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Photo-Cross-Linkable Polymer Micelles in Hydrogen-Bonding-Built Layer-by-Layer Films

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Photoactive micelles of a diblock copolymer composed of poly(ethylene oxide) and poly(7-(2-methacryloyloxyethoxy)-4-methylcoumarin) (PEO-*b*-PCMA) were layer-by-layer assembled with poly(acrylic acid) (PAA) using hydrogen-bonding between the PEO corona of the micelles and the PAA chains (pH < 3). In addition to characterizing the assembly process using a number of techniques, the tunable photo-cross-linking of polymer micelles through dimerization of the coumarin groups was used to generate interesting functions for the multilayer film. On the one hand, the easy tuning of the photo-cross-linking density could be used to control the release rate of hydrophobic guest molecules loaded in the film. On the other hand, after chemical cross-linking of PAA to stabilize the film, the photo-cross-linking of the micelles could be used to restrict the dissolution of PEO-*b*-PCMA chains in a good organic solvent; this cross-linking-dependent extraction of polymer micelles was utilized to vary the porosity of the film.

1. Introduction

A new direction in utilizing the versatile layer-by-layer (LBL) technique to build up nanostructured thin films is the exploitation of amphiphilic block copolymer micelles.[1−13] In aqueous solution, these micelles generally comprise a water-soluble polyelectrolyte corona of the hydrophilic block and an aggregated compact core of the hydrophobic block. The charged corona allows for the deposition of nanometer-sized polymer micelles in a LBL fashion. This new development is of interest for two reasons. First, it extends the inventory of polymers suitable for LBL assembly to block copolymers that are a field of excitement due to the large variety of nanostructures they can self-organize. Second, it provides a general way to introduce and organize hydrophobic polymers in multilayer films, which otherwise is undoable. The presence of a hydrophobic polymer can bring new functionalities into the film and enhance its capacity of encapsulating hydrophobic compounds, thus offering many new possibilities for the design of LBL-based nanomaterials. Two methods have been shown to be effective in assembling polymer micelles into a multilayer film. The first one is to alternately deposit a micelle having a charged corona and a molecularly dissolved polyelectrolyte of opposite charge.[1,2,7,8,12,13] In this way, the polyelectrolyte layer acts as a glue to bind with the micelles. The second method, reported by our group and others,[3−6,9−11] consists of alternate deposition of two different polymer micelles with a polycation and a polyanion corona, respectively, without the use of dissolved polyelectrolytes. In either way, electrostatic interactions are usually brought into play. However, H-bonding interactions are known to be also effective in assembling LBL films.[14−16] As a natural extension, recently it has been used for LBL assembly involving a polymer micelle.[8]

In this paper, we present a study of using H-bonding to LBL assemble poly(acrylic acid) (PAA) and micelles of a photoactive amphiphilic diblock copolymer, namely, poly(ethylene oxide)-*b*-poly(7-(2-methacryloyloxyethoxy)-4-methylcoumarin) (PEO-*b*-PCMA). It is known that, at pH < 3, PAA forms H-bonds with PEO between the nonionized COOH groups of the former and the ether groups of the latter.[16,17] Therefore, LBL assembly is possible via H-bonds between molecularly dissolved PAA chains and the PEO corona of PEO-*b*-PCMA micelles. As part of our ongoing effort on exploring coumarin-based photoactive polymers,[18−21] the primary purpose of this work is to investigate the possible new functions that can be imparted to the LBL film by introducing coumarin-containing polymer micelles. PCMA features a reversible photo-cross-linking through photodimerization of coumarin side groups upon exposure to $\lambda > 310$ nm UV light and photocleavage of cyclobutane rings under $\lambda < 260$ nm.[22] In addition to characterizations of the assembly process and the micelle-embedded LBL films, we investigated the use of photo-cross-linking to change the film porosity and to control the release of guest

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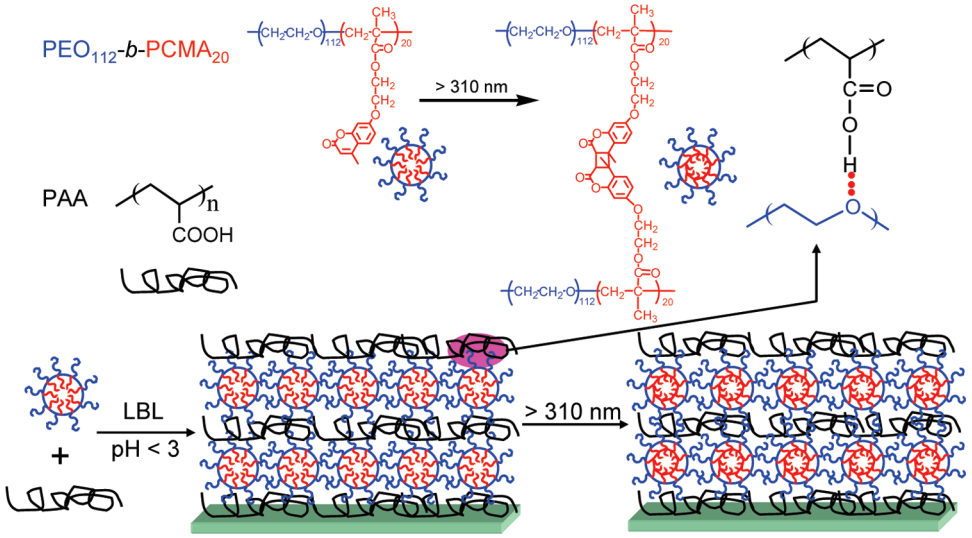

