Photoisomerization

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Optical Switching of Self-Assembly: Micellization and Micelle–Hollow-Sphere Transition of Hydrogen-Bonded Polymers[**]

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One attractive goal of supramolecular chemistry is to control molecular self-assembly by an external stimulus. Temperature and pH are the stimuli that have been studied primarily, although light irradiation is regarded as the most reliable external stimulus as it involves only photochemical processes, which are energy-saving and easily controllable. The isomerization of photochromic groups, particularly azobenzene groups, is a well-known photochemical process that has been extensively studied.[1] Clearly, when azobenzene groups are incorporated into the building-block molecules, light-induced changes in the structure of the photochromic groups will affect their self-assembly behavior as the two isomers possess different properties. Most work in this field deals with small-molecule systems containing azobenzene photochromic units.[2] However, the use of photoisomerization as a stimulus-responsive procedure in the construction of polymeric self-assembly systems has been largely unexploited.

Recently, Zhao et al.[3] achieved reversible morphological changes in micelles of block copolymers containing azobenzene mesogens, induced by exposure to UV and visible light. Harada et al.[4] constructed a photoresponsive hydrogel system based on molecular recognition between cyclodextrin and azobenzene units. Hatton et al.[5] obtained the light-controlled gelation of hydrophobically modified poly(acrylic acid) and a surfactant containing azobenzene groups. Fréchet et al.[6] reported a micellar system sensitive to infrared light through a two-photon photoreaction. An ABA-type triblock copolymer film with azobenzene groups in the side chains was found to possess a reversible photocontrolled 2D microphase separation.[7] Clearly, it still remains a great challenge to explore reversible optical switching in the construction of various polymeric self-assembly systems.

In recent years our group has succeeded in developing "block-copolymer-free" strategies to construct polymeric micelles and hollow spheres by interpolymer-specific interactions.[8] We are now able to use homopolymers, random

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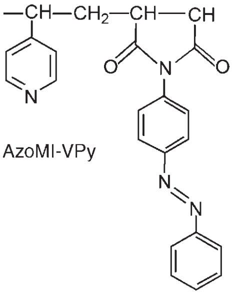
copolymers, and oligomers as building blocks to construct noncovalently connected micelles (NCCMs), in which core and shell are connected by hydrogen bonding only. Some of these NCCMs are highly sensitive to changes in temperature and pH.[8c,d] Herein, we report significant progress in the construction of NCCMs driven by the photoinduced isomerization of azobenzene groups incorporated into the polymer building blocks. Furthermore, reversible transition between micelles and hollow spheres is also achieved by the photoinduced isomerization.


AzoMI-VPy

Our photocontrollable self-assembly system contains a polymer pair comprising poly(4-phenylazomaleinanil-*co*-4-vinylpyridine) (AzoMI-VPy) and polybutadiene with a terminal carboxy group (CPB). The AzoMI-VPy synthesized by free-radical polymerization[9] contains azobenzene side groups that serve as photoresponsive units and pyridine residues as proton acceptors. The CPB with terminal carboxy groups as hydrogen-bonding donors was obtained by the free-radical polymerization of butadiene initiated by succinic peroxide.[10a]

Mixing of AzoMI-VPy and CPB in various ratios in their common solvent, toluene, is expected to give a soluble interpolymer complex through hydrogen bonding between the pyridyl and carboxy groups. Such complexation between these proton-donor and proton-acceptor groups was reported in our previous publications.[10] The transparent toluene solutions of the AzoMI-VPy/CPB interpolymer complex were then irradiated with UV light at room temperature and the process was monitored by UV/Vis spectroscopy. As shown in Figure 1, the absorption of *trans*-azobenzene (π–π* transition) becomes progressively weaker with increasing irradiation wavelength, with the peak shifting from about 330 to about 325 nm, while the absorption band near 440 nm (n–π* transition of *cis*-azobenzene) grows gradually stronger.

