Layer-by-Layer Assembly of Two Different Polymer Micelles with Polycation and Polyanion Coronas

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ABSTRACT: Layer-by-layer (LBL) assembly of two different polymer micelles was realized through alternating deposition of micelles with a polyanion and a polycation corona without the use of molecularly dissolved polyelectrolytes. The two micelles used were formed by the diblock copolymers of quaternized poly(4-vinylpyridine)-*b*-poly(*tert*-butyl acrylate) (PQ4VP-*b*-P*t*BA) and poly(acrylic acid)-*b*-poly(4-vinylpyridine) (PAA-*b*-P4VP) at pH > 7. The simultaneous loading of two hydrophobic dyes (pyrene and Nile Red) in the multilayer films through their preencapsulation in the micelles was investigated. The results show that the two dyes were redistributed in the micelle core regions in the films during the LBL buildup process.

Introduction

Layer-by-layer (LBL) assembly of polyelectrolytes has become a powerful means to build nanostructured thin films for many applications.[1] One recent development is the use of LBL to assemble particles or particle-like entities such as semiconductor nanocrystals,[2] vesicles,[3] and polymer micelles[4] into layered structures. In those studies, however, a polyelectrolyte was always utilized to bind the particles whose surface had the opposite charge of the polyelectrolyte. In this paper, we report a study of using LBL to assemble two different polymer micelles that have a polycation and a polyanion corona without the use of soluble polyelectrolytes. Considering the large body of knowledge on the micellar aggregates formed by amphiphilic block copolymers (star micelles, crew-cut micelles, vesicles, etc.) and the tremendous interest of using them as nanocarriers for hydrophobic agents (dyes, quantum dots, drugs, etc.),[5] we believe that the direct LBL assembly of different polymer micelles as demonstrated in this paper opens a general, versatile, and robust route to bringing hydrophobic polymers or functional agents into layered or ordered thin films.

The scheme for LBL assembly of two different polymer micelles is illustrated in Figure 1. The buildup process consists of sequential adsorption of micelles with oppositely charged polyelectrolyte coronas onto a substrate. The chemical structures of the materials utilized in this study are also shown. We used micelles formed by two diblock copolymers, one being composed of quaternized poly(4-vinylpyridine) and poly(*tert*-butyl acrylate) (PQ4VP-*b*-P*t*BA) and the other one being poly(acrylic acid)-*b*-poly(4-vinylpyridine) (PAA-*b*-P4VP). In aqueous solution, PQ4VP-*b*-P*t*BA forms micelles with hydrophobic P*t*BA core and positively charged PQ4VP corona, while at pH > 7, PAA-*b*-P4VP forms micelles with P4VP core and negatively charged PAA corona.[6] In addition to investigating the feasibility of LBL assembly of two micelles, we also wanted to know whether different dyes preencapsulated by the micelles in solution can be introduced into and organized in the multilayer film, as shown in Figure 1. Two hydrophobic dyes were used as model compounds for encapsulation, namely, pyrene (Py) and Nile Red (NR). The acronym PQ4VP-*b*-P*t*BA(NR) stands for micelles with cationic PQ4VP corona and NR-loaded P*t*BA core, while PAA-*b*-P4VP(Py) refers to micelles with anionic PAA corona and Py-entrapped P4VP core. Actually, each dye could be loaded in the two types of micelles, allowing for different combinations for LBL assembly. The results of this study show that different polymer micelles with oppositely charged coronas could be assembled into multilayer films using the LBL technique. However, spatial separation and organization of the two dyes could not be achieved through their physical preencapsulation in the micelles due to the diffusion occurred in the buildup process of the multilayer films.

Experimental Section

The two samples used, $PQ4VP_{97}$-*b*-P*t*BA_{52} and PAA_{52}-*b*-$P4VP_{97}$, were obtained from the same diblock copolymer of P*t*BA_{52}-*b*-$P4VP_{97}$ synthesized using atom transfer radical polymerization (ATRP).[6] Hydrolysis of the P*t*BA block gave rise to PAA_{52}-*b*-$P4VP_{97}$, while quaternization of the P4VP block resulted in $PQ4VP_{97}$-*b*-P*t*BA_{52}. Details on the synthesis of P*t*BA_{52}-*b*-$P4VP_{97}$, the preparation of PAA_{52}-*b*-$P4VP_{97}$, and investigation of the formation of micelles with PAA corona and P4VP core at pH > 7 were already reported[6] and will not be repeated here. Throughout this study, unless otherwise stated, all micellar solutions and rinsing water were held at pH > 7 to keep PAA in its ionized anionic state and to avoid the dissociation of assembled micelles. In the case of $PQ4VP_{97}$-*b*-P*t*BA_{52}, it was obtained through quaternization of P*t*BA_{52}-*b*-$P4VP_{97}$ with a 4-fold excess of ethyl bromide at reflux in ethanol for 48 h under nitrogen, followed by precipitation of the polymer in ether; complete quaternization was confirmed by ^{1}H NMR spectroscopy.[7]