Figure 1. Schematic illustration of the LBL assembly of PEO-*b*-PCMA micelles and PAA through H-bonding, as well as the polymer chemical structures and the photo-cross-linking reaction of coumarin side groups.

molecules loaded in the films. Figure 1 is an illustration of the LBL assembled film of PEO-*b*-PCMA micelles through H-bonding with PAA (with only two layers of micelles shown) and the controllable photo-cross-linking reaction of the domains of PCMA in the film, together with the chemical structures of the used polymers. The results we report herein show that the insertion of photocontrollable polymer micelles could offer new possibilities of tuning the properties of the LBL films.

2. Experimental Section

2.1. Preparation of Micelles. The details on the synthesis and characterization of PEO-*b*-PCMA were already reported[18] and will not be repeated here. The sample used in this study was PEO_{112}-*b*-$PCMA_{20}$. Since it could not be directly dissolved in water to form micelles, the following procedure was utilized to prepare the micellar aqueous solution required for LBL assembly with PAA. A total of 4 mg of the block copolymer was first dissolved in 10 mL of dimethyl sulfoxide (DMSO; a good solvent for both polymers) under stirring and subjected to ultrasonic dispersion. Then, to induce the formation of micelles, distilled water was added slowly (20 μL every 30 s) to reach 50% (v/v) DMSO, under stirring. Afterward, the micellar solution was dialyzed against distilled water (dialysis bag, Spectro/Pro; cutoff molecular weight, 3500) to remove DMSO. The aqueous micellar solution was then filtered through a 0.45 μm filter, and the pH adjusted to below 3 using 1 M HCl. Under these conditions, a stable dispersion of micelles in water, having a PEO corona and PCMA core, could be obtained.

2.2. Preparation of LBL Films. LBL films were fabricated manually using a block copolymer (BCP) micellar solution and a PAA solution. For the latter, the sample (from Aldrich, M_w = 450 000 g mol^{-1}) was dissolved in a water at a concentration of 2 mg mL^{-1}. Typically, to build up a LBL film, a cleaned quartz plate (treated in H_2SO_4/H_2O_2 3:1 mixture 1 h) was first dipped in the PAA solution for 15 min, followed by rinsing with water and drying with nitrogen flow at room temperature (the first layer of PAA can be deposited on the quartz plate through H-bonding with the hydroxyl groups on the treated quartz surface). The substrate was then dipped in the micellar solution for 15 min, rinsed, and dried. This led to the deposition of a bilayer of PAA/micelle (PEO-*b*-PCMA) on both sides of the substrate. The cycle of alternating deposition was repeated to obtain the desired number of bilayers. The number of bilayers (both in the text and the figures) refers to the number on one side of the substrate. All solutions (PAA, micelles, and rinsing water) were kept at pH = 2.5 in order to minimize the ionization of acid groups on PAA (pK_a = 4.5).[23] For all solutions, pH was adjusted using 1 M HCl and measured by using a pH meter (Orion 410Aplus).

2.3. Photo-Cross-Linking of Dye-Loaded LBL Films and Release Test. Nile Red (NR)-loaded films were cross-linked by using a UV−vis spot curing system (Expo Lite) combined with a 320−480 nm filter. Films were placed under the UV lamp, and the UV intensity was set at 30 mW/cm^2 (365 nm). The photo-cross-linking degree could be adjusted by changing the irradiation time and followed by the decrease of the coumarin absorption peak at 324 nm. For the release test, the NR-loaded film on quartz was immersed in a standard UV cell filled with acetone, and the amount of NR released into the solution, as a function of the cumulative time, was monitored by measuring the fluorescence emission of the chromophore at 610 nm (excitation at 550 nm) (the LBL film was set at the bottom of the solution and did not interfere with the excitation beam).

