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Cite this: *Soft Matter*, 2011, **7**, 10001

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**PAPER**

# Light-responsive block copolymer vesicles based on a photo-softening effect†

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***Received 4th June 2011, Accepted 3rd August 2011***
**DOI: 10.1039/c1sm06041d**



We report the synthesis and study of two series of amphiphilic block copolymers (BCPs) of which the hydrophilic block is either poly(acrylic acid) (PAA) or poly(*N*,*N*-dimethylacrylamide) (PDMA) and the hydrophobic block is a side-chain liquid crystalline polymer (SCLCP) bearing biphenyl mesogens in majority and azobenzene mesogens in minority, namely, a random copolymer of 6-[4-(4-cyanophenyl) phenoxyl]hexyl acrylate with 6-[4-(4-methoxyphenylazo)phenoxyl]hexyl acrylate (P(BiPA-*co*-Azo)). Samples of both BCPs, PDMA-*b*-P(BiPA-*co*-Azo) and PAA-*b*-P(BiPA-*co*-Azo), could form large vesicles in aqueous solution with a SCLCP membrane. The BCPs were designed for investigating photoinduced order-disorder transition of the mesogens confined inside the vesicle membrane as a result of the *trans–cis* photoisomerization of azobenzene and the LC cooperative effect. From photo-optical measurements on a BCP vesicle solution, we found evidence that a photoinduced LC order–disorder transition could occur inside the vesicle membrane in aqueous solution. Moreover, using a pH-sensitive fluorescent probe, we studied the photo-softening effect on the proton transfer across the vesicle membrane. Similar to plasticization of the vesicle membrane upon addition of a good solvent in aqueous solution, photo-induced softening could increase the rate of proton diffusion from inside to outside of the vesicle through the SCLCP membrane.

## Introduction

Amphiphilic block copolymers (BCP) can form stable vesicles (polymersomes) in aqueous solution.[1–3] If one (or more) constituting block of a BCP can respond to a change in temperature, or pH, or to the presence of a molecular species, or to irradiation, the vesicle of this BCP should also be stimuli-responsive. In this way, a variety of thermo-,[4–8] pH-,[9–13] redox-[14–17] and light-sensitive BCP vesicles[18–24] were prepared in recent years. The reaction of such BCP vesicles to a stimulus can have different consequences on their structure or morphology, including size change,[7,25,26] transformation to other types of aggregates[19,27–32] and dissociation.[4,14,18,22–24] The responsiveness to stimuli renders BCP vesicles more appealing for potential applications.[33–36]

The reversible *trans–cis* photoisomerization was often used in designing light-responsive BCP vesicles. Li and coworkers demonstrated an elegant approach.[23] They prepared giant asymmetric BCP vesicles of which the membrane is composed of two leaflets of polybutadiene (inner leaflet) and a side-on liquid crystalline polymer (LCP) with azobenzene mesogens (outer leaflet). Upon exposure to UV light, a LC-isotropic phase transition occurs in the outer leaflet resulting in a contraction of the outer monolayer along the membrane thickness direction, and the excess surface induces a curling instability that leads to the bursting of the vesicle membrane. In a report by Jin *et al.*,[24] the photo-responsive inclusion complexation of β-cyclodextrin with azobenzene has been used to achieve photoinduced assembly (with *cis* azobenzene under UV light) and disassembly (with *trans* azobenzene under visible). In the present study, we investigated a different and simpler approach as compared to the aforementioned methods. As depicted in Fig. 1, the idea is to make BCP vesicles whose membrane can be softened upon absorption of photons. To achieve this effect, we designed and synthesized two

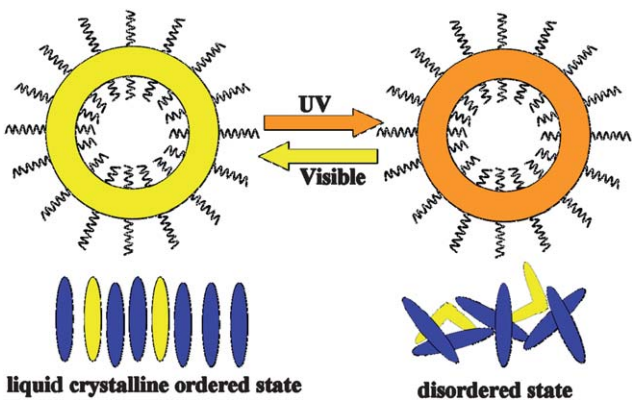


**Fig. 1** Schematic illustration of block copolymer vesicles of which mesogens inside the liquid crystalline polymer membrane can undergo an order–disorder transition induced by the *trans–cis* photoisomerization of azobenzene and the liquid crystal cooperative effect.

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† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/c1sm06041d/

series of diblock copolymers. They differ in the chemical identity of the hydrophilic block but possess the same hydrophobic block namely, a side-chain liquid crystalline polymer (SCLCP) bearing randomly distributed biphenyl (in majority) and azobenzene mesogens (in minority). Our working hypothesis is as follows. Upon formation of vesicles, the LC order of the SCLCP block inside the membrane may persist; while upon absorption of UV light, the *trans–cis* isomerization of azobenzene could induce a LC-isotropic phase transition of all mesogens due to the cooperative effect, exerting a softening effect on the vesicle membrane. Such photoinduced isothermal phase transition is well known for azobenzene-containing SCLCPs in the bulk[37] and in microphase-separated BCP thin films under confinement.[38] Moreover, a number of recent reports show that BCPs with a SCLCP block could readily form vesicles, sometime of very large sizes,[19–21,26] which may facilitate the direct observation of a photoinduced LC order–disorder transition. As reported in this paper, indeed the LC cooperativity-driven photoinduced order-disorder phase transition inside the membrane of BCP vesicles was observed, and the photo-softening effect was evidenced by monitoring the kinetics of proton diffusion across the vesicle membrane through changes in the fluorescence from a molecular probe.