The two types of polymer micelles were prepared by directly dissolving the block copolymers in aqueous solution with the desired pH value. Encapsulation of either Py or NR (Aldrich) was obtained using the following procedure. 4 mg of polymer was first dissolved in 9 mL of water to form the micelles; then 1 mL of dye solution in THF (concentration 1 mg mL^{-1}) was added into the micellar solution under stirring. After THF was removed by evaporation in air, the solution was filtered through a 0.45 μm membrane to eliminate the precipitated dye. Finally, water was added to reach 10 mL for the resultant dye-entrapped micellar solution. Thus, all solutions used to construct LBL multilayers had the same polymer concentration of 0.4 mg mL^{-1}.

The standard LBL deposition procedure of dipping−rinsing−drying was used.[1−4] Quartz slides were cleaned by immersion in a hot mixture of hydrogen peroxide and sulfuric acid (3/7, v/v) for 1 h, followed by rinsing with pure water and drying in hot air stream. The substrates both with negatively charged surfaces and coated with a primer of poly(allylamine hydrochloride) (PAH, $M \sim 70\,000$

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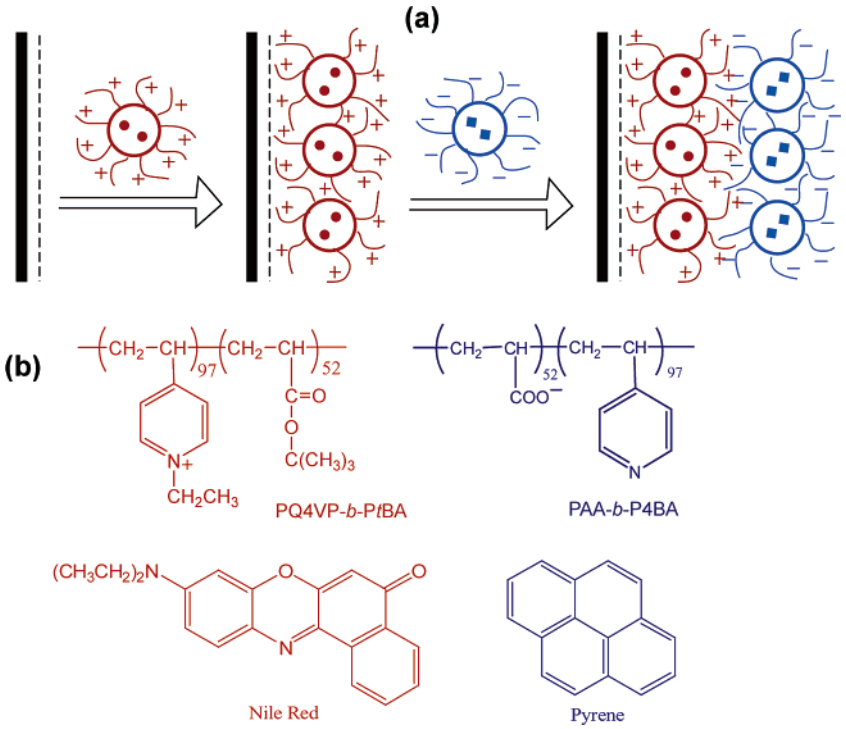

Figure 1. (a) Schematic illustration of LBL assembly of two different polymer micelles with encapsulated guests. (b) Chemical structures of the block copolymers and the hydrophobic dyes used.

g mol^{-1}, Aldrich), giving rise to positively charged surfaces, were employed in the study. To assemble the two types of micelles, the substrate was first dipped in the solution of the micelles whose corona had the opposite charge of the substrate surface for 15 min, then extensively rinsed using water with the same pH as the micellar solution, and finally dried by airflow. Subsequently, the substrate containing the first layer of micelles was immersed in the other micellar solution and subjected to the same treatment, yielding the bilayer of micelles on both sides of the substrate (only one side is sketched in Figure 1a). This alternating deposition process was then repeated to produce a film with the desired number of layers. Water used in all experiments was distilled and deionized using a Barnstead E-Pure system; pH was adjusted using 1 M NaOH or HCl and measured by a pH meter (Orion 410Aplus).

