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Rational Design of Light-Controllable Polymer Micelles

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ABSTRACT: Amphiphilic block copolymer (BCP) micelles are nanocarriers that hold promise for controlled delivery applications. This account highlights our recent works on light-dissociable BCP micelles. We have designed and developed light-responsive amphiphilic BCPs whose micellar aggregates (core-shell micelles and vesicles) can be disrupted by light exposure. The basic strategy is to incorporate a chromophore into the structure of the hydrophobic block, whose photoreaction can result in a conformational or structural change that shifts the hydrophilic/hydrophobic balance toward the destabilization of the micelles. Using various chromophores including azobenzene, pyrene and nitrobenzene, we have achieved both reversible and irreversible dissociation of BCP micelles upon illumination with UV/visible or near infrared light. The demonstrated rational design principle based on light-changeable or light-switchable amphiphilicity is general and can be applied to many polymer/chromophore combinations. This opens the door to developing photocontrollable polymer nanocarriers offering control over when and where the release of loaded agents takes place. © 2007 The Japan Chemical Journal Forum and Wiley Periodicals, Inc. Chem Rec 7: 286–294; 2007: Published online in Wiley InterScience (www.interscience.wiley.com) DOI 10.1002/tcr.20127

Key words: polymer micelles; light-responsive material; polymer nanocarrier; block copolymers; self-assembly

Introduction

Polymer micelles, usually self-assembled from amphiphilic block copolymers (BCPs), have attracted a great deal of attention. One reason is their potential utilization as nanocarriers for controlled delivery of drugs and other bioagents.[1] BCP micelles have some important advantages over micelles formed by small-molecule surfactants. They can be more stable due to a much lower critical micellization concentration and macromolecular nature (e.g., high T_g or crystallization at the core); their sizes can easily be adjusted to allow their preferential accumulation in porous cancer tissues through the enhanced permeation and retention mechanism.[1] In simplistic terms, an ideal controlled delivery consists of three steps. The first step is a stable encapsulation of the drug by BCP micelles. It means that after being administrated in the body, the micelle protects the drug and prevents it from leaking out quickly. The second step is a site-specific transportation of the drug. It means that the drug-loaded BCP micelle should be selectively captured by the target (pathological sites). The third step is that once

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arrived on the target, the BCP micelle "opens the door" to release the drug. This last step is not trivial. One may realize that a stable encapsulation of the drug, which is crucial to the whole controlled process, could also render the drug release from the micelle more difficult at a later time. Actually, for each of the three steps (or conditions), there has been much research effort aimed at developing effective strategies. For the stable encapsulation, the cross-linking of BCP micelles is useful to provide structural integrity and to slow down the diffusion of the drug through cross-linked polymer chains.[2] Regarding the site-specific transportation, the functionalization of the micelle with a targeting ligand that can be recognized by a receptor highly exposed by the target remains the most appealing approach.[3] Finally, to release the drug quickly or in a controlled fashion after the micelle arrives on the site, the micelle should be structurally disrupted. For this purpose, it is natural to think about BCP micelles that can react to an external stimulus to be disrupted. Most research works on stimuli-responsive BCP micelles have been exploring their pH[4] and thermal sensitivity.[5] Indeed, changes in pH and temperature are events that BCP micelles can encounter in the body. Particularly, tumor tissues are known to be slightly acidic (pH ~ 6.8), and the endosomal and lysosomal compartments of cells have even lower pH (pH ~ 5.0–6.0) with respect to the physiological pH 7.4.[4a] If BCP micelles contain acid-labile bonds in their structures, inside the cells, the acidic pH can break those chemical bonds and the structural disruption of the micelle can lead to the release of the loaded drug.[4a]

Over the past years, our group has been studying the use of light (illumination) to control the disruption of BCP micelles. In 2004, we have reported the first photocontrollable BCP micelle that can be reversibly dissociated by UV light and reformed by visible light in solution.[6] It should be emphasized that our research deals with *polymer* micelles that differ from photosensitive surfactant-type (small-molecule) micelles.[7] The concept of using light to trigger the disruption of BCP micelles and thus to control the release of encapsulated drugs or other bioagents is interesting. In addition to be complementary to other stimuli such as pH and temperature change, a light source can be manipulated from outside of the body. If the release essentially occurs when the BCP micellar nanocarrier is disrupted by light, the most appealing feature is the great selectivity of the time and the site of release, since, obviously, the release should take place when illumination is applied and only in the region exposed to light. A parallel can also be drawn between the use of light to control the release of drugs from such polymer nanocarriers and the photodynamic therapy where light is used to activate the drugs (photosensitizers). In this paper, we give a brief review of our research achievements on this topic, discuss what we have learned so far, and highlight the rational designing of photocontrollable BCP micelles.