2.4. Chemical Cross-linking of LBL Films. H-bonded LBL films can be stabilized by chemical cross-linking. With PAA, this can be achieved by reacting diamine molecules with the carboxylic acid groups.[24,25] In this work, to cross-link a LBL film of PAA/PEO-*b*-PCMA micelles, the following conditions were utilized. The film on quartz was dipped in a solution prepared by dissolving 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) hydrochloride (450 mg) and 2-morpholinoethane sulfonic acid (MES) (145 mg) in 15 mL of distilled water; after 10 min, 20 μL 2,2′-ethylenedioxybisethylamine was added. The reaction lasted 4 h at room temperature before the film was taken out of the solution, washed with distilled water, and dried by nitrogen flow. During the reaction, the solution pH was kept at 3. To test the stability of cross-linked films in aqueous solution at pH = 10 and in DMSO, the film was dipped in the solution for the desired time and then taken out of the solution, rinsed with water, and dried by nitrogen stream before the UV−vis measurements. To obtain a diamine-cross-linked film with embedded photo-cross-linked PEO-*b*-PCMA micelles, the cross-linked film was exposed to UV light (100 mW/cm^2 at 365 nm) to have a dimerization degree of 45% for coumarin groups.

2.5. Characterizations. LBL films of PAA/ PEO-*b*-PCMA micelles were characterized by means of a number of techniques.

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UV−vis spectra were taken using a Varian 50 Bio spectrophotometer, while steady-state fluorescence emission spectra were recorded on a Varian spectrometer (Cary Eclipse) with an excitation wavelength at 550 nm. 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. Quartz crystal microbalance (QCM) measurements were carried out using a Resonant Probes GmbH system (Goslar, Germany). The gold-coated quartz resonators were placed on a Teflon holder (Maxtek Inc., Cypress, CA), while data from the network analyzer (Agilent, Palo Alto, CA, HP4396A) were analyzed by the software from Resonant Probes. The resonator was cleaned in H_2SO_4/H_2O_2 (3:1, v/v) for 15 min and then rinsed by distilled water and dried. In this experiment, after the assembly of the first 20 layers, the film was put into the sample holder to obtain the frequency change upon the deposition of every bilayer, that is, the in situ measurement started from the 21st layer. With the resonator in the sample holder, the PAA solution (15 min), distilled water (5 min), and micelle solution (15 min) were alternately injected for the LBL process. All measurements were performed at three harmonics (15, 25, and 35 MHz corresponding to the overtones $n = 3, 5,$ and 7, respectively; the fundamental frequency of the crystal is 5 MHz). As the same results were obtained, only the data with 15 MHz are given in this paper.

3. Results and Discussion

3.1. LBL Assembly and Characterizations. The alternate deposition of PAA and PEO-*b*-PCMA micelles into LBL film can be monitored using the absorbance of coumarin moieties centered at 324 nm where PAA has no absorption. Figure 2 presents the results obtained using the copolymer micelles dispersed in aqueous solution right after dialysis against water and without further filtration, with the pH of all solutions being kept at ~2.5. The spectral changes upon deposition of 20 layers, with PAA as the first layer on a quartz plate and the micelles on the top layer (10 bilayers), indicate the assembly in a LBL fashion. The inset shows the plot of the absorbance of coumarin at 324 nm as a function of the number of layers, with odd numbers for PAA and even numbers for polymer micelles (the number zero is for the quartz plate). The amount of deposited polymer micelles increased linearly with increasing number of layers of PEO-*b*-PCMA, while after each deposition of a PAA layer on top the absorbance at 324 nm remained unchanged within experimental error, as it should be. These results clearly indicate that the film grew in a LBL controlled manner through the action of H-bonding between PAA and the micelle corona of PEO.

We also investigated the LBL assembly by varying experimental variables. Since PCMA features the reversible photo-cross-linking through dimerization of coumarin moieties,[18−22] prior to LBL assembly, copolymer micelles can be core-cross-linked to have the structural integrity while retaining the corona of PEO for H-bonding with PAA. Figure 3 shows an example of the results. The same experimental procedure was utilized as for Figure 2 except that the micellar solution was exposed to UV light at $\lambda >$ 320 nm to partially cross-link the micelles and then subjected to microfiltration to remove large aggregates. Estimated from the decrease in absorbance at 324 nm, the dimerization degree was about 45%. The reason for a partial cross-linking was to have the absorption peak of coumarin at 324 nm remain observable for the monitoring of LBL buildup. From the results in Figure 3, the same conclusion on the effectiveness of using H-bonding to LBL assemble polymer micelles can be reached. The amount of deposited cross-linked micelles increased linearly with the number of layers. Two notes need to be made. First, in Figure 3, the final film also contained 20 layers, with the top layer being PEO-*b*-PCMA micelles. Second, the smaller absorbance at 324 nm than that of the film in Figure 2 was due to the partial dimerization of coumarin moieties, rather than indicative of a smaller amount of cross-linked micelles deposited on the substrate.

