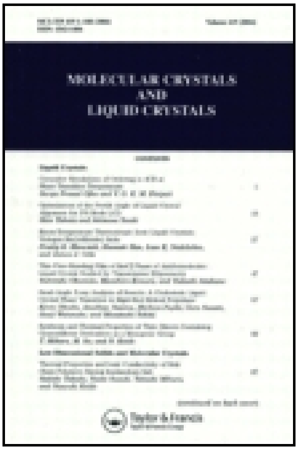

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Self-Assembly and Photoresponsive Behavior of Amphiphilic Diblock Copolymers Containing Azobenzene Moieties

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Self-Assembly and Photoresponsive Behavior of Amphiphilic Diblock Copolymers Containing Azobenzene Moieties

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*An amphiphilic diblock copolymer, poly(ethylene oxide)-*block*-poly {6-[4-(4-ethoxyphenylazo)phenoxy] hexyl methacrylate}, was synthesized using atom transfer radical polymerization. In the solution of tetrahydrofuran and water, the diblock copolymer formed micrometer scale vesicles by self-assembly. Under the irradiation of UV light at 365 nm, these microvesicles generated such photoresponsive behavior as photoinduced expansion, swelling and fusion due to* trans-cis *photoisomerization of azobenzene units. The self-assembled vesicles even enlarged to be about five times their original size because of photoinduced fusion.*

Keywords: amphiphilic block copolymer; azobenzene; microvesicle; photodeformation; self-assembly

INTRODUCTION

Due to *trans-cis* photoisomerization of azobenzene moieties, azo polymers materials have been reported to show various photoresponsive properties, such as photodeformation [1–4], surface relief gratings [5], change on wettability [6] and association/dissociation of aggregates in the solutions [7]. They have been extensively investigated in recent years, because these photoresponsive polymers are promising for application in sensors, actuators, artificial muscles, optical data-storage and other photodriven devices [8–9].

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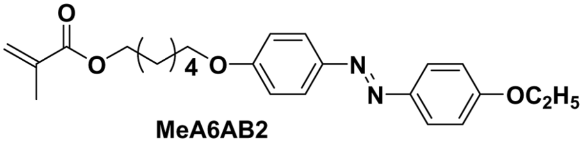
On the other hand, there has recently been a growing focus on self-assembly systems of amphiphilic block copolymers, including the block copolymers containing aromatic azobenzene chromophores, because they can form various nano- or micro- aggregates in the solutions and the ordered periodic structures in the solid state by self-assembly [10,11]. A large number of works indicate that such self-assembled aggregation states as micelles, vesicles, spheres and rods are determined by many factors, including selection of suitable solvents, the ratio of hydrophilic to hydrophobic segments, concentration, etc [12–14]. It is well known that vesicles have many potential applications, such as carriers of drug or specific chemical species, protective shells for cells or enzymes, containers and reactors. Especially those vesicles that can cause a corresponding change in response to external stimuli like temperature, pH, solvent composition, ionic strength, electric field and light attract much attention [15,16]. Compared to other stimuli, light has more advantages, because it may provide a rapid, remote and actuate control to the responsive materials. Therefore, photoresponsive vesicles or micelles have attracted increasing interest. Most of them have been prepared from the amphiphilic copolymers containing azobenzene moieties by atom transfer radical polymerization (ATRP) or reversible addition-fragmentation transfer (RAFT) polymerization [7,17–20]. For example, Zhao and coworkers reported the preparation of a copolymer containing hydrophobic polymethacrylate with azobenzene moieties in the side groups and hydrophiphilic poly(acylic acid) by ATRP and selective hydrolyzation [7]. Zhang and coworkers synthesized diblock copolymers based on acrylic acid and azobenzene monomer by RAFT polymerization [20]. Moreover, a random copolymer composed of hydrophiphilic poly(acylic acid) units and hydrophobic azobenzene-containing acrylate units was also prepared [21]. The aggregates formed by these copolymers showed interesting photoresponsive behavior caused by the photoisomerization of azobenzene chromophores.