## Experimental

Fig. 2 shows the chemical structures of the synthesized BCPs and a schematic illustration of their chain structure. The hydrophobic block expected to form the vesicle membrane is a random copolymer of 6-[4-(4-cyanophenyl)phenoxyl]hexyl acrylate with 6-[4-(4-methoxyphenylazo)phenoxyl]hexyl acrylate (denoted as P(BiPA-*co*-Azo)) which is a SCLCP with biphenyl mesogens in majority and a small amount of photoisomerizable azobenzene mesogens. In order to examine the generality of obtaining birefringent BCP vesicles, two hydrophilic blocks were utilized, being

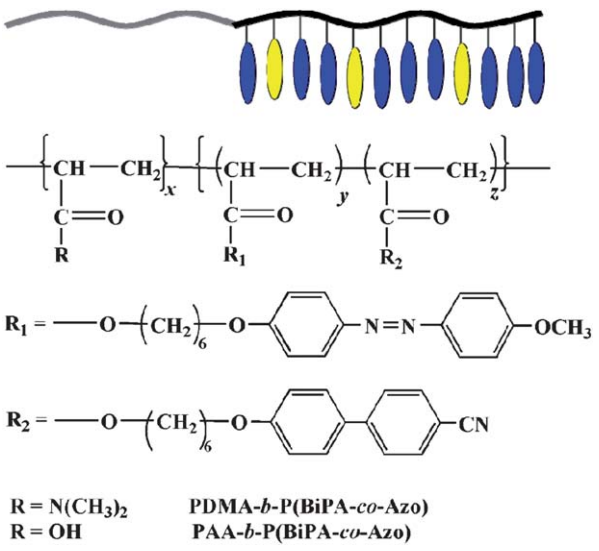


**Fig. 2** Schematic illustration and the chemical structures of synthesized amphiphilic block copolymers whose hydrophobic block is a side-chain liquid crystalline random copolymer bearing biphenyl and azobenzene mesogens.

either poly(acrylic acid) (PAA) or poly(*N*,*N*-dimethylacrylamide) (PDMA). The two series of BCPs are referred to as PAA-*b*-P(BiPA-*co*-Azo) and PDMA-*b*-P(BiPA-*co*-Azo) respectively. They were synthesized by using reversible addition fragmentation chain transfer polymerization (RAFT). Details on their synthesis and characterizations using $^1$H NMR, DSC and polarizing microscopy are given in Supporting Information. BCP vesicles were obtained by first dissolving a polymer sample in THF (5 mg mL$^{-1}$ unless otherwise stated), followed by the addition of an equal volume of deionized water to the solution at a rate of 0.01 mL/min. Afterward, the solution was quenched in 4-fold water (with respect to the solution volume). After removing THF by dialysis, an aqueous solution of vesicles was obtained. For the proton diffusion experiment, the encapsulation of the pH-indicator dye followed the procedures described in some literatures.[25,39]

## Results and discussion

### 1. Block copolymer synthesis and characterization

The characteristics of the two series of BCP samples are summarized in Table 1. In both cases, the hydrophilic block was first synthesized using RAFT to yield a macromolecular chain transfer agent (macro-CTA), which was then used to grow the hydrophobic SCLCP block of P(BiPA-*co*-Azo). For PDMA-*b*-P(BiPA-*co*-Azo), the same macro-CTA, PDMA$_{37}$-CTA, was utilized. By varying the feed ratio of biphenyl and azobenzene monomers, BCP samples with different lengths and compositions of the SCLCP block were prepared (P0–P6 in Table 1). In the case of PAA-*b*-P(BiPA-*co*-Azo), a poly(*tert*-butyl acrylate) macro-CTA, P*t*BA$_{40}$-CTA, was synthesized and used to prepare BCP samples of P*t*BA-*b*-P(BiPA-*co*-Azo); the latter was then subjected to a hydrolysis reaction to remove *tert*-butyl groups, yielding the target amphiphilic BCP of PAA-*b*-P(BiPA-*co*-Azo) (P7–P12). For each BCP sample, the composition was determined from its $^1$H NMR spectrum by comparing the integrals of the resonance peaks of azobenzene at $\sim$ 7.83 ppm, biphenyl group at 7.40–7.72 ppm, methyl groups of PDMA at 2.9–3.2 ppm and methyl groups of P*t*BA at 1.5 ppm (spectra in Supporting Information). Their number-average molecular weight ($M_n$), calculated from $^1$H NMR and estimated from GPC using polystyrene (PS) standards, are also shown in Table 1. All samples have a low polydispersity index (PDI). Fig. 3 shows examples of GPC curves, confirming well-controlled growth of the SCLCP block with the two series of samples. All BCP samples display liquid crystalline (LC) phases as can be noticed from the examples of DSC heating curves in Fig. 4. On the one hand, for PDMA-*b*-P(BiPA-*co*-Azo) (Fig. 4a), the PDMA block alone, PDMA$_{37}$-CTA (sample P0), is amorphous and has a $T_g$ at $\sim$78 °C. For the BCP sample P1, whose SCLCP block contains only biphenyl mesogens, $T_g$ decreases to about 40 °C while the LC-isotropic endotherm arising from the PBiPA$_{61}$ block is observed at around 90 °C. The presence of azobenzene mesogens in the SCLCP block in sample P2, while having a similar number of biphenyl groups, merely causes the clearing temperature to increase by about 10 °C. This behaviour is expected for such a random copolymer because the SCLCP with only azobenzene mesogens has