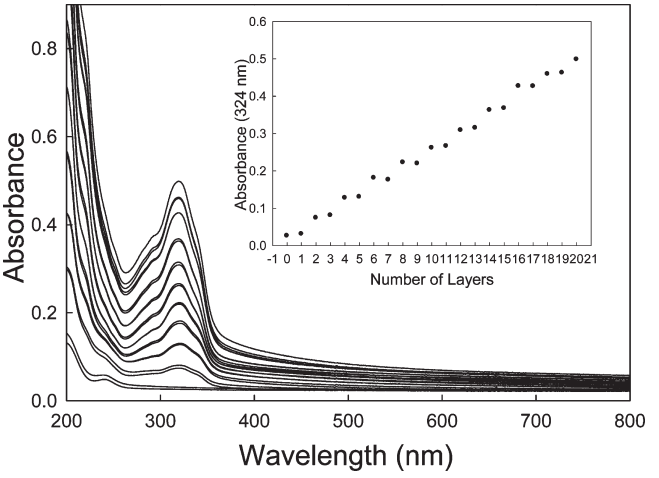

Figure 2. UV−vis spectra of LBL assembled PAA and PEO-*b*-PCMA micelle up to 10 bilayers. The inset shows the plot of absorbance of coumarin groups at 324 nm versus number of layers (odd numbers for PAA layers, even numbers for micelle layers, and number zero for the quartz plate), showing a stepwise increase because PAA contains no coumarin groups.

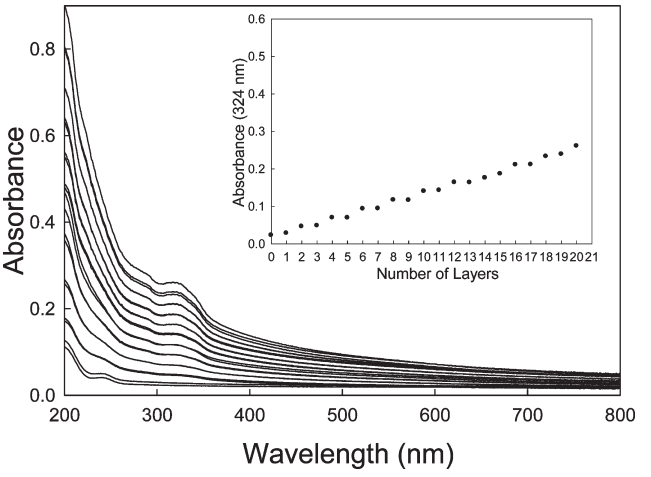

Figure 3. UV−vis spectra of LBL assembled PAA and photo-cross-linked PEO-*b*-PCMA micelle up to 10 bilayers. The inset shows the plot of absorbance of coumarin groups at 324 nm versus number of layers (odd numbers for PAA layers, even numbers for micelle layers, and number zero for the quartz plate).

QCM measurements were conducted to get more insight into the LBL assembly process involving a BCP micelle. As is known,[26,27] the QCM frequency decrease ($-\Delta F$) is proportional to an increase in mass on the QCM resonator surface. In our system, the mass increase of each deposited bilayer, Δm, is related to the frequency shift through $\Delta m = -C\Delta F/n$, where n is the overtone and C is the mass sensitive constant ($C = 17.7$ ng cm^{-2} Hz^{-1}). As mentioned above (Experimental Section), each of the first 10 bilayers was prepared using the normal process prior to the QCM measurement in the dry state. Figure 4 shows the frequency decrease with increasing the number of bilayers.

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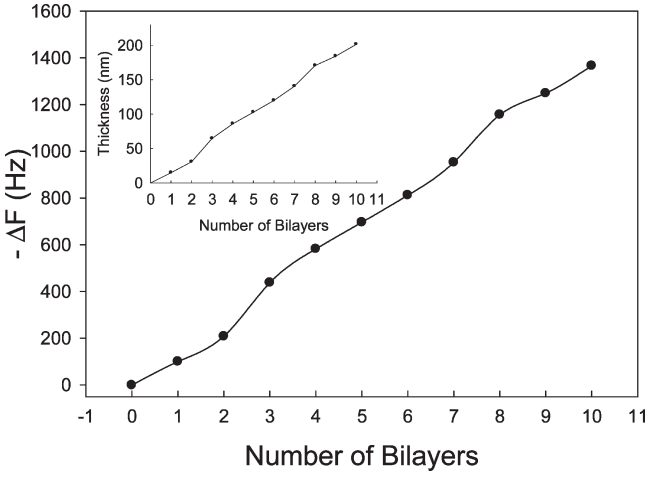

Figure 4. QCM frequency shift as a function of the number of deposited bilayers of PAA/PEO-*b*-PCMA micelle. The inset shows the increase in the estimated thickness with increasing the number of bilayers.