The multilayer films of polymer micelles were mainly characterized by means of UV−vis and fluorescence spectroscopy. UV−vis spectra were taken using a Hewlett-Packard 8452A diode array spectrophotometer, while steady-state fluorescence emission spectra recorded on a SPEX 1680 double-monochromator spectrophotometer. The surface morphology of the films was examined using a Hitachi S-4700 field-emission-gun scanning electron microscope (SEM) operating at 3 kV as well as a Nanoscope 3A atomic force microscope (AFM) in tapping mode.

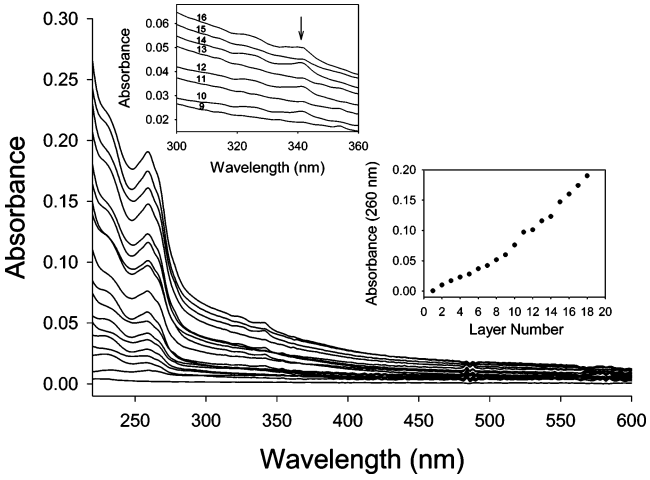

Figure 2. UV−vis spectra of LBL assembled PQ4VP-*b*-P*t*BA(NR) (micellar solution pH = 8) and PAA-*b*-P4VP(Py) (micellar solution pH = 11) up to 18 layers. The lower inset shows the plot of absorbance at 260 nm vs number of layers, while the upper inset is an expansion of UV−vis spectra in the 300−360 nm region for the numbered layers.

Results and Discussion

We start by revealing the general behavior of LBL assembly of two dye-encapsulated polymer micelles using an example of results. In this case, the first layer adsorbed on the negatively charged surface of substrate (quartz) was PQ4VP-*b*-P*t*BA(NR), and then the second layer of PAA-*b*-P4VP(Py) was deposited on top of the first layer; the sequence was repeated nine times. The micellar solution of PQ4VP-*b*-P*t*BA(NR) was set at pH 8, while the solution of PAA-*b*-P4VP(Py) at pH 11. It should be mentioned that throughout the paper the number of layers refers to the layers deposited on one side of the quartz slide, while UV−vis and fluorescence spectra were recorded with layers on both sides. Figure 2 shows the UV−vis spectra recorded after each deposition. The upper inset is an expansion of the spectra for the numbered layers in the 300−360 nm region showing the absorption bands of Py, the change of which will be discussed later. Absorption of NR around 540 nm is indiscernible partly due to the weak amount of dye loaded in the multilayer film. The lower inset is the plot of absorbance at 260 nm (from the pyridyl groups of PQ4VP and P4VP) vs the number of layers, which indicates a proportional (nearly linear) increase of the amount of polymers with increasing the number of layers. The results indicate the LBL buildup from the two block copolymers in the form of micelles.

Fluorescence emissions of Py (λ_{ex} = 340 nm) and NR (λ_{ex} = 550 nm) after the deposition of each layer of micelles were recorded and used to monitor the variation in concentration of the two dyes with increasing the number of layers. Figure 3a shows the emission spectra of Py and NR; for the sake of clarity, only those for the last 8 layers, numbered 11−18, are