This result indicates isomerization of the *trans*-azobenzene group into *cis*-azobenzene.[3a,11] Meanwhile, this UV irradiation makes the solution turn faintly blue and opalescent, which indicates the formation of polymeric assemblies. AzoMI-VPy/CPB solutions over a broad range of composition and undergoing UV exposure for 30 min were studied by dynamic light scattering (DLS). The results (Table 1) showed that assembled particles with a diameter around 250 nm appeared in the solution. The UV-induced particles possess a relatively narrow size distribution; for example, a low polydispersity index (PDI) is obtained when the molar ratio of pyridyl units to carboxy units (AzoMI-VPy/CPB) is in the range from 1.0:0.4 to 1.0:1.0.

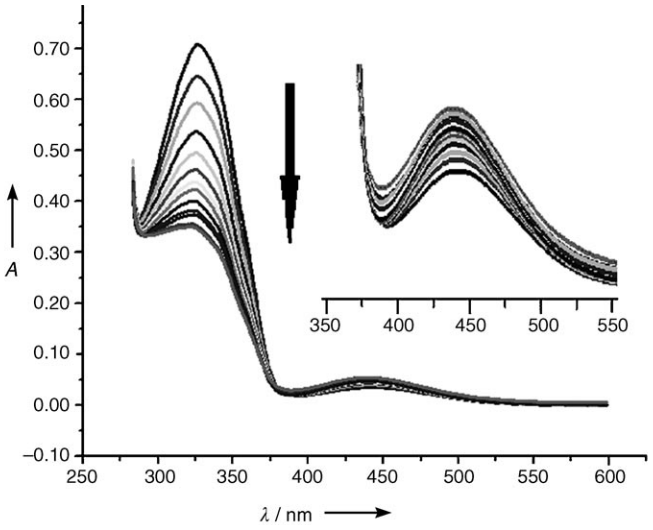


Figure 1. UV/Vis spectra of AzoMI-VPy/CPB (1.0:0.5) solutions, from the top down (visible part enlarged in insert, from the bottom up), for UV irradiation for 0, 3, 6, 9, 12, 15, 18, 21, 24, 27, 30, 33, and 36 min.

Scanning electron microscopy (SEM) revealed spherical particles with diameters around 200 nm in the UV-irradiated solutions (Figure 2 A), in agreement with the DLS results. To obtain an insight into the structure of the aggregate, we also carried out transmission electron microscopy (TEM) experiments. As shown in Figure 2 B, the aggregates are spherical with diameters around 100 nm, much smaller than the values from SEM and DLS. This difference may be caused by the low shell-to-background contrast as a result of the low chain density of the solvated CPB chains. This conjecture finds support from the TEM image shown in Figure 2 C, which shows that when the sample is stained with RuO_4, the particle size reaches about 180 nm as a result of the CPB shell becoming visible. This core–shell structure can further be revealed by the ^{1}H NMR spectrum of AzoMI-VPy/CPB (1.0:0.5) in deuterated toluene (see Supporting Information). The intensity ratio of the −CH= signal of CPB to that of the *o*-H of the azobenzene moiety of AzoMI-VPy is 13:1 when the two polymers are dissolved and form a soluble complex. After UV irradiation the ratio is dramatically increased to 96:1, as the proton signals of AzoMI-VPy drop sharply while those of the CPB remain unchanged. This finding demonstrates that in the micelles, the CPB chains remained soluble and formed the micellar shells, while the AzoMI-VPy chains aggregated and formed cores with low chain mobility.

On the basis of the above results, we may rationalize the photoinduced formation of micelles as follows. The AzoMI-VPy with azobenzene units in the *trans* conformation can be dissolved in nonpolar toluene. Under UV irradiation, the azobenzene units isomerize into the *cis* isomer with a higher polarity (Scheme 1), and thus the AzoMI-VPy tends to precipitate in the nonpolar toluene solvent.[9a,12] However, driven by the hydrogen bonding between the end carboxy group in CPB and the pyridyl group in AzoMI-VPy, the CPB chains may gather around the AzoMI-VPy aggregates and

Table 1: Characteristic data of the UV-induced micelles for various AzoMI-VPy/CPB molar ratios, measured by DLS.

