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Photocontrolled Self-Assembly and Disassembly of Block Ionomer Complex Vesicles: A Facile Approach toward Supramolecular Polymer Nanocontainers

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A new concept of designing a photocontrollable supramolecular polymer nanocontainer through the electrostatic association between an azobenzene-containing surfactant (AzoC10) and a double-hydrophilic block ionomer, poly(ethylene glycol)-*b*-poly(acrylic acid) ($PEG_{43}-PAA_{153}$), is described. Such a block ionomer complex can self-assemble in aqueous solution and form vesicle-like aggregates, which are composed of a poly(ethylene glycol) corona and a poly(acrylic acid) shell associated with azobenzene-containing surfactant. The photoisomerization of azobenzene moieties in the block ionomer complex can reversibly tune the amphiphilicity of the surfactants, inducing the disassembly of the vesicles. Such block ionomer complex vesicles are further evaluated as nanocontainers capable to encapsulate and release guest solutes on demand controlled by light irradiation. For example, the vesicles encapsulating the fluorescein sodium display clear spherical images observed by fluorescence microscopy. However, such fluorescence-marked images disappear after releasing the solute from the vesicles triggered by the UV light. Such novel materials are of both basic and practical significance, especially as prospective nanocontainers for cargo delivery.

Introduction

Self-assembly of amphiphilic block copolymers induces formation of nanosized polymeric micelles or vesicles, which have been widely explored as carriers for enzymes or nonbiological catalysts as well as containers for drug or gene delivery.[1] Since amphiphilicity is the principal basis of such self-assembly, some approaches have been developed to modulate the polymeric assemblies for controlled drug delivery through tuning the amphiphilicity of the block copolymers.[2] Generally, the drug species encapsulated in or attached to the polymeric assemblies can be released via reversible[3] or irreversible[4] disassembly of the hydrophobic core-forming segments. However, the self-assembly of amphiphilic block copolymers usually involves the use of organic solvents and suffers from complicated preparation processes. More than a decade ago Kataoka's group[5] and Kabanov's group[6] developed a concept for preparing block copolymer assemblies on the basis of electrostatic interactions. This new family of polymeric assemblies is formed by double-hydrophilic block copolymers, containing ionic and nonionic water-soluble segments (block ionomers), and can incorporate many charged polymers, including synthetic polyions,[7] enzymes,[8] DNA,[9] RNA,[10] and others. One great advantage of this approach is that such assemblies are formed in water, and no organic solvent is required for their preparation. Moreover, the block ionomers with appropriate molecular weight and composition can also form micelle-like or vesicle-like aggregates. The basic mechanism of the formation of such polymeric assemblies involves the core precipitation of the charged blocks of block ionomers with the oppositely charged polyions. Besides the

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block ionomer−polyion systems, Kabanov et al. proposed a simple method to prepare block ionomer complexes by electrostatic complexation of block ionomers with oppositely charged surfactants.[11] Such block ionomer complex can be depicted as an amphiphilic supramolecular block copolymer, in which the nonionic block functions as the hydrophilic part while the electrostatic complex of the ionic block and aggregated surfactant counterions serves as the hydrophobic part. It is known that by introducing stimuli-responsive moieties onto the surfactants, the surfactant aggregates can be tuned toward controllable disassembly.[12] Herein, for the first time we demonstrate a possibility of controlled self-assembly and disassembly of the block ionomer and surfactant complex vesicles through tuning the amphiphilicity of the surfactants.

It is well-known that the *trans*- and *cis*-forms of azobenzene-bearing surfactant have different critical micelle concentration (cmc), and this can be used to realize the destruction and formation of the micellar structure in solution upon alternatively treatment of UV light and visible light.[13] Inspired by this work, we attempted to introduce the azobenzene-bearing surfactant into the block copolymer complex and to develop a new concept of stimuli-responsive block ionomer complex. In addition, we wondered if the complex is able to form photocontrolled vesicle-like structure and this stable vesicle-like structure can be used as polymeric nanocontainer for cargo delivery. For this purpose, in the present work, we prepared a positive-charged azobenzene-containing surfactant, 1-[10-(4-phenylazophenoxy)decyl]triethylamine bromide (AzoC10), and a double-hydrophilic block copolymer of poly(ethylene glycol)-*block*-poly(acrylic acid) (PEG_{43}−PAA_{153}). We have demonstrated that the electrostatic complexation between the single-tail surfactant and the PAA block of the block copolymer leads to the spontaneous formation of block ionomer complex vesicles. The block ionomer complex vesicles are found to disassemble when the azobenzene moiety changes from *trans*- to *cis*-form as a result of UV light irradiation. Furthermore, such block ionomer complex vesicles can be used as nanocontainers for encapsulation and release of guest molecules controlled by UV light irradiation.