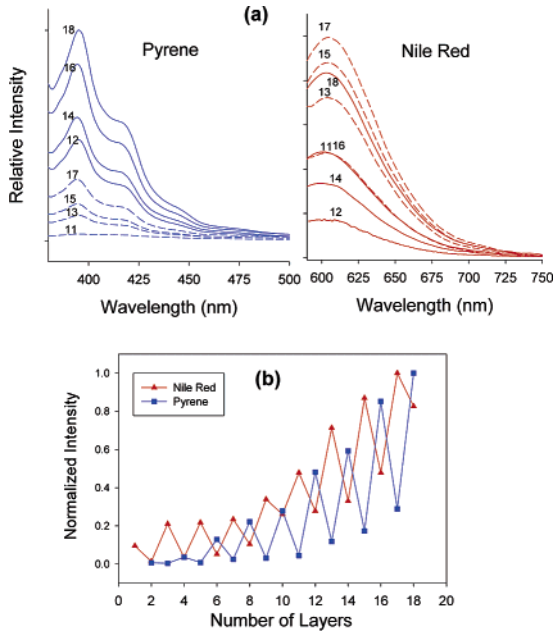

Figure 3. For samples in Figure 2: (a) Changes in fluorescence emission spectra of pyrene (λ_{ex} = 340 nm) and Nile Red (λ_{ex} = 550 nm) as a function of the number of layers, with odd numbers for films with a top layer of PQ4VP-*b*-P*t*BA(NR) (spectra in dashed line) and even numbers for films with a top layer of PAA-*b*-P4VP(Py) (spectra in solid line). (b) Normalized fluorescence intensity of pyrene (396 nm) and Nile Red (610 nm) vs the number of layers.

given. The odd numbers of layers had the micelles of PQ4VP-*b*-P*t*BA(NR) on top (spectra in dashed line), while the even numbers of layers had the micelles of PAA-*b*-P4VP(Py) on top (spectra in solid line). It can be seen that changes in fluorescence emissions of the two dyes exhibit a peculiar pattern. The fluorescence intensity of Py increased after each deposition of an PAA-*b*-P4VP(Py) layer on top of the film (even numbers), but it dropped following the deposition of an PQ4VP-*b*-P*t*BA(NR) layer on top (odd numbers). The same behavior can be noticed for the fluorescence of NR, which increased with the number of layers when the top layer was PQ4VP-*b*-P*t*BA(NR) but decreased when the top layer was PAA-*b*-P4VP(Py). This pattern of change is better depicted in Figure 3b by plotting the fluorescence intensity of NR and Py normalized at 610 and 396 nm, respectively, against the number of layers. The fluorescence emission of both NR and Py displays an oscillating variation with increasing the number of layers. If one looks at the fluorescence of NR after each deposition of PQ4VP-*b*-P*t*BA(NR), it essentially increases proportionally with the number of layers. However, after each deposition of PAA-*b*-P4VP(Py) on top, the fluorescence of NR decreases, before it is recovered again with the subsequent top layer of PQ4VP-*b*-P*t*BA(NR). If one looks at the fluorescence change of Py, the same observation can be made, with the fluorescence of Py oscillating with the number of layers, but in the opposite direction of NR. We have performed a number of experiments under different conditions, including changing the pH of the micellar solutions and the use of a prime layer of PAH on the surface of quartz; similar results were obtained in all cases. Figure 4 shows one more example of the results obtained with the micellar solutions of PQ4VP-*b*-P*t*BA(NR) and PAA-*b*-P4VP(Py), both with pH 9. Figure 4a indicates the LBL assembly of the two types of micelles, but the lower absorbance at 260 nm (inset) as compared to Figure 2 suggests that lowering pH of the micellar solution of PAA-*b*-P4VP, from pH 11 to pH 9, resulted in a decrease in the amount of polymer micelles deposited. This behavior should be related to the pH-sensitive state of ionized PAA corona. Despite the smaller amount of polymers deposited, Figure 4b shows the same pattern of fluorescence change of the two dyes with increasing the number of layers.

Back to Figure 2, the enlarged UV−vis spectra in the region showing the absorption of Py provide a clue to what happens in the LBL buildup process that leads to the change in fluorescence of loaded dyes. Every time when PQ4VP-*b*-P*t*BA(NR) is deposited on top (odd numbers), the absorption bands of Py become very small, which accounts for the reduced fluorescence emission of Py. By contrast, after PAA-*b*-P4VP(Py) is deposited on top (even numbers), the absorption bands of Py become much more prominent and essentially increase with the total number of the layers of PAA-*b*-P4VP(Py) in the film, which explains the recovered fluorescence of Py and its continuous increase with the number of layers (Figure 3). This result implies the following mechanism for the oscillating fluorescence intensity of the two dyes with increasing the number of layers. When the film on substrate is immersed in the micellar solution of PQ4VP-*b*-P*t*BA(NR) for the deposition of a new layer of micelles, most Py molecules entrapped in the film are released into the micellar solution, regardless of the total number of layers. This reequilibrium process occurs not only due to the concentration gradient-induced diffusion of Py,