ratio	1.0:0.1	1.0:0.2	1.0:0.3	1.0:0.4	1.0:0.5	1.0:0.6	1.0:0.7	1.0:0.8	1.0:0.9	1.0:1.0
D_h [nm]	211	216	217	236	231	230	258	256	253	212
PDI $[\mu_2/\langle \Gamma \rangle^2]$	0.50	0.28	0.19	0.17	0.080	0.025	0.12	0.12	0.046	0.13

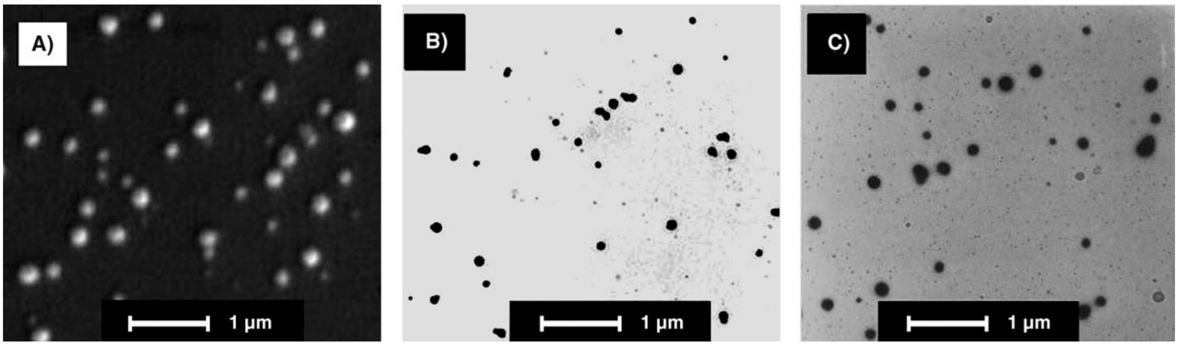
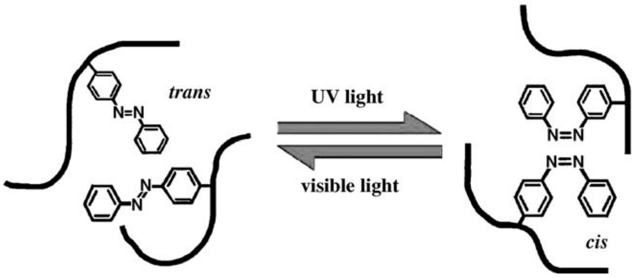


Figure 2. Morphology of UV-induced micelles of AzoMI-VPy/CPB (1.0:0.5) observed by SEM (A) and TEM (B) unstained; C) stained with RuO_4).



Scheme 1. Illustration of the UV-induced isomerization of azobenzene groups attached to polymer chains.

consequently stabilize them, thus forming stable core–shell micelles. The micellar structure in this case clearly differs from that of micelles of block copolymers, as the CPB shell and AzoMI-VPy core are linked by hydrogen bonding instead of covalent bonding; hence our appellation "noncovalently connected micelles".[8a]

When the solutions of UV-induced micelles were irradiated by visible light they turned transparent within a couple of minutes, which indicates dissociation of the micelles. The UV/Vis spectra showed that in this process, the *cis*-azobenzene groups returned to their *trans* state (Figure 3 A). As the *trans* form of azobenzene is thermodynamically more stable, the *cis*-to-*trans* isomerization can be achieved thermally as well.[13] We obtained the UV/Vis spectrum of the micelle solution at 40 °C in the dark as a function of time. As shown in Figure 3 B, over 30 min only a very small proportion of the azobenzene molecules in the *cis* form thermally reverted to the *trans* form, as the absorbance increased merely from 0.35 to 0.37 (A1 to B1). In contrast, under visible light the isomerization was almost complete within 3 min (A1 to A2), with the absorbance increasing to 0.70 and staying at that value with further irradiation. Clearly, under our experimental conditions, isomerization from the *cis* to the *trans* conformation was predominantly photoinduced.

A solution of the soluble complex is transparent whereas a micellar solution scatters light strongly, and thus a change in the turbidity of the solution is a good indicator of micellization or demicellization. As shown in Figure 4, the reversible changes in the turbidity of the solution caused by alternate UV and visible light irradiation proved that the micellization is a completely photoinduced reversible process.

