How Can Azobenzene Block Copolymer Vesicles Be Dissociated and Reformed by Light?

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · DECEMBER 2005

Impact Factor: 3.3 · DOI: 10.1021/jp0524274 · Source: PubMed

4 AUTHORS, INCLUDING:

Guang Wang
Northeast Normal University
52 PUBLICATIONS **1,206** CITATIONS
SEE PROFILE

Armand Soldera
Université de Sherbrooke
95 PUBLICATIONS **896** CITATIONS
SEE PROFILE

How Can Azobenzene Block Copolymer Vesicles Be Dissociated and Reformed by Light?

Xia Tong, Guang Wang, Armand Soldera, and Yue Zhao*

Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

Received: May 10, 2005; In Final Form: September 8, 2005

The underlying mechanism of UV light-induced dissociation and visible light-induced reformation of vesicles formed by an azobenzene diblock copolymer was investigated. These processes were studied in situ by monitoring changes in optical transmittance of the vesicular solution while being exposed to UV or visible light irradiation. The results indicate that the UV-induced dissociation of the vesicles results from their thermodynamic instability due to a shift of the hydrophilic/hydrophobic balance arising from the trans−cis isomerization, while their reaggregation takes place upon visible light irradiation that shifts the hydrophilic/hydrophobic balance in the opposite direction after the reverse cis−trans isomerization. The study suggests a specific design principle for obtaining UV light-dissociable and visible light-recoverable vesicles based on azobenzene block copolymers. On one hand, the structure of azobenzene moiety used in the hydrophobic block should have a small (near zero) dipole moment in the trans form and a significantly higher dipole moment in the cis form, which ensures a significant increase in polarity of the hydrophobic block under UV light irradiation. On the other hand, the hydrophilic block should be weakly hydrophilic. The conjunction of the two conditions can make the light-induced shift of the hydrophilic/hydrophobic balance important enough to lead to the reversible change in vesicular aggregation.

Introduction

Micellar aggregates (including star micelles, crew-cut micelles, and vesicles) formed by amphiphilic block copolymers in aqueous solution have attracted much interest. In view of the potential for drug delivery application, polymer micelles responsive to changes in temperature[1,2] and, more particularly, in pH[3−7] have been the focus of many studies. Generally, polymers are designed in such a way that their micelles can be disrupted, thus triggering the release of encapsulated molecules, in acidic conditions with pH below the physiological pH 7.4, or at temperatures higher than the normal body temperature of about 37 °C. For example, to make polymer micelles sensitive to acidic pH, Gillies and Frechet used acid-labile acetal bonds in the structure of the hydrophobic block, whose cleavage at pH 5 increases the hydrophilicity of the block leading to the destabilization of micelles.[3] Deming et al. designed amphiphilic peptide block copolymers, for which a helix-to-coil conformational change of the hydrophobic block at pH 3 results in the disruption of vesicles.[4] pH sensitive dendritic core−shell nanocarriers were also designed and studied.[8] Regarding thermosensitive polymer micelles, the poly(*N*-isopropylacrylamide) (PNIPAAm)-based hydrophilic block is often used, whose lower critical solution temperature (LCST) can be adjusted to above 37 °C through copolymerization with a hydrophilic comonomer.[9] Those polymer micelles can be stable at $T <$ LCST, but are disrupted by the phase separation at $T >$ LCST.[1,2] Some noticeable recent developments include the design of block copolymers that are sensitive to both pH and temperature,[10] and polymer core−shell nanoparticles whose thermal sensitivity is tuned by its response to pH changes.[11] Other external stimuli investigated for the destabilization of polymer micelles include change in ionic strength,[12] oxidation reaction,[13] and ultrasound.[14]

Although many systems of light-responsive micellar aggregations based on small-molecule surfactants have been studied,[15−21] the use of light as an external stimulus to disrupt polymer micellar aggregates remains largely unexploited until now.[22,23] The photoactivity of azobenzene-containing surfactants or amphiphilic polymers is expected to arise from the trans−cis photoisomerization of the chromophore. Recently, we have reported the synthesis, through atom transfer radical polymerization (ATRP), of an amphiphilic diblock copolymer whose micellar aggregates (both core−shell micelles and vesicles) can be strongly disrupted by UV light and reassembled under subsequent visible light irradiation.[22] The hydrophobic block of this system, PAzo, is a methacrylate-based azobenzene-containing side-chain liquid crystalline polymer (Azo-SCLCP), while the hydrophilic block is a random copolymer of poly(*tert*-butyl acrylate-*co*-acrylic acid) (*t*BA-AA). Considering the fact that for azo block copolymers in the solid state, the liquid crystalline (LC) phases formed by azobenzene mesogens can remain in the nanometer scale, microphase-separated domains of the azo polymer even though the phase transition temperatures are likely to be affected by the confinement,[24−29] we speculated that for azo block copolymers forming micellar aggregates in solution, LC phases may survive in the compact regions of the hydrophobic Azo-SCLCP. We thus went on to suggest that the observed disruption of azo block copolymer micelles upon UV light irradiation could be due to the plasticization of the compact regions as a result of the light-induced LC-to-isotropic phase transition[30] that weakens the micelles and makes them easily dissociable.[22] However, we note that a recent work by Gan and co-workers found little effect of UV light irradiation on micelles formed by another azo amphiphilic block copolymer.[31]

It is safe to say that any parameter that is known to affect the formation of polymer micelles could be responsible for, or contribute to, the reaction to light of azo block copolymer

* Address correspondence to this author. E-mail: yue.zhao@usherbrooke.ca.