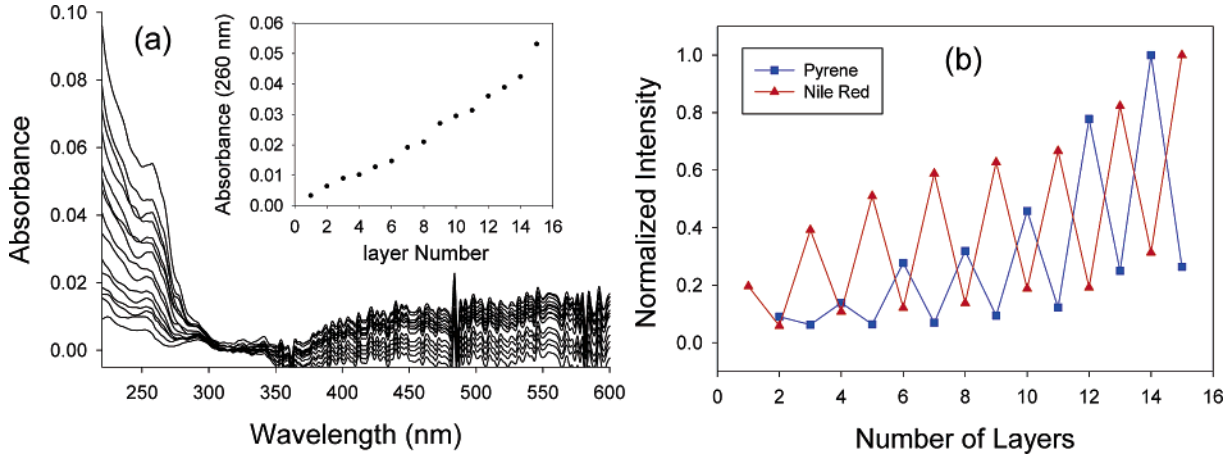

Figure 4. (a) UV−vis spectra of LBL assembled PQ4VP-*b*-P*t*BA(NR) (micellar solution pH = 9) and PAA-*b*-P4VP(Py) (micellar solution pH = 9) up to 15 layers, with the inset showing the plot of absorbance at 260 nm vs number of layers. (b) Normalized fluorescence intensity of pyrene (396 nm) and Nile Red (610 nm) vs the number of layers.

but may be enhanced by the PQ4VP-*b*-P*t*BA micelles present in the solution whose hydrophobic cores tend to solubilize the hydrophobic Py dye. In the same time, NR enters the film, not only through the deposition of the top layer of PQ4VP-*b*-P*t*BA(NR) micelles but also via the opposite equilibrium process, making NR molecules diffuse into the film. This analysis explains why after each deposition of PQ4VP-*b*-P*t*BA(NR) the fluorescence emission of Py from the film drops drastically, while the fluorescence of NR is recovered. The fact that the amount of NR solubilized by the film seems to be proportional to the total number of layers suggests that the diffusion of NR molecules into the film, during the immersion in the micellar solution of PQ4VP-*b*-P*t*BA(NR), was not limited to the surface region. It is easy to imagine that during the subsequent deposition of PAA-*b*-P4VP(Py) micelles, with the film immersed in the micellar solution of PAA-*b*-P4VP(Py), the whole reequilibrium process is reversed, with Py reentering the film and NR coming out. It can be noticed in Figure 3 that the release of NR from the film into the solution is less important than for Py leaching. Under the stated conditions, one possible reason for this behavior is that in the micellar solution of PAA-*b*-P4VP(Py), which is a double-hydrophilic block copolymer,[6,8] the micelle core of P4VP is much more polar than the core of P*t*BA; this difference means that the solubilization propensity of NR by PAA-*b*-P4VP(Py) micelles could be less important than the solubilization of Py by PQ4VP-*b*-P*t*BA(NR) micelles. However, such an effect due to different polarities of the micelle cores apparently becomes much smaller in Figure 4, suggesting that other variables such as the pH value and the amount of micelles deposited on the substrate could also affect the release of the dye into the micellar solution. Basically, the release of a hydrophobic dye from LBL-assembled micelle film immersed in a micellar solution is similar to the release of a hydrophilic dye entrapped in LBL polyelectrolyte film dipped in aqueous solution.[9] We mention that after each deposition the dye removed by the micellar solution from the LBL film gave rise to no noticeable fluorescence from the micellar solution, which is likely due to the dilution of a very small amount of dye released into the large volume of the micellar solution used in this study (10 mL).