In this work, we synthesised an amphiphilic azobenzene diblock copolymer by ATRP, which consists of a hydrophilic poly(ethylene oxide) (PEO) segment instead of above-mentioned poly(acylic acid) and an azobenzene-cantaining liquid crystalline (LC) polymethacrylate (PAzoMA). With this diblock structure, firstly, nonionic PEO block cannot be influenced by pH and the ionic strength of aqueous solution; secondly, hydrophobic PAzoMA LC block is easy to form regular aggregation and compact packing, which are favorable for the diblock copolymer to generate a self-assembled regular structure when added to water; thirdly, azobenzene mesogens can exhibit a photoresponsive property [22–24]. Microvesicles were prepared through the



MeA6AB2

FIGURE 1 Structure and abbreviation of the azobenzene monomer.

self-assembly of the copolymer in the solution of tetrahydrofuran (THF) and H_2O. Their photoresponsive behavior including expansion, swelling and fusion was also investigated.

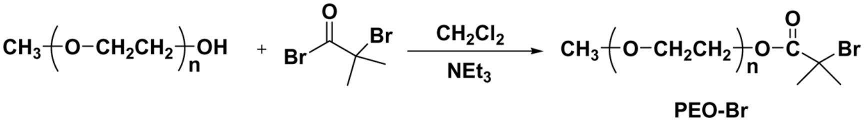
EXPERIMENTAL

Materials

2-Bromo-2-methylpropionyl bromide (Alfa Aesar), copper (I) bromide (Aldrich) and methacryloyl chloride (Tokyo Kasei Co.) were used without further purification. Polyethylene glycol monomethylether ($M_n = 1900$) was obtained from Alfa Aesar, which was dried by azeotropic distillation with toluene before use. All the solvents were freshly distilled before use. The ligand tris[2-(dimethylamino)-ethyl]amine (Me6Tren) used for ATRP was synthesized according to the literature [25]. The azobenzene monomer 6-[4-(4-ethoxyphenylazo) phenoxy]-hexyl methacrylate (MeA6AB2) shown in Figure 1 was synthesized according to the procedure similar to the reported method [26,27]. ^{1}H-NMR (500 MHz, $CDCl_3$): δ: 1.5–1.8 (m; 11H, $–O–CH_2–C\underline{H}_3$, $–O–CH_2–(C\underline{H}_2)_4–CH_2–O–$), 1.9 (s; 3H, $–CH_2{=}C(C\underline{H}_3)–$), 4.0–4.2 (m; 6H, $–O–C\underline{H}_2–CH_3$, $–O–C\underline{H}_2–(CH_2)_4–C\underline{H}_2–O–$), 5.5 (d; 1H, *trans*–$C\underline{H}_2{=}C(CH_3)–$), 6.1 (d; 1H, *cis*–$C\underline{H}_2{=}C(CH_3)–$), 7.0 (m; 4H, –Ar), 7.9 (m; 4H, –Ar). FTIR (KBr), cm^{-1}: 1710 v(C=O)(–COO–), 1640 v(C=C) ($C{=}CH_2$), 1250 v(C–O–C) (–COO–), 1050 v(C–O–C) (C–O–Ar).

Synthesis of PEO-Br Macroinitiator

The synthesis of the macroinitiator is shown in Scheme 1. Polyethylene glycol monomethylether (5.0 g, 0.26 mmol) and triethylamine

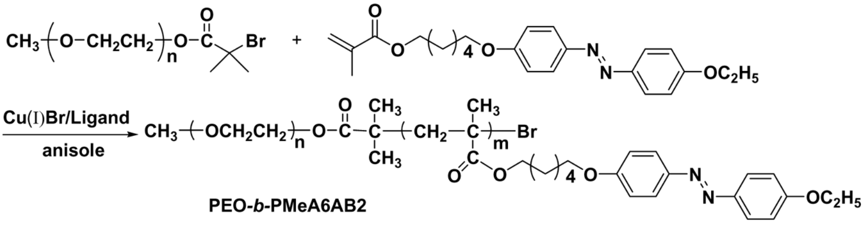


SCHEME 1 Synthetic route of PEO-Br macroinitiator.