10.1021/jp0524274 CCC: $30.25
Published on Web 10/08/2005

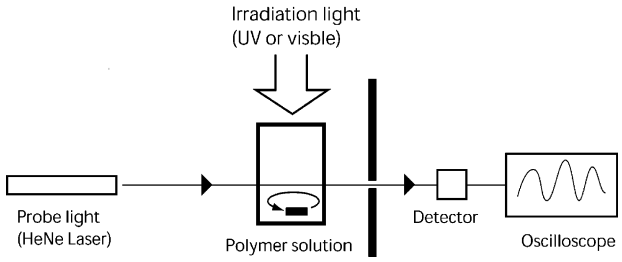
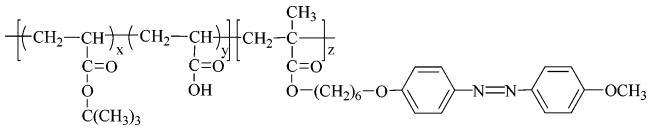


Figure 1. Schematic illustration of the setup used to measure changes in optical transmittance of the vesicle solution under UV or visible light irradiation, the shear effect on the solution being controlled by adjusting the speed of rotation of the stirring magnetic bar.

micelles if this parameter is influenced by the photoisomerization of azobenzene. It is important to understand the process of light-induced disruption of azo polymer micelles as well as the underlying mechanisms in order to establish the design principles for new amphiphilic azo polymers whose micelles would be strongly disrupted by light. With this in mind, we have carried out a detailed study on samples of PAzo-*b*-(*t*BA-AA). Using an optical setup, we have been able to monitor the processes of UV and visible light-induced changes in polymer vesicles in situ. Even without ruling out the possible optical plasticization effect, the results of this study point to a dominant effect arising from the conjunction of a change in polarity of azobenzene moieties on the hydrophobic block, resulting from the trans−cis photoisomerization, with the relative strength of hydrophilicity of the hydrophilic block. This effect may alter the hydrophilic/hydrophobic balance enough to dissociate or reform the micelles under UV or visible light irradiation.

Experimental Section

Details on the synthesis and characterization of the amphiphilic diblock copolymer PAzo-*b*-(*t*BA-AA) (structure shown below) have been reported previously.[22] Two samples were chosen for the present study. Unless otherwise stated, the results discussed in this paper were obtained with use of a sample designated as $PAzo_{74}$-*b*-($t BA_{46}$-AA_{22}), i.e., it contains about 74 units of Azo in the hydrophobic block and, in the hydrophilic block, 46 units of *t*BA and 22 units of AA. According to the scanning (SEM) and transmission electron microscope (TEM) observations, both core−shell micelles and vesicles formed by adding water in dioxane solution of this sample could be reversibly disrupted and reformed upon alternating UV and visible light irradiation of the micellar solution.[22] A second sample, designated as $PAzo_{31}$-*b*-($t BA_{19}$-AA_{33}), was also used for comparison.



The optical setup utilized to monitor the processes of disruption and reformation of polymer vesicles in solutions exposed to UV or visible light irradiation is given in Figure 1. A low-power He−Ne laser (633 nm, 4 mW) was used as the probe light to measure the optical transmittance of the micellar solution, about 1.5 mL of which was placed in a standard quartz cuvette, with a small magnetic bar for stirring (the stirring plate beneath the cuvette is not drawn). The stirring rate could be adjusted by changing the speed of rotation of the magnetic bar. The irradiation UV or visible light was applied vertically from the top of the cuvette (∼5 cm distance). A UV−visible spot curing system (Novacure) was used to produce UV (∼360 nm) and visible light (∼440 nm) by changing the filter; the intensity of irradiation, measured at these wavelengths by a powermeter, could be adjusted. The spot of irradiation was about 1 cm^2, which covered the whole opening of the cuvette. By using a nontransparent plate with a small hole (∼2 mm diameter) allowing only the probe laser beam to pass, the irradiation light, which could scatter by the vesicular solution, had no effect on the transmitted intensity of the probe light measured by a high-speed photodetector (Displaytech). The digital oscilloscope (Tektronix, TDS 420A) connected to the photodetector could thus record changes in transmittance of the vesicular solution under UV or visible light irradiation. To have large changes in optical transmittance, unless mentioned otherwise, polymer vesicles formed in the dioxane/water mixture were not diluted or quenched by adding an excess volume of water.

With use of a Hitachi S-4700 Field-Emission-Gun scanning electron microscope operating at 3 KV, SEM was also used to observe changes in the morphology of micellar aggregates obtained by casting the solution, either without or after UV or visible light irradiation, on a silicon wafer, followed by drying at room temperature. The results were correlated with the optical measurements.

Results and Discussion

The reliability of the optical setup was first examined with a vesicle solution of $PAzo_{74}$-*b*-($t BA_{46}$-AA_{22}), prepared by adding 16% of water in a dioxane solution (v/v) with the initial polymer concentration of 1 mg mL^{-1}.[22] As can be seen from Figure 2, after UV light (18 mW cm^{-2}) was applied to the solution under stirring, the optical transmittance increased and reached a plateaulike value after about 20 s; longer UV irradiation then only resulted in a very slight increase in transmittance. This behavior is consistent with UV light-induced dissociation of polymer vesicles, which reduces the scattering of the probe light as a result of the reduced number and/or size of the aggregates. When the irradiation was switched to visible light (440 nm, 24 mW cm^{-2}; it took ∼10 s to change the filter), the optical transmittance dropped quickly, suggesting the reformation of the aggregates in the solution. The transmittance after 50 s of visible light exposure remained slightly higher than the initial transmittance (before UV irradiation). The changes as implied by the optical measurement were confirmed by SEM observations on samples cast from the solution before UV irradiation (marked by A in Figure 2), after 40 s of UV irradiation (B) and after 40 s of visible irradiation (C). SEM images show the formation of polymer vesicles in A, the disappearance of vesicles in B, and the reformation of vesicles in C. The average size of the aggregates reformed under visible light exposure appears to be a little smaller than that in the initial solution, which accounts for the slight difference in optical transmittance. This is likely to be caused by the short period of time available for polymer vesicles to recover. Also shown in Figure 2 is the result of a control test. The transmittance of the same polymer solution without addition of water, thus with no vesicles, was recorded under the same conditions (before and after UV and visible irradiation). While the reversible trans−cis photoisomerization of azobenzene moieties on the dissolved block copolymer took place, no meaningful changes in transmittance of the solution were observed. The results in Figure 2 unambiguously confirm that the optical setup can be used to follow in situ the processes of UV light-induced dissociation and visible light-induced reformation of polymer vesicles. However, the sensitivity of the setup is not good enough to monitor changes in transmittance