How to Make Light-Dissociable BCP Micelles?

BCPs can self-organize into micelles in solution if the solvent is good for one block but bad for the other, i.e., being block selective. In the case of amphiphilic BCPs, their micelles in aqueous solution have a compact core region formed by the hydrophobic block and a shell (corona) formed by the hydrophilic block that ensures their solubility (or dispersion) in water. Like micelles of small-molecule surfactants, the decisive parameter controlling the non-covalent micellar association of BCPs is the hydrophilic/hydrophobic balance that is governed by variables such as the relative lengths of the two blocks and

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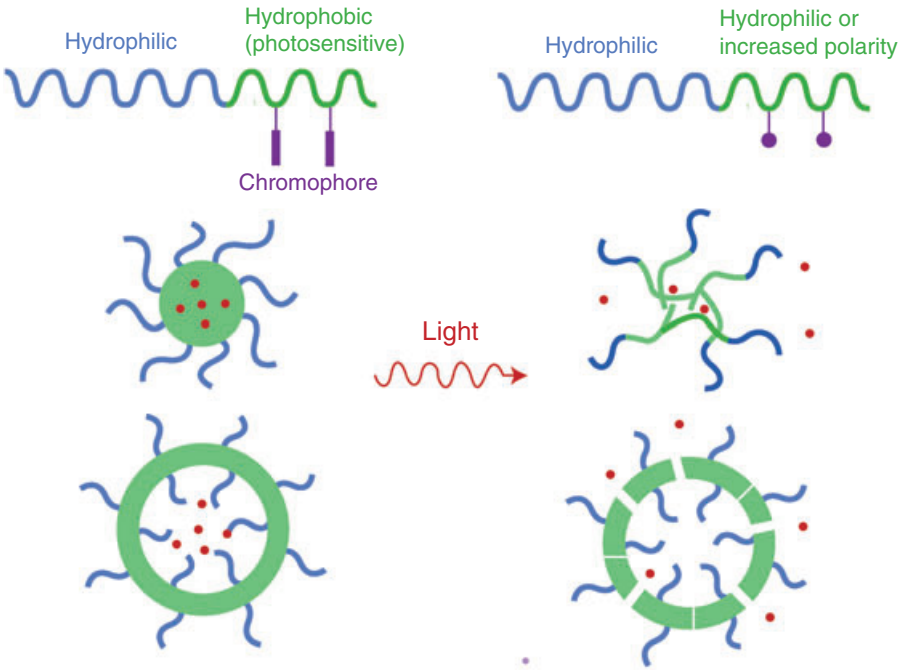

Fig. 1. Schematic illustration of the rational design of light-dissociable block copolymer core-shell micelles or vesicles. The photoreaction of the chromophore on the hydrophobic polymer either increases its polarity or converts it into a hydrophilic polymer; in both cases, the hydrophilic/hydrophobic balance can be shifted toward the destabilization of the micellar association.

their interactions with water determined by their chemical structures. Our studies in recent years have established a general design principle for light-dissociable BCP micelles, which is schematically illustrated in Figure 1. The hydrophobic block of the amphiphilic BCP is designed to be a light-responsive polymer having a chromophore in its structure as pendent groups. The BCP can form core-shell micelles or vesicles for encapsulation of hydrophobic and hydrophilic agents, respectively (polymer vesicles can also load hydrophobic agents in the membrane, which is not depicted in Fig. 1). Upon illumination, the photoreaction of the chromophore shifts the hydrophilic/hydrophobic balance toward the dissociation of the micellar aggregates. Two types of photoreactions can lead to this result. In one, the photoreaction of the chromophore increases significantly the polarity of the hydrophobic polymer so that it is no longer hydrophobic enough to hold the micellar association. In the other case, the photoreaction of the dye causes such a structural change that the hydrophobic polymer is simply converted into a hydrophilic one. In the latter case, the basic condition for BCP micelle formation is gone, and their micelles should be dissociated by light. On the basis of this rational design scheme, we have synthesized and studied various BCPs for light-dissociable polymer micelles.