(NEt_3, 1 mL) were mixed in dichloromethane (CH_2Cl_2, 50 mL) at 0°C. With stirring, a solution of 2-Bromo-2-methylpropionyl bromide (1 mL) in 20 mL CH_2Cl_2 was added dropwise. After this addition completed, the mixture was stirred at room temperature for 48 h. The reaction mixture was poured into water. Then the organic layer was collected and further washed with hydrochloric acid (1 M) and sodium hydroxide (1 M) aqueous solution successively and dried over anhydrous magnesium sulfate. After being concentrated, the solution of crude product was reprecipitated in ethyl ether for several times. After recrystallization from ethanol, the final product was dried in vacuum to give white solid powder of PEO-Br (2.0 g). Yield: 40%. M_n (GPC) = 5200, $M_w/M_n = 1.15$. ^1H NMR (500 MHz, $CDCl_3$): δ 1.94 (s, 6H, $BrC(CH_3)_2$), 3.38 (s, 3H, OCH_3), 3.64 (s, 4*n*H, OCH_2CH_2).

Synthesis of Diblock Copolymer

The synthetic route of the diblock copolymer of poly(ethylene oxide)-*block*-poly{6-[4-(4-Ethoxyphenylazo)phenoxy] hexyl methacrylate} (PEO-*b*-PMeA6AB2) is shown in Scheme 2. The preparation was performed with Cu(I)Br complexed with Me6Tren as the catalyst and PEO-Br as the macroinitiator. In a 25-mL Schlenk reaction flask, PEO-Br (0.2 g, 0.04 mmol), Cu(I)Br (6 mg, 0.04 mmol) and MeA6AB2 (0.3 g, 0.7 mmol) were added, degassed and filled with argon. Me6Tren (16 μL, 0.06 mmol) in deoxygenated anisole (4 mL) was added through a syringe. The mixture was degassed three times using freeze-thaw-pump cycles and sealed. Finally, the flask was placed in an oil bath at 70°C for 48 h. Conversion was determined as 92% by ^1H-NMR. The solution was then diluted with THF and passed through an alumina column in order to remove the metal complex. After being concentrated, it was reprecipitated in methanol for three times. The yellow product was collected by filtration and dried under vacuum. Yield: 280 mg (56%). M_n (GPC) = 17700, $M_w/M_n = 1.48$.



SCHEME 2 Synthetic route of PEO-*b*-PMeA6AB2 diblock copolymer.

Preparation of Microvesicles

PEO-*b*-PMeA6AB2 was dissolved in THF to obtain a solution with the initial concentration of 2.0 $mg{\cdot}mL^{-1}$. The solution was stirred overnight and then settled for 48 h at room temperature. The self-assembly was performed by adding Milli-Q water into the THF solution at a rate of 5 $\mu L{\cdot}s^{-1}$ with durative stirring. Self-assembled microvesicles were obtained when the content of water reached 25 vol %.

Measurements

Content of the block containing azobenzene moieties in the diblock copolymer was determined by ^1H NMR. Molecular weight and polydispersity ($PDI = M_w/M_n$) of PEO-Br and PEO-*b*-PMeA6AB2 were measured by gel permeation chromatography (GPC) with a Shimadzu system equipped with RID-10A Shimadzu refractive index detector. THF was used as the eluent (elution rate, 0.8 $mL{\cdot}min^{-1}$), and polystyrene standards were used for calibration. Thermaldynamic properties were examined using a DuPont 910 differential scanning calorimeter (DSC) with a heating rate of 10°$C{\cdot}min^{-1}$. Photoisomerization upon the irradiation of UV light (365 nm, 10 $mW{\cdot}cm^{-2}$) was measured with a UV-Vis Tu-1800 spectrophotometer (Purkinje General Inc., China).

