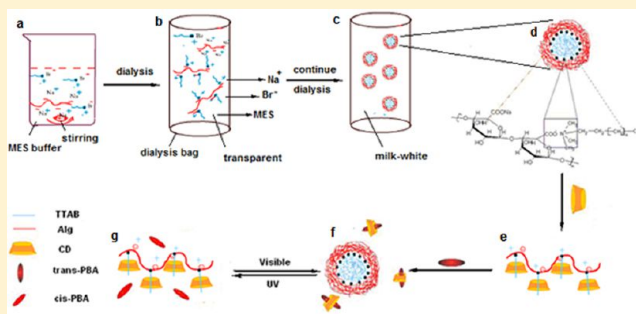


Photoreversible Polymer–Surfactant Micelles Using the Molecular Recognition of α -CyclodextrinZhen-Qiang Dong,[†] Ya Cao,[†] Xiao-Juan Han,[†] Min-Min Fan,[†] Qi-Juan Yuan,[†] Yi-Fu Wang,[†] Bang-Jing Li,^{*,‡} and Sheng Zhang^{*,†}[†]State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China[‡]Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041, China

Supporting Information

ABSTRACT: Photoreversible micelles were achieved by a combination of commercially available components sodium alginate (Alg), tetradecyltrimethylammonium bromide (TTAB), α -cyclodextrin (α -CD), and 4-(phenylazo)benzoic acid (PBA). Under visible light irradiation, α -CD interacted more favorably with PBA than with alkyl chains of TTAB. Therefore, polymer–surfactant micelles were formed by the self-assembly of Alg and TTAB through electrostatic attraction. After UV irradiation, micelles were disrupted because PBA in the cis form lost its ability to complex with α -CD, and then the latter was interacted with TTAB to prevent the association of alkyl chains of TTAB. On alternating irradiation of this quaternary system with UV and visible light, this reversible micellization process can be recycled many times.



1. INTRODUCTION

Stimuli-responsive self-assembling micelles have recently attracted significant attention because of their potentials in a broad range of field, such as drug/gene delivery, sensor system, and nanodevices.^{1–7} As a type of “smart” assembly, their formation and disruption can be controlled by external stimuli such as the pH, temperature, and light. So far, many stimuli-responsive micelles have been achieved by modified amphiphiles in which responsive groups such as ferrocene, azobenzenes, amylases, and amines are covalently introduced.^{8–15} However, people find that the special force such as hydrogen bonds and ion–ion interactions could be the driving forces for the formation of noncovalently connected micelles (NCCM).^{16–18} Assembly through noncovalent interaction offers a number of advantages over chemical synthesis: it does not require complicated preparative procedures and the reactions are typically fast. The combination of NCCM with the responsive nature furnishes an attractive means of taking advantage of both. However, to the best of our knowledge, only a few NCCMs with reversible responses have been reported.^{19–22}

It has been reported that polyelectrolyte can bind with oppositely charged surfactants through electrostatic attraction, resulting in the formation of a micelle-like domain.^{23–28} In this article, we endowed responseless polymer–surfactant micelles with photoreversible abilities by the simple introduction of α -CD and PBA. It is demonstrated that this composite exhibits reversible changes in micellar aggregates under alternating UV and visible light illumination. It should be noted that all the

components of these photoresponsive composites—sodium alginate (Alg), tetradecyltrimethylammonium bromide (TTAB), α -cyclodextrin (α -CD), and 4-(phenylazo)benzoic acid (PBA)—are commercially available components. Alg was selected as the polymer matrix because it is very easy to obtain (from marine algae) and it is much cheaper, biocompatible, and biodegradable.

2. MATERIALS AND METHODS

2.1. Materials. Pure sodium alginate (Alg) with medium viscosity (1.05–1.15 Pa s) was purchased from Tianjin Yuanhang Chemical Co., China. Tetradecyltrimethylammonium bromide (TTAB), with a purity of $\geq 99\%$, was purchased from Xianmen Innovation Chemical Co., China. α -Cyclodextrin (α -CD) and 4-(phenylazo)benzoic acid (PBA) were purchased from Tokyo Chemical Industry Co. Ltd., Japan. Pyrene and Nile red were purchased from Sigma-Aldrich Co., Inc. Morpholinoethanesulfonic acid (MES) was a local commercial product. All of these products were used without further purification.