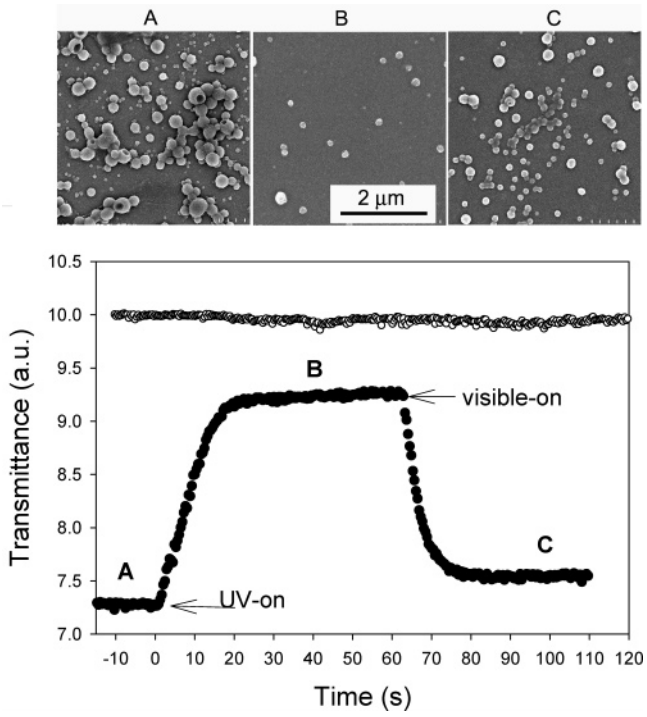


Figure 2. Changes in transmittance for a vesicle solution of $PAzo_{74}$-*b*-(*t*BA_{46}-AA_{22}) exposed to UV (360 nm, 18 mW cm^{-2}) and visible (440 nm, 24 mW cm^{-2}) light irradiation, vesicles being formed by adding 16%, in volume, of water in a dioxane solution with initial polymer concentration of 1 mg mL^{-1}. Typical SEM images (with the same scale bar) for samples cast from the solution at different times indicated in the figure show the vesicles before irradiation, their dissociation under UV irradiation, and the reformation after visible light exposure. For comparison, also shown is the transmittance of the diblock copolymer solution in dioxane (no water added to induce the aggregation) subjected to the same conditions of UV and visible light irradiation. The abscissa of time is shifted to have the origin correspond to the application of UV irradiation.

related to the formation of small core−shell micelles (∼15 nm) of the copolymer. Therefore, the study reported herein was focused on larger polymer vesicles.

As mentioned in the Introduction, to explain the UV light-induced dissociation of polymer vesicles (also core−shell micelles), we initially speculated an optical plasticization of the compact hydrophobic compartments resulting from the LC-isotropic phase transition related to the trans−cis isomerization of azobenzene mesogens.[22] In other words, the kinetic stability of the aggregates would be decreased owing to softened compact regions, which make them easily breakable. Should this be the case, it would be expected that the rate of dissociation of polymer vesicles under UV light irradiation should be sensitive to the rate of stirring of the solution that provides the shearing force to break the vesicles. And if the kinetic stability were the only factor, no dissociation of polymer vesicles would be expected to occur in the absence of any shear effect, i.e., the solution is still with no stirring. Using the same UV irradiation intensity of 18 mW cm^{-2}, we recorded the change in optical transmittance of the vesicular solution with no stirring and with stirring at different rates by adjusting the rotation speed of the magnetic bar between about 50 and 300 rmp (Figure 3). Before the UV irradiation was turned on, the vesicular solution had the same transmittance regardless of the stirring rate, indicating that the shear effect under the mixing conditions could not break the polymer vesicles. Data of transmittance for different stirring rates in Figure 3 are shifted along the ordinate to better show the changes under the UV light irradiation. For the still solution,

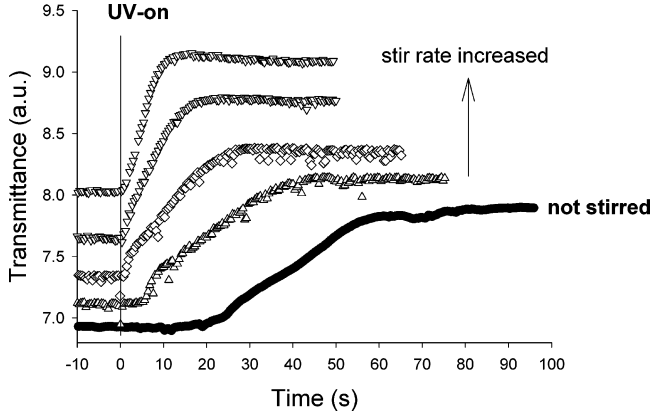


Figure 3. Changes in transmittance of the vesicle solution of $PAzo_{74}$-*b*-(*t*BA_{46}-AA_{22}) subjected to UV light irradiation (18 mW cm^{-2}), the solution being still (with no stirring) and stirred by a magnetic bar at different speeds of rotation (about 50, 100, 200, and 300 rpm). Data of transmittance for different stirring rates are shifted along the ordinate for the sake of clarity.