The photoresponsive process of the vesicle solution was induced by a UV-LED irradiator (Omron ZUV-C30H) with the wavelength of 365 nm under the stirring. Once the UV light was turned off, the vesicle solution was immediately transferred into a glass cell (17 mm × 6 mm × 200 um), which was then sealed for optical microscopy observation. The morphologies and sizes of polymeric aggregates were observed by Olympus BH-2 optical microscope. Images were taken and recorded using an Olympus digital camera.

RESULTS AND DISCUSSION

Synthesis and Characteristics

The amphiphilic diblock copolymer was synthesized by ATRP; therefore, their structure, molecular weight and content of azobenzene moieties can be finely controlled. Figure 2 shows the ^1H NMR spectra of the copolymer PEO-*b*-PMeA6AB2, macroinitiator PEO-Br and monomer MeA6AB2. Comparing Figure 2(a) with Figure 2(c), we can see that two peaks at 5.5 ppm and 6.1 ppm assigned to vinyl protons of the methacrylate group disappear from the spectrum of

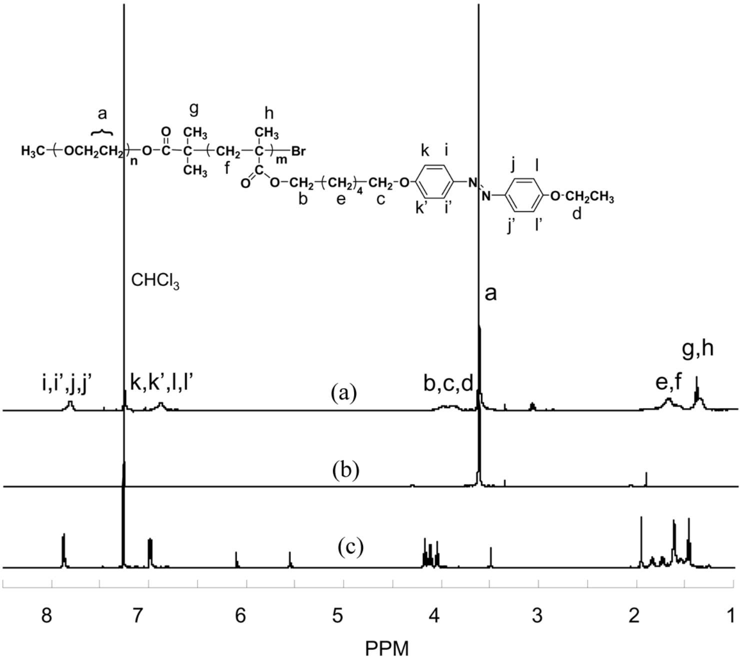


FIGURE 2 ^{1}H-NMR spectra of PEO-*b*-PMeA6AB2 (a), PEO-Br (b) and MeA6AB2 (c).

PEO-*b*-PMeA6AB2, indicating that there are not unpolymerized monomers remaining in the copolymer. Moreover, comparing Figure 2(a) with Figure 2(b), it is clear that two new peaks located at 6.9 ppm and 7.8 ppm assigned to protons of the azobenzene group appear in the spectrum of PEO-*b*-PMeA6AB2, showing that MeA6AB2 is incorporated with PEO-Br. Obviously, PEO-*b*-PMeA6AB2 was successfully prepared.

The DSC measurement indicates that PEO-b-PMeA6AB2 containing a polymethacrylate LC block with azobenzene mesogens in the side chains shows a nematic phase, whose temperature range is from 26°C to 55°C as Table 1 lists.

Characteristics of the macroinitiator and copolymer analyzed with GPC and ^{1}H NMR are also given in Table 1. The data of GPC measurements show that the polydispersity of PEO-*b*-PMeA6AB2 diblock copolymer is larger than that of PEO-Br macroinitiator, caused by using the ligand Me6Tren with a higher activity instead of generally-used pentamethyldiethylenetriamine (PMDETA) or hexamethyldiethylenetriamine (HMTETA). The number average molecular

TABLE 1 Characteristics of the Macroinitiator and Copolymer

Sample	Phase transition temperature (°C)	Content of azobenzene-containing block (wt %)[b]	M_n (GPC)	M_w/M_n (GPC)	M_n (NMR)
PEO-Br	–	–	5200	1.15	4000
PEO-*b*-PMeA6AB2	G 26 N 55 I[a]	60	17700	1.48	10100

[a] G, glass; N, nematic; I, isotropic.
[b] Calculated from ^{1}H-NMR data.