2.2. Preparation of Alg/TTAB Micelles. Alg (0.4 g) was added to 60 mL of MES buffer (pH 6.0) at room temperature. After the Alg completely dissolved, 0.067 g of TTAB was added to the above solution and stirred for 30 min. Then the mixture was dialyzed with water (three times a day for 2 days at 30 °C). A milky white Alg/TTAB micelle emulsion (200 mL) was achieved.

A known amount of pyrene in methanol was added to a flask, and the methanol evaporated at 40 °C. Then a measured amount of Alg/

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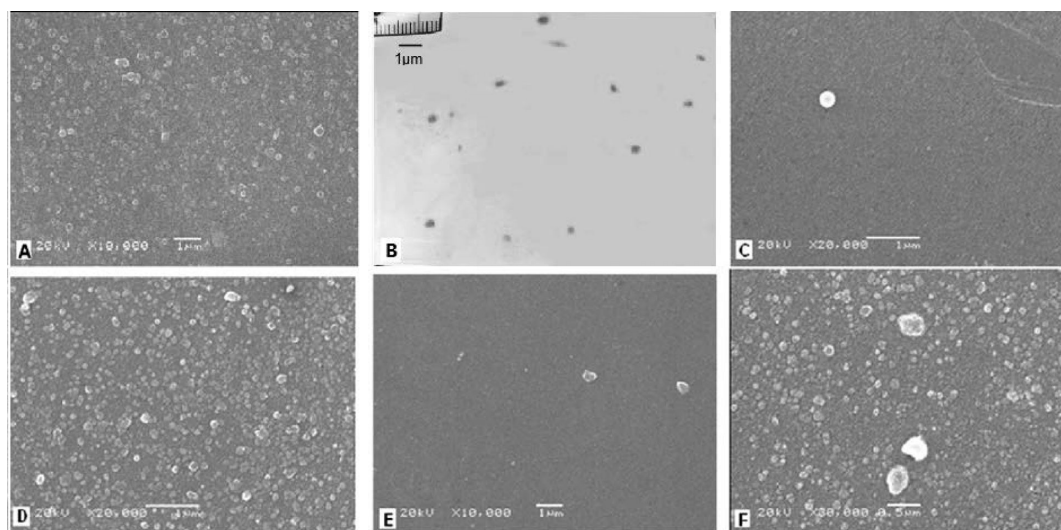


Figure 1. (A) SEM micrograph of Alg/TTAB. (B) TEM micrograph of Alg/TTAB. (C) SEM micrograph of Alg/TTAB/ α -CD. (D) SEM micrograph of Alg/TTAB/ α -CD/PBA. (E) SEM micrograph of Alg/TTAB/ α -CD/PBA after exposure to UV light for 2 h. (F) SEM micrograph of Alg/TTAB/ α -CD/PBA after exposure to visible light for 2 h.

TTAB solution was added to the flask, and the mixture was heated for 3 h at 65 °C to equilibrate the pyrene and the micelles. Subsequently, the mixture was cooled overnight at room temperature. The final concentration of pyrene was 1.0×10^{-6} M. Fluorescence spectra were recorded using a fluorescence spectrophotometer with slit widths of 5.0 and 2.5 nm for excitation and emission, respectively. The fluorescence emission spectra of pyrene were recorded using an excitation wavelength of 335 nm, and intensities I_1 and I_3 were measured at the wavelengths corresponding to the first and third vibronic bands located at 373 and 384 nm, respectively.

2.3. Preparation of Alg/TTAB/ α -CD/PBA Micelles. The Alg/TTAB micelle emulsion (2.25 mg/mL, 4.0 mL, transmittance 60%) was adjusted to pH 13 by adding 0.1 M NaOH. Five milligrams of α -CD was added to the above micelle system with stirring for 5 min, and then the milky white solution became clear. When 1.2 mg of PBA was added to the Alg/TTAB/ α -CD solution, after stirring for another 30 min, the solution gradually became turbid, indicating the formation of Alg/TTAB micelles.