after the UV irradiation was applied, it showed no change in transmittance during the first 20 s; then the transmittance increased gradually over the next 40 s or so to reach the plateau. For stirred solutions, the process of vesicle dissociation became faster as the stirring rate increased. Even with the slowest stirring rate, the apparent induction period of ∼20 s before the beginning of the dissociation observed for the still solution was reduced to about 6 s. At higher stirring rates, the process took place once the UV irradiation was applied. With the various stirring rates used, the time of UV irradiation for the completion of the vesicle dissociation process ranges from about 40 to 10 s. The occurrence of UV light-induced dissociation of polymer vesicles in the solution with no stirring, i.e., in the absence of any shear effect, suggests that a weakened kinetic stability of the vesicles due to the trans−cis isomerization of azobenzene mesogens would not be the cause; rather the vesicles in the still solution under UV irradiation become thermodynamically unstable, which leads to their dissociation. The effect of the stirring rate on the rate of the vesicle dissociation process is also understandable. On one hand, when polymer vesicles become thermodynamically unstable as azobenzene moieties are converted to the cis isomer, a stronger shear effect arising from a higher stirring rate should speed up the breaking of the aggregates and thus reduce the time needed for the polymer to reach the equilibrium state. On the other hand, considering the strong absorption of the azobenzene chromophore,[22] with the large volume of the vesicular solution used in the experiment (∼1.5 mL) and the low irradiation intensities, it is likely that only azobenzene moieties in the vesicles located in a region a short distance from the surface of the solution (Figure 1) would be excited and undergo the trans−cis photoisomerization (the actual distance varies as a function of polymer concentration and irradiation intensity). This means that a faster mixing at a higher stirring rate should allow all azobenzene moieties to be exposed to the UV irradiation more quickly and, consequently, complete the vesicle dissociation process in a shorter period of time.

For the same reasons, a similar effect of the stirring rate on the process of reformation of polymer vesicles upon visible light irradiation, which induces the reverse cis−trans isomerization of azobenzene mesogens, is no surprise. The results in Figure 4 were obtained by applying a visible light irradiation of the same intensity (24 mW cm^{-2}) on the polymer solution, whose vesicles were beforehand dissociated by UV light, with no stirring and under different stirring rates. Similar to the

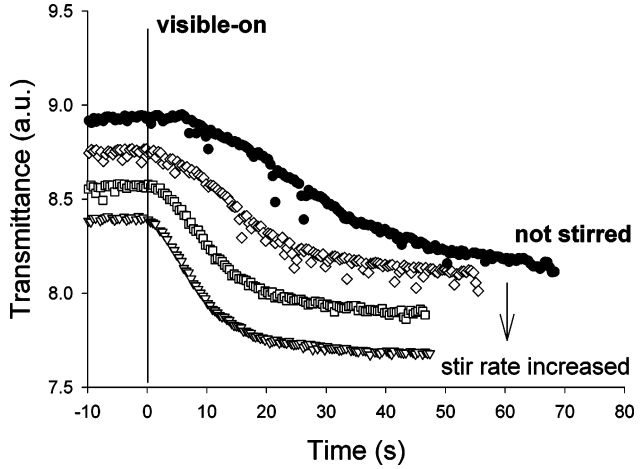


Figure 4. Changes in transmittance of the clear solution of $PAzo_{74}$-*b*-(*t*BA_{46}-AA_{22}) subjected to visible light irradiation (24 mW cm^{-2}), the solution being still and stirred by a magnetic bar at different speeds of rotation (about 100, 200, and 300 rpm). For each set of experiments, the clear solution was obtained after the dissociation of vesicles by UV irradiation. Data of transmittance for different stirring rates are shifted along the ordinate for the sake of clarity.

dissociation process (Figure 3), before visible light was turned on, the transmittance of the clear solution showed no change under the various stirring rates (data in Figure 4 are shifted for the sake of clarity), while it decreased due to the reformation of the vesicles after visible light was applied. Even in the still solution, polymer vesicles can reform, but it takes longer than in solutions under stirring. The rate of the reformation process increases with increasing the stirring rate of the solution.

With a constant stirring rate (~200 rpm of the magnetic bar), the intensity of UV and visible light irradiation can also be used to change the rates of dissociation and reformation, respectively, of polymer vesicles. Figure 5 shows the results obtained with three different intensities of UV irradiation for the dissociation process (Figure 5a) and visible irradiation for the reformation process (Figure 5b). In both cases, the kinetic process becomes faster with increasing the irradiation intensity. This effect can easily be understood by the fact that increasing the irradiation intensity can increase the number of azobenzene mesogens being excited and undergoing the trans−cis or the reverse cis−trans isomerization, which should speed up any changes associated with the photoisomerization process. Also shown in Figure 5b are changes in optical transmittance of the solution, after the UV irradiation was turned off, in the absence of visible light irradiation while keeping the probe He−Ne laser on the solution. No noticeable change occurred over 160 s, indicating that the probe light (633 nm) had no influence on the reverse cis−trans isomerization of azobenzene mesogens. Actually, after 1 h of illumination with the He−Ne laser, there was only ~3% decrease in transmittance of the solution, revealing the appreciable thermal stability of azobenzene moieties in the cis form. Significant decrease in transmittance was recorded only after much longer times as a result of thermally induced cis−trans isomerization (~50% decrease after 4 h).

