Multi-layer films of block copolymer micelles adsorbed to colloidal templates

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Alternating layers of cationic and anionic block copolymer micelles have been deposited onto colloidal silica particles using a layer-by-layer approach. The resulting films have been investigated using a number of characterization techniques including zeta potential measurements, dynamic light scattering, thermo-gravimetric analysis and microscopy. The micelles used here demonstrate pH-responsive behaviour both in solution and when adsorbed at interfaces. It has been shown that block copolymer micelles can selectively encapsulate and release hydrophobic materials; therefore, the incorporation of such responsive species within films has the potential to offer increased functionality. The formation of films onto colloidal particles is of great interest as it can provide pathways to direct encapsulation of materials along with surface modification. This study aims to provide new insights into the nature and properties of responsive films. Such studies will allow for the future development of novel delivery systems that have potential application within a number of industrial sectors including personal care products, pharmaceuticals and agro-chemicals.

Keywords: layer-by-layer; block copolymer; micelles; pH responsive; colloidal

1. Introduction

In recent years, the layer-by-layer (LbL) technique has been employed as a robust method for depositing polyelectrolyte multi-layer films onto a number of substrates (Caruso 2001). This technique has been used to develop highly functional coatings with a broad range of potential applications. Initially demonstrated on planar surfaces (Decher 1997), the deposition process has also been carried out using colloidal substrates (Radtchenko et al. 2000), notably nanoparticles (Caruso & Möhwald 1999), emulsion droplets (Lu et al. 2004; Wackerbarth et al. 2009) and liquid crystals (Tjipto et al. 2006; Priest et al. 2008).

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Hollow capsules have been created by selective dissolution of the colloidal template, leading to further interest in this area (Donath et al. 1998). Recently, developments have been reported whereby one or more of the polyelectrolyte layers are replaced by a particulate component (Caruso et al. 1998), including quantum dots (Lavasanifar et al. 2002), liposomes (Stadler et al. 2009) and micelles (Ma et al. 2005; Cho et al. 2006), thus increasing the number of possible systems and the range of proposed applications.

In our research group, we have focused recently on studying the adsorption of amphiphilic block copolymers to solid surfaces, including their incorporation within multi-layer films (Webber et al. 2004; Smith et al. 2007; Sakai et al. 2008). This is recognized as an important topic in materials science and engineering owing to the large number of potential technologies that could use such systems. For example, such responsive copolymer systems may allow the formation of functional surface coatings that respond to environmental conditions in order to produce nanoscale variations in friction and adhesion. Alternatively, solutions containing block copolymer micelles have the potential to selectively encapsulate and subsequently release active materials in response to changes in bulk conditions, suggesting possible applications within many delivery systems, most notably pharmaceuticals. An excellent review of literature covering the encapsulation of molecules within amphiphilic copolymers in aqueous solution has been published (Rodriguez-Hernandez et al. 2005). This research has largely focused on examining micelles in solution. In contrast, research on micelle adsorption to solid surfaces and its effect on the ability of these micelles to encapsulate/release chemical compounds is much more limited, with only a small number of systems having been investigated in the research groups of Hammond (Nguyen et al. 2007; Kim et al. 2008a, b) and Cho et al. (2004, 2006). For certain applications, immobilization of block copolymer micelles at a solid interface may allow for enhanced and localized concentrations of active materials. Furthermore, adsorption at an interface may hinder (or even prevent) micelle dissolution upon dilution of such systems. Thus, with the use of stimulus-responsive polymers, an adsorbed layer of loaded micelles may allow researchers to design versatile ways for encapsulating and selectively delivering active materials.

In our laboratories we have extensively worked with a pair of oppositely charged block copolymer micelles: poly2-(dimethylamino) ethyl methacrylate-block-poly2-(diethylamino) ethyl methacrylate (PDMA-PDEA) and poly (2-(diethylamino) ethyl) methacrylate-block-poly(methacrylic acid) (PDEA-b-PMAA), with the latter being a polyampholyte. The PDMA-PDEA copolymer is molecularly dispersed at low pH, but forms well-defined PDEA-core micelles in alkaline solution (Bütün et al. 2001b). The unimer-to-micelle transition occurs over a relatively narrow pH range (pH 7–9), which depends on both the molecular weight and the block composition of the copolymer. Bütün et al. showed that the PDMA blocks of these copolymers can be selectively quaternized by reaction with simple alkyl halides to produce permanent cationic blocks. This derivatization ensures that the coronal PDMA blocks retain their cationic character, and the assembled structures remain colloidally stable in alkaline media (Bütün et al. 2001a). Recently, the synthesis of zwitterionic AB diblock copolymers has also been reported (Lowe et al. 1998). The aqueous solution behaviour of PDEA-PMAA is considerably more complex...
than that seen for the PDMA-\textit{b}-PDEA copolymers owing to the pH sensitivity of both blocks and electrostatic attractions between the oppositely charged blocks. PDEA-PMAA copolymers are known to form micelles with an anionic coronal PMAA block and a hydrophobic PDEA core in alkaline solution (Lowe \textit{et al.} 1998).