 

**Table 1** Characteristics of synthesized amphiphilic liquid crystalline block polymers

| Sample | Abbreviation and composition[a] | $M_n$ (GPC) | $M_n$(NMR) | PDI (GPC) |
|---|---|---|---|---|
| P0 | $PDMA_{37}$-CTA | 3000 | 3700 | 1.09 |
| P1 | $PDMA_{37}$-*b*-$PBiPA_{61}$ | 20700 | 29100 | 1.13 |
| P2 | $PDMA_{37}$-*b*-P($BiPA_{50}$-*co*-$Azo_6$) | 18900 | 23600 | 1.14 |
| P3 | $PDMA_{37}$-*b*-P($BiPA_{40}$-*co*-$Azo_2$) | 14700 | 18800 | 1.21 |
| P4 | $PDMA_{37}$-*b*-P($BiPA_{35}$-*co*-$Azo_3$) | 13700 | 17300 | 1.19 |
| P5 | $PDMA_{37}$-*b*-P($BiPA_{26}$-*co*-$Azo_4$) | 11200 | 14500 | 1.23 |
| P6 | $PDMA_{37}$-*b*-P($BiPA_{21}$-*co*-$Azo_4$) | 10300 | 12700 | 1.22 |
| P7 | P*t*$BA_{40}$-CTA | 3900 | 4500 | 1.05 |
| P8[b] | $PAA_{40}$ | — | — | — |
| P9 | P*t*$BA_{40}$-*b*-P($BiPA_{56}$-*co*-$Azo_2$) | 24700 | 29100 | 1.11 |
| P10 | $PAA_{40}$-*b*-P($BiPA_{56}$-*co*-$Azo_2$) | — | — | — |
| P11 | P*t*$BA_{40}$-*b*-P($BiPA_{36}$-*co*-$Azo_{12}$) | 16900 | 23600 | 1.22 |
| P12 | $PAA_{40}$-*b*-P($BiPA_{36}$-*co*-$Azo_{12}$) | — | — | — |
| P13 | P*t*$BA_{40}$-*b*-P($BiPA_{18}$-*co*-$Azo_{18}$) | 12900 | 18800 | 1.26 |

[a] PDMA-CTA = poly (N, N-dimethylacrylamide) chain transfer agent. P*t*BA-CTA = poly (*tert*-butyl acrylate) chain transfer agent. P(BiPA-*co*-Azo) = random copolymer of 6-[4-(4-methoxyphenylazo)phenoxyl]hexyl acrylate (Azo) and 6-[4-(4-cyanophenyl)phenoxyl]hexyl acrylate (BiPA). PAA = poly (acrylic acid). In the sample abbreviation, the subscript indicates the number of repeat monomer units. $M_n$ (GPC) = number-average molecular weight (g $mol^{-1}$) measured by gel permeation chromatography using polystyrene standards for calibration. $M_n$ (NMR) = number-average molecular weight (g $mol^{-1}$) estimated from $^1$H NMR spectra based on $M_n$ (NMR) of PDMA-CTA or P*t*BA-CTA and the block copolymer composition, comparing the integrals of the resonance peaks of azobenzene at 7.83 ppm, biphenyl group at 7.40–7.72 ppm, PDMA methyl groups at 2.9–3.2 ppm, or P*t*BA methyl groups at 1.5 ppm. PDI (GPC) = polydispersity index. [b] All samples of or with PAA were obtained by hydrolysis of their P*t*BA counterparts in $CH_2Cl_2$ with addition of 5-fold molar excess of $CF_3COOH$ (with respect to *t*-butyl groups) at room temperature for 24 h. The complete hydrolysis of *t*-butyl groups was confirmed by $^1$H NMR spectroscopy.

a higher LC-isotropic transition temperature.[40] Comparing sample P4 with P2, the reduced LC–isotropic transition temperature is interpreted as being caused by the lower molecular weight of the SCLCP block (Table 1). In these PDMA-bearing BCP samples, the $T_g$ of the hydrophilic block is hardly discernible as compared to the $PDMA_{37}$-CTA (sample P0).

In the case of PAA-*b*-P(BiPA-*co*-Azo) (Fig. 4b), the $PAA_{40}$ block is also amorphous with a $T_g$ lying at about 108 °C, while the BCP samples all show a LC-isotropic transition peak similar to those observed in PDMA-*b*-P(BiPA-*co*-Azo) (Fig. 4a). Comparing samples P12 and P10, the higher content of azobenzene mesogens in P12 results in a higher LC-isotropic phase transition temperature than that displayed by P10. Interestingly, P11, which is the precursor of sample P12 before hydrolysis of the P*t*BA block, has a lower thermal stability of the LC phase, suggesting that PAA has different interfacial interactions with P(BiPA-*co*-Azo) than P*t*BA does. It is possible that P*t*BA has a better miscibility with the SCLCP block which could result in a reduction of the clearing temperature. For all amphiphilic LC-BCP samples, the $T_g$ of the amorphous hydrophilic block (PDMA and PAA) is not visible in the thermograms (*i.e.*, Fig. 4a and 4b, respectively) likely due to their very small weight fractions in the BCPs (<20% for samples in Fig. 4).

