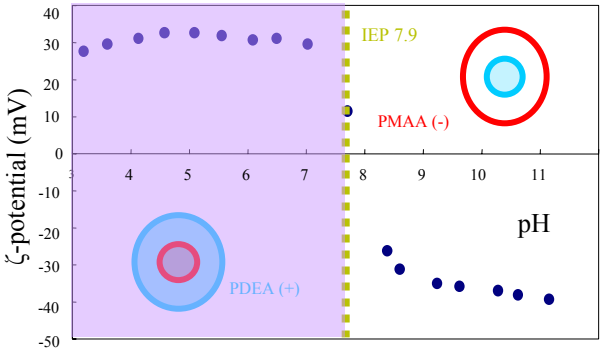

Figure 4: Zwitterionic behaviour of $PDEA_{50}$-$PMAA_{50}$ diblocks. Critical point pH 7.9

Zeta potential measurements, after deposition and absorption of each of the micellar layers, confirmed charge reversal of the particle surface, as indicated in Figure 5. Figure 6 shows some of the TEM images obtained after deposition of each of the successive layers (layer 0- layer 5).

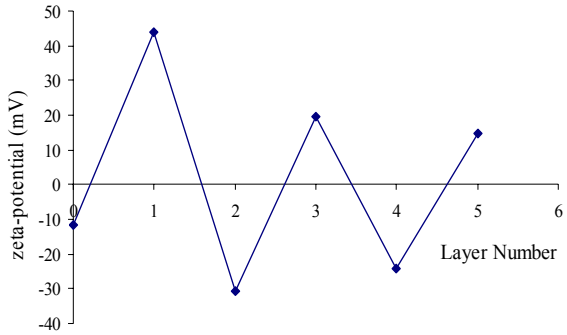

Figure 5: ζ-potential versus layer number. Charge reversibility is observed after sequential absorption of up to five layers, of the micellar diblock copolymers $PDMA_{96}$-$PDEA_{26}$ and $PDEA_{50}$-$PMAA_{50}$, onto the negatively charged (at pH 9) MF particle

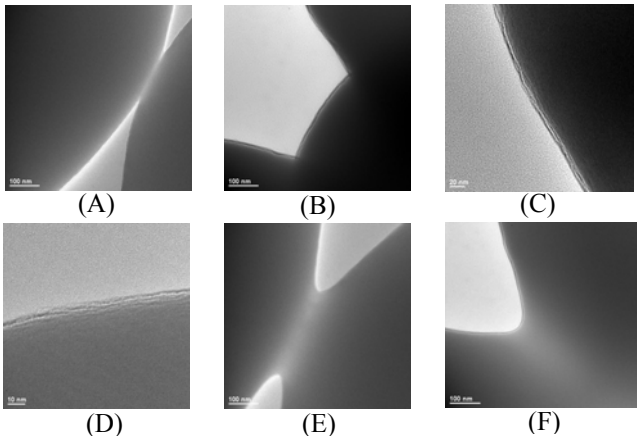

Figure 6: TEM images of all consecutive layers onto the 2μm diameter MF particles; (A) MF particle (layer 0), (B) layer 1, (C) layer 2, (D) layer 3, (E) layer 4, (F) layer 5

Before embarking into the study of the dissolution of the encapsulated MF, let us initially consider their decomposition in HCl as naked particles. A 0.01%wt MF particle suspension, made in 10mM KNO_3 electrolyte, was exposed to HCl solution of a pH of 1.4. As can be observed in Figure 7, the suspension turns from cloudy white to clear, denoting MF resin decomposition to oligomers. [5]

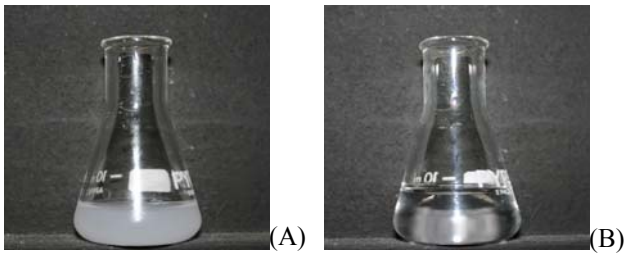

Figure 7: Bare MF particles (A) before and (B) after dissolution in 0.1M HCl

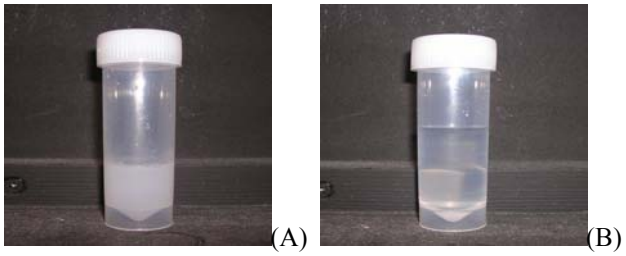

Figure 8: Coated MF particles (A) before and (B) after dissolution in 0.1M HCl

In the same way, MF core particles coated with either one or five layers of the diblock copolymer micelles, were dissolved away. Dissolution of the MF particles was undertaken at a pH 1-2. As can be observed in Figure 8 the suspension goes from milky to clear, much in the same way as the naked MF particles after decomposition. Samples were tested both before and after cross-linking with BIEE.