Our initial investigation of the self-assembly of mono- and multi-layer films was conducted on planar surfaces, typically silica and quartz. The use of \textit{in situ} atomic force microscopy (AFM) has allowed the individual micelles present within a layer to be imaged and conformational changes as a result of changing bulk conditions to be observed (Webber \textit{et al.} 2004). Furthermore, the use of quartz crystal microbalance and optical reflectometry (OR) has provided us with adsorption isotherms from which we have deduced the level of hydration of these block copolymer micellar films (Sakai \textit{et al.} 2006\textit{a},\textit{c},\textit{d}). More recently we have started to investigate the formation of LbL assembled films comprising block copolymer micelles onto curved surfaces, specifically charged colloidal particles (Biggs \textit{et al.} 2007). The electrostatic assembly of coatings onto micron- and submicron-sized particles presents a number of exciting opportunities in the development of smart surface coatings and stimulus responsive particles. As demonstrated by Donath \textit{et al.} (1998), employing a sacrificial particle for the deposition of such films, one can form functional capsules after selective dissolution of the supporting template. In employing sacrificial templates such as polystyrene latex (Addison \textit{et al.} 2008) and calcium carbonate (Addison \textit{et al.} 2010), we have been able to generate hollow polymeric capsules, with membranes that are composed exclusively of multi-layers of block copolymer micelles (Addison \textit{et al.} 2008, 2010).

Our previous work has shown that, upon surface immobilization within a film or membrane, the individual block copolymer micelles retain their core/shell structure (Biggs \textit{et al.} 2007). We demonstrated that the pH-responsive nature of the surface adsorbed micelles is retained, thus allowing hydrophobic material encapsulated within the micelle core to be selectively released as a function of changes in pH. This is caused by changes in the conformation of the surface adsorbed structures induced by rearrangement of the individual copolymer chains resulting in the loss of the hydrophobic domain from the aggregates. The aim of the present work is to provide further insight into the nature of multi-layers comprising PDMA-PDEA/PDEA-PMAA micelles adsorbed to colloidal templates. Specifically, a more detailed characterization will examine the extent of polymer adsorption, the film thickness and the response of these films to pH changes. Where appropriate, comparison will be drawn with the observations we have made in examining equivalent multi-layer films on flat surfaces. In addition, this study will investigate how modification of PDMA-PDEA micelles via quaternization of the PDMA block influences the formation of the micelle films. For this purpose, colloidal silica was identified as a suitable particle on which to deposit multi-layer films. This is because it possesses a high degree of anionic charge in basic conditions, i.e. where the two block copolymers exist as anionic/cationic micelles. It is also readily available in monodispersed samples, which should allow for accurate estimation of surface area, which is necessary to calculate adsorbed amounts. Furthermore, much of our investigation of such films on flat surfaces was carried out on silica substrates (Sakai \textit{et al.} 2006\textit{b},\textit{d}).

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2. Results and discussion

Analysis of film deposition on particulate substrates can be achieved by measuring the electrokinetic potential of the coated colloidal particles. However, estimating the zeta potentials of flat surfaces using streaming potentials generally requires a more complex analysis. Previously, zeta potential measurements have been commonly used to characterize the formation of multi-layer films onto both planar and colloidal surfaces. Because such films are typically adsorbed by consecutively adsorbing each layer, each corresponding adsorption cycle should result in a charge reversal of the surface, indicating that a successful coating has been performed. In some cases, however, reliance on a zeta potential measurement alone to confirm charge reversal of the particle surface as evidence for application of a coating may be misleading. It is entirely possible, for example, that the second layer does not deposit onto the particles and instead the solution strips (either partially or fully) the initial layer from the surface. This would result in the exposure of a bare silica surface (anionic), giving the false impression of a successful coating. In order to further investigate the nature of the micellar films, a series of acid/base zeta potential titrations were carried out on 250 nm silica particles that had been coated with a layer of block copolymer micelles. Such titrations give estimates of the zeta potentials of the particles as a function of pH and can provide additional information about how such micellar coatings respond to changes in their chemical environment.

For this purpose, a 250 nm silica sol was coated with PDMA-PDEA micelles having different levels of quaternization (permanent charge) at pH 9. Following washing and redispersion, data for the zeta potential as a function of pH were recorded. These data have been plotted in figure 1.