As mentioned earlier in the discussion of the results in Figure 3, the dissociation of polymer vesicles in the still solution (with no stirring) under UV irradiation suggests that the vesicles become thermodynamically unstable as a result of the trans−cis isomerization of azobenzene mesogens on the PAzo block, even though a possible decrease of the mechanical stability of the vesicles due to an optical plasticization effect could not be ruled out. This would be possible if the content of water in dioxane needed to induce the vesicle aggregation became

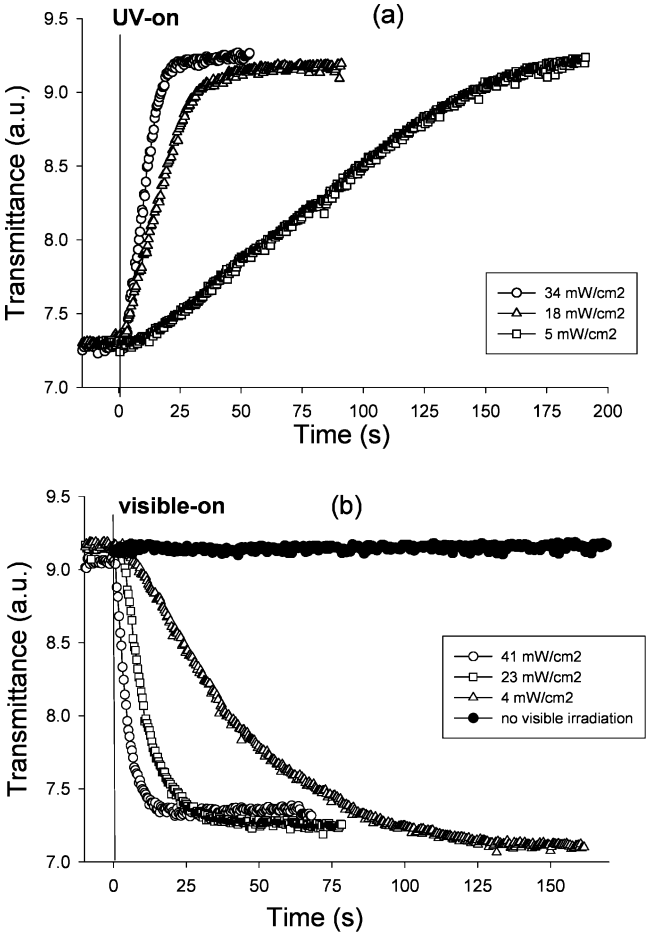


Figure 5. Transmittance vs time for the vesicle solution of $PAzo_{74}$-*b*-(*t*BA_{46}-AA_{22}) (a) under UV irradiation of different intensities (for the process of dissociation of vesicles) and (b) under visible light irradiation of different intensities (for the process of reformation of vesicles), the same stirring rate (about 200 rpm) being used for all the measurements. For comparison, also shown in part b are changes in transmittance for the solution under only the probe light (He−Ne laser, 633 nm) illumination with no visible light irradiation applied.

significantly higher under UV irradiation. Using the optical setup, we measured changes in transmittance as a function of water content (% in volume with respect to the volume of dioxane) for solutions without and with UV irradiation; the results are shown in Figure 6. In two separate experiments, 2 mL of dioxane solution with an initial polymer concentration of 1 mg mL^{-1} was placed in the cuvette (Figure 1); after each addition of a small amount of water, in one case, the solution was stirred for 3 min before the transmittance was measured, while in the other case, the solution was stirred under UV light irradiation (18 mW cm^{-2}) for 3 min, then UV was turned off and the transmittance of the solution was recorded. In the absence of UV irradiation, the transmittance starts to decrease significantly after addition of about 13% of water, which would correspond to the formation of polymer vesicles. The water content to induce core−shell micelles could not be noticed due to the limited sensitivity of the setup. For the solution exposed to UV light, indeed, the apparent polymer aggregation process begins at a much higher water content of about 21%, and the transmittance drops more quickly than for the solution without UV irradiation.

SEM observations were made on samples prepared from the two solutions with three different water contents marked by letters in Figure 6, and representative images were shown in Figure 7. For the solution without UV irradiation, core−shell

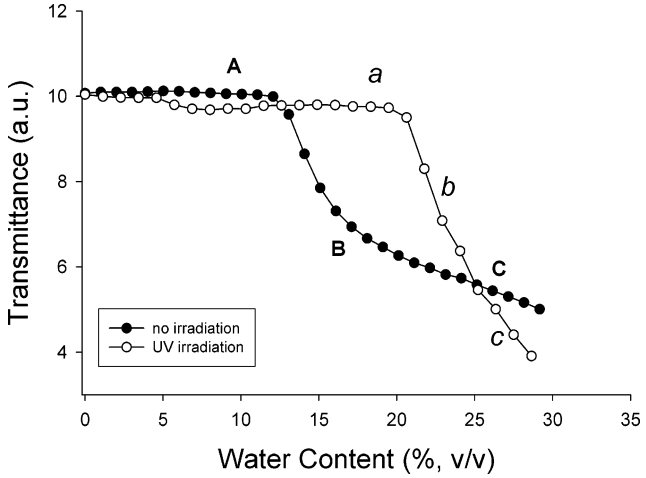


Figure 6. Transmittance vs water content added to the dioxane solution of $PAzo_{74}$-*b*-(*t*BA_{46}-AA_{22}) (initial concentration, 1 mg mL^{-1}) without and with UV light irradiation. Polymer aggregation states in both solutions with three different water contents indicated by letters were observed by SEM.

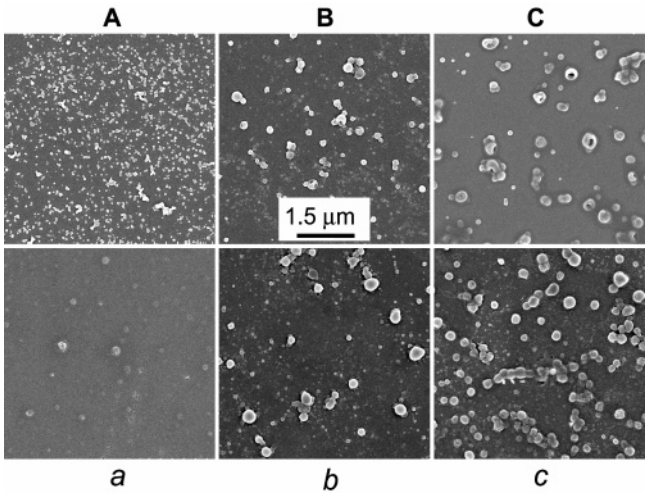


Figure 7. SEM images of polymer aggregates in solutions indicated in Figure 6. The scale bar is the same for all images.