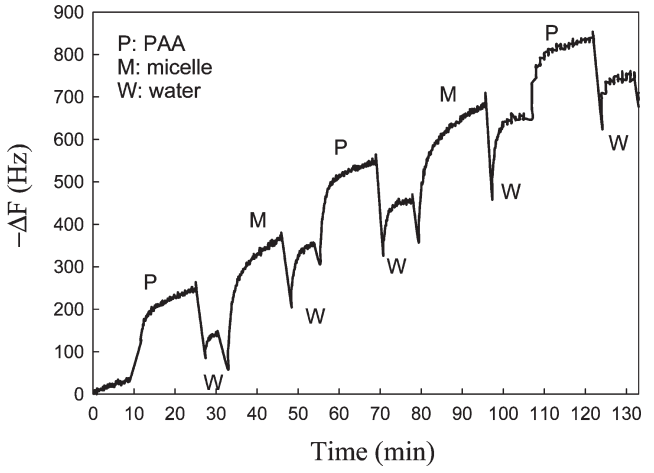

Figure 5. In situ QCM frequency shift upon repeating cycles of deposition of PAA solution, rinsing with water and deposition of micellar solution.

Assuming a density of 1.2 g cm^{-3} for polymers,[28,29] the thickness increase of the LBL film could be calculated, and the result is shown in the inset. Each bilayer has a thickness of about 20 nm. This value is much smaller than the size of micelles observed on surface (see Figure 6), suggesting that the micelles were compressed in the LBL film.[3,9]

Then, from the 21st layer to the 25th layer, real-time monitoring of the formation of the PAA/PEO-*b*-PCMA micelle multilayers was attempted. For these measurements, the QCM resonator was retained in the holder; the PAA solution, distilled water, and the micellar solution were alternately introduced from a circulation tube for 15, 5, and 15 min, respectively. From the frequency changes, two observations can be made. First, the deposition of PAA and micelles did not reach the equilibrium after 15 min (it actually took about 2 h to get a constant frequency). Second, when rinsing water was injected, the quick increase in frequency indicates the instant removal of most matter (PAA or micelles) deposited during the last cycle, and the subsequent decrease in the frequency suggests that part of the removed matter stayed in the rinsing water and some was redeposited. Under the used conditions, the apparent frequency decrease is about 200 Hz after deposition of a micelle layer, compared to about 100 Hz after deposition of a PAA layer. However, due to the kinetic nature of the deposition and rinsing processes as mentioned above, and considering the fact that different amounts of water molecules could be retained with PAA and the micelles, these values could not be used to estimate the amounts of deposited PAA and micelles during each cycle. Nevertheless, the real-time monitoring shows the successive deposition of PAA and the micelles.

The surface morphology of the film in Figure 2 was examined by using an SEM and AFM. As can be seen from Figure 6, PEO-*b*-PCMA micelles remain distinguishable on the surface and, considering the condensation and coalescence that could occur during the LBL assembly process, their sizes are quite consistent with those in aqueous solution (~120 nm from dynamic light scattering measurements). The height profile of the AFM image shows that such LBL films have a highly rough surface. Similar results were obtained with LBL films containing cross-linked polymer micelles.

3.2. Effect of Micelle Photo-Cross-Linking on the Release of Loaded Guest Molecules. After confirming the feasibility of using H-bonds between PAA and PEO to LBL assemble PEO-*b*-PCMA micelles, we investigated the possibilities of using the photoactivity of the micelles to enable new functions. One interesting feature of having polymer micelles in the LBL films is to encapsulate hydrophobic guest molecules by the micelles (undoable with polyelectrolyte films) and then to release them in solution. On the one hand, with a LBL film built up through H-bonding involving nonionized carboxylic acid groups, the release of loaded molecules can be achieved in aqueous solution by increasing the pH to ionize the acid groups that destabilizes the film.[8] On the other hand, if the hydrophobic micelle core can be cross-linked, the cross-linking degree should affect the release of loaded guest molecules by controlling their diffusion rate through polymer chains. With our PEO-*b*-PCMA micelles, the easily tunable photodimerization reaction of coumarin groups provides an easy way to tune the cross-linking degree of the micelles.

We performed the following experiment. Nile Red (NR), a hydrophobic dye, was loaded in PEO-*b*-PCMA micelles using a previously reported procedure,[18] and three LBL films of PAA/PEO-*b*-PCMA micelle were prepared using the same PAA and micellar solutions and under the same conditions (10 bilayers). Two of the NR-loaded films were then exposed to UV light (>320 nm) to obtain a dimerization degree of 5% and 10% respectively, while the other one remained uncross-linked. The UV−vis spectra of the three films are shown in Figure 7a. Before discussing the release experiment, two points should be emphasized. First, with the used rather low UV intensity (30 mW/cm^2) and the short irradiation times (20 and 40 s respectively), the possible photodegradation effect on the loaded NR molecules, which absorb little photons of $\lambda > 320$ nm, was minimized (little change in the fluorescence emission of NR in the films after the UV exposure). This ensured an appropriate comparison of the release of NR from the three films immersed in solution. Second, the apparent photodimerization degree is an average value for all coumarin groups, while in reality the top layer of micelles could be more severely cross-linked than the layers close to the bottom (substrate surface) because coumarin groups on top can be more easily excited.[20] In other words, there may be a gradient of the cross-linking density along the thickness direction. The release experiment was carried out by dipping the NR-loaded LBL films in acetone, in which the films are stable