When contrasted to the zeta/pH titration of the silica sol (see the electronic supplementary material, figure S1) it is evident from figure 1 that successful coatings of the silica particles have been achieved. In all cases, the adsorption is driven by electrostatic interactions between the cationic PDMA-PDEA coronas and the highly anionic silica particles. In the case of the 0qPDMA-PDEA copolymer, the electrostatic interactions will be much weaker; however, it is clear from these data that the 0qPDMA-PDEA still adsorb to the particle surfaces and do not desorb during the washing steps. These results are in agreement with our previous findings on planar silica surfaces (Sakai et al. 2006b). All of the PDMA-PDEA coatings demonstrate an increasingly positive zeta potential as the solution pH is decreased. This can be explained by protonation of the tertiary amine groups in both the PDMA and PDEA block as more acidic conditions are achieved. These datasets also show that the gradient in zeta potential between basic and acidic conditions is larger for micelles with less permanent cationic charge. This behaviour is logical as lower quaternization of the PDMA results in a greater density of available amine groups that can undergo a reversible protonation owing to changes in the solution pH. In weakly acidic conditions (pH 4) all of the PDMA-PDEA samples have a significant degree of cationic charge associated with them; however, for a given pH, increasing the permanent charge associated with the PDMA block gives rise to an overall higher value of zeta potential. At low pH, it may be expected that the majority of the tertiary amine groups present on the copolymers will be protonated, and thus all samples should demonstrate similar zeta potentials. Inspection of figure 1 shows that this is not
the case, with a possible explanation being that the weak/unquaternized PDMA-PDEA micelles show significantly more desorption upon transitioning to low pH following adsorption at pH 9 (Addison et al. 2008). Furthermore, rearrangement of the copolymer chains upon exposure to acidic conditions produces layers with significantly different morphologies (see the electronic supplementary material, figure S3; Webber et al. 2004). Both of these factors could be contributing to the differences observed in the zeta potentials of the coated silica sols at low pH. These results serve to demonstrate that all of the PDMA-PDEA samples can produce a successful coating of the silica particles. Additionally, it is clear that the pH-responsive nature of the copolymer chains is retained upon adsorption to a colloidal template.

Following the coating of the silica particles with a monolayer of 50qPDMA-PDEA micelles, an additional layer of anionic PDEA-PMAA micelles (pH 9) was deposited as a second over-layer. Following washing and redispersion of the particles, an initial zeta potential measurement at a single pH confirmed a charge reversal of the particles from cationic to anionic. However, in order to gain further insight into the nature of the two-layer surface coating, data for the zeta potential as a function of pH were also recorded (figure 2).

The data in figure 2 clearly show the pH-dependent response of the PDEA-PMAA, which is adsorbed as the outermost layer of the film. Above pH 8, negative zeta potentials are reported owing to deprotonation of the coronal PMAA block. In contrast, below pH 6 cationic zeta potentials are reported because of protonation of the tertiary amines on the PDEA block and the concomitant loss of charge on the PMAA blocks as these residues are protonated. Figure 2 also contains data for the reverse titration, i.e. from acidic back to basic conditions. In acidic conditions, both the first and the second polymer micelle
Figure 2. Zeta potential as a function of pH for a sample of 250 nm silica particles coated with a polymeric bilayer consisting of an under-layer of 50qPDMA-PDEA and an over-layer of PDEA-PMMA. The first titration was performed in 10 mM KNO₃ with an initial pH of 9.5 by titrating to acidic conditions (circles). The coated silica sample used for the first titration was retained and redispersed in acidic 10 mM KNO₃ following centrifugation of the particles. This sample was then titrated from pH 3.5 back to basic conditions (crosses).

layers are expected to be positively charged; this may cause some desorption of the outermost (PDEA-PMAA) layer of the film. However, titration to basic pH shows clearly that the anionic/cationic nature of the second micelle over-layer coating is still observed. It is probable that substantial desorption and interpenetration may have occurred within the film owing to the conformational changes associated with the initial titration to pH 4. However, the response of the particles during the reverse titration suggests that a significant number of PDEA-PMAA chains are still present within the outermost polymeric layer. This result is potentially significant as it demonstrates that, in transitioning from a weakly basic environment to weakly acidic conditions, the pH-sensitive two-layer film is sufficiently robust to not desorb completely from the particle surface. This result is encouraging for the use of such responsive films as smart membranes with a possibility to deliver different materials as a function of a range of stimuli.