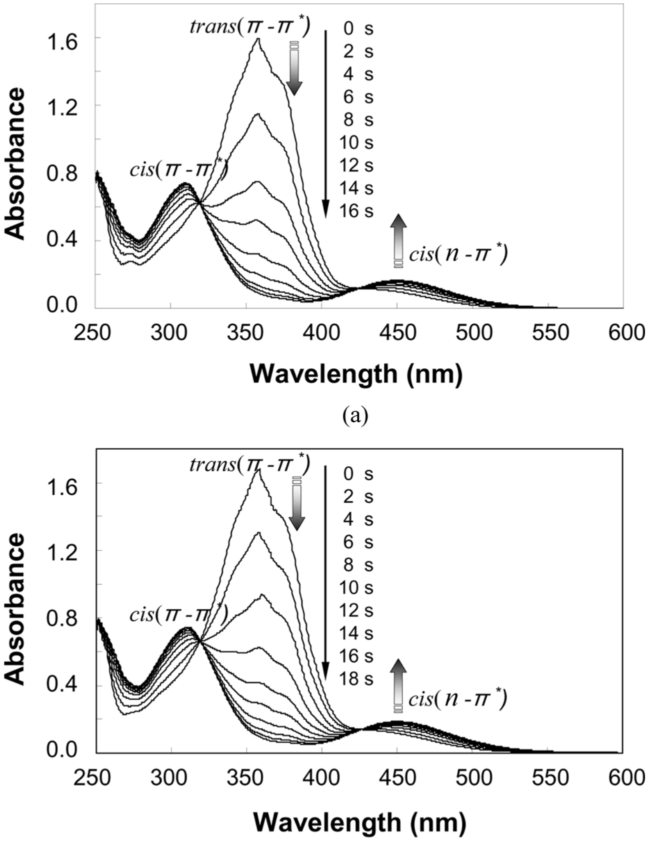
weight measured by GPC is larger than that obtained from ^{1}H NMR, because the GPC data are only relative rather than absolute, which is relevant to hydrodynamic volume; however, ^{1}H NMR spectra can directly reveal absolute molecular weight of the polymer and the mass ratio of two polymers. The content of the block containing azobenzene moieties in the copolymer is calculated to be 60 wt% according to the following equation:

$$\text{Content(wt\%)} = \frac{1}{1 + \frac{n_{7.8} I_{3.6}}{n_{3.6} I_{7.8}} \cdot \frac{M_{EO}}{M_{AZO}}} \times 100\%$$

where $I_{3.6}$ and $I_{7.8}$ are the integration values at 3.6 ppm assigned to four protons of the ethylene oxide group and at 7.8 ppm assigned to four phenyl protons of the azobenzene group, respectively. $n_{3.6}$ and $n_{7.8}$ are both equal to 4, which are the number of protons in the above two groups. M_{EO} and M_{AZO} are representative of the molar mass of ethylene oxide and azobenzene units, which are 44 and 410, respectively.

Photoisomerization Study with UV-Vis Spectroscopy

Azobenzene groups can undergo a reversible photochemical reaction between *trans* form and *cis* form, therefore the UV-Vis spectra were measured to investigate the photoisomerization of MeA6AB2 and PEO-*b*-PMeA6AB2. The THF solution of MeA6AB2 was irradiated with UV light at 365 nm with the light intensity of 10 mW·cm^{-2} for different time, and the UV-Vis spectra given in Figure 3(a) were recorded until the photostationary state reached. The maximum absorption at 360 nm and the absorption around 450 nm are due to the π-π^* transition of *trans*-azobenzene groups and the n-π^* transition of *cis*-azobenzene groups, respectively. Upon the irradiation of UV light, the former absorbance decreased and the latter