Experimental Section

Materials and Instruments. All reagents and solvents were purchased from Beijing Chemical Reagent Co., China. Triethylamine was dried by NaOH before use. The block copolymer PEG_{43}−PAA_{153} was synthesized by atom transfer radical polymerization (ATRP).[14] AzoC10 was synthesized according to the synthetic route shown in Figure 1, in which the synthesis of compounds **1** and **2** has been described before.[12c]

Synthesis of 1-[10-(4-Phenylazophenoxy)decyl]triethylamine Bromide (AzoC10). Excessive triethylamine (0.5 mL) was added to compound **2** (0.1425 g, 0.3 mmol)−acetonitrile solution. The mixture was kept stirring for 8 h at 60 °C under an Ar atmosphere. After evaporation of acetonitrile, the yellow solid was dissolved in tetrahydrofuran. The solution was added stepwise with magnetic stirring to a plenty of petroleum ether, and the yellow precipitate was filtered and dried in a vacuum oven. Final characteristics of AzoC10 were as follows: ^{1}H NMR (solvent: $CDCl_3$): δ 7.99−7.90 (q, 4H), δ 7.52−7.46 (m, 3H), δ 7.02−7.00 (d, 2H), δ 4.07−4.03 (t, 2H), δ 3.54−3.47 (q, 6H), δ 3.29−3.24 (t, 2H), δ 1.83 −1.32 (m, 25H). ^{13}C NMR (solvent: $CDCl_3$): δ 161.89, 152.70, 146.82, 130.47, 129, 14, 124, 94, 122,60, 114,82, 68.40, 57.68, 53.67, 29.38. 29.30, 29.21, 26.56, 26.01, 22.21, 8.23. MS: $[M-Br]^+$ calculated, 438.35; found, 438.33. Anal. Calcd for $C_{28}H_{44}BrN_3O$ (AzoC10): C, 64.85; H, 8.55. Found: C, 64.88; H, 8.50.

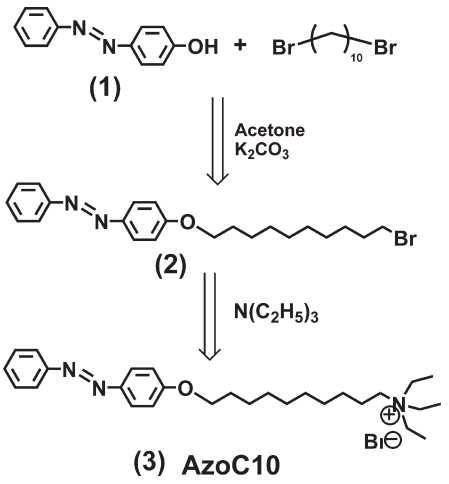

Figure 1. Synthetic route of AzoC10.

^{1}H NMR spectra were recorded using a JEOL JNM-ECA300 spectrometer. The electrospray ionization mass spectrometry (ESI-MS) was performed using a PE SciexAPI 3000 spectrometer. UV/vis and fluorescence spectra were obtained using Hitachi U-3010 and Hitachi F-7000 spectrophotometers, respectively. A high-pressure mercury lamp with an optical fiber and an intensity of 900 mW/cm^2 was used as the irradiation light source for photoisomerization of azobenzene. The two band-pass filters with the wavelengths 365 ± 10 and 450 ± 10 nm were used to produce the UV light (365 nm) and visible light (450 nm), respectively. To reduce the error in the kinetic measurement of photoisomerization, the solutions were irradiated in an in situ mode using the UV/vis spectrophotometer with the optical fiber. Additionally, to avoid the heat generated by light irradiation, the optical fiber was kept 3 cm away from the sample. The transmission electron microscopy (TEM) was performed on a JEMO 2010 electron microscope, operating at an acceleration voltage of 110 kV. The samples were prepared by drop-coating the aqueous solution on the carbon-coated copper grid and stained with 0.2% phosphotungstic acid hydrate before TEM observation. The dynamic light scattering (DLS) measurements were performed using ALV/DLS/SLS-5022F laser light scattering measurement system. The light wavelength was set at 633 nm, which is much longer than the absorption band of *trans*- or *cis*-azobenzene group. The fluorescent images were captured using an OLYMPUSBX 51 fluorescence microscope by straightly casting the block ionomer complex incorporating FNa, before or after UV irradiation, on a clean glass.