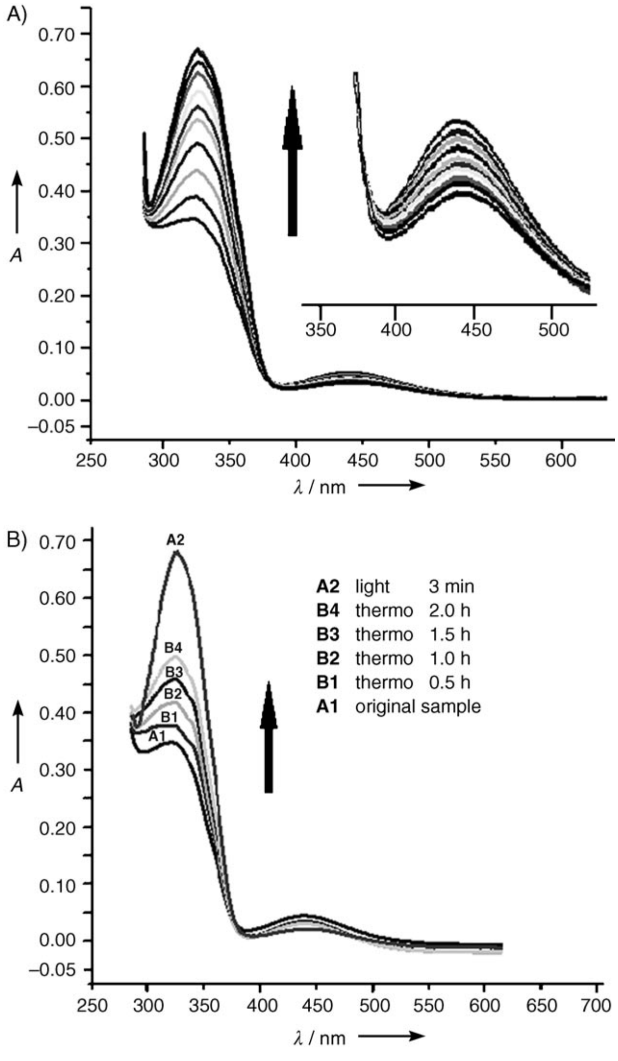


Figure 3. UV/Vis spectra A) of AzoMI-VPy/CPB (1.0:0.5) solutions, from the bottom up (visible part enlarged in the insert, from the top down), for visible light irradiation for 0, 20, 40, 60, 80, 100, 120, 140, 160, 180, and 200 s; B) showing visible-light and thermal (treatment at 40 °C) recovery.

Furthermore, the structure of the micelles induced by UV irradiation can be fixed simply through core cross-linking of the pyridyl groups with 1,4-diiodobutene at room temper-

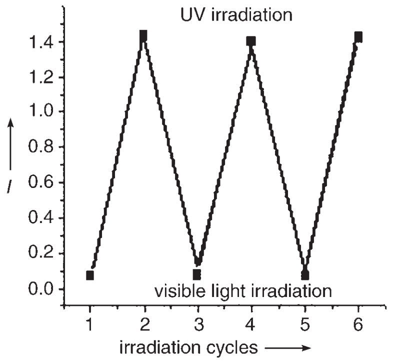


Figure 4. Turbidity of the AzoMI-VPy/CPB (1.0:0.5) solution under alternate UV and visible light irradiation.