Polymer Micelles With Reversible Light-Controlled Dissociation and Formation

Figure 2 shows the chemical structure of the first BCP we prepared for light-controllable polymer micelles. While the hydrophilic block is a random copolymer of poly(*tert*-butyl acrylate-co-acrylic acid) [P(*t*BA-*co*-AA)], the hydrophobic block (PAzoMA) is a side-chain liquid crystalline polymethacrylate bearing the azobenzene chromophore that can undergo the reversible trans-cis photoisomerization upon UV and visible light irradiation.[6] This diblock copolymer, P(*t*BA-*co*-AA)-*b*-PAzoMA, was prepared by synthesizing first P*t*BA-*b*-PAzoMA using atom transfer radical polymerization (ATRP) and then by partially hydrolyzing the *t*BA units. Polymer core-shell micelles and vesicles were obtained, and they displayed light-controllable reversible dissociation and formation. The behavior can be explained by the photoisomerization of pendent azobenzene groups as depicted in Figure 2. Upon illumination of the micellar solution with UV light, trans-azobenzene moieties are converted into the cis isomer. This photoreaction results in a large change in the polarity of PAzoMA. Indeed, due to the almost symmetrical structure of the azobenzene moiety, the trans form has a near-zero dipole moment (no charge separation), while the bent cis form dis-

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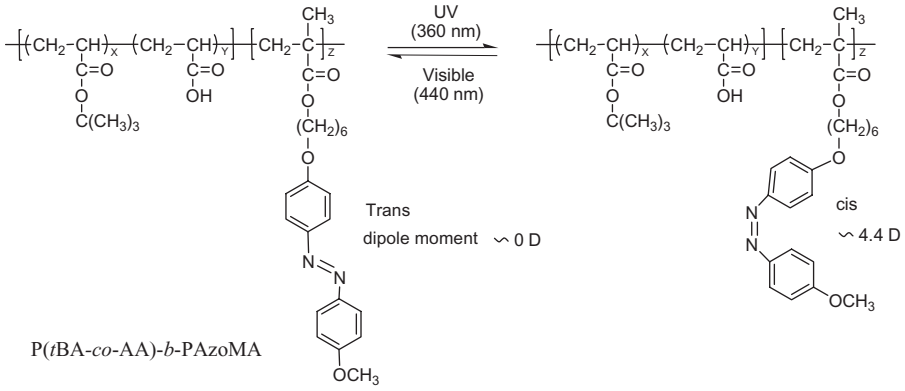

Fig. 2. Chemical structure of an amphiphilic diblock copolymer whose hydrophobic block contains the azobenzene chromophore. The polarity of the hydrophobic block can be switched upon illumination with UV and visible light as a result of the reversible trans-cis photoisomerization of azobenzene. This can lead to the reversible light-controlled dissociation and formation of polymer micelles.

plays a dipole moment of ~4.4 D according to a density functional theory calculation using 4,4′-dimethoxyazobenzene as the model compound.[8] Consequently, when a micellar solution of P(*t*BA-*co*-AA)-*b*-PAzoMA is exposed to UV light, the polarity of the PAzoMA block increases significantly; as the PAzoMA block is no longer hydrophobic enough to preserve the micellar association, BCP micelles are dissociated. Subsequently, when visible light is applied to the solution with dissolved BCP chains (dissociated micelles), the reverse cis-trans isomerization takes place. As azobenzene moieties on the PAzoMA block are returned to the trans form, the initial hydrophilic/hydrophobic balance is recovered, resulting in the reformation of micelles.

We have unambiguously demonstrated the light-controlled dissociation and reformation of BCP micellar aggregates. Shown in Figure 3 is an example of the result with a vesicule solution prepared by adding 16% of water (v/v) in a dioxane solution of P(tBA$_{46}$-*co*-AA$_{22}$)-*b*-PAzoMA$_{74}$ (polymer concentration in dioxane, 1 mg mL^{-1}). The larger vesicles (~200 nm), as compared with core-shell micelles (~15 nm), made it possible to monitor their structural changes in solution upon UV and visible light irradiation through the measurement of the transmittance of a probe light (633 nm).[8] Upon application of a UV light (360 nm, 18 mW cm^{-2}) to the solution (~1.5 mL) under stirring, the optical transmittance increased quickly due to the dissociation of vesicles. Under the used conditions, this process was completed after about 20 s. When the irradiation was switched to visible light (440 nm, 24 mW cm^{-2}), the opposite process occurred immediately; the transmittance dropped as a result of the reformation of vesicles. These reversible changes were confirmed by scanning electron microscope (SEM) observations on samples cast from the solution before UV irradiation (marked by A), after 40 s UV irradiation (B) and after 40 s visible irradiation (C). The higher