Preparation of the Block Ionomer Complex. To prepare the block ionomer complex, two precursors of AzoC10 and PEG_{43}-PAA_{153} were separately dissolved in water, and their concentrations were 2.0×10^{-4} M and 0.06 mg/mL, respectively. 0.5 mL of PEG_{43}-PAA_{153}, in which the molar concentration of carboxylate group is 7.3×10^{-4} M, was added in a tube, following with addition of AzoC10 solution and water until the total volume is 5 mL. The composition of the mixture (Z value) was expressed

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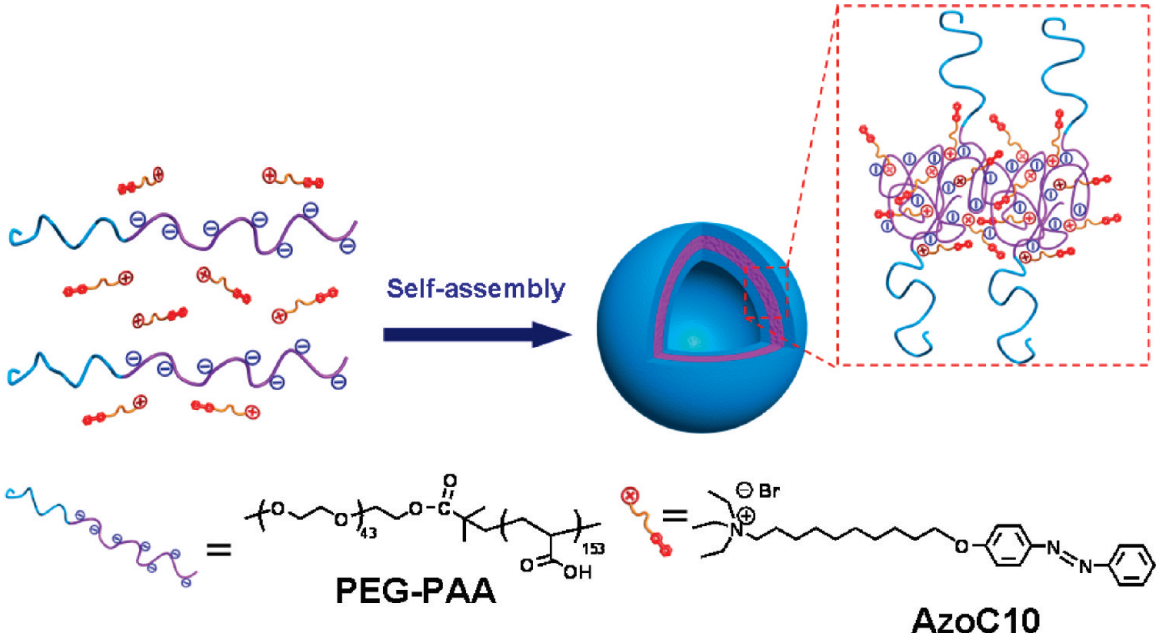
Scheme 1. Schematic Illustration of the Self-Assembly of the Block Ionomer Complex Vesicles



as the molar ratio of the positive-charged AzoC10 and negative-charged carboxylate groups of $PEG_{43}-PAA_{153}$, Z = [AzoC10]/[COO^-]. For example, when 2 mL of AzoC10 was mixed with 0.5 mL of $PEG_{43}-PAA_{153}$, and the mixture was further diluted by water to 5 mL, the final concentrations of carboxylate and AzoC10 were 7.3×10^{-4} and 8.0×10^{-4} M, respectively, and the Z value in the mixture solution was around 1.1.

Turbidity Measurements. The turbidity was measured at different Z values during titration of the corresponding polymers with AzoC10 in aqueous solution. The absorbance of the mixture solution at 550 nm was measured by a UV/vis spectrometer. The turbidity was calculated as turbidity $= 1 - 10^{-A}$, where A is the UV absorbance of the mixture.

Kinetic Photoisomerization of AzoC10. The reversible photoisomerization of azobenzene moiety is induced by alternating UV (365 nm) and visible light (450 nm) irradiation. Usually the photoisomerization of azobenzene group proceeds as the first-order reaction. The first-order plot for *trans*−*cis* photoisomerization is determined by the following equation:

$$\ln \frac{(A_0 - A_{eq})}{(A_t - A_{eq})} = k_t t$$

where A_0, A_t, and A_{eq} are the initial absorbance, the absorbance at time t, and the absorbance at the photostationary state of azobenzene group of AzoC10 at 340 nm, respectively; k_t is the rate constant of the *trans*−*cis* isomerization. For the *cis*−*trans* conversion of azobenzene, the kinetic equation needs to be changed to

$$\ln \frac{(A_{eq} - A_0)}{(A_{eq} - A_t)} = k_c t$$

in which k_c is the rate constant of the *cis*−*trans* photoisomerization.