Thirty microliters of a 0.05 mg/mL stock solution of Nile red in dichloromethane was added to an empty vial, which was then placed under vacuum for at least 2 h to ensure complete solvent removal. Then, we added 4 mL of a dilute Alg/TTAB/ α -CD/PBA micelle solution (pH 13, 1.6 mg/mL) to this vial and shook the mixture vigorously and allowed it to equilibrate at room temperature for at least 2 h. Fluorescence measurements were taken at an excitation wavelength of 550 nm, and the emission was monitored from 560 to 700 nm.

2.4. Measurements. The 2D ^1H NOESY NMR spectra were recorded on an Advance Bruker 600 NMR spectrometer at room temperature. Transmission electron microscopy (TEM) observations were performed on a Jeol JEM-100CX electron microscope at an accelerating voltage of 80 kV. Scanning electron microscopy (SEM) observations were performed on a Jeol JSM-S900LV electron microscope at an accelerating voltage of 20 kV. The specimens were coated with gold before SEM observations. The zeta potential of Alg/TTAB micelles was measured using a Zetasizer model Nano-ZS, Malvern Instruments, England. PBA was isomerized by photo-irradiation using a 400 W Xe lamp equipped with a cutoff filter and a band-pass filter (360 nm UV light or visible light, 2 h). The distance between the sample cell and the lamp was fixed at 40 cm. The transmittance changes in our whole experiment were recorded using a UNICO 2008 UV/vis spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Preparation and Characterization of Reversible Micelles.

First, Alg was mixed with cationic surfactant TTAB in aqueous solution. Two component solutions were transparent because the Alg was a water-soluble polymer and the concentration of TTAB (1.05×10^{-3} mol/L) was lower than the TTAB critical micelle concentration (1.6×10^{-3} mol/L).²⁹ However, the mixed solution of Alg/TTAB gradually became turbid, indicating the formation of some kind of aggregates. DLS measurements showed that the hydrodynamic diameter (D_h) of the Alg/TTAB aggregates was about 390 nm under neutral and basic conditions (Figure S1a). The formation of these domains can be traced to the electrostatic attraction between TTAB and Alg. It has been reported that the interactions between polyelectrolytes and oppositely charged surfactants in solution can lead to the formation of a micelle-like domain in which the surfactant served as alkyl side chains to form a hydrophobic core and the hydrated polyelectrolyte formed an outer shell.^{23–28} Figure 1A,B showed the morphology of Alg/TTAB aggregates studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It can be seen that the Alg/TTAB aggregates were spherical in shape and their diameters were about 200 nm. The diameter of the particles in Figure 1 is a little smaller than D_h , which may result from the shrinkage of particles during the process of solvent evaporation during sample preparation. The zeta potential of Alg/TTAB aggregates was -30.0 mV, confirming that the surface of the particles was covered with protonated Alg blocks.

The fluorescence probe technique was applied to study the self-aggregation behavior of Alg/TTAB conjugates on a molecular level. Pyrene was chosen as the fluorescent probe because of its photophysical properties.³⁰ As shown in Figure 2, at low Alg/TTAB concentration the I_1/I_3 ratio of pyrene is about 1.70, which corresponds well to the value where pyrene was dissolved in distilled water. With the Alg/TTAB concentration increasing, the I_1/I_3 ratio starts to decrease and reaches a constant value of 1.19, indicating constant polarity of the local environment sensed by pyrene. From the plots of the pyrene I_1/I_3 ratio, we can estimate that the critical micelle

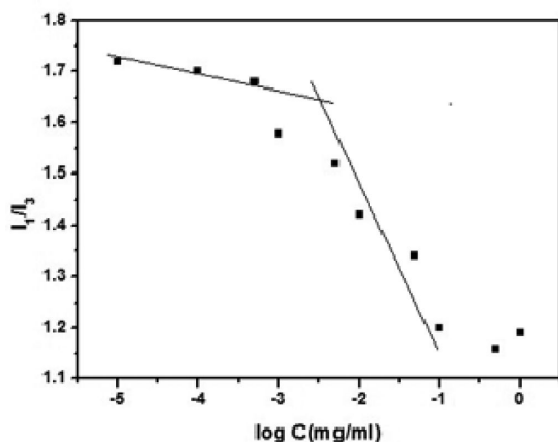


Figure 2. Plot of the fluorescence intensity of pyrene as a function of the Alg/TTAB concentration.