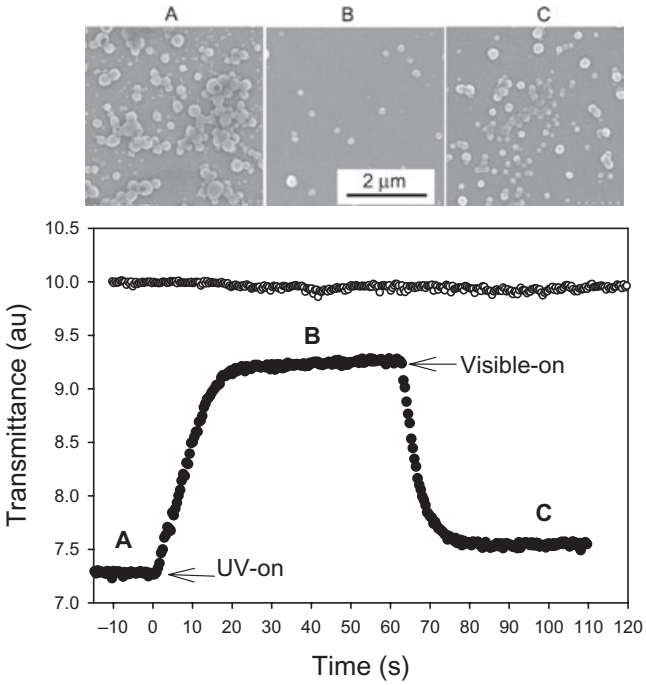

Fig. 3. Changes in transmittance for a vesicle solution of P(*t*BA-*co*-AA)-*b*-PAzoMA illuminated with UV and then visible light. Scanning electron microscope images show the vesicles prior to UV illumination, their dissociation under UV, and their reformation under visible light exposure. The higher and unchanged transmittance is from the diblock copolymer dissolved in solution (with no vesicles) subjected to the same conditions of UV and visible light irradiation (reprinted with permission from Tong et al.,[8] copyright 2005, American Chemical Society).

and essentially unchanged transmittance in Figure 3 was obtained with the same BCP solution without addition of water (no formation of vesicles) subjected to exactly the same UV and visible light irradiation for the reversible trans-cis

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photoisomerization of azobenzene moieties on the dissolved BCP. Note that this reversible process was also observed on SEM for small core-shell micelles.[6]

To our knowledge, this is the first reported polymer micelle with reversible light-controlled dissociation and formation in solution. More importantly, the general design principle revealed by our studies[6,8] obviously can be adapted to design many such BCP micelles using a variety of bi-stable photoswitching dye molecules such as spiropyrans and diarylethenes,[9] to name only a few. The main requirement is that the chromophore can switch between two isomeric forms upon illumination at two different wavelengths and that the two isomers exhibit significantly different dipole moments. An additional comment is worth being made regarding the use of azobenzene and its derivatives. The substitution pattern on the azobenzene moiety can be important. In many azobenzene polymers, especially for those used to generate photoinduced orientation, the azobenzene moiety carries an electron-donor and an electron-acceptor group in the para positions.[10] Using such an azobenzene-containing polymer, the dissociation of BCP micelles upon UV irradiation is unlikely to occur because the cis isomer has a lower dipole moment than the trans isomer, in contrast to the azobenzene structure that we used (Fig. 2). Ultimately, the efficiency for the photocontrol of BCP micelles depends on how the hydrophilic/hydrophobic balance changes, which is determined by the combination of a number of parameters. For instance, if the photoinduced increase in the polarity of the hydrophobic block is relatively small, a short hydrophilic block can still shift the hydrophilic/hydrophobic balance and make the BCP micelles thermodynamically unstable. After our reports, other groups have exploited the use of azobenzene[11] as well as spiropyran[12] to make reversible photocontrolled polymer micellar aggregates.