A greater understanding of the nature of multi-layer films containing block copolymer micelles and their response to stimuli can be achieved through the quantification of the amount of adsorbed polymer within each layer. Correlating these data to the aggregation numbers of the micelles, one can determine the number of micelles per unit area which, as demonstrated later, can be used to analyse uptake and release of material from such films. Previous studies of polymeric films on planar substrates have used a number of different techniques to produce adsorption isotherms (Sakai et al. 2006a,c,d). It has been shown that OR can be used to detect changes in electron density, and thus refractive index at an interface owing to the adsorption of polymeric material. In addition, a quartz

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Figure 3. Graph showing the amount of polymer within each layer of multi-layer films (composed of alternating PDMA-PDEA and PDEA-PMAA layers) adsorbed to 250 nm silica particle templates. Each datum point represents the amount of polymer adsorbed within an individual layer. The values given for the adsorption are calculated per surface area of the silica colloid and are not cumulative. Adsorption of four different films was investigated: 0qPDMA-PDEA/PDEA-PMAA (squares), 10qPDMA-PDEA/PDEA-PMAA (circles), 50qPDMA-PDEA/PDEA-PMAA (crosses), 100qPDMA-PDEA/PDEA-PMAA (triangles).

crystal microbalance is able to detect the combined mass of surface adsorbed polymer chains and bound water associated with a quartz crystal according to the Sauerbrey equation (Sauerbrey 1959).

For the colloidal silica templates used here, quantification of the copolymer adsorption to the particle surface was carried out by two different approaches. We used a chemical titration method as described below as well as TGA. These techniques were used to characterize samples obtained from different stages of the coating of 250 nm silica spheres with six layers of alternating PDMA-PDEA and PDEA-PMAA. In the case of the chemical titration, after each adsorption cycle the particles were settled via centrifugation and a sample of the supernatant removed for subsequent analysis. The analysis procedure involved the titration of the anionic potassium vinyl sulphate (PVSK) aqueous solution against the cationic copolymer solutions (carried out at acidic pH where PDEA-PMAA is cationic). The PVSK solution complexes with the protonated tertiary amines of the PDEA and PDMA and, at the end point, this causes precipitation of the copolymer chains resulting in a colour change. Comparison of experimental results with a calibration curve (see the electronic supplementary material, figure S2) obtained by titrating against known polymer concentrations allows for determination of the concentration of the supernatant and thus the amount of polymer adsorbed to the particles. Plotted in figure 3 are the adsorption data obtained with this technique as a function of layer number for the four PDMA-PDEA copolymer samples with the PDEA-PMAA copolymer micelles. Note that these data are non-cumulative and the amount adsorbed is specific to the given layer number.

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Exposure of the colloid sample coated with a layer of $0q$PDMA-PDEA to a solution of PDEA-PMAA micelles causes significant desorption of the weakly bound PDMA-PDEA chains. If desorption of the underlying PDMA-PDEA layer during exposure to a PDEA-PMAA layer is too great, determination of the PDEA-PMAA concentration in the resulting supernatant is compromised owing to the presence of the desorbed PDMA-PDEA. As a result, the data for layers 2, 4 and 6 of the $0q$PDMA-PDEA/PDEA-PMAA multi-layer have been excluded; however, the results for the cationic layers (1, 3 and 5) should remain reliable. Figure 3 shows that varying the quaternization of the PDMA block creates large variations in the amount of adsorbed PDMA-PDEA within the cationic layers, i.e. layers 1, 3 and 5. It is clear that the weakly charged $0q$PDMA-PDEA adsorbs with the greatest density and, as the degree of quaternization of the PDMA-PDEA is increased, less adsorption is recorded. This is in good agreement with our studies on flat surfaces which showed that the larger $0q$PDMA-PDEA micelles adsorb as a more closely packed layer, thus facilitating the adsorption of greater amounts. For reference purposes, contained within the electronic supplementary material (table S1) are the hydrodynamic diameters of the micelles in solution. The data recorded for the anionic layers, i.e. layers 2, 4 and 6, are generally in good agreement to one another for all four of the PDMA-PDEA/PDEA-PMAA copolymer pairs investigated here. There is some suggestion from the data that the underlying layer of positively charged micelles influences the amount of adsorbed negatively charged micelles as the adsorption recorded slightly increased with the degree of quaternization of the micelles in the underlying layer. A general trend of the data is that as more layers are added the amount of adsorption of both the anionic and cationic layers gradually increases. This may be rationalized through the increasing hydrodynamic diameter of the colloids as the surfaces are coated by each layer effectively increasing the available surface area to which subsequent layers can adsorb.