concentration was about 3.98×10^{-3} mg/mL by means of the method used by Shen et al.³¹ The cmc value for Alg/TTAB complexes is 2 orders of magnitude lower than those for low-molecular-weight surfactants such as TTAB 5.38×10^{-1} mg/mL (1.6×10^{-3} mol/L).²⁷

Interestingly, the solution transmittance changed dramatically from 67% to nearly 98% after adding 5 mg of α -CD ($[\alpha\text{-CD}] = 1.29 \times 10^{-3}$ mol/L) to 4 mL of the turbid Alg/TTAB complex solution. It was noted that the concentration of α -CD was present in small excess compared to TTAB ($[\text{TTAB}] = 0.5 \times 10^{-3}$ mol/L) to ensure that every TTAB molecule can form an inclusion complex with α -CD. The scattering intensity of the solution became very low, resulting in the DLS measurement not being made. This phenomenon indicated that the concentration of micelles was very low and suggested that most of the Alg/TTAB micelles dissociated. SEM

observation confirmed that almost no micelles existed after the addition of α -CD to Alg/TTAB solution (Figure 1C).

CDs are one of the most important host compounds in supramolecular chemistry. The conical structure of CDs contains a cavity allowing CDs to include guest molecules ranging from small organic/inorganic compounds to polymers.^{32,33} The interaction of α -CD with Alg/TTAB was investigated by 2D ^1H NOESY NMR spectra. Figure 3 showed the NOESY spectrum for the Alg/TTAB/ α -CD mixture. It can be seen that the signals of inner protons (H3, H6, and H5) of α -CD were correlated with the resonance of the alkyl chain of TTAB, indicating that alkyl chains of TTAB threaded through the cavity of α -CD to form an inclusion complex. The formation of an inclusion complex between a long alkyl chain and α -CD in an aqueous medium has also been reported by other research groups.^{34–36} For example, Harada et al. found that α -CDs formed inclusion complexes with dodecyl side chains attached to poly(acrylic acid) and the formation of inclusion complexes suppressed the associations of hydrophobic alkyl chains.³⁵ In this study, the association constant for α -CD and TTAB was studied by ^1H NMR. On addition of α -CD, the peaks of methyl and methylene in TTAB shifted to a lower field (Figure S2). Peak shift reciprocals were calculated and plotted against the reciprocal concentration of α -CD to make the Benesi–Hildebrand plot (Figure S3). These plots were fitted well with a straight line ($[\alpha\text{-CD}] < 5 \times 10^{-3}$ M), indicative of the formation of a 1:1 inclusion complex of α -CD with TTAB. From the straight line, the association constant for α -CD and TTAB ($K_{\alpha\text{-CD-TTAB}}$) was determined to be 1.4×10^3 M $^{-1}$. Because α -CD was threaded onto the C14 chains of TTAB, the hydrophobic association of C14 chains was prevented, resulting in the dissociation of Alg/TTAB micelles.

To dissociate the complex of α -CD and TTAB, competitive guest PBA was added to the Alg/TTAB/ α -CD ternary system. It was found that the transparent Alg/TTAB/ α -CD solution became turbid again by the addition of PBA (molar ratio of α -