## 2. Birefringent block copolymer vesicles in aqueous solution

Most BCP samples in Table 1 can self-assemble into vesicles under the preparation conditions described above. Generally, the vesicles of PAA-*b*-P(BiPA-*co*-Azo) are larger than those of PDMA-*b*-P(BiPA-*co*-Azo) and can be observed in aqueous solution directly with an optical microscope. In solution, the vesicles appear as birefringent particles that twinkle constantly due to motion. A polarizing photomicrograph of such a solution is shown in Fig. 5a, along with TEM images of the vesicles of both BCPs in the dry state shown in Fig. 5b and 5c. The

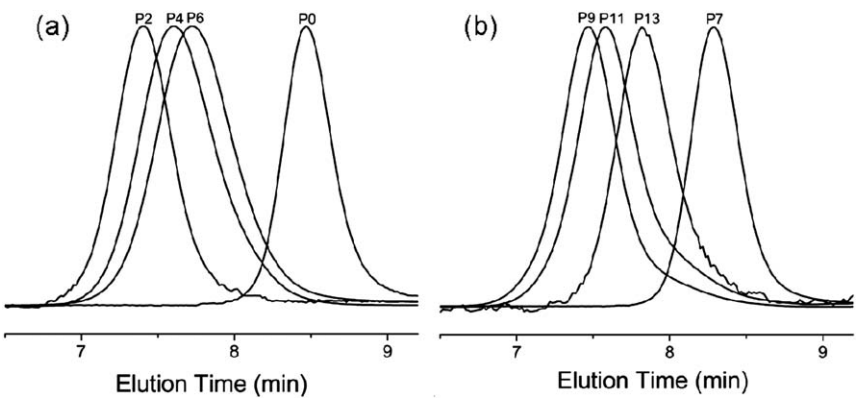


**Fig. 3** GPC curves of various samples of (a) PDMA-*b*-P(BiPA-*co*-Azo) and (b) P*t*BA-*b*-P(BiPA-*co*-Azo). Samples characteristics are shown in Table 1.

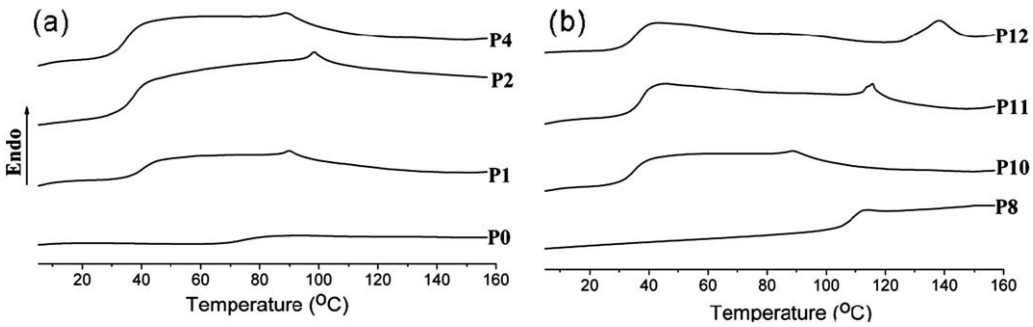


**Fig. 4** DSC heating curves (second scan) of various samples for (a) PDMA-*b*-P(BiPA-*co*-Azo) and (b) PAA-*b*-P(BiPA-*co*-Azo) and P*t*BA-*b*-P(BiPA-*co*-Azo). Samples characteristics are shown in Table 1.



birefringence of the vesicles in solution, as demonstrated under crossed polarizers observations with optical microscopy, is a straightforward indication that the SCLCP block forms a LC membrane.

An interesting phenomenon was observed with PDMA-*b*-P(BiPA-*co*-Azo) polymersomes. In deionised water, the vesicles are not big enough to be visible with an optical microscope. However, by adding a salt to the solution while keeping all other conditions the same, the vesicle formed become large enough and observable by optical microscopy. Fig. 6 shows an example of this phenomenon. By adding KI in a solution of P2, birefringent vesicles becomes discernible at a salt concentration of $\sim$ 0.01 M, and their average size increases with increasing salt concentration, reaching diameters on the order of several micrometres. This can be noticed from the polarizing photomicrographs in Fig. 6a and 6b, and TEM image in Fig. 6c. Moreover, there is a clear LC texture appearing under crossed polarizers: most vesicles appear to display a dark cross which is reminiscent of the texture characterizing LC droplets within which mesogens adopt a radial configuration where LC directors orient normal to the spherical interface. A vesicle is a hollow capsule, but if biphenyl and azobenzene mesogens in the vesicle membrane formed by P(BiPA-*co*-Azo) are aligned normal to the interface with hydrated PDMA chains, such a LC texture could be expected. It is well known that ions in aqueous solution could affect the interactions between LC molecules and induce a perpendicular anchoring at the interface.[41] It seems that by interacting with the polymer and water molecules, dissolution of KI in the vesicle solution of PDMA-*b*-P(BiPA-*co*-Azo) could affect the BCP self-assembly behaviour and the order of mesogens inside the membrane. Other salts (KBr, KCl, $K_2CO_3$) were also utilized and similar effects were observed.

The above results show evidence that both PAA-*b*-P(BiPA-*co*-Azo) and PDMA-*b*-P(BiPA-*co*-Azo) can form large vesicles with a LC membrane in aqueous solution. On the basis of TEM images, the membrane thickness for sample P10 is about 16 nm while that for sample P2 is close to 12 nm. The vesicle membrane is a nanoscale domain and the mesogens inside should be subjected to confinement effects, which could affect the LC ordering with respect to the bulk state. To get some insight into the identity of the LC phase that reside inside the membrane, vesicles formed from sample P2 in aqueous solution were prepared, collected by freeze-drying, and used for DSC and X-ray diffraction measurements. No salt was added in the solution in order to avoid complications due to the presence of salt crystals that may form in freeze-dried samples. X-ray diffraction measurements showed the absence of any smectic ordering in the freeze-dried vesicles samples, similarly to observations made in bulk polymer samples (data not shown). This suggests that mesogens form a nematic phase inside the vesicle membrane. As for DSC analyses, the first heating scan of the vesicle samples displayed a large enthalpy relaxation endotherm around Tg, which disappeared in the second scan; the LC-isotropic phase transition occurred at temperatures similar to those displayed by bulk samples of P2 (ESI†).