Polymer Micelles With Irreversible Light-Induced Dissociation

The reversibility in the photocontrolled dissociation and reformation process of BCP micelles is certainly interesting and can eventually be exploited for specific applications. However, for light-controlled release of drugs or other bioagents as discussed in the Introduction, the reversibility is unnecessary. On the basis of the same principle of photocontrolled change in the hydrophilic/hydrophobic balance, we have further designed, synthesized, and studied BCP micelles that can be dissociated irreversibly by light.[13,14] Figure 4 shows the chemical structures of two such amphiphilic diblock copolymers which we synthesized using ATRP, as well as their photoreactions responsible for the irreversible dissociation of their micelles. The basic photoreaction involved in this type of BCP is that upon illumination, dye-pendent groups can be cleaved from the hydrophobic block and the resulting structural change simply transforms the hydrophobic polymer into a hydrophilic one. When this happens, it is easy to understand that the hydrophilic/hydrophobic balance is shifted drastically toward the dissociation of polymer micelles. The first BCP is composed of a hydrophilic poly(ethylene oxide) (PEO) block and a hydrophobic block of poly(1-pyrenylmethyl methacrylate) (PPyMA), while the second BCP also has PEO as the hydrophilic polymer but poly(2-nitrobenzylmethyl methacrylate) (PNBMA) as the hydrophobic block. For PEO-*b*-PPyMA, upon illumination of its micellar aqueous solution with UV light, the photosolvolysis of pyrenylmethyl esters results in the cleavage of 1-pyrenemethanol converting the ester groups to carboxylic acid groups and the hydrophobic PPyMA to the hydrophilic poly(methacrylic acid) (PMA).[13] In the case of PEO-*b*-PNBMA, the used 2-nitrobenzyl chromophore is even more interesting. In addition to the photolysis reaction that results in the cleavage of 2-nitrosobenzoldehyde and transforms the hydrophobic PNBMA block into the hydrophilic PMA, the photoreaction of 2-nitrobenzyl is an intramolecular rearrangement process that can occur both in solution and in the solid state,[15] in contrast with pyrenylmethyl esters whose photosolvolysis requires the presence of a nucleophilic solvent.[16] Another interesting feature of 2-nitrobenzyl is that its photolysis can be induced either via one-photon absorption of UV light or via two-photon absorption of near infrared (NIR). The disruption of BCP micelles triggered by two-photon absorption of NIR (~700–1000 nm) is particularly attractive for biomedical applications. NIR has a deeper penetration through water and tissues than UV due to the reduced absorption and scattering, and it is also less detrimental to healthy cells than UV.[17]

Figure 5 shows an example of the results obtained with PEO-*b*-PPyMA. The SEM images (Fig. 5A) revealed a complete dissociation of the BCP micelles in solution after UV irradiation. In this experiment, the core-shell micelles (~15 nm in diameter) were obtained by adding 15 wt% of water into a tetrahydrofuran (THF) solution of PEO_{45}-*b*-$PPyMA_{72}$ (polymer concentration, 0.25 mg mL^{-1}). The micelles disappeared after the micellar solution (~3.5 mL) was illumined with UV light for 15 min (365 nm; total intensity, ~2 W). Since such BCP micelles can readily solubilize hydrophobic compounds through their hydrophobic cores, the encapsulation of a hydrophobic dye, Nile red, was examined. Figure 5B are pictures of an aqueous micellar solution with solubilized Nile red. Before UV irradiation, the solution appeared pink due to the absorption of visible light by Nile red. However, after UV irradiation, the pink color disappeared; accompanied by an increase in turbidity of the solution. These changes were caused by the cleavage of pyrenemethanol from the BCP and the release of Nile red from disrupted micelles into water where both pyrenemethanol and Nile red were insoluble. Note that dye-loaded