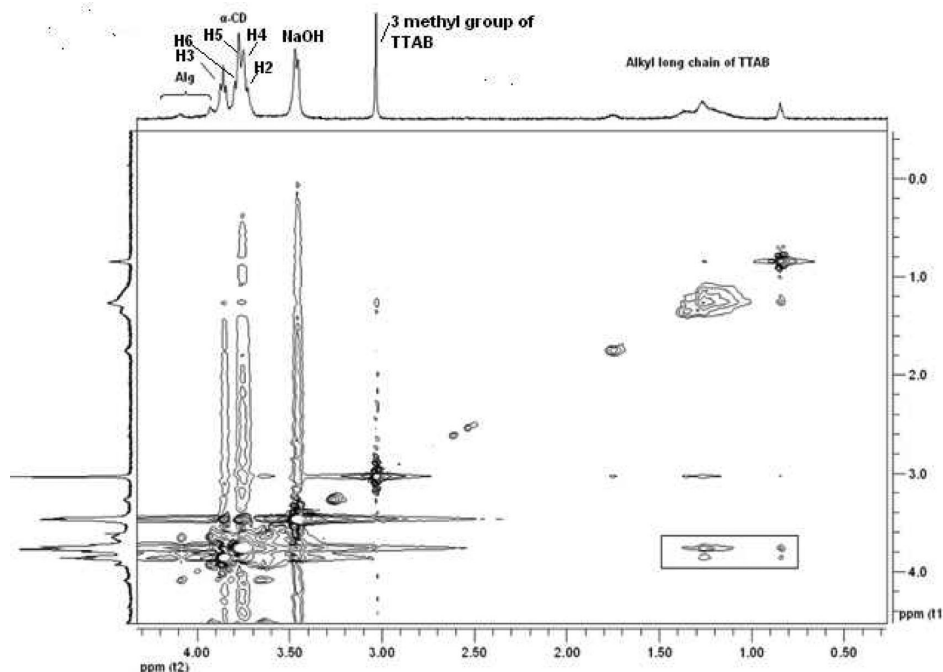


Figure 3. Two-dimensional NOESY spectra of Alg/TTAB after the addition of α -CD (Alg/TTAB/CD) in D₂O at pH 13.

CD and PBA was 1:1). As shown in Figure 1D, a large number of micelles were formed again. Figure 4a shows the NOESY

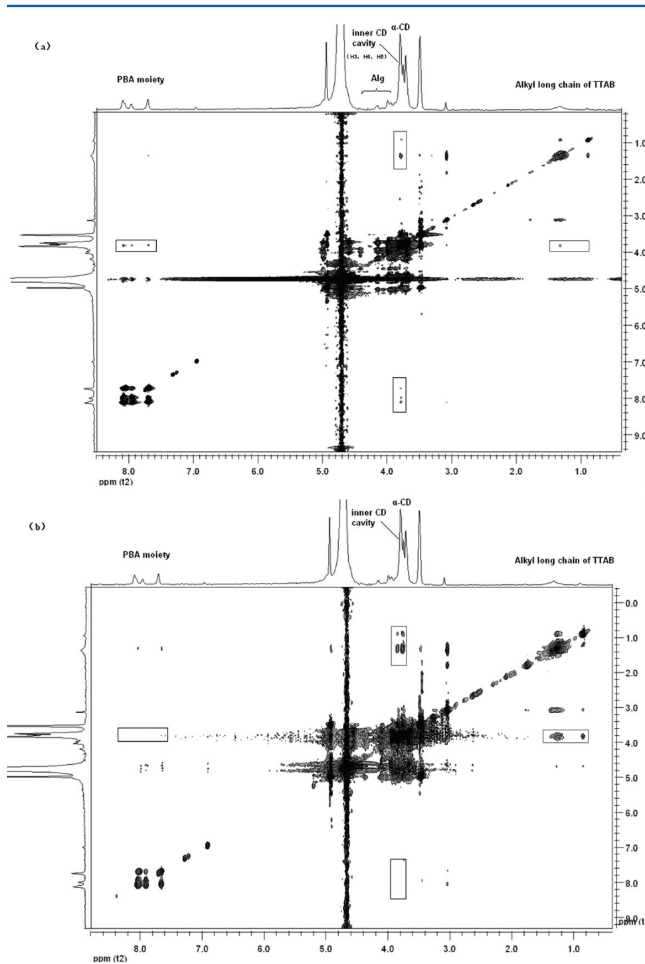


Figure 4. Two-dimensional NOESY spectra of Alg/TTAB/ α -CD/PBA before (a) and after (b) UV in D_2O at pH 13.

spectrum for the Alg/TTAB/ α -CD/PBA mixture. It can be seen that protons in both the phenyl group of PBA and the alkyl moieties of TTAB showed correlation peaks with inner protons in α -CD, indicating that α -CD formed an inclusion complex not only with the long alkyl chain of TTAB but also with PBA.