Loading of Fluorescent Molecules. Taking fluorescein sodium (FNa) as an example, the loading procedure is described as follows. First, three components, 1 mL of FNa (1×10^{-4} M), 4 mL of AzoC10 (2×10^{-4} M), 1 mL of $PEG_{43}-PAA_{153}$ (0.06 mg/mL), and 4 mL of water were simply mixed together. The Z value in this mixture was equal to 1.1. Second, after stirring for half an hour, the mixture solution was dialyzed against water to remove the excess of FNa, which did not incorporate into vesicles. After 4 day dialysis (water changed twice every day), the separation of FNa was complete as confirmed by lack of fluorescence in the filtrate. No loss of the block copolymer was postulated because the pore size of semipermeable bag was small enough to prevent block copolymers from passing through. Based on this, the final Z value of the block ionomer complex was calculated using AzoC10 concentration (3.5×10^{-4} M) in the residue determined by the UV spectra, the initial amount of $PEG_{43}-PAA_{153}$ (0.06 mg), and the volume of the residue solution which was measured as 9.8 mL after the dialysis.

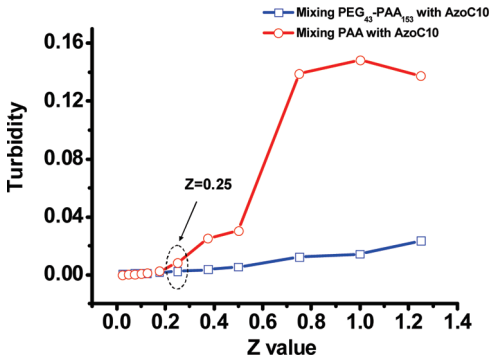


Figure 2. Turbidity of the mixtures of AzoC10 with the block copolymer $PEG_{43}-PAA_{153}$ and homopolymer PAA as a function of the molar ratio between AzoC10 and carboxylate groups of the polymer (Z value). [COO^-] = 7.3×10^{-5} M. The UV measurement was carried out by gradually increasing the concentration of AzoC10.

Results and Discussion

Formation of Block Ionomer Complex Vesicles. The strategy employed to prepare block ionomer complex vesicles is illustrated in Scheme 1. The azobenzene-containing surfactant, AzoC10, and the block copolymer, $PEG_{43}-PAA_{153}$, used herein as its sodium salt, are both water-soluble. Therefore, all experiments were carried out in aqueous solutions at pH 9.0. The concentrations of the reagents were set to ensure that at every Z value the concentration of AzoC10 was much lower than its cmc, which was measured as high as 1.3×10^{-4} M. This allowed avoiding self-assembly of AzoC10 alone. However, in the

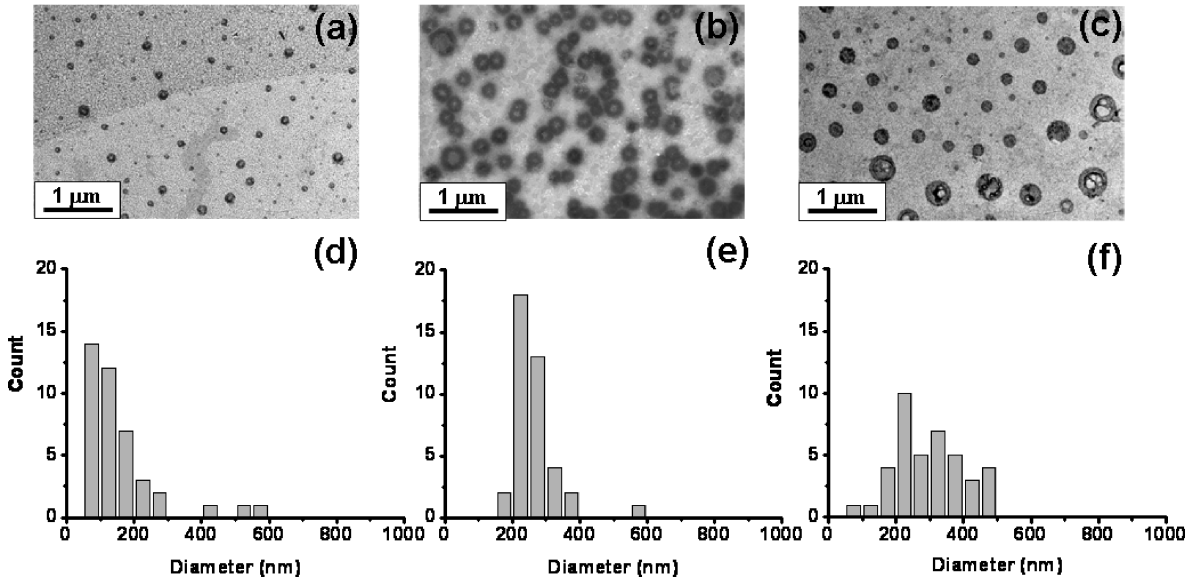


Figure 3. TEM observation of block ionomer complex vesicles (a) at $Z = 0.25$, (b) $Z = 0.5$, and (c) $Z = 1$ and the size distribution of block ionomer complex vesicles (d) at $Z = 0.25$, (e) $Z = 0.5$, and (f) $Z = 1$. The concentration of PEO_{43}−PAA_{153} is kept at 6×10^{-3} mg/mL, which corresponds to $[COO^-] = 7.3 \times 10^{-5}$ M.