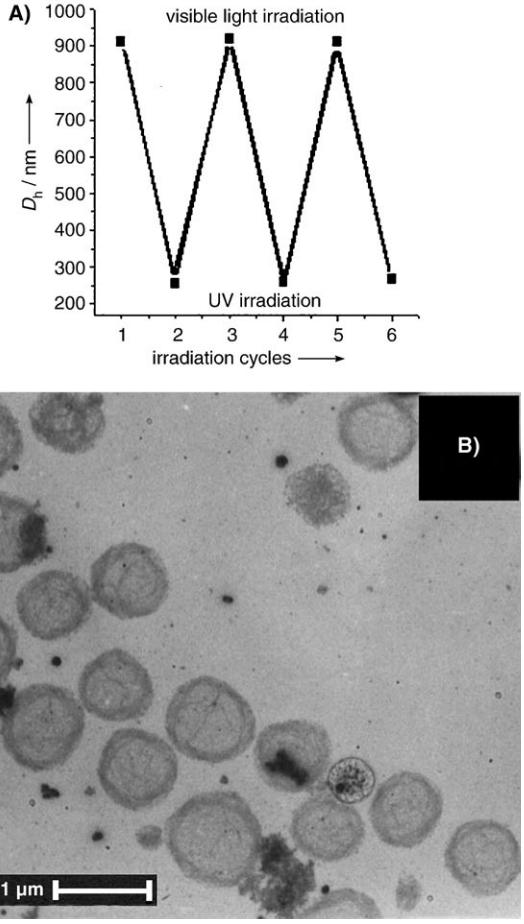


Figure 5. A) $\langle D_h \rangle$ of the micelle–hollow-sphere transition of an AzoMI-VPy/CPB (1.0:0.5) solution after cross-linking under alternate UV and visible light irradiation. B) TEM image of visible-light-induced hollow spheres of cross-linked AzoMI-VPy/CPB (1.0:0.5) micelles.

ature for 48 h.[14] As a control example, a micelle solution without the cross-linker was treated under the same conditions. After irradiation with visible light for 5 min, micellar structures were still maintained in the cross-linked sample, whereas the micelles were totally dissociated in the control sample and the solution turned transparent. Moreover, DLS revealed a dramatic increase in the size of the core-cross-linked micelles from 250 to about 900 nm under irradiation by visible light (Figure 5 A). This remarkable size expansion of the micelles can be attributed to isomerization of the azobenzene from the *cis* to the *trans* state, which gives the cross-linked AzoMI-VPy chains a much higher affinity to the solvent, thus making them greatly swelled.

In TEM experiments, the spheres irradiated with visible light showed a clear contrast between a dark periphery and a gray central part (Figure 5 B), typical of hollow spheres.[15,16]. When the solution was again irradiated with UV light, the hollow spheres collapsed and returned to micelles with diameters of about 250 nm (measured by DLS; Figure 5 A) as the *trans* isomer reverted to the *cis* isomer. The DLS measurements also indicate that the transition between micelles and hollow spheres induced by alternate UV and visible light irradiation is reversible (Figure 5 A). Thus, optical switching of the micelle–hollow-sphere transition was achieved.

As summarized in Figure 6, we have demonstrated that reversible optical switching of self-assembly can be achieved by the incorporation of azobenzene units into one of the polymeric building blocks, with the aid of the hydrogen-bonding interaction between the polymer pair of AzoMI-VPy and CPB. First, the AzoMI-VPy/CPB can form "graftlike" interpolymer complexes in toluene thanks to the hydrogen-bonding interaction between carboxylic acid and pyridine. The complex is soluble in toluene when the azobenzene units of AzoMI-VPy are in the *trans* conformation. Then under UV irradiation, the azobenzene units are transformed into the polar *cis* conformation and thus make the AzoMI-VPy chains aggregate. However, macroscopic precipitation is inhibited by the soluble CPB chains surrounding the AzoMI-VPy aggregates through hydrogen-bonding interactions. Thus, core–shell micelles are formed with a volume about 250 nm across. Upon irradiation with visible light, the micelles are quickly disassociated into a transparent interpolymer complex as the azobenzene *cis* form returns to the *trans* form.

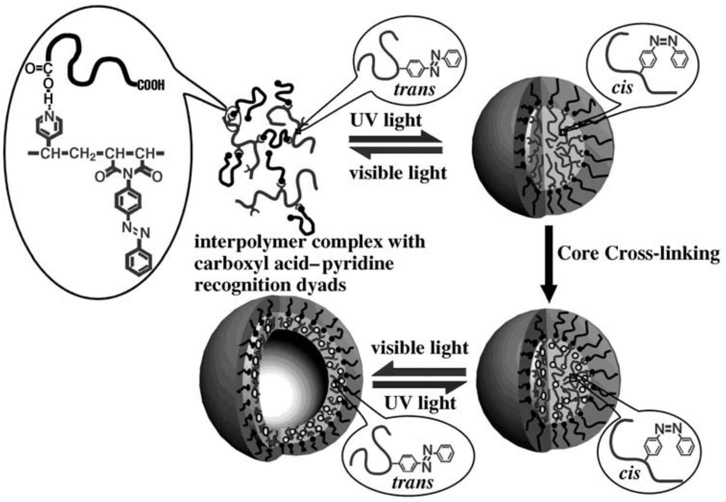


Figure 6. Illustration of the reversible photoinduced micellization and micelle–hollow-sphere transition of hydrogen-bonded polymers.