micelles were formed with 10% water (image A). The drop of optical transmittance resulted from the transformation of core−shell micelles into much larger vesicles, as revealed by the morphologies of aggregates in solutions with 15% and 26% of water (images B and C). By contrast, with the solution exposed to UV light, no core−shell micelles were formed even at 19% of water; only a few larger aggregates were observable (image a). As the water content increased to above 21%, the aggregation of polymer took place, resulting in aggregates with similar sizes to the vesicles observed in the solution without UV irradiation. The increase in water content from 23% (image b) to 26% (image c) mainly increased the number of the aggregates, some of which looked like vesicles. The results in Figures 6 and 7 corroborate well with the UV light-induced dissociation of polymer vesicles prepared with 16% of water, and their reformation upon visible light irradiation. Under the conditions used (solvent and initial polymer concentration), Figure 6 indicates that vesicles formed at water content between about 15% and 20% would display strong optical dissociation and reformation. Vesicles formed at higher water content cannot be disrupted by UV light because of the aggregation of the polymer under UV irradiation. Using the same experimental conditions but a different solvent, tetrahydrofuran (THF) instead

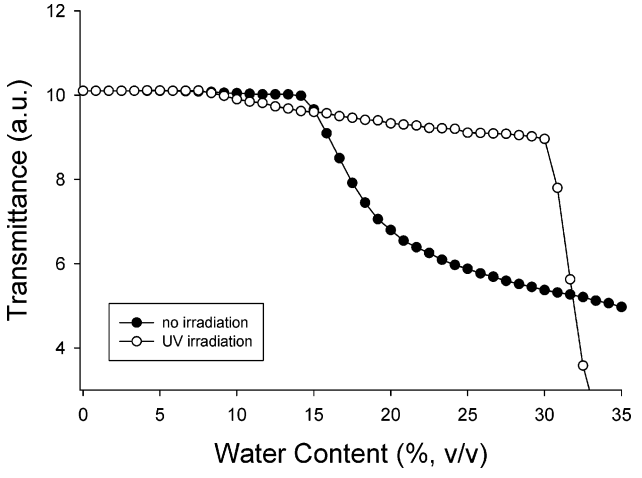


Figure 8. Transmittance vs water content added to the tetrahydrofuran solution of $PAzo_{74}$-*b*-(*t*BA_{46}-AA_{22}) (initial concentration, 1 mg mL^{-1}) without and with UV light irradiation.

of dioxane, the results in Figure 8 confirm the increase in the water content needed to induce the formation of vesicles in the solution exposed to UV light. With THF as solvent, the change is even greater, which means a larger window for optical dissociation and reformation of polymer vesicles. It is seen from Figure 8 that the drop of transmittance was observed at about 15% in the solution without UV irradiation, while this critical water content increased to 30% for the solution irradiated by UV light.

The above results basically indicate that the vesicles formed by the diblock copolymer of $PAzo_{74}$-*b*-(*t*BA_{46}-AA_{22}) can become unstable and be dissociated when azobenzene mesogens on the hydrophobic block undergo the trans−cis isomerization upon UV irradiation. A shift of the hydrophilic/hydrophobic balance arising from the configurational change of azobenzene would explain the thermodynamic instability of the vesicles. For the azobenzene molecule with no substituents attached to it, the trans−cis isomerization is known to result in a significant increase in dipole moment, from 0 D (no dipole moment) for the trans isomer to 3 D for the cis isomer.[32] The azobenzene moiety used in our block copolymer has a methoxy group on the 4′ position and is linked to the methacrylate backbone via an alkyl group on the 4 position. The nearly same substituents in the para positions should give the azobenzene moiety a very small dipole moment in the trans form, while the dipole moment of the bent cis isomer should increase.

Using 4,4′-dimethoxyazobenzene as the model compound, we have calculated the dipole moment of the cis configuration by means of the Density Functional Theory (DFT) formalism using the DMol3[33] program (from Accelrys) under the Materials Studio 3.2 environment. The RBPE[34] gradient corrected functional for exchange and correlation terms was used, and the numerical Double Numerical plus Polarization (DNP) was considered as the basis set, which is equivalent in size and quality to the extended 6-31G(d,p). DFT calculations were first performed on the cis configuration of azobenzene with no substituents; a dipole moment of 3.2 D was obtained, which is in good agreement with the reported value of 3 D.[32] In the case of 4,4′-dimethoxyazobenzene, due to symmetry the trans configuration exhibits a zero-dipole moment. The cis configuration, however, shows three minima (one is doubly degenerated) depending on the dihedral angles of the two methoxy groups. Figure 9 shows the lowest energy conformation and summarizes the results of calculation including the relative energy and the dipole moment components along the three axes (μ_x, μ_y, and μ_z

φ (deg.)	ϕ (deg.)	Energy (kJ/mol)	μ_x (D)	μ_y (D)	μ_z (D)
-0.3	-0.3	0.0	0.00	0.00	-1.36
178.7	178.7	0.4	0.00	0.00	-5.37
1.8	178.5	1.2	1.80	-1.53	-4.35
178.3	1.6	1.2	-1.80	1.53	-4.36

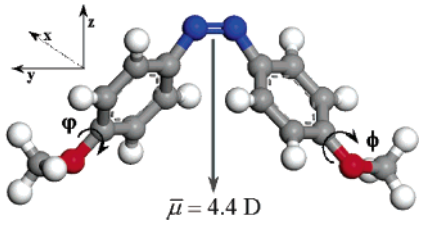


Figure 9. Lowest energy conformation of 4,4′-dimethoxyazobenzene in the cis form (N blue, O red, C gray, H white). The calculated relative energies and dipole moment components of the four stable conformations are shown, with the total dipole moment being computed as the average over the four conformations.