(a)

(b)

FIGURE 3 UV-Vis absorption spectra of MeA6AB2 (10^{-5} mol·L^{-1}) (a) and PEO-*b*-MeA6AB2 (10^{-6} mol·L^{-1}) (b) in THF upon the irradiation of UV light (365 nm, 10 mW·cm^2).

absorbance increased gradually. Furthermore, when the isomerization continued, more *cis* isomers generated, resulting in the increment of the absorbance at 315 nm assigned to the π-π^* transition of *cis* isomers. At last, the wavelength of maximum absorption gradually shifted from 360 nm to 315 nm. These variations indicate the *trans*-to-*cis* isomerization of the azobenzene groups. The THF solution of PEO-*b*-PMeA6AB2 was also measured with the same method, and the similar results were obtained as Figure 3(b) shows.

Self-Assembly of the Diblock Copolymer

In the aqueous solution, morphologies and sizes of the diblock copolymers generally depend to a great extent on the ratio of hydrophilic to hydrophobic blocks, the molecular weight and polydispersity of the copolymers and the interaction between solvent molecules and polymer segments. If the content of hydrophobic block is relatively lower, the block copolymers are not able to form larger micrometer scale aggregates, which can be directly observed by optical microscope. In contrast, if the hydrophobic block is much longer than the hydrophilic block, the copolymers are easy to generate precipitation because of the phase separation. Therefore, an appropriate length ratio between two blocks is crucial to obtain regular aggregates. In this study, the mass ratio of hydrophilic block of PEO to hydrophobic block of PMeA6AB2 in the amphiphilic diblock copolymer was 40 to 60 (Table 1). It was found that PEO-*b*-PMeA6AB2 self-assembled into microvesicles in the solution of THF and H_2O. As shown in Figure 4, the size range of these formed vesicles is from 0.4 μm to 0.7 μm. The inhomogeneity of their size distribution results from the larger polydispersity of the amphiphilic diblock copolymer.

Photoresponsive Behavior of the Self-Assembled Microvesicles

Photoresponsive behavior of the self-assembled microvesicles in response to UV light was observed by optical microscope. Figure 5(a) shows the initial state. After the irradiation of UV light (365 nm,

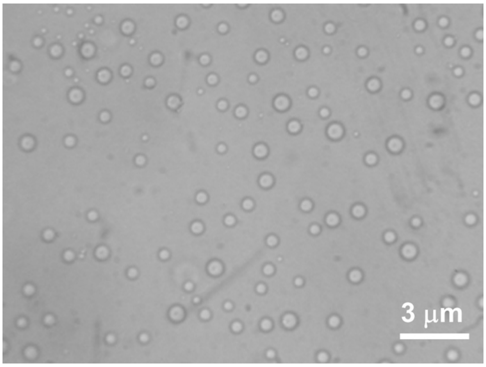


FIGURE 4 Optical microscopic photos of microvesicles self-assembled in THF/H_2O solution.