In this work we have also quantified the polymer adsorption of each micelle layer using TGA, by recording the mass change of the coated particle samples as a function of increasing temperature. Using silica particles as the template, this technique can easily differentiate the decomposition of the polymer layer from that of the particle itself as they occur at very different temperatures ($>800^\circ C$ for inorganic silica and $\approx 300^\circ C$ for the polymer). By carrying out TGA on samples of particles after each coating has been applied we have estimated the polymer content of each layer per unit surface area of colloid. Plotted in figure 4 are the data obtained from the TGA of 250 nm silica particles coated with one to five alternative layers of $50q$PDMA-PDEA and PDEA-PMAA micelles.

All the plots in figure 4 show a similar trend until approximately $300^\circ C$ owing to the loss of bound water in the system. When increasing the temperature further, significant differences are found owing to the decomposition of the surface adsorbed polymer. As expected, as more polymer micelle layers are added to the particles, the polymer content of the sample increases. By subtracting the expected water content (based on the pristine silica sample) from each of the coated silica samples, it is possible to obtain an estimate of the adsorbed amount of polymer in each layer. These data have been plotted in figure 5 along with the corresponding data from the $50q$PDMA-PDEA/PDEA-PMAA colloidal titration.
Figure 4. Thermo-gravimetric analysis of samples of 250 nm silica particles coated with alternating 50qPDMA-PDEA/PDEA-PMAA layers. Pristine particles (line), one layer (squares), two layers (triangles), three layers (circles), four layers (crosses) and five layers (stars).

Figure 5. The extent of polymer adsorption in a multi-layer film composed of alternating layers of 50qPDMA-PDEA and PDEA-PMAA adsorbed to 250 nm silica particles. Each datum point is cumulative and includes the total amount of polymer adsorbed to the silica following the addition of the number of layers as given by the $x$-axis. As determined by TGA (squares), colloidal titration (circles).

Inspection of figure 5 shows the two datasets to be in excellent agreement with each other. The two techniques measure different parameters and so will each have their own errors associated. For example, the colloidal titrations are based on the changes in concentration of an adsorbing polymer solution; it is assumed that the
entirety of the polymer that is removed from the solution is bound to the particles. In comparison TGA directly measures the polymeric content of dried particles removed from solution. Prior to drying the particles, it is necessary to remove the excess polymer from the suspension by carrying out a number of washing cycles, it is expected that these washing cycles will remove loosely bound copolymer chains, meaning that the particles will have less polymer bound to them than would be suggested by the decrease in concentration of the supernatant alone. On the other hand, the estimates obtained by TGA require an assumption that the moisture content of coated particles is the same as that for pristine particles. In reality it is probable that as more layers are added to the particles the residual water content increases. Despite this, the fact that both sets of data are in excellent agreement tends to suggest that such experimental artefacts have been kept to a minimum and both techniques offer a viable means of estimating the extent of polymer complexation in the multi-layer films.

Determining the thickness of multi-layer films is of interest as it provides insight into the film properties, specifically their permeability and mechanical properties. Accurate determination of the thickness of films adsorbed to flat substrates is possible with techniques such as OR. However, this generally requires the film to be composed of a number of discrete layers that are optically homogeneous and isotropic (Arsov et al. 2003). Any violation to these requirements hinders measurements and requires complex variations to the technique. Dynamic light scattering (DLS) is a relatively straightforward colloidal characterization technique which can be used to estimate the hydrodynamic diameter of particles in solution (Hassan 2009). Providing that the particles are sufficiently small or of a density close to that of the dispersant to not undergo significant settling over the course of a measurement, DLS can give highly accurate estimates of the diameters of spherical particles. In the case of polymer-coated particles, providing the particles can be completely redispersed following adsorption/washing and do not undergo aggregation in solution, DLS can be used to estimate the thicknesses of adsorbed polymer layers. By using monodispersed colloidal templates, DLS measurements have the potential to offer a quick and convenient way of monitoring the formation and response of multi-layer films. Such an approach will negate potential problems caused by the possible interpenetration of diffuse micelle layers (Smith et al. 2007), which may hinder measurements made with elipsometry-based techniques.

For such measurements, silica particles (250 nm) were coated with a monolayer of PDMA-PDEA micelles. Once again the four experiments were performed with the quaternization being varied (0q, 10q, 50q and 100q). These adsorptions were performed at pH 4 and pH 9. Following a number of washing cycles a sample of the particles were redispersed in electrolyte solution and the hydrodynamic diameter determined using DLS measurements. These data are given below in table 1.

The data in table 1 indicate that, for all samples of PDMA-PDEA, adsorption at acidic pH results in thin layers of between 2 and 10 nm based on a determined particle size of 249 nm ± 1 nm. Under acidic conditions PDMA-PDEA copolymers do not undergo micellization in solution, so it is reasonable to assume that copolymers adsorb as individual chains to the particle surface in order to compensate for the surface charge. In contrast, when the PDMA-PDEA solutions are adsorbed at pH 9, much thicker films are formed on the particles, corresponding to the presence of adsorbed copolymer micelles. Furthermore,
Table 1. Hydrodynamic diameters of 250 nm silica colloids coated with PDMA-PDEA monolayers in acidic (pH 4) and basic (pH 9) conditions.