The complex formation behavior of α -CD with PBA was investigated by UV-vis absorption spectra. On addition of α -CD, the absorption of PBA around 330 nm shifted to a longer-wavelength region as a result of the formation of inclusion complexes of α -CD with PBA (Figure S4). Reciprocals of the peak shift for the wavelength at the absorption maximum ($\Delta\lambda_{\max}$) were calculated and plotted against the reciprocal of the concentration of α -CD to make the Benesi-Hildebrand plot (Figure S5). These plots were fitted well with a straight line, indicative of the formation of 1:1 inclusion complexes of α -CD with PBA. From the straight line, the association constant for α -CD and *trans*-PBA ($K_{\alpha\text{-CD}/\text{trans-PBA}}$) was determined to be $1.8 \times 10^4 \text{ M}^{-1}$. Because $K_{\alpha\text{-CD}/\text{trans-PBA}}$ is larger than $K_{\alpha\text{-CD}/\text{TTAB}}$, upon addition of PBA to the Alg/TTAB/ α -CD mixture, α -CD interacted more favorably with PBA than with the alkyl chains of TTAB, which induced the dissociation of inclusion complexes of α -CD and TTAB to restore the hydrophobic association of alkyl chains and then

resulted in the formation of micelles. DLS measurement showed that the D_h of the micelles is about 388 nm (Figure S1b), which is almost the same as the size of Alg/TTAB aggregates.

The Alg/TTAB/ α -CD/PBA quaternary system showed photoresponsive behavior. As shown in Figure 5, the Alg/

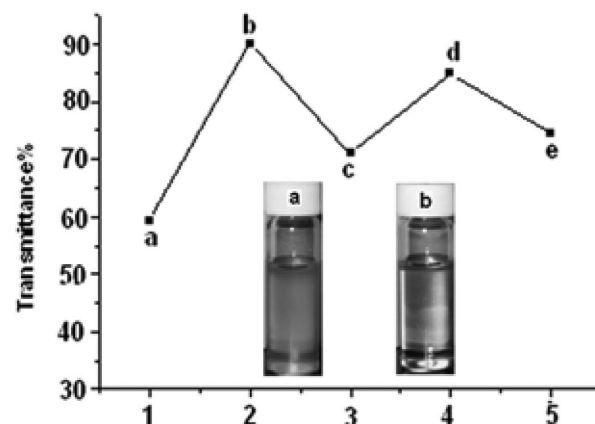


Figure 5. (a) Initial transmittance of Alg/TTAB/ α -CD/PBA. (b) Transmittance changes after (a) exposure to UV light for 2 h. (c) Transmittance changes after (b) exposure to visible light for 2 h. (d) Transmittance changes after (c) re-exposure to UV light for 2 h. (e) Transmittance changes after (d) re-exposure to visible light for 2 h.

TTAB/ α -CD/PBA solution under visible light was turbid, indicating the formation of aggregates. The SEM photograph revealed that the aggregates were particles with a size of around 200 nm (Figure 1D), which were smaller than those used in the DLS measurement (388 nm, Figure S1b) as a result of the shrinkage of the aggregates for sample preparation. UV irradiation at 360 nm made the Alg/TTAB/ α -CD/PBA solution change from turbid to transparent, and the DLS measurement cannot be made because of the low scattering intensity of solution, suggesting the dissociation of micelles. SEM confirmed that almost no micelles remained in the solution after 2 h of UV exposure (Figure 1E). The resulting transparent solution became turbid again as it was irradiated with visible light. The SEM images in Figure 1E,F indicate the reappearance of a large number of micelles. DLS measurement showed that the D_h of the micelles was 395 nm (Figure S1c), which is the same size as micelles before UV irradiation, confirming that micelles formed again after visible light irradiation.