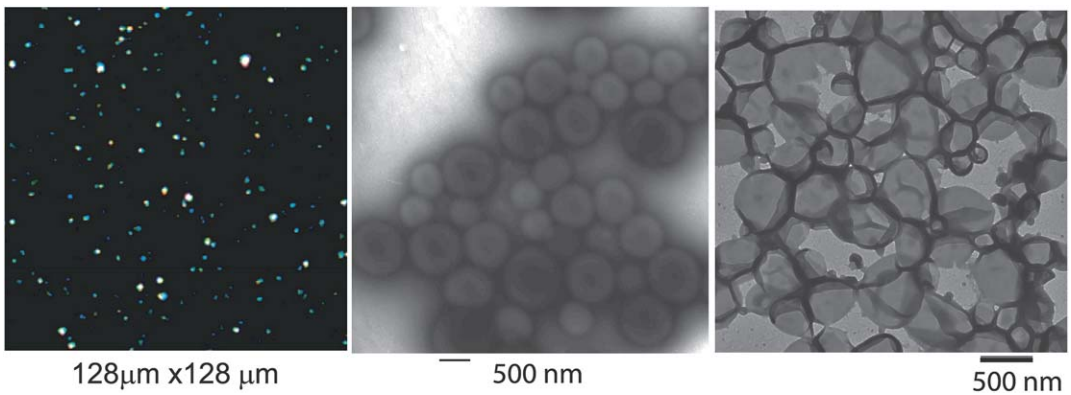


**Fig. 5** (a) and (b) Polarizing optical micrograph and TEM image of vesicles of $PAA_{40}$-*b*-P($BiPA_{56}$-*co*-$Azo_2$) in aqueous solution and in the dry state, respectively. (c) TEM image of vesicles of $PDMA_{37}$-*b*-P($BiPA_{50}$-*co*-$Azo_6$) in the dry state.

 

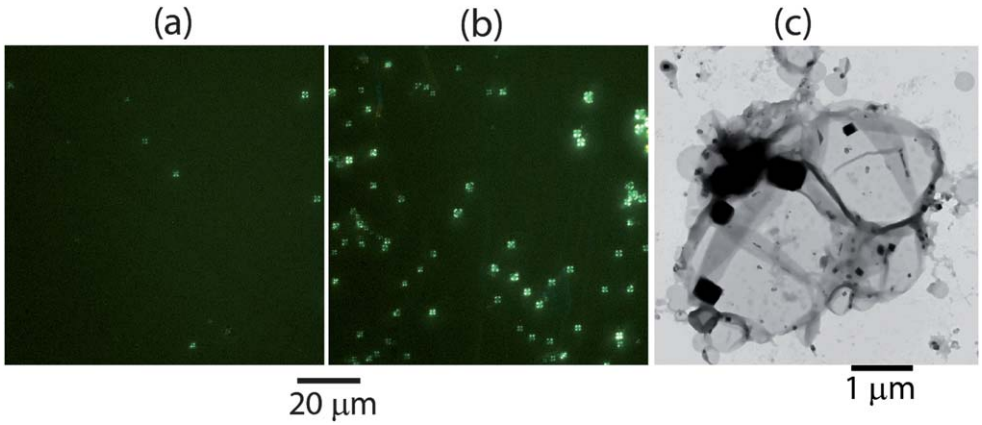


**Fig. 6** (a) and (b) Polarizing optical micrograph of $PDMA_{37}$-*b*-P($BiPA_{50}$-*co*-$Azo_6$) in aqueous solution with KI at two concentrations of 0.01 M and 0.08 M, respectively. (c) TEM image of vesicles in the dry state, cast from the solution with 0.08 M KI.



### 3. Photoinduced order–disorder phase transition inside vesicle membrane

By solubilizing a small amount of an azobenzene compound in a small-molecule liquid crystal host, and inducing the *trans–cis* isomerization of the chromophore by UV irradiation, multiple isothermal photochemical processes can take place, including phase transition and phase separation.[38,42] The stable *trans* azobenzene provides an elongated core for mesogens, while the bent *cis* form is incompatible with and able to disrupt an ordered LC phase, allowing photochemical control over the order-disorder transition processes. In the case of SCLCPs that bear a small amount of azobenzene moieties mixed with another type of mesogens, like in P(BiPA-*co*-Azo), the photoinduced order-disorder phase transition can readily occur due to a LC cooperative effect, especially at temperatures close to that of the LC-isotropic phase transition.[37] In thin films of azobenzene-containing BCPs, such photoinduced order–disorder transition was also evidenced.[37] However, the process is slower than in random copolymers due to the presence of confinement exerted by microphase-separated nanodomains. In the present study, it is of fundamental interest to know whether photoinduced and LC cooperativity-driven order–disorder transition can occur inside vesicle membranes in aqueous solution. As already mentioned, our working hypothesis is that such photoinduced order–disorder transition could provide an optical softening effect on the vesicle membrane. We carried out investigations with the vesicles of P2 and the results confirmed our working hypothesis.