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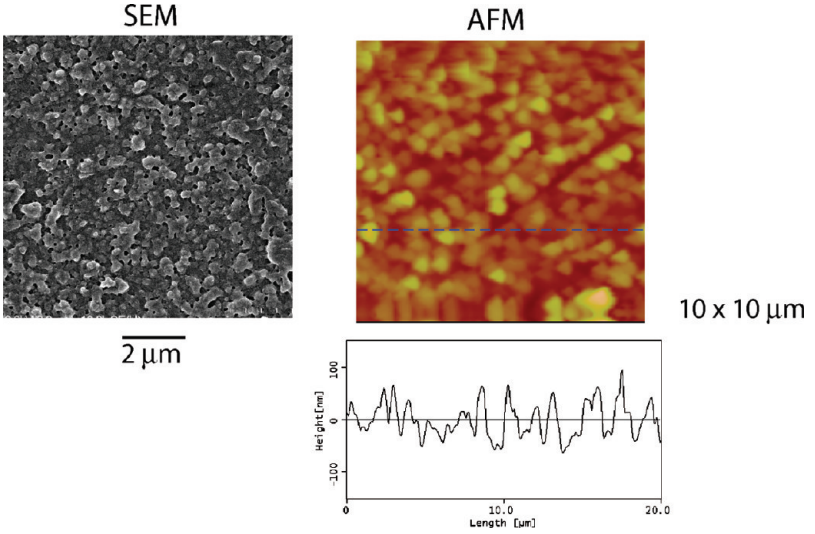

Figure 6. (a) SEM image and (b) AFM image of a 10-bilayer LBL film of PAA and PEO-*b*-PCMA micelles. The height profile corresponds to the marked line.

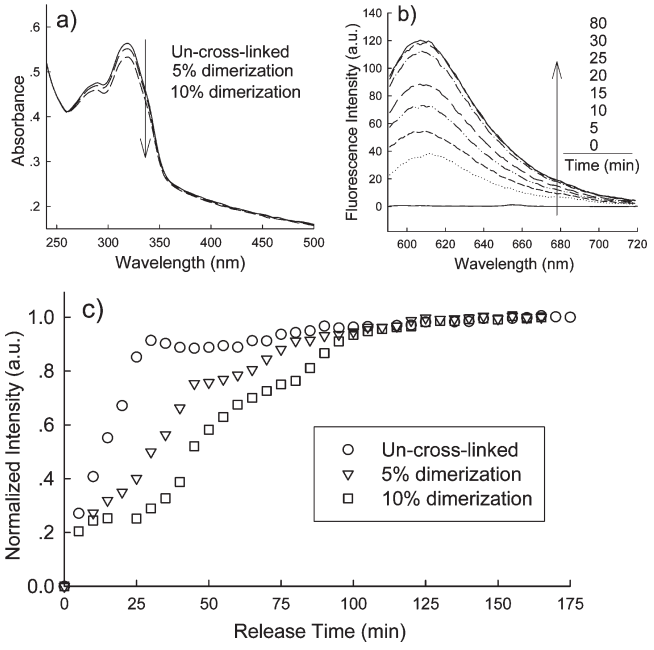

Figure 7. (a) UV−vis spectra of NR-loaded 10-bilayer films with different photo-cross-linking densities for PEO-*b*-PCMA micelles. (b) Fluorescence emission spectra of NR (λ_{ex} = 550 nm) recorded with the film containing uncross-linked micelles immersed in acetone for different times. (c) Plots of normalized fluorescence intensity versus time for the films with different photo-cross-linking densities of the micelles.

while NR can easily be dissolved; and the amount of NR diffused into the solution was monitored by measuring the fluorescence emission of NR (λ_{ex} = 550 nm) as a function of time. Using the uncross-linked film as an example, Figure 7b shows a series of variable time emission spectra (the spectrum labeled 0 min is that of the solvent before immersion of the film). Figure 7c gives the plots of normalized fluorescence emission intensity versus time for the three films. It is clear that the release rate of NR is sensitive to the cross-linking density of the PEO-*b*-PCMA micelles. The release of NR was increasingly slowed down with increasing cross-linking density. Therefore, without destroying the LBL film, in contrast to the pH effect, the photocontrollable cross-linking of the polymer micelles offers a means to control the release of loaded guest molecules. Finally, we note that since the photo-cross-linking of coumarin groups is reversible,[18−21] the photocleavage of cyclobutane rings upon UV irradiation (λ < 260 nm) could be used to reduce the number of cross-links, enhancing the flexibility in tuning the cross-linking density. However, in the present work, we were unable to show the benefit of the reversibility for the controlled release of NR due to the photodegradation of NR molecules that becomes serious upon absorption of short wavelength UV photons. In principle, the reversible control of cross-linking density could be explored by using systems where the photodegradation of loaded molecules is not a problem, or using the two-photon absorption of visible light of coumarin to achieve the reversible photoreaction.[22]