in debye) for each of the conformations. For the calculation, the molecule was oriented with the two nitrogen atoms being placed along the *y*-axis and the center of mass of the molecule forming the *yz*-plane with the two nitrogen atoms. Considering that the barrier height is in the order of 15.5 kJ/mol, and that the difference in energy between the minima is small as compared to *kT* at room temperature, the total dipole moment of the cis configuration was taken as the average over the four conformations and computed according to the following equation:

$$\bar{\mu} = \sqrt{(\overline{\sum_{\text{conf}} \mu_x})^2 + (\overline{\sum_{\text{conf}} \mu_y})^2 + (\overline{\sum_{\text{conf}} \mu_z})^2}$$

where the summation runs over the four conformations, and the upper bar represents the average. As indicated in Figure 9, the obtained dipole is directed along the *z*-axis, with a magnitude of 4.4 D.

The results of this calculation thus confirm that upon UV light irradiation, the conversion from trans to cis configuration can result in a significant increase in dipole moment of pendant azobenzene mesogens of the diblock copolymer. This means that when UV light induces the trans−cis isomerization, the polarity of the hydrophobic PAzo block forming the compact region of micellar aggregates could increase significantly, which alters the hydrophilic/hydrophobic balance and thus destabilizes the aggregates. From this analysis it becomes clear that the substituents on azobenzene would be important. Many azo polymers have strong electron-donor and electron-acceptor groups on azobenzene (for use, for example, as chromophores for nonlinear optical materials), for which the trans isomer has a larger dipole moment than the cis isomer.[35] If such an azobenzene polymer is used as the hydrophobic block in amphiphilic block copolymers, it can be expected that irradiation would have little disruption effect on micellar aggregates, since the change in polarity resulting from the trans−cis isomerization should shift the hydrophilic/hydrophobic balance in the opposite direction that is unfavorable to dissociation of the aggregates.

A significant increase in dipole moment of azobenzene moieties on the hydrophobic block under UV irradiation is necessary but may not be enough to lead to the dissociation of micellar aggregates. Indeed, another sample of the block copolymer $PAzo_{31}$-*b*-(*t*BA_{19}-AA_{33}) was found to display limited response to UV and visible light irradiations. As compared to

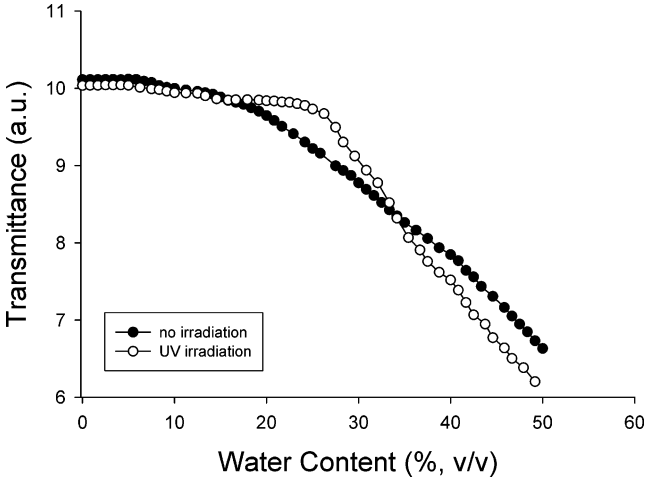


Figure 10. Transmittance vs water content added to the dioxane solution of $PAzo_{31}$-*b*-(*t*BA_{19}-AA_{33}) (initial concentration, 1 mg mL^{-1}) without and with UV light irradiation.

$PAzo_{74}$-*b*-(*t*BA_{46}-AA_{22}), the second sample has a much shorter hydrophobic PAzo block and a more hydrophilic block due to the relative length and the higher ratio of the number of AA units to that of *t*BA units. Using the same conditions as in Figure 6, the optical transmittance of the dioxane solution of $PAzo_{31}$-*b*-(*t*BA_{19}-AA_{33}), both without and with UV light irradiation, was measured as a function of water content. The results in Figure 10 show much smaller differences between the two solutions. For this sample, only large micelle-like aggregates (∼200 nm) coexisting with core−shell micelles (∼15 nm) were observed by adding water in dioxane solution; UV and visible light irradiation only resulted in changes in the number of aggregates.[22] The same increase in dipole moment for azobenzene mesogens takes place in this sample upon UV light irradiation, but the resulting increase in polarity of the PAzo block is not important enough to alter significantly the hydrophilic/hydrophobic balance due to the stronger hydrophilicity of the *t*BA-AA block. Therefore, it appears that the prominent light-induced dissociation and reformation observed for the vesicles of $PAzo_{74}$-*b*-(*t*BA_{46}-AA_{22}) were the result of an increase in polarity of the hydrophobic PAzo block in conjunction with the weakness of hydrophilicity of the hydrophilic block (the relative length and chemical nature). Under such a conjugation, the reversible trans−cis isomerization of azobenzene moieties can alter reversibly the hydrophilic/hydrophobic balance in the two directions, which determines the state of aggregation of the diblock copolymer.

Although the light-induced change in thermodynamic stability of the polymer vesicles has been found to be the primary cause of their dissociation and reformation, we note that a possible contribution from an optical plasticization effect due to the LC-isotropic phase transition of azobenzene mesogens, or simply from the change in their packing state as a result of the photoisomerization process, cannot be ruled out. Investigations aiming at elucidating these effects are underway in our laboratory, and the results will be reported at due time.