presence of the PEG_{43}−PAA_{153} due to electrostatic complexation with PAA segment AzoC10 aggregated becoming a part of the block ionomer complex.

The critical Z value corresponding to the onset of the formation of the block ionomer complex was estimated from the turbidity measurements. As shown in Figure 2, the turbidity of the PEG_{43}−PAA_{153} and AzoC10 mixtures starts to increase slightly at $Z = 0.25$, suggesting formation of the colloidal aggregates. Even more pronounced are the turbidity changes in the case of the homopolymer PAA ($M_w = 2000$), which was used as the positive control to observe its association with AzoC10. In this case the onset of the turbidity increase was also observed at $Z = 0.25$. Furthermore, at $Z = 0.5$ the dispersion became highly turbid due to precipitation of an insoluble complex of PAA and AzoC10. In contrast, the complexes of PEG_{43}−PAA_{153} and AzoC10 did not precipitate, and the dispersion remained relatively clear at Z as high as 1.25. The difference in the aggregation behavior of the complexes formed by the block copolymer and homopolymer is noteworthy and suggests that contrary to PAA the PEG_{43}−PAA_{153} forms with AzoC10 small colloidal aggregates, which remain stable in dispersion. The TEM microphotographs suggest that these aggregates at various Z values are vesicles of nanoscale size (Figure 3). The formation of the vesicles was also independently confirmed using fluorescence probes as described further.

Photocontrolled Self-Assembly and Disassembly of the Vesicles. The data in Figure 4 demonstrate that the molecules of AzoC10 incorporated the block ionomer complex can undergo reversible photoisomerization. Specifically, upon irradiation with UV light of 365 nm for 300 s, the absorption band at around 340 nm decreased remarkably. Concomitantly the absorption band around 430 nm increased. These absorption bands at 340 and 430 nm are ascribed to π−π^* and n−π^* transitions, respectively. Therefore, the change of the absorption bands is indicative of the photoisomerization of AzoC10 from *trans*- to *cis*-form induced by UV irradiation. The opposite transition was observed upon irradiation of the *cis*-form by the visible light of 450 nm for 900 s. In this case the π−π^* absorption increased while the n−π^* absorption decreased. This suggests that AzoC10 inverts from *cis*- back to *trans*-form.

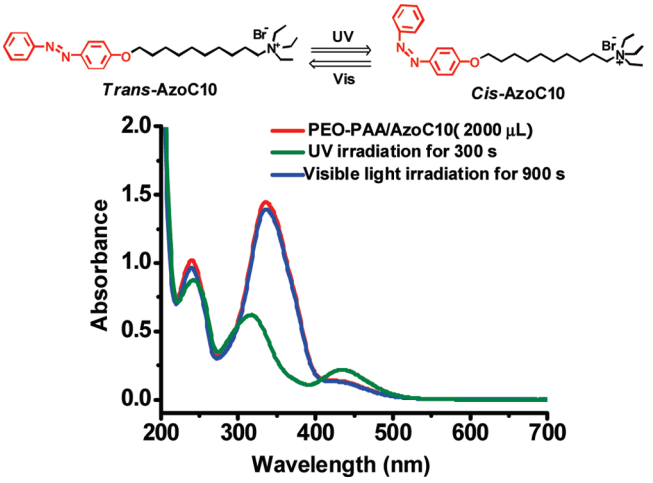


Figure 4. Photoisomerization of AzoC10 in the block ionomer complex vesicles ($Z = 1$). $[PEG_{43}$-$PAA_{153}] = 0.06$ mg/mL; $[AzoC10] = 8 \times 10^{-5}$ M which is below its cmc (1.3×10^{-4} M).