<table>
<thead>
<tr>
<th>PDMA quaternization (%)</th>
<th>Hydrodynamic diameter following coating at pH 9 (nm) (^a)</th>
<th>Hydrodynamic diameter following coating at pH 4 (nm) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>291 ± 2</td>
<td>254 ± 2</td>
</tr>
<tr>
<td>10</td>
<td>274 ± 2</td>
<td>257 ± 2</td>
</tr>
<tr>
<td>50</td>
<td>267 ± 2</td>
<td>258 ± 2</td>
</tr>
<tr>
<td>100</td>
<td>260 ± 2</td>
<td>256 ± 2</td>
</tr>
</tbody>
</table>

\(^a\) As determined by DLS (10 mM KNO\(_3\), pH ≈ 9).

Increasing quaternization of the micelles results in thinner films. Contrasting these results with the measured diameters of the micelles in solution (see the electronic supplementary material, table S1) it is clear that larger micelles correlate well with thicker surface adsorbed films. However, in all cases, the layer thicknesses are smaller than might be expected if a monolayer coverage of non-collapsed micelles is assumed. A possible explanation of this is due to the relaxation and thus flattening of the micelles to the silica surface on adsorption, which we have reported previously on flat surfaces \(\text{Sakai et al. 2008}\). These data are in good agreement with our observations on flat silica surfaces as the more highly charged, smaller PDMA-PDEA micelles undergo a larger relaxation. These results provide good evidence that the PDMA-PDEA copolymer chains are adsorbing as aggregate structures at pH 9. Furthermore, it confirms that DLS measurements are sufficiently sensitive to detect subtle variations in film thickness originating from the different hydrodynamic diameters of the adsorbed PDMA-PDEA micelles.

In order to further investigate the pH-responsive nature of the surface-adsorbed PDMA-PDEA micelles, 250 nm silica particles were first coated with the PDMA-PDEA micelles at pH 9. Following a standard washing/redispersion protocol, the solution pH was then lowered to pH 4 and the hydrodynamic diameters of the coated particles measured. These data are given in figure 6.

The data in figure 6 show the response of PDMA-PDEA monolayers to changes in solution pH. These results are in good agreement with observations seen on flat silica surfaces where the 0q and 10qPDMA-PDEA undergo a degree of swelling upon transitioning to acidic pH resulting in increasing diameters. Conversely, the highly quaternized PDMA-PDEA micelles (50q and 100q) experience a modest reduction in size, which may be caused by micelle dissociation and copolymer desorption. A possible explanation of these observations is that the adsorbed 0qPDMA-PDEA and 10qPDMA-PDEA aggregates transition from micelle-like structures to polymeric brushes upon transitioning to acidic pH. This transitioning results in the surface-adsorbed copolymer chains adopting a less flattened conformation and consequently increasing the recorded hydrodynamic diameter of the particles. This behaviour is in good agreement with our observations on planar surfaces, with a more detailed explanation of this being available elsewhere \(\text{Webber et al. 2005}\). A schematic diagram of this behaviour adapted from a previous publication is provided within the electronic supplementary material (figure S3).
Multi-layers of PDMA-PDEA/PDEA-PMAA were adsorbed to 250 nm silica templates. After the formation of each layer, a sample of particles was investigated using DLS; these data are plotted in figure 7.

The data in figure 7 show that, with the addition of each layer, the hydrodynamic diameter of the particles increases. Additionally, the multi-layers containing the larger, less charged PDMA-PDEA micelles are coated with a thicker film than those containing the more highly charged PDMA-PDEA samples. It is reasonable to assume that larger micelles will result in thicker adsorbed films; however, when multiple layers of micelles have been deposited it is probable that significant interpenetration of the layers occurs, making further analysis of these data difficult to quantify. Despite this, these data serve to provide additional evidence that with each adsorption cycle a successful coating is being adsorbed.