Concluding Remarks

This study suggests a specific principle for the designing of amphiphilic azobenzene block copolymers whose vesicular aggregates can be strongly disrupted by light. First, the azobenzene chromophore in the structure of the hydrophobic block should have a significant increase in dipole moment when it converts from the trans to the cis configuration upon UV

irradiation. For this, azobenzene moieties with the same substituents on the para positions would be most useful. Azobenzene structures with strong electron-donor and electron-acceptor groups should not be used in this design due to the opposite change in dipole moment. Second, the hydrophilic block should be weakly hydrophilic, though enough to induce polymer aggregation in block-selective solvents. Reducing the length of the hydrophilic block with respect to the hydrophobic block could control this parameter. The conjugation of the two conditions is necessary. Since polymer vesicles are generally formed by amphiphilic block copolymers whose hydrophobic block is much longer than the hydrophilic block, applying this design principle would be effective to obtain polymer vesicles that can be dissociated and reformed upon UV and visible light irradiation.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada, le Fonds québécois de la recherche sur la nature et les technologies of Québec is acknowledged. We are grateful to the Centre for Self-Assembled Chemical Structures (Quebec) and le Centre d'étude en matériaux optiques et photoniques de l'Université de Sherbrooke (CEMOPUS). A.S. also thanks Canadian Funds for Innovation for technical support.

References and Notes

(1) Chung, J. E.; Yokoyama, M.; Yamato, M.; Aoyagi, T.; Sakurai, Y.; Okano, T. *J. Controlled Release* **1999**, *62*, 115.
(2) Chung, J. E.; Yokoyama, M.; Okano, T. *J. Controlled Release* **2000**, *65*, 93.
(3) Gillies, E. R.; Frechet, J. M. J. *Chem. Commun.* **2003**, 1640.
(4) Bellomo, E. G.; Wyrsta, M. D.; Pakstis, L.; Pochan, D. J.; Deming, T. J. *Nat. Mater.* **2004**, *3*, 244.
(5) Bae, Y.; Fukushima, S.; Harada, A.; Kataoka, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 4640.
(6) Liu, F.; Eisenberg, A. *J. Am. Chem. Soc.* **2003**, *125*, 15059.
(7) Tang, Y.; Liu, S. Y.; Armes, S. P.; Billingham, N. C. *Biomacromolecules* **2003**, *4*, 1636.
(8) Haag, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 278.
(9) Taillefer, J.; Jones, M.-C.; Brasseur, N.; Van Lier, J. E.; Leroux, J.-C. *J. Pharm. Sci.* **2000**, *89*, 52.
(10) Schilli, C. M.; Zhang, M.; Rizzardo, E.; Thang, S. H.; Chong, Y. K.; Edwards, K.; Karlsson, G.; Muller, A. H. E. *Macromolecules* **2004**, *37*, 7861.
(11) Soppimath, K. S.; Tan, D. C.-W.; Yang, Y.-Y. *Adv. Mater.* **2005**, *17*, 318.
(12) Zhang, L.; Eisenberg, A. *Macromolecules* **1996**, *29*, 8805.
(13) Napoli, A.; Valentini, M.; Tirelli, N.; Muller, M.; Hubbell, J. A. *Nat. Mater.* **2004**, *3*, 183.
(14) Rapoport, N.; Pitt, W. G.; Sun, H.; Nelson, J. L. *J. Controlled Release* **2003**, *91*, 85.
(15) Shin, J. Y.; Abbott, N. L. *Langmuir* **1999**, *15*, 4404.
(16) Porcar, I.; Perrin, P.; Tribet, C. *Langmuir* **2001**, *17*, 6905.
(17) Shum, P.; Kim, J.-M.; Thompson, D. H. *Adv. Drug Delivery Rev.* **2001**, *53*, 273.
(18) Orihara, Y.; Matsumura, A.; Saito, Y.; Ogawa, N.; Saji, T.; Yamaguchi, A.; Sakai, H.; Abe, M. *Langmuir* **2001**, *17*, 6072.
(19) Einaga, Y.; Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *J. Am. Chem. Soc.* **1999**, *121*, 3745.
(20) Shang, T.; Smith, K. A.; Hatton, T. A. *Langmuir* **2003**, *19*, 10764.
(21) Lee, C. T.; Smith, K. A.; Hatton, T. A. *Macromolecules* **2004**, *37*, 5397.
(22) Wang, G.; Tong, X.; Zhao, Y. *Macromolecules* **2004**, *37*, 8911.
(23) Jiang, J.; Tong, X.; Zhao, Y. *J. Am. Chem. Soc.* **2005**, *127*, 8290.
(24) Mao, G.; Wang, J.; Clingman, S. R.; Ober, C. K.; Chen, J. T.; Thomas, E. L. *Macromolecules* **1997**, *30*, 2556.
(25) Tian, Y.; Watanabe, K.; Kong, X.; Abe, J.; Iyoda, T. *Macromolecules* **2002**, *35*, 3739.
(26) Cui, L.; Zhao, Y.; Yavrian, A.; Galstian, T. *Macromolecules* **2003**, *36*, 8246.
(27) Tong, X.; Cui, L.; Zhao, Y. *Macromolecules* **2004**, *37*, 3101.
(28) Cui, L.; Tong, X.; Yan, X.; Liu, G.; Zhao, Y. *Macromolecules* **2004**, *37*, 7097.
(29) Han, Y.-K.; Dufour, B.; Wu, W.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 9355.
(30) Ikeda, T.; Tsutsumi, O. *Science* **1995**, *268*, 1873.
(31) Ravi, P.; Sin, S. L.; Gan, L. H.; Gan, Y. Y.; Tam, K. C.; Xia, X. L.; Hu, X. *Polymer* **2005**, *46*, 137.
(32) Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915.
(33) Delley, B. J. *J. Chem. Phys.* **1990**, *92*, 508.
(34) Hammer, B.; Hansen, L. B.; Norskov, J. K. *Phys. Rev. B* **1999**, *59*, 7413.
(35) Perdersen, T. G.; Johansen, P. M.; Pedersen, H. C. *J. Opt. A. Pure Appl. Opt.* **2000**, *2*, 272.