The resultant capsule samples were then imaged using a Scanning Electron Microscope. Through SEM observations the difference between the un-dissolved and dissolved particles is readily apparent. Furthermore, there is a visible difference between the particles that were cross-linked before dissolution and the ones that were not. Figure 9 gives representative images. Figure 9(A) shows MF particles coated with five micelle layers and Figure 9(B) shows the same sample after it has been cross-linked; the influence of the cross-linking being clearly visible in the region between the particles shown. In Figure 9(C) and 9(D) the same samples are shown after the core particles have been dissolved. Here the effect of the cross-linker is again evident; the BIEE cross-linking offers increased stability for the shell cross-linked micelles. The size of the uncross-linked hollow capsule decreases by about 0.5μm, to approximately 1.5μm, whereas the size of the cross-linked capsule remains virtually the same at approximately

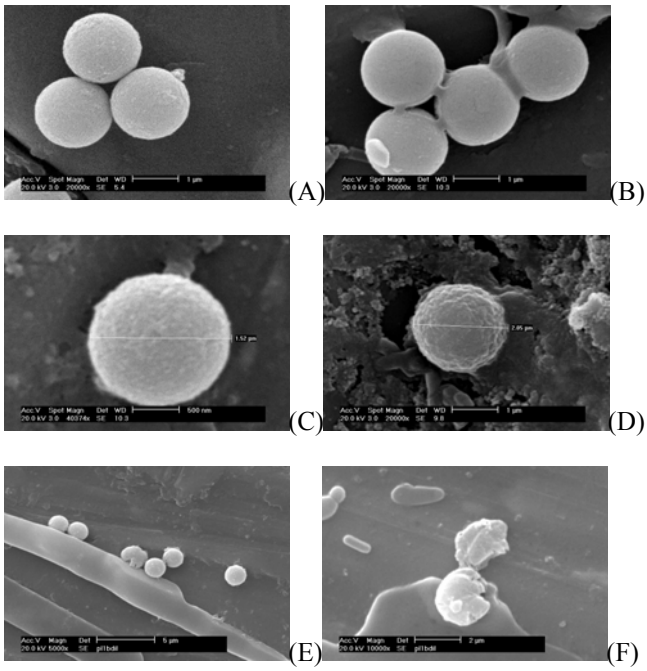

Figure 9: SEM images of (A) 5 layer coated MF particles, (B) 5 layer coated MF particles and cross-linked with BIEE, (C) 5 layer coated MF particles and dissolved in 0.1M HCl, (D) 5 layer coated MF particles, cross-linked and dissolved in 0.1M HCl, (E) & (F) 1 layer coated MF particles, cross-linked and dissolved, where it is clearly visible that some of the particles have "burst"

2μm. The use of the BIEE, therefore, provides additional structural rigidity to the capsules. Figures 9(E) and 9(F) show similar images after deposition of only one micelle layer and dissolution of the core. Note that both these images utilize a cross-linked sample. Stability and rigidity of those particles is still surprisingly good, probably due the inherent structural integrity of the encapsulating micelles. In some cases, a few particles "burst" during the core dissolution as can be seen in these last two images. Previously, it has been suggested from investigations using simply homopolymer systems that a low yield of stable capsules is obtained when the number of deposited layers is less than 4. [5] Our results using micellar layers suggest that the micelles themselves may offer some increased stability with less layers being deposited.

4 CONCLUSIONS

MF inorganic colloidal particles were successfully coated with multilayers of diblock copolymer micelles in a 10mM KNO_3 polyelectrolyte solution at pH 9, via the layer-by–layer technique. The MF core was then successfully dissolved when exposed to an acidic environment of 0.1M HCl, at a pH of 1.6. SEM supported the formation of hollow capsules.

After dissolution of the core the pH was quickly adjusted back to pH 9 by addition of 1M and 0.01M KOH. At pH 9 the capsule shells appear stable and do not seem to degrade.

Applications. In the recent years there has been an increasing interest in the production of 'smart' surface coatings for specific applications in the field of nanotechnology. Coatings with regular 3-dimensional morphology may offer a range of advantages even though there are generally some limitations to this "top-down" approach; they are complex, time consuming and expensive procedures in comparison to the "bottom-up" approaches. Nevertheless, the advantages can very well outweigh the above limitations. Applications on the fields of drug delivery (for the controlled release of active agents and sensitive contents), biomedicine, food industry and even their functionality as steric stabilisers have proven that.

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