Additional loading and release experiments were carried out to further confirm the mechanism. LBL films were first prepared by alternating deposition of the micelles of PQ4VP-*b*-P*t*BA and PAA-*b*-P4VP containing no dyes. The films were then immersed in a dye-encapsulated micellar solution of either PQ4VP-*b*-P*t*BA or PAA-*b*-P4VP, and the absorption of the dye by the LBL film was monitored through UV−vis and fluorescence measurements. Plotted in Figure 5 is the normalized fluorescence intensity of the two dyes (610 nm for NR and 396 nm for Py) in the LBL film vs time of immersion of the film in the dye-containing micellar solution; the results were obtained using a 16-layer film immersed in PQ4VP-*b*-P*t*BA(Py), PQ4VP-*b*-P*t*BA(NR), and their binary mixture (50/50, v/v). In all solutions, at pH 8 the total polymer concentration was kept 0.4 mg mL^{-1}, meaning that in the mixture the concentration of either dye was reduced by a factor of 2 with respect to their corresponding micellar solution. The results show that both hydrophobic dyes solubilized by the micelles in solution can be loaded into the LBL film quickly, and on the basis of the change in normalized fluorescence intensity with time, the rate of loading is similar for Py and NR. For both dyes, their relative amounts in the film equilibrated with the mixture of the two micellar solutions was diminished to about half the amount loaded using the separate micellar solutions, indicating that the concentration of dye in the micellar solution is a determining factor for the amount of dye that can be solubilized by the film.

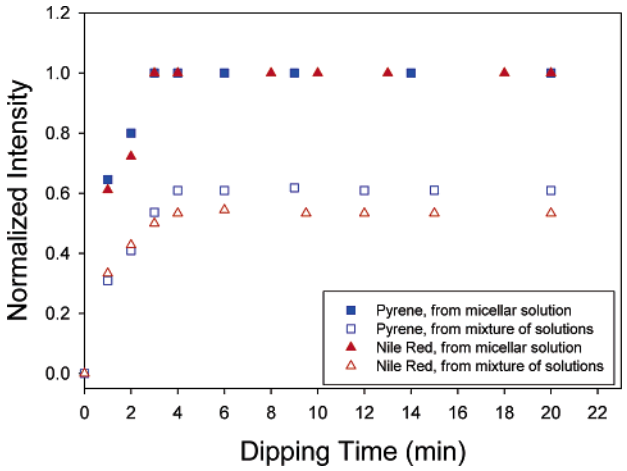

Figure 5. Normalized fluorescence intensity of pyrene (396 nm) and Nile Red (610 nm) vs dipping time for a 16-layer film of two polymer micelles immersed in dye-encapsulated micellar solutions (pH 8) of PQ4VP-*b*-P*t*BA(Py), PQ4VP-*b*-P*t*BA(NR), and their binary mixture (50/50, v/v), showing the uptake of the dyes by the film.

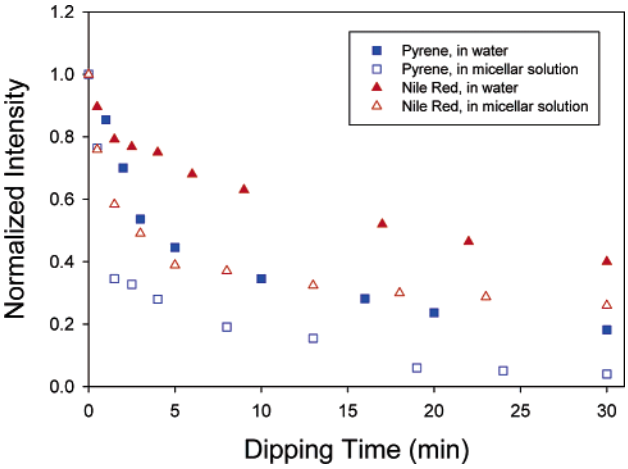

Figure 6. Normalized fluorescence intensity of pyrene (396 nm) and Nile Red (610 nm) vs dipping time for the film with absorbed dyes immersed in water and in the micellar solution of PQ4VP-*b*-P*t*BA at pH 8, showing the release of the two dyes.

The release of the two dyes from the LBL film into aqueous solutions with and without polymer micelles was also investigated. In this experiment, the multilayer film containing both Py and NR was immersed in a micellar solution of PQ4VP-*b*-P*t*BA containing no dyes and, for comparison, also in aqueous solution without any micelles at the same pH of 8. The simultaneous release of both dyes was indicated by the decrease in fluorescence intensity of the film with the time of immersion. The results in Figure 6 show that the release of both dyes is indeed faster in the micellar solution than in the solution without micelles. The solubilization of the hydrophobic dyes by the hydrophobic micelle core enhances the propensity for dye molecules to come out of the film and thus speeds up the release process. In both water and the micellar solution, the release of Py apparently is quicker than NR, which should be related to their differing aqueous solubility, intermolecular interactions with micelles in the film, and loaded amount in the film. On the other hand, as expected, the release rate is also sensitive to pH of the aqueous solution (without micelles). When the dye-loaded LBL film was dipped in solution at pH 3, the release was much faster, being completed within the first 2 min (results