It is known that azobenzene (azo) derivatives are isomerized from *trans* to *cis* and from *cis* to *trans* under irradiation with UV and visible light, respectively.³⁷ As shown in Figure S7, after 10 min of 400 W irradiation, most azo moieties completed the isomerization. α -CD can interact with *trans*-azobenzene to form a 1:1 inclusion complex but cannot include the *cis*-azobenzene to form an inclusion complex because of the mismatch between the host and guest.^{38–40} Our investigation also confirmed that α -CD did not interact or interacted very weakly with *cis*-PBA. The absorption band at 430 nm due to the $n-\pi^*$ transition of *cis*-PBA exhibits no significant spectral change upon addition of varying concentrations of α -CD (Figure S6). The structure of Alg/TTAB/ α -CD/PBA after UV irradiation was also explored with a 2D NOESY spectrum. As shown in Figure 4b, after UV irradiation, protons in *cis*-PBA exhibited almost no correlation peaks with α -CD. In contrast, the correlation peak between

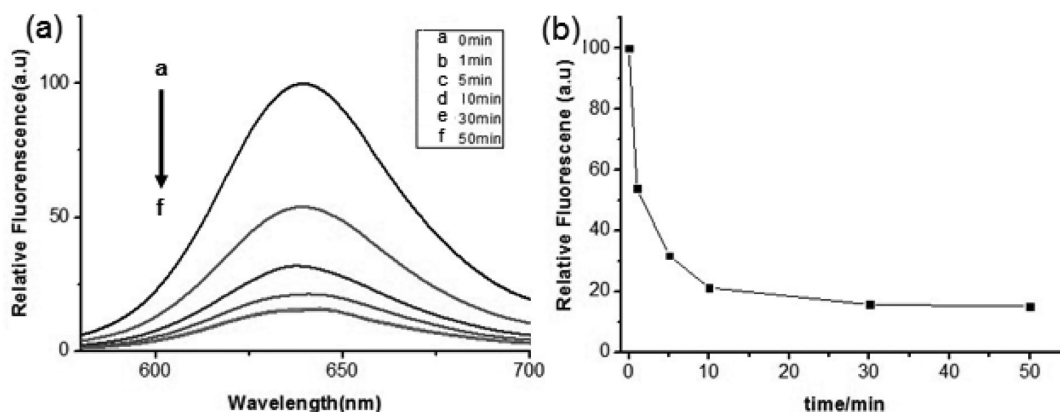


Figure 6. (a) Emission spectra of Nile red ($\lambda_{\text{ex}} = 550 \text{ nm}$) encapsulated in Alg/TTAB/ α -CD/PBA under UV irradiation at 365 nm. (b) Fluorescence emission intensity of Nile red at 640 nm versus the irradiation time.

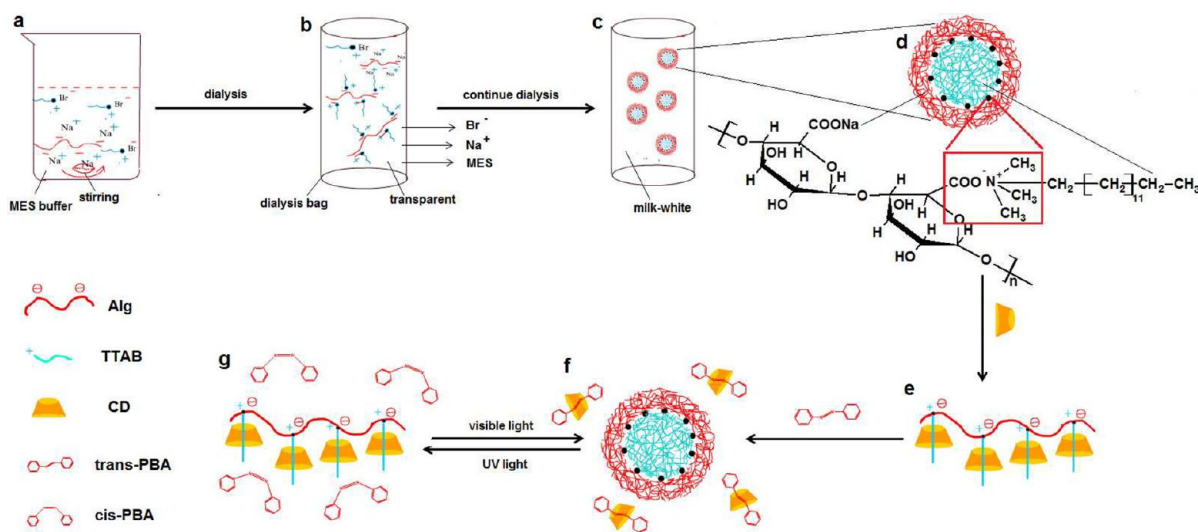


Figure 7. Schematic illustration of the preparation process of the Alg/TTAB/ α -CD/PBA composite and its double responsive behavior with UV and visible light.

protons in α -CD and alkyl chains of TTAB was much stronger. These results indicated that α -CD interacted less favorably with PBA than with alkyl chains of TTAB when PBA took the cis form in Alg/TTAB/ α -CD/PBA quaternary mixtures. Therefore, the associations of hydrophobic alkyl chains were suppressed by the formation of TTAB/ α -CD inclusion complexes, leading to the dissociation of micelles.