3.3. Nanoporous Films Prepared Using Chemical and Photo-Cross-Linking. In the case of LBL films of PAA and PEO assembled with H-bonding, it has been reported that the cross-linking of PAA chains by reacting with a diamine could make the film stable in alkaline solution.[24,30] Therefore, with our films of PAA/PEO-*b*-PCMA micelles, it is possible either to chemically cross-link PAA chains or to photo-cross-link PEO-*b*-PCMA micelles, or to do both. Using an 8-bilayer film, we investigated the effect of cross-linking on the film stability both in aqueous solution at basic pH = 10 and in dimethyl sulfoxide (DMSO). In these tests, unless otherwise stated, the film on quartz was immersed in a solution for 1 h before being taken out of the solution, dried and used for the UV−vis measurement. The state of the film remaining on the substrate could be readily assessed from the absorption of coumarin groups. The results are summarized in Figure 8. For the uncross-linked film (Figure 8a), the film was almost totally dissolved in alkaline solution but showed some resistance to DMSO, since about half of the coumarin absorption could still be seen. For the film with uncross-linked PAA chains but photo-cross-linked PEO-*b*-PCMA micelles (dimerization of coumarin ~45%) (Figure 8b), it was again completely disintegrated in alkaline solution, indicating that although cross-linked micelles are not molecularly dissoluble in the solution, they cannot stay due to the destruction of H-bonds between PAA and PEO chains. By contrast, in DMSO, the film became stable, indicating

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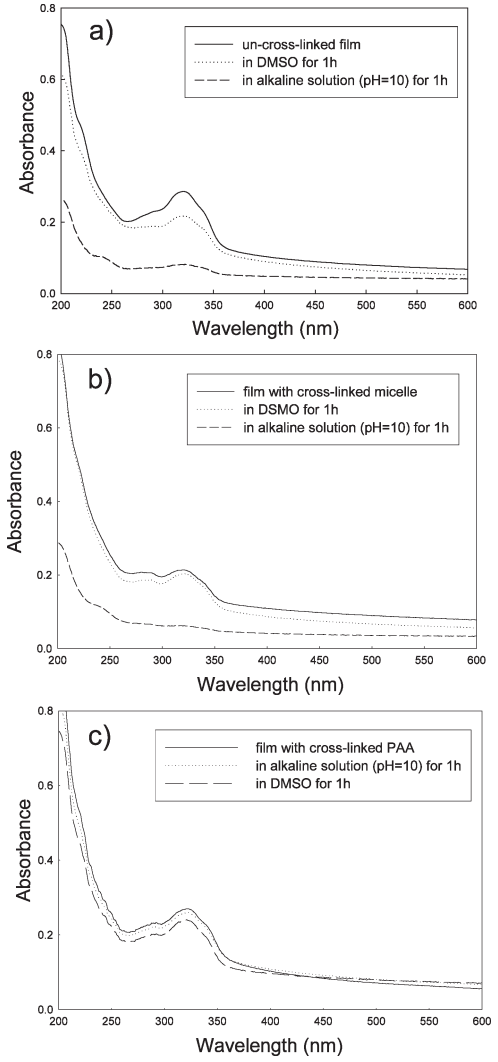

Figure 8. UV−vis spectral changes for (a) a 8-bilayer film with uncross-linked PAA and uncross-linked micelles, (b) an 8-bilayer film with uncross-linked PAA but cross-linked micelles, and (c) an 8-bilayer film with cross-linked PAA but uncross-linked micelles, after 1 h immersion in DMSO or in an alkaline solution (pH = 10).

that this organic solvent could not destroy the H-bonds and the cross-linking of the micelles prevent the dissolution of PEO-*b*-PCMA chains. In the case of the film with chemically cross-linked PAA chains and uncross-linked micelles (Figure 8c), the film was stable in alkaline solution and quite stable in DMSO as well. In DMSO, however, a substantial amount of PEO-*b*-PCMA chains could be dissolved at longer times such as 2 h (spectrum not shown). This result implies that, despite the presence of large polymer micelles in the film, PAA chains on different layers could still interact with themselves through diffusion across the micelle layers, and that the reaction with diamine molecules could still give rise to cross-linked PAA that stabilizes the whole film in alkaline solution. Of course, the hydrophobic nature of PCMA chains helps the stability in aqueous solution. The unchanged spectrum after 1 h in the alkaline solution shows the absence of hydrolysis of the coumarin groups that are confined inside the hydrophobic micelle cores in the LBL film. These results indicate that the chemical cross-linking of PAA chains is key to the stability of the film in alkaline solution, while the resistance to DMSO, which is a good solvent for PEO-*b*-PCMA, could be enhanced by photo-cross-linking of the micelles.