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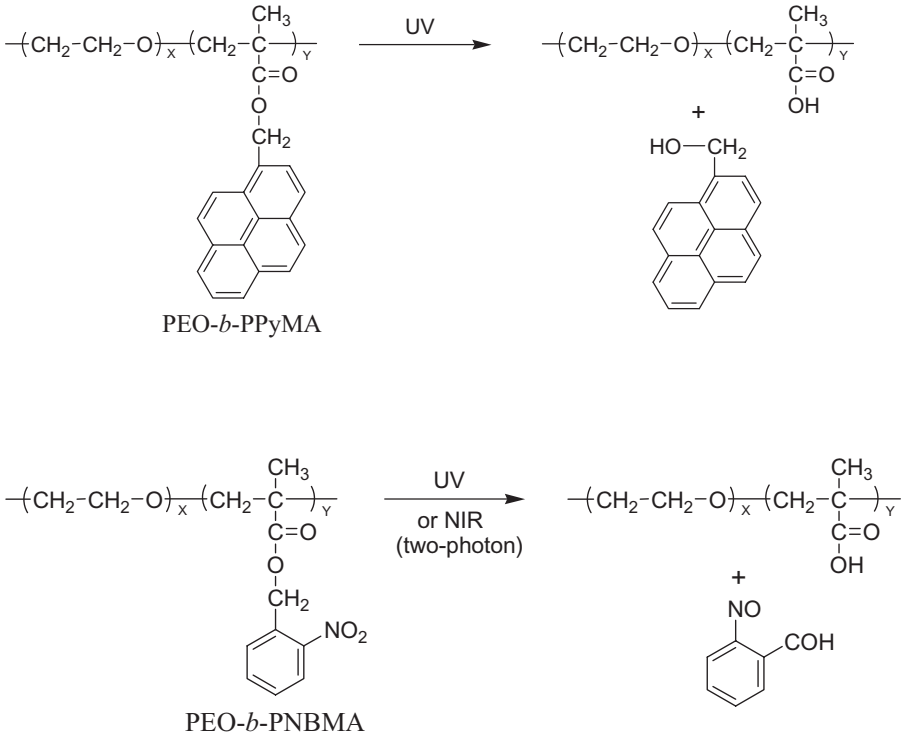

Fig. 4. Chemical structures of two amphiphilic diblock copolymers whose hydrophobic blocks contain the pyrene and 2-nitrobenzyl chromophore, respectively. In both cases, the photolysis reaction results in the cleavage of the chromophore and converts the hydrophobic polymethacrylate into the hydrophilic poly(methacrylic acid). This can lead to the irreversible light-induced dissociation of polymer micelles.

polymer micelles in aqueous solution can be prepared by adding water into a THF solution of the BCP and Nile red, followed by removal of precipitated Nile red through microfiltration and of THF through evaporation or dialysis. Other characterization results also confirmed the UV light-induced dissociation of the micelles of PEO-*b*-PPyMA, including ^{1}H NMR that allowed the degree of cleavage to be estimated as a function of UV irradiation time.[13]

Likewise, micelles of PEO-*b*-PNBMA can be irreversibly dissociated in solution upon UV irradiation for the same reason as for PEO-*b*-PPyMA. Using Nile red as a hydrophobic model compound, we investigated the photocontrolled release from micelles of PEO-*b*-PNBMA upon absorption of one-photon UV (365 nm) and two-photon NIR (700 nm).[14] The release of Nile red from the hydrophobic core of PNBMA into water can be monitored through its fluorescence emission as the intensity decreases and the maximum emission wavelength red shifts.[17] Figure 6A shows an example with the fluorescence spectra ($\lambda_{ex} = 550$ nm) of Nile red-loaded micelles of PEO_{45}-*b*-$PNBMA_{167}$ in an aqueous solution upon UV irradiation (145 mW cm^{-2}, 0.7 mL solution), the red shift of λ_{em} being about 10 nm after 420 s. The change in the normalized fluorescence intensity as a function of irradiation time reflects the kinetic process of the photoinduced release of Nile red. Figure 6B shows the results obtained for the same micellar solution exposed to UV light of different intensities. It can be seen that under the used conditions, no release takes place in the absence of UV light, while the release becomes faster with increased UV light intensity, since high light intensity speeds up the photolysis of 2-nitrobenzyl and, consequently, the disruption of BCP micelles. This result demonstrates the photocontrollability of the release of encapsulated guest molecules by varying the intensity of UV light. We also utilized a femtosecond IR laser (Ti: sapphire, 700 nm, ~80 fs pulse, pulse energy density ~50 mJ cm^{-2}) to illuminate the same Nile red-loaded micellar solution (0.3 mL). The fluorescence measurements showed the release of Nile red, but much more slowly than with the UV light (in tens of minutes as compared to tens of seconds).[14] This slow disruption of BCP micelles was attributed to the low efficiency of two-photon absorption of the used 2-nitrobenzyl chromophore.