The occurrence of the reversible *trans–cis* photoisomerization of azobenzene mesogens inside the membrane of the BCP vesicles in aqueous solution was first confirmed from UV-vis spectroscopic measurements. Fig. 7 shows the absorption spectra of a vesicle solution of P2. At the a vesicle concentration of 0.5 mg $mL^{-1}$, the absorption features from azobenzene mesogens in the *trans* form at around 360 nm, as well as the absorption features due to the biphenyl mesogens near 300 nm, are much too strong to be analysed. However, after UV exposure of the solution, the appearance of an absorption shoulder band near 450 nm clearly indicates the formation of *cis* azobenzene. The thermal stability of the azobenzene mesogens inside the vesicle membrane can be noticed from the fact that absorption spectra from vesicles solutions remain essentially unchanged by keeping the solution in the dark 40 min after UV exposure. After subsequent visible irradiation, the absorption band of *cis* azobenzene disappears indicating the reverse *cis–trans* photoisomerization. Of course, the thermally activated *cis–trans* isomerization becomes faster when the vesicle solutions are heated to higher temperatures. In order to detect the photoinduced order-disorder transition inside the vesicle membrane, we carried out the following experiment. A drop of the vesicle solution was deposited on a glass slide inside a temperature-controlled hot stage that was positioned on the stage of an optical microscope. The transmission intensity of the illuminating light through the vesicle solution between crossed polarizers was measured by using a high-speed photodetector connected to a digital oscilloscope.[42] As the photodetector replaces a digital camera on the microscope, the sampling area of the solution corresponds to the photomicrograph frame whose size is determined by the objective. Irradiation with UV or visible light could be applied from the top of the solution through a quartz window. Fig. 8 shows the results. At 25 °C, no change in transmittance is observed upon exposure of the vesicle solution to

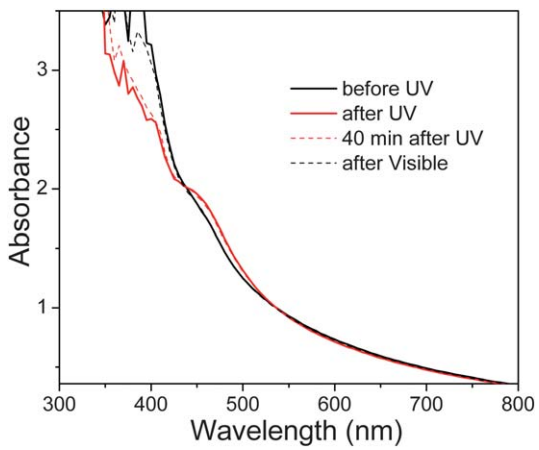


**Fig. 7** UV-vis spectra of a vesicle solution of $PDMA_{37}$-*b*-P($BiPA_{50}$-*co*-$Azo_6$) (2 mL, 0.5 mg $mL^{-1}$) before, right after UV irradiation (365 nm, 85 mW $cm^{-2}$, 3 min), after 40 min in the dark and after subsequent visible irradiation (400–500 nm, 40 mW $cm^{-2}$, 5 min).

UV and visible light. This is understandable because the solution temperature is below the $T_g$ of the SCLCP membrane and far from the clearing temperature of the mesogens (~ 100 °C). Although the *trans–cis* photoisomerization of azobenzene takes place under UV irradiation, the lack of mobility and high viscosity prevents the disordering of biphenyl mesogens. By contrast, at 65 °C, with the SCLCP membrane in the LC phase and closer to the clearing temperature, the transmittance decreases upon exposure of the solution to UV light, indicating the occurrence of order–disorder transition inside the membrane. The transmittance level remains unchanged after turning off the UV light for about 40 s, which is consequence of the high thermal stability of the *cis* isomer. Subsequently, upon exposure of visible light, the transmittance increases as a result of the reverse *cis–trans* isomerization of azobenzene that restores the LC order inside the membrane. Interestingly, despite the small signal changes, which is due to the limited number of vesicles in the small sampling area (~750 μm × 1125 μm), the characteristics of the order-disorder transition are similar to what is known with azobenzene BCPs when the photochemical process occurs in the solid state under confinement within microphase separated nanodomains.[38] That is, the photo-induced transition from an ordered to a disordered state proceeds faster than the recovery of order from a disordered state. Also shown in Fig. 8 are photomicrographs of the vesicle solution taken before (Fig. 8a) and after (Fig. 8b) UV light irradiation, and after subsequent visible light irradiation (Fig. 8c). The reversible change in the sample birefringence, resulting in the decrease or increase of the solution transmittance under crossed polarizers, is clearly visible. It can be noticed that the transmittance level prior to UV irradiation is lower at 65 °C than at 25 °C. This may reflect a reduced LC order inside the vesicle membrane at elevated temperatures. These results provide evidence that the photoinduced order–disorder phase transition of all mesogens arising from the *trans-cis* photoisomerization of a small amount of azobenzene moieties can occur inside the membrane of BCP vesicles in aqueous solution. A final note is that based on the change in the birefringence of the vesicle solution, photoinduced order-disorder transition was also observed for vesicles of PAA-*b*-P(BiPA-*co*-Azo) at solution temperatures close to the clearing temperature of the SCLCP membrane.