With respect to observation of these coated films, electron microscopic techniques such as SEM and TEM generally require dry samples; thus necessitating the removal of the particles from solution. However, such imaging techniques can still provide information on the nature of the adsorbed films that would be difficult to obtain if working with a flat substrate. Shown below in figure 8b are SEM images of a single micelle layer adsorbed to silica particles to be contrasted to an image of a bare silica particle (figure 8a). It is clear from these SEM images that, following adsorption, washing and drying of the particles, a coating is still present. Furthermore, it is evident that a degree of structuring is present within the dehydrated coating, which gives further evidence that the 0qPDMA-PDEA chains are adsorbing as structured aggregates.
Figure 7. DLS-determined hydrodynamic diameters of 250 nm silica particles coated with alternating layers of PDMA-PDEA/PDEA-PMAA as a function of layer number. Measurements were carried out at pH 9 with a 10 mM KNO₃ electrolyte. Four unique multi-layer films were investigated: 0qPDMA-PDEA/PDEA-PMAA (squares), 10qPDMA-PDEA/PDEA-PMAA (circles), 50qPDMA-PDEA/PDEA-PMAA (triangles) and 100qPDMA-PDEA/PDEA-PMAA (crosses).

Figure 8. (a) SEM image of a 500 nm silica particle. (b) 500 nm silica particle following adsorption of a single 0qPDMA-PDEA micelle layer. Scale bar, 100 nm.

Nano-sized structures (10–15 nm) present on the particle surface are smaller than the corresponding 0qPDMA-PDEA micelles in solution (23 nm). A probable cause of this is dehydration of the micelles resulting in flattening and shrinkage. This could also be causing the apparent porous nature of the coating seen within the SEM image.
Figure 9. (a) TEM image of a 250 nm silica particle coated with a 50qPDMA-PDEA micelle monolayer. (b) A single 250 nm silica particle following deposition of four alternating 50qPDMA-PDEA and PDEA-PMAA micelle layers. Scale bar, 50 nm.

Inspection of the TEM images in figure 9 shows that a thin film of polymer is present on the particles following adsorption of a single layer of 0qPDMA-PDEA micelles; following the adsorption of a pair of 0qPDMA-PDEA/PDEA-PMAA bilayers it is clear that the apparent surface roughness of the particles has increased significantly, thus indicating the formation of a more substantial polymeric coating.

3. Experimental

(a) Materials

The materials were provided by the following sources: KOH (reagent grade, ≥90%, flakes), Sigma-Aldrich; KNO₃ (SigmaUltra, ≥99.0%), Sigma-Aldrich; HNO₃ (ACS reagent, 70%), Sigma-Aldrich; PVSK (1/400N poly(potassium vinyl sulphate) aqueous solution), Wako Pure Chemicals; toluidine blue indicator solution, Wako Pure Chemicals; 250 nm silica particles (Angstromsphere), Fiber Optic Center Inc.; 500 nm silica particles, Bangs Labs. All chemicals were used as received. The water used in all experiments was prepared from a Millipore Milli-Q Ultrapure Water Purification System with a resistivity of 18.2 MΩ cm⁻¹ (25°C).

(b) Copolymer synthesis and characterization

The PDMA-PDEA diblock copolymer was synthesized using group transfer polymerization (GTP). Full details of this synthesis may be found elsewhere (Bütün et al. 2001b). The quaternization procedure was carried out using MeI, as described previously (Bütün et al. 2001a). The mean degree of quaternization of the PDMA blocks was assessed using ¹H NMR and was found to be 10, 50 and 100 per cent for the three quaternized samples.
The synthesis of the zwitterionic PDEA-PMAA diblock copolymer was also carried out using GTP. Full details of the synthesis may be found elsewhere (Lowe et al. 1998). For the copolymer used in this sample, on the basis of the $^{1}H$ NMR spectra, the mean degrees of polymerization were calculated to be 50 for the PDEA block and 50 for the PMAA block. The isoelectric point of this copolymer sample in solution was estimated with zeta potential measurements and found to be 7.8 ± 0.2.

(c) Preparation of PDMA-PDEA/PDEA-PMAA multi-layer film

Copolymer micelle multi-layers were prepared on silica colloids (Angstrom-sphere) via a modified LbL methodology. An aqueous solution of PDMA-b-PDEA at pH 9 (10 ml, 1000 ppm) was added to a dispersion of the silica sol at the same pH (10 ml, 7500 ppm) and tumbled for 12 h to ensure full equilibration. The sample was then centrifuged (3000 r.p.m., 20 min) to separate the colloidal particles from the non-adsorbed copolymer. Approximately 19 ml of supernatant was removed, replaced by an equivalent volume of pH 9 electrolyte solution and the sedimemented particles were redispersed. This purification protocol of separation, supernatant removal/replacement, and redispersion was repeated twice, with the final solution volume being made up to 10 ml. Finally, the solution pH was checked, and readjusted to pH 9 if necessary by addition of small volumes of dilute acid (HNO$_3$) or base (KOH). A solution of PDEA-b-PMAA (10 ml, 1000 ppm) at pH 9 was added to develop the second layer, and allowed to adsorb for 12 h. The separation/replacement/redispersion procedure was repeated as above. Successive additions of either cationic or anionic copolymer micelles produced a five-layer coating on the silica particles. All solutions used during the multi-layer preparation were 10 mM in KNO$_3$.