Concluding Remarks and Perspectives

Our works in recent years clearly demonstrate that BCP micelles can be designed to be effectively dissociable upon illumination either in a reversible or irreversible fashion. The established rational design principle based on the photocon-

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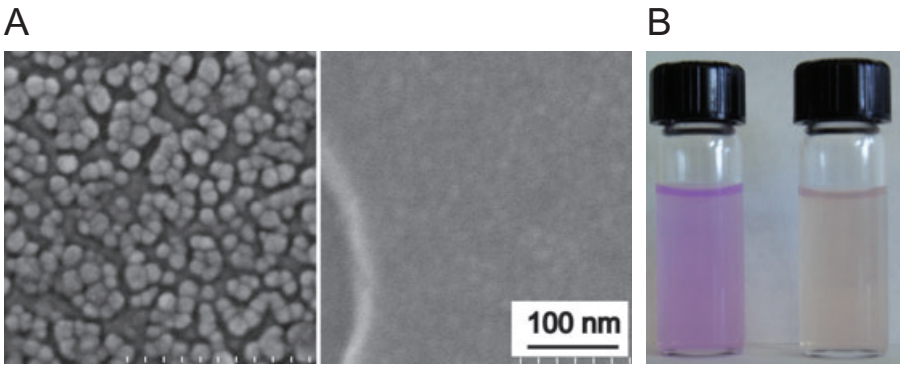

Fig. 5. (A) Scanning electron microscope images showing the micelles formed by PEO-*b*-PPyMA (left) and their dissociation upon illumination of the micellar solution with UV light (right). (B) Photos showing an aqueous PEO-*b*-PPyMA micellar solution equilibrated with the hydrophobic dye of Nile red before (left) and after (right) UV light exposure (reprinted with permission from Jiang et al.,[13] copyright 2005, American Chemical Society).

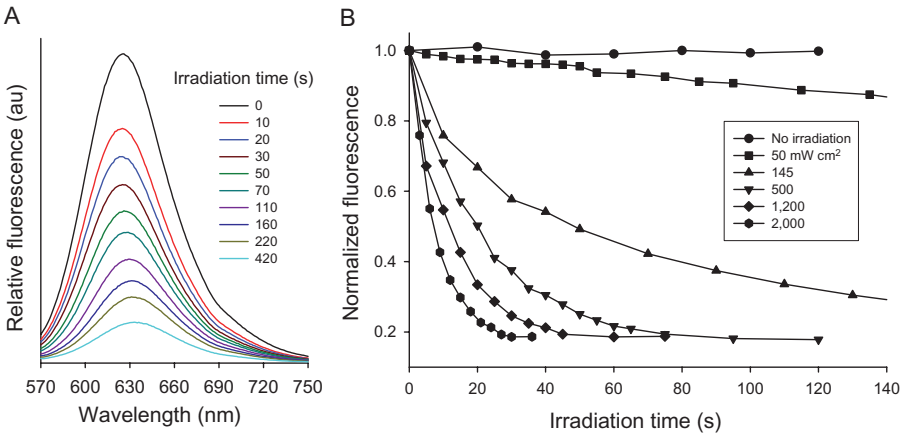

Fig. 6. (A) Fluorescence emission spectra ($\lambda_{ex} = 550$ nm) of Nile red-loaded micelles of PEO-*b*-PNBMA in an aqueous solution upon illumination with UV light (145 mW cm^{-2}), showing the decrease and red shift of the fluorescence emission of Nile red due to its exposure (release) to water. (B) Normalized fluorescence vs. irradiation time for the same Nile red-loaded micellar aqueous solution exposed to UV light of various intensities, showing the increase in release rate with increased UV light intensity (reprinted with permission from Jiang et al.,[14] copyright 2006, American Chemical Society).

trolled hydrophilic/hydrophobic balance (or light-mediated amphiphilicity) is general and can be applied to many polymer/chromophore combinations. However, much work remains to be done before the use of light would become a truly appealing and viable modality for controlled polymer micelle-based drug delivery. What follows is a discussion on a number of issues in this field. Although some of the issues are the subjects of ongoing studies in our laboratory, we hope that this account would help to spark off more interest in developing light-controllable polymer micelles as well as other types of self-assembled molecular systems.