### 4. Photo-softening effect on proton diffusion through vesicle membrane

Eisenberg *et al.* showed that the plasticization of the vesicle membrane of BCPs by an organic solvent added to the aqueous solution could result in faster proton diffusion across the membrane, from the vesicle interior to the outside solution.[39a]

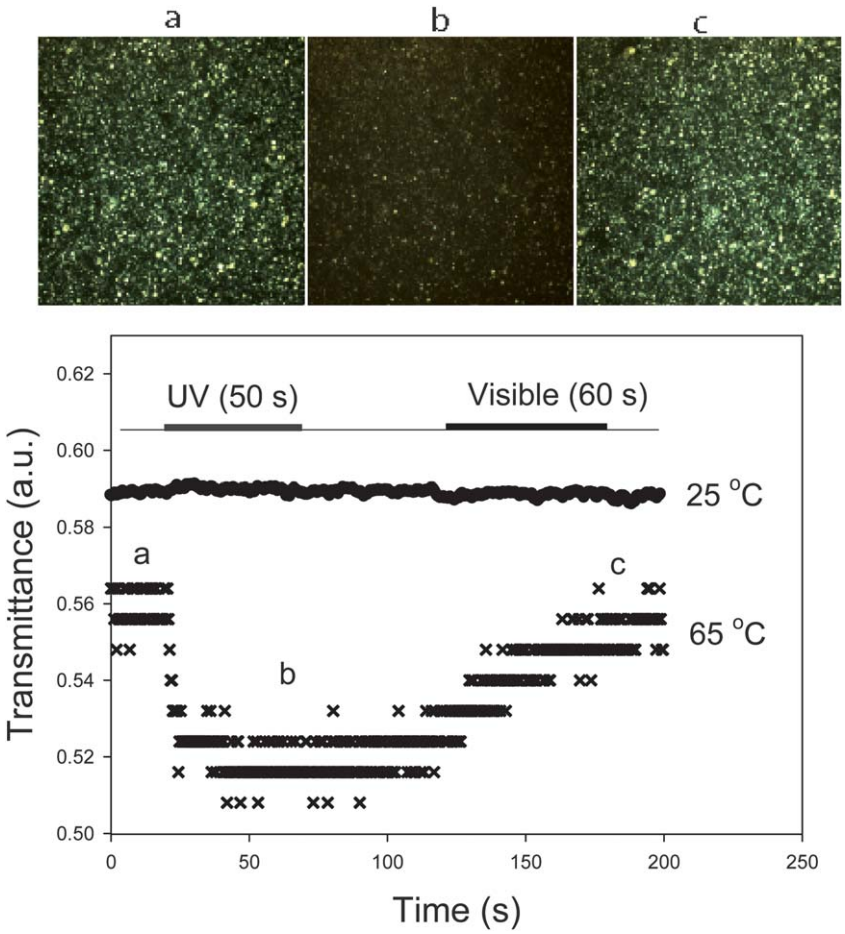


**Fig. 8** Change in transmittance of a vesicle solution of $PDMA_{37}$-*b*-$P(BiPA_{50}$-*co*-$Azo_6)$ (0.08 M KI) upon UV irradiation (365 nm, 10 mW $cm^{-2}$) for 50 s, after turning off UV for 50 s and upon visible irradiation (400–500 nm, 1 mW $cm^{-2}$) for 60 s, at 25 and 65 °C. The polarizing optical micrographs were taken with the solution: (a) before UV irradiation, (b) after UV irradiation and (c) after subsequent visible irradiation. Image area: 71 μm × 71 μm.

 

The proton diffusion kinetics could be monitored by recording the excitation spectrum of 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS) of which the ratio of the intensities of the band peaked at 454 nm to that peaked at 403 nm ($\lambda_{em}$ = 509 nm) is dependent on the pH of the solution.[43] To investigate the photo-softening effect on the membrane of the LC-BCP vesicles, we employed HPTS to examine the proton diffusion kinetics before and after the *trans–cis* photoisomerization of azobenzene mesogens within the membrane. The photoinduced order–disorder transition inside the vesicle membrane is more prominent at elevated solution temperatures. However, the thermal relaxation of *cis* azobenzene also becomes faster, which makes it impossible to follow the proton diffusion process in the disordered state because of the rapid *cis*-to-*trans* thermal isomerization rate which restores the ordered state quickly. In principle, the effect can be monitored under continuous UV exposure which preserves the disordered state, but the fluorescent probe HPTS is sensitive to UV irradiation, which could potentially interfere with the monitoring of the proton transport kinetics.[43] Taking the above into consideration, we first carried out measurements of HPTS fluorescence at room temperature by using vesicles of P2 formed in water without salt. In this vesicle solution, the actual $T_g$ of the SCLCP membrane may be in the vicinity of room temperature. Moreover, even in the glassy state, it is known that the *trans-cis* photoisomerization of azobenzene results in a plasticization effect that is the origin of the photoinduced surface relief gratings.[32,45,46]

For this experiment, after dissolving P2 in THF at a concentration of 5 mg $mL^{-1}$, water at pH = 3 was added to induce the formation of vesicles. Upon removal of THF by evaporation and dilution of the solution to a BCP concentration of 0.5 mg $mL^{-1}$ using water at pH = 3, an aqueous vesicle solution with pH~3 for both inside and outside the vesicles was obtained at equilibrium (pH measured using a pH meter). Afterwards, NaOH (0.1 N) was added and the solution stirred for 3min to reach pH = 8.9, triggering a net proton diffusive flux from inside to outside of the vesicles across its membrane. Immediately after this pH change, an aliquot of the solution (1.5 mL) was placed in a cuvette and exposed to UV light (365 nm UV, 85 mW $cm^{-2}$, 3 min), while the other part (1.5 mL) was stored in the dark without exposure to light. Then, to the two solutions, of which one has *trans* azobenzene mesogens and the other one has *cis* isomers inside the vesicle membrane, a HPTS solution (0.4 mM) was added to obtain a probe concentration of ~ 0.1 μM, and their excitation spectra ($\lambda_{em}$ = 509 nm) were recorded over time. Fig. 9 shows the excitation spectra of the vesicle solution after UV exposure taken at various times after the pH change. The spectral changes indicate that the proton diffusion in this system is a very slow process. As more protons pass through the membrane and migrate to the outside of the vesicles, the band at 403 nm becomes more intense at expense of the 454 nm band, as a result of the decreasing pH in the outside solution. From the relative intensities of the two bands, the change in the proton concentration could be calculated.[25,39,43] The results obtained for the two solutions with, respectively, *trans* azobenzene (before UV irradiation) and *cis* azobenzene (after UV irradiation) are shown in Fig. 10. It is clear that the *trans-cis*