The TEM data suggest that the block ionomer complexes undergo drastic structural changes upon irradiation-induced photoisomerization of the surfactant. Specifically, the vesicles formed by the block copolymer and *trans*-form of AzoC10 in the case of $Z = 1$ appeared to be partially destroyed after UV irradiation (Figure 5a,b). This was accompanied by a substantial increase in the particle size. As shown in Figure 5c, before UV irradiation, the main diameter distribution of the block ionomer complex was around 80 nm. After UV irradiation, the number intensity decreased dramatically and the size of the particles increased to several hundred nanometers. Such remarkable changes in the morphology and size before and after UV irradiation must be related to the photoisomerization of the azobenzene moiety of AzoC10. A similar phenomenon was demonstrated by Zhao et al. in their azo-copolymers.[15] It is remarkable that the visible light irradiation of the block ionomer complex subjected to

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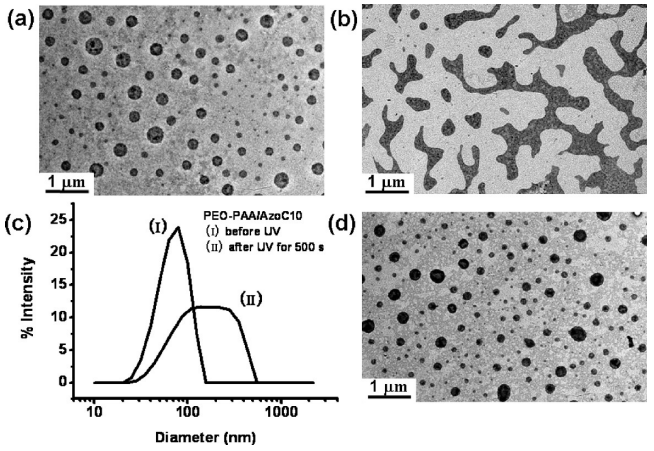

Figure 5. TEM images of the block ionomer complex (Z = 1) (a) before UV irradiation, (b) after UV irradiation for 300 s, and (c) DLS results: (I) before UV irradiation; (II) after UV irradiation. (d) The recovery of block ionomer complex after further visible light irradiation for 900 s.

prior UV irradiation appears to induce the recovery of the vesicle-like structures (Figure 5d). Moreover, we have tried two cycles to confirm the reversibility of assembly and disassembly.

To understand if the ratio between the block copolymer and AzoC10 can influence self-assembly and disassembly of vesicle-like aggregates, we changed the composition of the mixture to Z = 0.5; i.e., the concentration of AzoC10 is the half of that of carboxylate groups. As indicated by TEM observation in Figure 6a, the vesicles can also form under this condition. As shown by DLS, the main diameter distribution of the vesicles is around 70 nm (Figure 6b). Different from the previous case of Z = 1, the block ionomer complex vesicles at Z = 0.5 can be completely disassembled upon UV irradiation (Figure 6c). The complete disassembly is also supported by DLS, which shows no DLS signal in this case. Therefore, the block ionomer complex at Z = 0.5 is suitable for guaranteeing the fully reversible change of the vesicles before and after UV irradiation. When irradiated by visible light, the block ionomer complex vesicles can be reassembled again, as expected. (Figure 6d). However, as well as confirmed by DLS (Figure 6e), the size distribution increases slightly comparing with the original vesicles without light irradiation, although the mechanism behind is not fully understood.

The self-assembly and disassembly of block ionomer complex vesicles are also reflected by different photoisomerization kinetics of AzoC10 under various conditions. As shown in Table 1, the initial *trans*−*cis* photoisomerization rate constants (k_t) of AzoC10 in the presence of PEG_{43}−PAA_{153} are always lower than those of the absence of the copolymer. However, the *cis*−*trans* photoisomerization rate (k_c) of AzoC10 in the presence of the block copolymer after UV irradiation remains similar to that of free AzoC10. These data indicate that AzoC10 become densely packed upon incorporation in the block ionomer complex, responsible for the significant decrease of k_t. In the case of *cis*-form of AzoC10, it cannot well form aggregates with the block copolymer, which agrees well with the situation of disassembly as discussed above.

Loading and Release of Solutes in the Vesicles. FNa and sodium 1-pyrenesulfonate ($PySO_3Na$) were used as model fluorescent probes to evaluate whether the block ionomer complex vesicles can encapsulate and release guest molecules. The block ionomer complexes were prepared in the presence of the solutions of these probes. The mixtures were then dialyzed as described in the Methods section. As expected, the UV and fluorescence spectra clearly indicate that FNa remained in the vesicles after the dialysis (Figure 7a,b). Notably, part of AzoC10 was lost during the dialysis, resulting in the effective decrease of Z value from 1 to around 0.5. Nevertheless, as discussed above, the vesicles can be formed at such Z value, as shown in Figure 7c. Successful loading of FNa in the block ionomer complex vesicles is reinforced by fluorescence microscopy, as shown in Figure 7e. With the excitation wavelength at 500 nm, clear spherical aggregates were captured, which should be ascribed to the block ionomer complex vesicles encapsulating FNa. The apparently larger size of vesicles observed compared to TEM image may be due to the luminescence effect. Interestingly, after the UV irradiation of the block ionomer complexes the punctuate fluorescence was greatly diminished, suggesting that most of the vesicles were disintegrated which is confirmed by TEM observation (Figure 7d), and simultaneously, FNa was released (Figure 7f). Additionally, there was no effect of UV irradiation on the fluorescence intensity of FNa, indicating that there is no photobleaching that could contribute to a decrease of fluorescence in Figure 7d.