(d) Zeta potential measurements

A Malvern NanoSeries ZetasizerNano-ZS (Malvern Instruments) equipped with a helium–neon laser source (wavelength 633 nm, power 4.0 mW) was used for measuring the zeta potential of the silica sols (typical particle concentration 1000 ppm) before and after micelle coating. Auto-titration involved addition of small volumes of dilute KOH and HNO$_3$ solutions to give zeta potential versus pH curves. All measurements were performed in 10 mM KNO$_3$ solution. A typical datum point represents the average of at least 100 individual measurements.

(e) Dynamic light scattering

DLS experiments were performed using a Brookhaven BI-200SM equipped with a 633 nm helium–neon laser source (power 35 mW). In a typical experiment, 5 cm$^{-3}$ of solution containing approximately 50 ppm solids was placed into a quartz cuvette. Prior to use cuvettes were washed with a combination of surfactant, mechanical action, ultrasound treatment and organic solvents. A scattering angle of 90° was used and each datum point was typically made up of at least five individual measurements. The hydrodynamic diameter of the 250 nm silica particles was found to be 249 ± 1 nm.
(f) Colloidal titration

The copolymer concentration in the supernatant was determined using colloidal titration. Briefly, the copolymer supernatant was titrated by 1/400 N poly(potassium vinyl sulphate) aqueous solution in the presence of 1ml of 0.1M HNO₃ and two drops of toluidine blue indicator solution. At the end point, the solution colour changes dramatically from blue to light pink; the copolymer concentration is determined by comparing the absorbance of the unknown copolymer solution with that of the calibration curve.

(g) Thermogravimetric analysis

Thermogravimetric analysis was performed on a Perkin-Elmer Pyris1 instrument using samples of approximately 5mg which had been oven-dried (50°C) for 24h prior to analysis. Samples were heated under a nitrogen purge from room temperature to 625°C at a heating rate of 10°C per minute.

(h) Scanning electron microscopy

Scanning electron microscopy (SEM) images were obtained using a LEO 1530 Field Emission Gun SEM instrument operating at 3kV.

(i) Transmission electron microscopy

Transmission electron microscopy (TEM) grids were prepared by depositing one drop of the sample onto a Holey Carbon Film 400 Mesh Cu (50) grid. The grid was dried for 24h in a dessicator before observation with a Philips CM100 microscope operating at 80kV.

4. Conclusions

In summary we have demonstrated that multi-layer films of PDMA-PDEA and PDEA-PMAA micelles can be successfully deposited onto colloidal silica particles. As reported previously by us, the introduction of permanent charge to the PDMA block of the PDMA-PDEA copolymers results in variations in resulting micelles in terms of hydrodynamic diameter, coronal charge and pH response. The observations made in this work show that such variations in physicochemical characteristics of the micelles result in variations to the nature of the adsorbed films, including film thickness, adsorption density and response to pH changes. Direct comparison of these observations with equivalent multi-layers deposited onto flat surfaces is difficult because of the inherent differences between the characterization techniques. Despite this, the observations between the two surfaces are largely in agreement with each other. In both cases the micelles that are adsorbed as the outermost layer of the membrane determine the zeta/pH response of the coated surface; furthermore, micelles of PDMA-PDEA with a lesser degree of quaternization, i.e. less permanent charge, demonstrate a larger zeta potential gradient upon transitioning to acidic conditions. In terms of adsorption density, the larger, less charged micelles of PDMA-PDEA adsorb with a greater density than the highly charged, smaller micelles. This is consistent with our observation on flat surfaces and agrees with our proposed model of smaller
micelles with greater charge adopting a more flattened/relaxed conformation. To further verify these observations, DLS was used to monitor the film thickness of coated particles and showed that larger, weakly charged micelles of PDMA-PDEA resulted in thicker membranes. Furthermore the response of these films to pH transitions was investigated using DLS. As has been reported on flat surfaces using in situ AFM, the 0qPDMA-PDEA and 10qPDMA-PDEA monolayers undergo swelling owing to rearrangement and extension of the copolymer chains into the bulk. Conversely, 50qPDMA-PDEA and 100qPDMA-PDEA monolayers undergo shrinkage, which is possibly being caused by dissociation of the micelles.

When combined with our previous findings these results serve to demonstrate how films and capsules composed of responsive micelle systems have the potential to be tailored towards specific applications and functionality via small chemical modifications to the structure of the block copolymers. These findings have the potential to provide new insight for the development of functional delivery materials.

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References


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