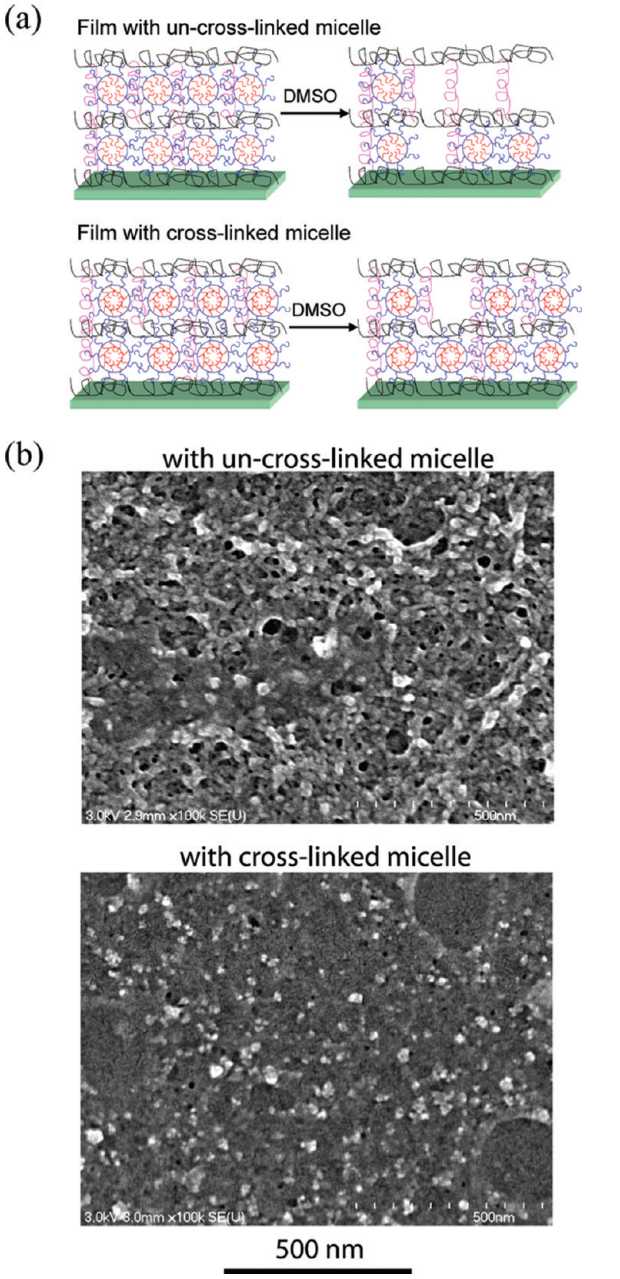

Figure 9. (a) Schematic illustration of micelle-cross-linking-dependent removal of PEO-*b*-PCMA in DMSO for a LBL film with cross-linked PAA. (b) SEM images for an 8-bilayer film with uncross-linked micelles and a 8-bilayer film with cross-linked micelles after a 2 h treatment in DMSO, showing different surface morphologies.

On the basis of the above observations, we investigated the possibility of using the solubility difference between photo-cross-linked and uncross-linked PEO-*b*-PCMA micelles to generate LBL films with a varying degree of porosity. The concept is schematically illustrated in Figure 9a. In a good solvent for PEO-*b*-PCMA, while chemically cross-linked PAA ensures the integrity of the film, uncross-linked polymer micelles could be more easily dissociated and removed from the LBL film, which creates more pores, than photo-cross-linked micelles. Qualitatively, this was confirmed by experiments using the same starting diamine-cross-linked 8-bilayer films of PAA/PEO-*b*-PCMA micelles. For one film, micelles were photo-cross-linked (dimerization of coumarin ~45%), while another film contained uncross-linked

micelles. Figure 9b shows SEM images of the two films treated in DMSO for 2 h. Much larger pores can be observed for the film with uncross-linked micelles, while the pore sizes appear smaller for the film treated with photo-cross-linked micelles. Therefore, in principle, photocontrollable cross-linking degree of polymer micelles could be explored to control the porosity by removing the micelles from LBL assembled films. More studies are needed to optimize the design and quantitatively control the porosity using photoactive polymer micelles.

4. Conclusions

We showed that photo-cross-linkable PEO-*b*-PCMA micelles can be LBL assembled with PAA (at pH < 3) into multilayer films through H-bonding between PEO corona of micelle and PAA chains. The controllable photo-cross-linking of the micelle-core-forming PCMA chains through dimerization of coumarin groups imparted interesting functions to the multilayer films. On the one hand, the easy tuning of the micelle cross-linking degree could be used to control the release rate of loaded hydrophobic guest molecules by affecting their diffusion through the polymer film. On the other hand, after chemically cross-linking PAA chains that stabilized the LBL film, the dissolution of polymer micelles in a good organic solvent could be affected by their photo-cross-linking, which could be used to prepare films with different nanoporosities.

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