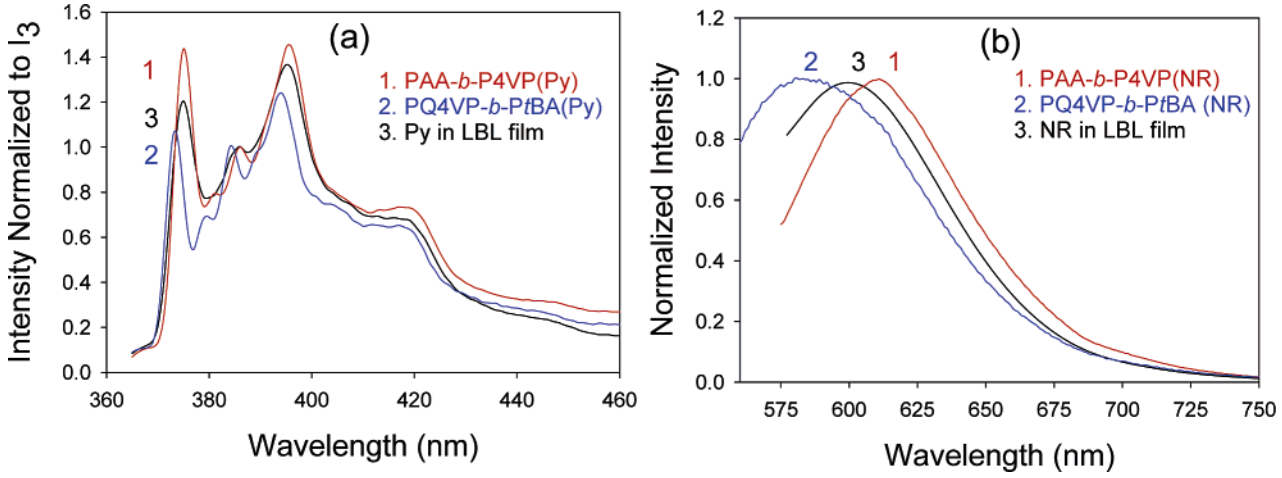

Figure 7. Fluorescence emission spectra of (a) pyrene and (b) Nile Red for films cast from dye-encapsulated micellar solutions and for the LBL assembled film with the two dyes absorbed from solutions as shown in Figure 5.

not shown). At pH 3, PAA-*b*-P4VP can no longer form micelles with polyanion corona because of the removal of negative charges from PAA, while the protonated P4VP core becomes hydrophilic and can no longer sequester the hydrophobic dyes. These changes should destabilize the LBL film and accelerate the release of the dyes into the solution.

The above results show that two different polymer micelles with polycation and polyanion coronas can be directly assembled through the LBL technique. However, spatially organizing two hydrophobic dyes inside the multilayer films through their preencapsulation in the micelles will be challenging. Despite the apparently proportional increase of the amount of dye with the number of layers, each dye actually undergoes an alternating process of release from and reuptake by the film during the LBL buildup. The consequence of this is that in the end the two dyes are not confined in their respective micelles but should be dispersed throughout the film, like in the case of direct loading of dyes by the LBL film (Figure 5). Since the two dyes used are hydrophobic in nature, it would be expected that they would tend to be solubilized more in the hydrophobic core regions than in the polyelectrolyte corona areas in the LBL film of micelles. We performed spectroscopic measurements to get some insight into the location of the dyes inside the multilayer films. Figure 7 compares the fluorescence emission spectra of the two dyes absorbed by the multilayer film (Figure 5) with the spectra recorded on thin films prepared by casting the solution of micelles with one loaded dye. In the latter case, dye molecules were essentially confined in the core region. For Py (Figure 7a), the peak ratio of I_1/I_3 is smaller for PQ4VP-*b*-P*t*BA(Py) than PAA-*b*-P4VP(Py), indicating that the P*t*BA micelle core is more hydrophobic than the micelle core of P4VP.[10] This difference is also revealed by the spectra of NR (Figure 7b), which displays a blue shift of the maximum emission wavelength in PQ4VP-*b*-P*t*BA(NR).[11] The intermediate I_1/I_3 value for Py and emission maximum for NR in the multilayer film indicate that dye molecules were located in an environment that, on average, was more hydrophobic than P4VP but less hydrophobic than P*t*BA, basically implying that they were solubilized by the two types of micelle cores with no significant preference for the more hydrophobic core region of P*t*BA. Similar fluorescence emission spectra were obtained with LBL films prepared using the two micelles with preencapsulated Py and NY (spectra not shown for the sake of clarity), confirming that dye molecules were uniformly distributed within the layers of the two micelles during the buildup procedure.