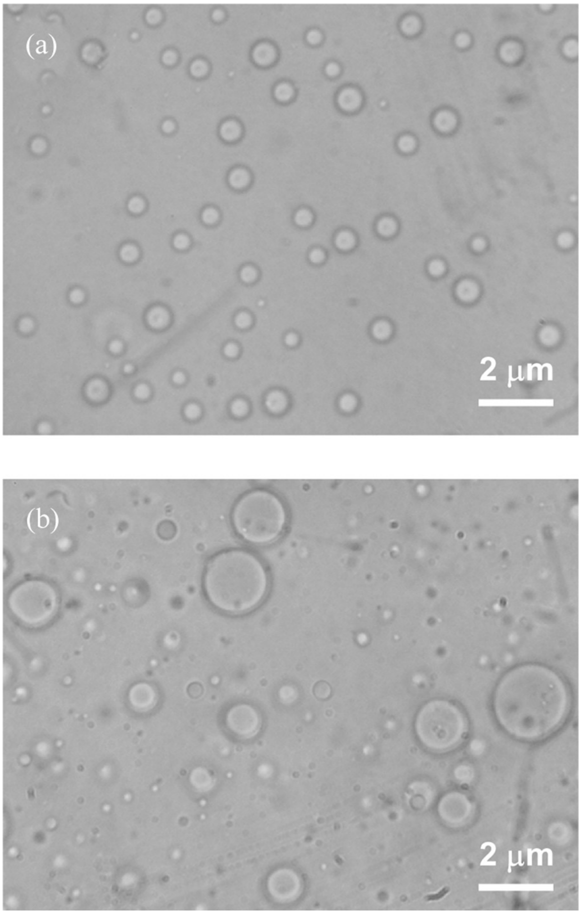


FIGURE 5 Optical microscopic photos of the microvesicles before (a) and after (b) the irradiation of UV light.

10 mW·cm^{-2}, 60 s), photoinduced increase in vesicle size from 0.4 ∼ 0.7 µm to 1 ∼ 2 µm was observed as shown in Figure 5(b). Actually, as Figure 6 shows, the vesicles underwent photoinduced fusion upon the irradiation of UV light. Figure 6(a) showed two adjacent vesicles with a diameter below 1 µm. Subsequently, both of them began to close contact and then merge as displayed in Figure 6(b) and 6(c). Finally, a bigger vesicle with the size beyond 1 µm was formed as shown in Figure 6(d). The generation of photoinduced fusion is mainly derived from the photoisomerization of azobenzene units. Because the rod-like *trans*-azobenzene units

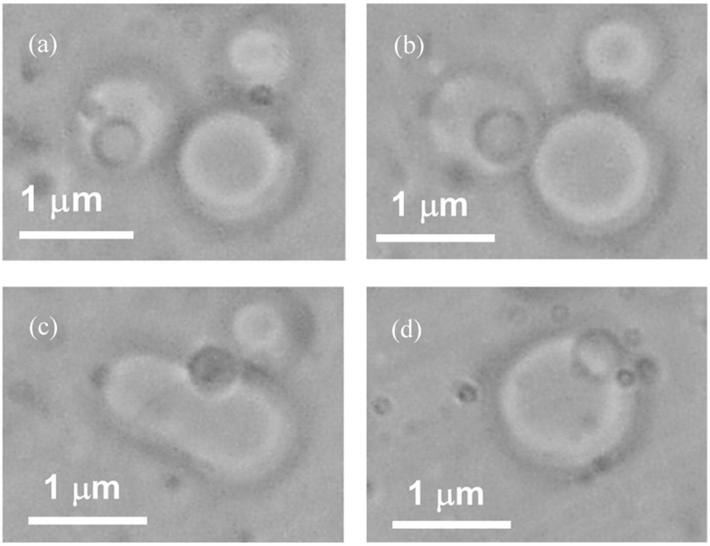


FIGURE 6 Optical microscopic photos of the vesicles from the initial state (a) to close contact state (b), fusion state (c), and a bigger vesicle (d).

are easy to form a relatively tight packing, whereas the bent *cis* isomers can only bring a loose stacking formation in the vesicle wall. When *trans*-to-*cis* photoisomerization is induced upon the irradiation of UV light, the expansion and swelling appear in these vesicular walls. The resulted increase in surface free energy leads to the fusion of vesicles. This fusion process of the vesicles is similar to that reported in branched polymersomes [28].

CONCLUSIONS

The amphiphilic block copolymer of PEO-b-PMeA6AB2 with hydrophilic PEO segment and a hydrophobic poly(methacrylate) segment containing azobenzene moieties was successfully synthesized by ATRP. The diblock copolymer can self-assemble into micrometer scale vesicles in THF/H_2O solution. Under the irradiation of UV light, these microvesicles underwent photoinduced fusion processes, including photoinduced expansion, swelling and fusion, derived from the photoisomerization of azobenzene units. Due to this photoinduced fusion, the microvesicles enlarged to be about five times their original size.

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