The encapsulation of hydrophobic molecules by Alg/TTAB/ α -CD/PBA and the UV-light-induced release were investigated. Nile red, a hydrophobic fluorescent probe, was selected as a model molecule. It is known that Nile red shows relatively low fluorescence emission ($\lambda_{\text{max}} = 660 \text{ nm}$) in water because of its poor solubility. However, if Nile red resides in a hydrophobic environment, such as the interior of a micelle, then its fluorescence emission intensity increases dramatically and experiences a blue shift.⁴¹ Figure 6a shows the fluorescence spectra ($\lambda_{\text{ex}} = 550 \text{ nm}$) of the micellar solution with encapsulated Nile red before and after UV light exposure. It can be seen that micelles with Nile red emitted extensive radiation at 640 nm, indicating that Nile red was encapsulated in the hydrophobic core of micelles. After UV irradiation, the fluorescence intensity decreased significantly, revealing that hydrophobic Nile red molecules were released into the water.

Figure 6b shows the relative fluorescence intensity at 640 nm as a function of irradiation time. In 10 min, the fluorescence intensity decreased 80%, suggesting that the UV irradiation resulted in the efficient disruption of micelles.

3.2. Proposed Mechanism. The mechanism of formation of these photoreversible micelles is proposed as follows (Figure 7). First, Alg and TTAB formed polymer–surfactant micelles in which the surfactant served as alkyl side chains to form a hydrophobic core and hydrated polyelectrolyte formed an outer shell (Figure 7a–c). These polymer–surfactant micelles were disrupted or reformed as a result of the competition of host–guest interactions (Figure 7d–g). Under visible light, α -CD interacted more favorably with PBA than with alkyl chains of TTAB. Therefore, polymer–surfactant micelles were formed by the self-assembly of Alg and TTAB through electrostatic attraction. After UV irradiation, micelles were disrupted because PBA in the cis isomer lost its ability to complex with α -CD and then the latter interacted with TTAB to prevent the association of alkyl chains of TTAB. On alternating irradiation of this quaternary system with UV and visible light, this reversible micellization process can be recycled many times (Figure 7f,g).

4. CONCLUSIONS

The responseless noncovalently connected polymer–surfactant micelles formed by Alg and TTAB were endowed with photoresponsive abilities by the simple introduction of α -CD and PBA. All components of these micelles are commercially available. SEM, TEM, DLS, and transmittance measurements confirmed that the micelles were formed under visible light but disrupted under UV light illumination. 2D ^1H NOESY NMR results indicated that this photoresponsive behavior was a result of the competition of host–guest interactions. Compared to stimuli-responsive micelles prepared by modified amphiphiles, the micelles developed in this study sidestep the difficult syntheses relying on the use of the molecular recognition of CDs. CDs are well known as host compounds capable of responsive binding with a range of guest molecules, such as redox-responsive binding with ferrocene derivatives and pH-responsive binding with aliphatic amines. Therefore, this study suggests that using the competition of host–guest interactions may be a general, versatile, and economical way to fabricate stimuli-responsive assemblies. Furthermore, the features of this Alg/TTAB/ α -CD/PBA system, including commercial availability and photoreversibility, may benefit from application in various fields such as encapsulation, drug delivery, and reaction vessels.

■ ASSOCIATED CONTENT

Supporting Information

Details on ^1H NMR spectra of TTAB in the absence and presence of α -CD. Benesi–Hildebrand plot for inclusion complexes of α -CD with TTAB and α -CD with PBA. UV–vis absorption spectra of PBA. UV–vis absorption spectra of PBA in the trans state. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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