The UV-light-induced micelles can be readily cross-linked by the pyridyl units reacting with 1,4-diiodobutene. The core-cross-linked micelles respond to light irradiation with reversible and remarkable morphological changes: visible light causes the formation of hollow spheres as a result of intense swelling of the core as the *cis*-azobenzene turns into the *trans* form, while UV light causes the hollow spheres to return to micelles as a result of isomerization in the opposite direction. In short, we have achieved reversible optical switching of micellization and the micelle–hollow-sphere transition in a system containing common, readily prepared polymers.

Experimental Section

Polymer synthesis: CPB was prepared by the free-radical polymerization of butadiene initiated by succinic peroxide in solution. Most of the resultant polybutadiene chains carried carboxy groups at both ends because of the dominance of the combination termination of the propagating free radicals. The carboxy content determined by chemical titration was 0.561 mmol g^{-1}, and hence the calculated number-average molecular weight was 3565. The PDI obtained by gel permeation chromatography (GPC) with polystyrene standards was 2.85. AzoMI-VPy was synthesized by the free-radical polymerization of 4-vinylpyridine (10.0 mmol) and 4-phenylazomaleinanil (10.0 mmol) in 1,4-dioxane (20 mL) at 70 °C for 24 h in a 100-mL round-bottomed flask fitted with a nitrogen bubbler, with azobisisobutyronitrile as initiator (0.03 g, 0.2 mmol). The copolymer was isolated by precipitation into a fivefold excess of cold methanol, washed with methanol, and dried at 40 °C under reduced pressure. The number-average molecular weight was 1984 and the PDI obtained by GPC analysis with polystyrene standards was 2.39.

UV and visible light exposure: UV irradiation was carried out with a 300-W high-pressure mercury lamp coupled with UV filters ($<$360 nm). Irradiation by visible light was performed using a 200-W incandescent light bulb ($>$440 nm).

The fixation of micelles through core cross-linking was performed by adding an equivalent of 1,4-diiodobutene, based on the pyridine units in the micellar solution, and stirring the mixture at room temperature for 48 h in the dark.

Measurements: A Malvern Autosizer 4700 laser-light-scattering spectrometer, equipped with a multi-τ digital time correlator and a solid-state laser as light source, was used. All the DLS measurements were carried out at (25.0 ± 0.1) °C and at a scattering angle of 90°. UV/Vis spectra were recorded on a Perkin-Elmer Lamda 35 UV/Vis spectrophotometer. The turbidity of the micellar solutions was measured at 700 nm, which was far from the absorption of the azobenzene chromophore.

TEM experiments were performed on a Philips CM 120 electron microscope at an accelerating voltage of 80 kV. The specimens were prepared by placing the micelle solution (5 μL) on a copper grid and allowing it to dry in a desiccator. SEM was conducted with a Tescan 5136 MM scanning electron microscope. Samples were prepared by placing the micelle solution (5 μL) on freshly cleaved mica and allowing it to dry in a desiccator.

The molecular weights of the polymers were measured by Agilent 1100 size-exclusion chromatography with THF as the eluent. The ^{1}H NMR measurements were performed on a Bruker DMX500 spectrometer in dimethyl sulfoxide (or toluene) with tetramethylsilane as an internal reference.

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[16] On prolonging the cross-linking time to far more than 48 h, microspheres without a central cavity were observed by TEM. In our opinion, the strengthening of the cross-linking reaction enabled the reaction to occur in the center as well as the periphery of the core. Thus, slightly swollen micelles instead of hollow spheres were obtained (see Supporting Information).