First, in view of the biomedical applications, BCP micelles sensitive to NIR light need to be developed. The key to such BCPs is the use of a chromophore that has a large two-photon absorption cross section for NIR and its photoreaction is able to cause a structural change of the BCP to shift the hydrophilic/hydrophobic balance. Our ongoing works found that the synthesis of NIR-sensitive BCPs might be more difficult. Among the issues, a chromophore effective in two-photon absorption of NIR may be even more sensitive to UV and visible light so that it can easily be decomposed by light or heat during the synthesis process. On the other hand, the two-photon absorption of NIR requires the use of a femtosecond IR laser with high-energy pulses. If continuous-wave NIR from a diode laser can be used to disrupt BCP micelles, this cheaper

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and more accessible NIR light source would make the concept of light-controlled drug delivery more appealing. However, we are not aware of chromophores that display the required structural changes depicted in Figure 1 upon one-photon absorption of NIR light. The development of such NIR chromophores would be exciting and certainly challenging.

Second, light-controlled dissociation or disruption of BCP micelles may need to be combined with other functions. As aforementioned, an ideal controlled drug delivery requires stable encapsulation, site-specific transportation and on-site release. If a light-dissociable BCP micelle cannot prevent the loaded guest from leaking immediately after being administrated in the body, the ability of dissociation upon illumination is of no use. Recently, we reported a study in that direction even though the photoinduced change of amphiphilicity was not involved.[18] We have designed and synthesized an amphiphilic diblock copolymer whose hydrophobic block contains coumarin moieties. After the formation of BCP micelles, the micelle core can be cross-linked by light (at $\lambda > 310$ nm) through the photodimerization of the chromophore to afford the micellar stability. To destabilize the micelle at a later time, the micelle can be de-cross-linked by light at a different wavelength ($\lambda < 260$ nm) through the cleavage of cyclobutane (coumarin dimer). The basic idea here is to stabilize BCP micelles first and then to disrupt them at a required time. We believe there are many opportunities of rationally designing BCP micelles that combine the stability, the use of a targeting ligand for site-specific transportation, and light-controlled disruption (de-cross-linking or change in amphiphilicity).

Third, the application of the principle to designing biocompatible and biodegradable BCPs is one step forward to light-responsive polymer micelles for biomedical applications. To this regard, the choice of PEO as the hydrophilic block is good because it has high water solubility, enables steric stabilization, and can inhibit the surface adsorption of biological substances.[1,4,19] The chromophore-containing hydrophobic blocks that we studied so far are polymethacrylates mainly due to the use of ATRP for the BCP synthesis. Hydrophobic biodegradable poly(amino acids) such as poly(aspartic acid) and poly(glutamic acid) can be made light-responsive through the incorporation of chromophores. Their synthesis requires the use of ring-opening polymerization. The choice of the chromophore whose photoreaction triggers the micellar disruption is another issue. Of course it is better to select biocompatible chromophores that are safe (i.e., not toxic) and that have already been used in biomaterials.[20,21]

Fourth, more basic studies remain to be done to understand the underlying mechanisms in the photocontrolled micellar disruption and release processes. There are three closely related but distinct events: (i) the photoreaction of the chromophore (isomerization or cleavage) responsible for shifting the hydrophilic/hydrophobic balance, (ii) the disruption/dissociation of BCP micelles as a result of the photoreaction, and (iii) the release of loaded guest molecules from the micelles. Depending on the relative lengths of the two blocks and their chemical structures, the critical degree of photoisomerization or photocleavage that causes the micellar dissociation may vary. Our studies found that the dissociation of BCP micelles could take place well before the complete photocleavage reaction.[13] On the other hand, loaded guest molecules would not wait until the complete dissociation of micelles to get out of them. How the release kinetics is determined by the structural perturbation of the micelles and how it is related to the photoreaction are unclear at this point. In principle, with increasing the illumination time, the change in sizes and their distribution of BCP micelles can be studied using dynamic light scattering, while the kinetics of release can be monitored spectroscopically if guest molecules display significant changes in absorption or fluorescence emission like Nile red. However, when the photocleaved chromophore is insoluble in water, which is the case for pyrenemethanol and 2-nitrosobenzoldehyde (Fig. 4), the photocleavage degree cannot be determined using ^{1}H NMR in aqueous solution. To obtain a complete picture and a deep understanding of the photocontrolled release in aqueous solution, the kinetics of the three events need to be characterized simultaneously. This could be done with a BCP micelle for which the photoreaction does not involve the cleavage of water-insoluble chromophore and can be analyzed using ^{1}H NMR.

As a final note, we believe that the interest of the demonstrated rational design based on light-changeable or light-switchable amphiphilicity goes beyond BCP micelles. This strategy can be exploited for more self-assembled amphiphilic polymer or material systems, for which optical control of properties or functions may be interesting.

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