We have also confirmed that the block ionomer complex vesicles can be applied for loading of $PySO_3Na$. Contrary

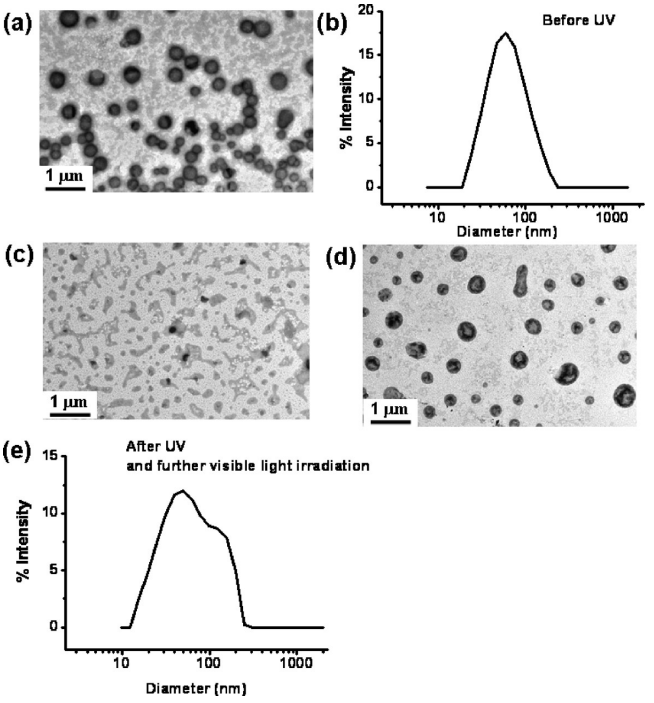

Figure 6. Formation of block ionomer complex vesicles (Z = 0.5) is indicated by (a) TEM observation and (b) DLS. (c) The vesicles are disrupted upon UV irradiation for 300 s. (d) TEM observation and (e) DLS result of the reassembled block ionomer complex vesicles by further visible light irradiation for 900 s.

Table 1. Photoisomerization of AzoC10 at Different Concentration in the Absence or Presence of the Block Copolymer

C(AzoC10) [M]	k_t [s^{-1}]	k_c [s^{-1}]
2×10^{-5} M	0.0840	0.0083
2×10^{-5} M (PEG_{43}−PAA_{153}, Z = 0.25)	0.0256	0.0084
4×10^{-5} M	0.0501	0.0050
4×10^{-5} M (PEG_{43}−PAA_{153}, Z = 0.5)	0.0220	0.0044
8×10^{-5} M	0.0321	0.0027
8×10^{-5} M (PEG_{43}−PAA_{153}, Z = 1)	0.0152	0.0031