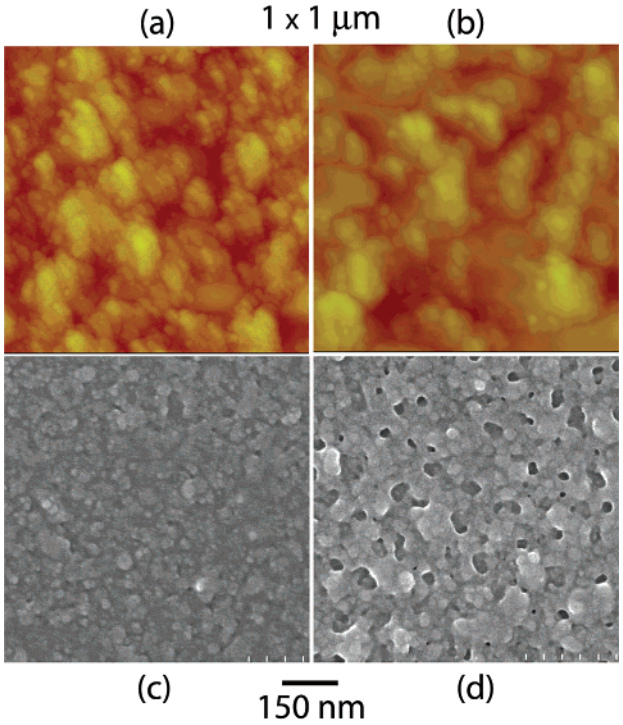

Figure 8. AFM and SEM images of LBL assembled films with either a top layer of PQ4VP-*b*-P*t*BA (odd numbers) or a top layer of PAA-*b*-P4VP (even numbers): (a) 12 layers, (b) 13 layers, (c) 17 layers, and (d) 18 layers.

Finally, we mention that the surface morphology of the multilayer films was observed using AFM and SEM. Figure 8 shows some representative images obtained after the deposition of the top layer of either PQ4VP-*b*-P*t*BA (odd numbers) or PAA-*b*-P4VP (even numbers). The two types of micelles on the surface are visible, the sizes of which are similar to the micelles observed on SEM by direct casting of the micellar solutions on a silicon wafer. AFM images show an average surface roughness of about 35 nm for the 12-layer film and 41 nm for the 13-layer film. After scratching the film in some areas, AFM was used to measure the thickness of the multilayer films, resulting in an estimation of about 20−30 nm per layer of micelles. Even though further studies are required to characterize the bulk structure or morphology of the polymer micelles in the multilayer film, the results unambiguously show the introduction of hydrophobic P*t*BA and less polar P4VP (compared to ionized PAA) domains in form of micelle cores in the

thin films through the LBL buildup. These domains are responsible for the efficient uptake of the hydrophobic dyes.

Concluding Remarks

We present a study of LBL assembly of two different polymer micelles with polycation and polyanion coronas. Compared to LBL assembly involving one polymer micelle or vesicle with one molecularly dissolved polyelectrolyte,[4] we believe our approach may offer a more robust and versatile way to incorporate and organize different hydrophobic species into thin films of layered structures, which may expand the power of LBL assembly in designing nanomaterials with more complex structures and functionalities. Despite the finding in this study that layering of two hydrophobic dyes cannot be achieved through their physical encapsulation by the micelles prior to LBL assembly, it can easily be envisioned that covalently attaching the two dyes onto the hydrophobic blocks of the polymers, which will not compromise the use of the LBL technique, would allow their ordering and layering in the multilayer films. Given the large body of knowledge on polymer micelles, other means can also be envisaged. For instance, using ABC-type triblock copolymer micelles, for which A block form the polyelectrolyte corona, B block offers a cross-linked shell, and C block form the hydrophobic core, preencapsulated hydrophobic guests can be organized into a layered and ordered structures in LBL-assembled films. This would be possible because the cross-linked shell could improve the stability of encapsulation[12] to prevent the diffusion in and out of guest molecules during the film buildup process. Perhaps more importantly, the demonstrated assembly of different polymer micelles represents a general strategy to bring and organize hydrophobic functional polymers into nanostructured thin films using the LBL technique, which otherwise is not possible. Work is underway in our lab, and the results will be reported in due course.

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