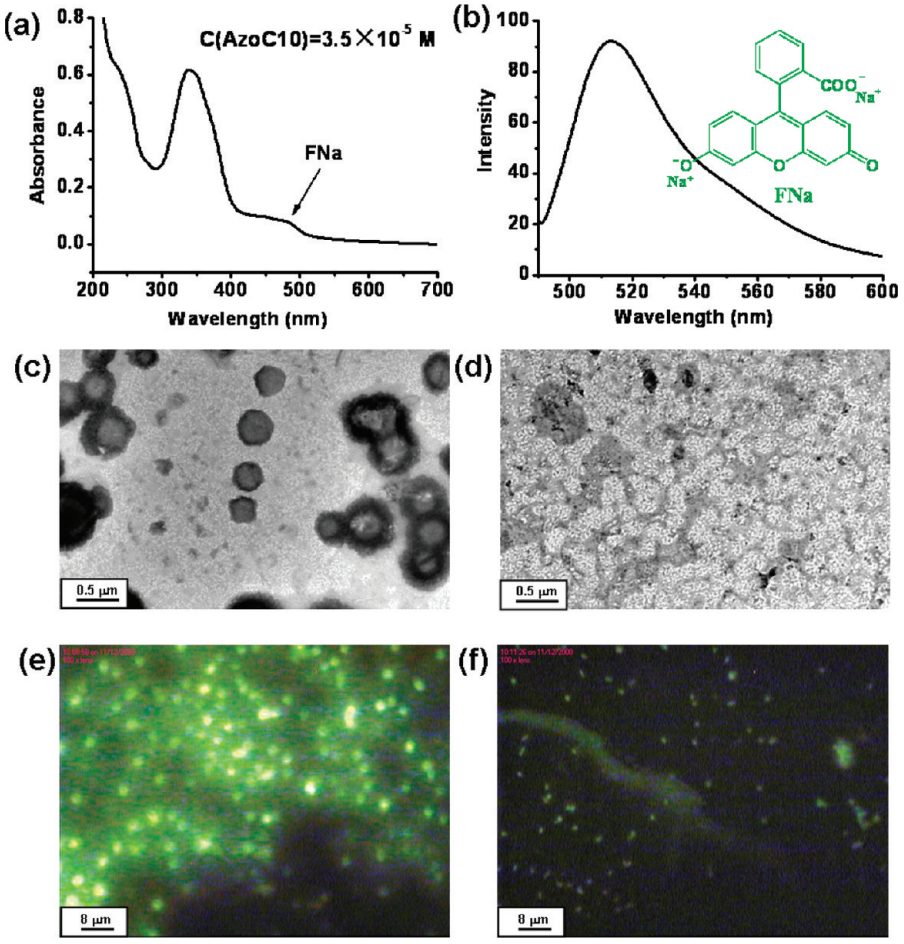

Figure 7. Encapsulation of and release of FNa in block ionomer complex vesicles demonstrated by (a) UV spectrum, (b) fluorescence spectrum (λ_{ex} = 485 nm), and (c, d) TEM images; (e, f) fluorescence microscopy images of the block ionomer complexes prepared in presence of FNa (a−c, e) before and (d) after UV irradiation.

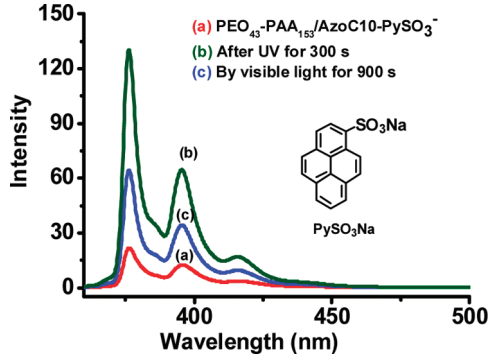

Figure 8. Fluorescence spectra (λ_{ex} = 339 nm) of the block ionomer complex vesicles encapsulating $PySO_3Na$: (a) before UV irradiation, (b) after UV irradiation, and (c) after visible light irradiation.

to FNa, $PySO_3Na$ has poor solubility in water and in the dispersions of the block ionomer complexes most likely would localize in the hydrophobic areas formed by the surfactant molecules. Since $PySO_3Na$ can be quenched by *trans*-azobenzene moiety (mainly because of energy transfer),[16] the fluorescence quenching of $PySO_3Na$ can be indicative of interaction of this probe with the surfactant structures containing *trans*-azobenzene. Indeed, as seen in Figure 8a, $PySO_3Na$ showed weak fluorescence in the presence of the block ionomer complex vesicles. However, after UV irradiation, the fluorescence increased, as shown in Figure 8b, because *cis*-azobenzene does not quench $PySO_3Na$. Moreover, upon visible light irradiation, the probe fluorescence decreased (Figure 8c), which is consistent with the restoration of the *trans*-form of AzoC10. However, since after the recovery the fluorescence intensity did not quench completely to the same level than that observed before UV-light irradiation, we speculate that part of $PySO_3Na$ was irreversibly released from the interior of the block ionomer complex vesicles.

Conclusion

In conclusion, we have demonstrated for the first time that a block ionomer complex can be obtained by electrostatic complexation between block copolymer and photoresponsive azobenzene-containing surfactant. More importantly, this block ionomer complex can form UV-responsive vesicles, which can be explored as supramolecular polymer nanocontainers for controlled loading and release of solutes. This represents a simple method for fabricating stimuli-responsive block ionomer complex vesicles. The method can be adopted for introducing different azobenzene-containing surfactants and even other stimuli-responsive moieties. By introducing stimuli-responsive surfactants into the block ionomer complex, one may broaden the application of this new class of supramolecular materials. Such

(16) Puntoriero, F.; Ceroni, P.; Balzani, V.; Bergamini, G.; Vögtle, F. *J. Am. Chem. Soc.* **2007**, *129*, 10714.

novel materials are of both basic and practical significance, especially as prospective nanocontainers for drug delivery.

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Supporting Information Available: Cmc measurement of AzoC10 and details for the kinetic photoisomerization of AzoC10 in different conditions. This material is available free of charge via the Internet at http://pubs.acs.org.