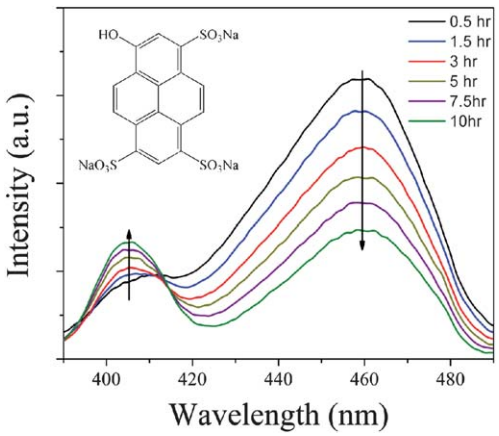


**Fig. 9** Evolution of the fluorescence excitation spectrum ($\lambda_{em}$ = 509 nm) over time for HPTS (structure shown as inset) added in a vesicles solution of $PDMA_{37}$-*b*-P($BiPA_{50}$-*co*-$Azo_6$) with a pH gradient. Before adding HPTS, the vesicle solution was exposed to UV light to obtain *cis*-azobenzene in the vesicle membrane.

photoisomerization of azobenzene mesogens has a drastic effect on the kinetics of the proton diffusion. With *cis* azobenzene in the membrane, the proton diffusion rate increases considerably as compared to *trans* azobenzene. After 5 h, the proton concentration with *cis* azobenzene in the vesicle membranes, as sensed by HPTS, is more than 20 times that with *trans* azobenzene. It should be mentioned that due to the very small fraction of the solution inside the vesicles (~ 0.01%), the pH decrease of the outside solution as a result of the proton diffusion is rather small. Measurements were also performed with vesicle solutions at 40 °C. At this temperature, the SCLCP membrane is slightly above $T_g$ and in the LC phase; the order-disorder transition arising from the *trans–cis* photoisomerization is allowed to occur, but to a lesser extent than at higher temperatures. Although the thermally activated relaxation of *cis* azobenzene back to the *trans* form becomes much faster than at room temperature, the effect of the remaining *cis*

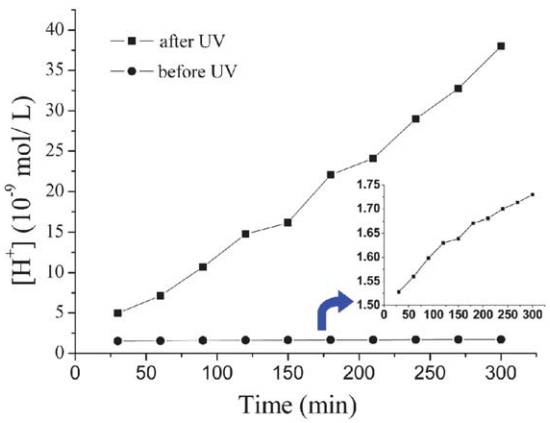


**Fig. 10** Plot of proton concentration [$H^+$] (calculated from the excitation spectra of HPTS) *vs.* time for a vesicle solution of $PDMA_{37}$-*b*-P($BiPA_{50}$-*co*-$Azo_6$) with a pH gradient at room temperature. The inset is the rescaled result obtained with the solution without UV irradiation.

azobenzene on the proton diffusion could still be observed at this temperature. In other words, 40 °C is a temperature of compromise, where the photochemical order–disorder transition is allowed, while the thermal relaxation of *cis* azobenzene is not yet too fast to make the photoinduced effect indictable. Fig. 11 shows the results. Prior to UV irradiation (with *trans* azobenzene), the proton diffusion appears to be only very slightly faster than at room temperature. After UV irradiation (with *cis* azobenzene and the resulting order–disorder transition), the proton diffusion becomes much faster. After 5 h, the difference in the ratio of the proton concentrations in the solutions after and before photoisomerization is about 7 as compared to >20 at room temperature (Fig. 10). This smaller photoinduced effect observed at 40 °C can be explained by the faster thermal relaxation of *cis* azobenzene inside the vesicle membrane, resulting in a smaller and continuously decreasing amount of *cis* azobenzene and the concomitant recovering of LC order. This can also be noticed from the apparent stabilization in the proton concentration at 40 °C after 250 min UV irradiation.

The above results show that the *trans–cis* photoisomerization of azobenzene mesogens inside the SCLCP vesicles can induce a softening effect that increases the proton diffusion rate through the membrane. This phenomenon is similar to the plasticization effect observed by adding a good solvent for the membrane in an aqueous vesicle solution.[39a] Since the photoisomerization of azobenzene is reversible upon alternating UV (~360 nm) and visible light (~440 nm) irradiation, the photosoftening effect should also be reversible. However, since the fluorescent dye HPTS used in this work is sensitive to both UV and visible light, the reversibility of the photoinduced effect (with, for example, repeated cycles of UV and visible light exposures) could not be measured with certainty since the irradiations could also contribute to changes in the excitation spectra of the dye. This is the reason for which the measurements in Fig. 10 and 11 were performed with HPTS added after the *trans-cis* photoisomerization.

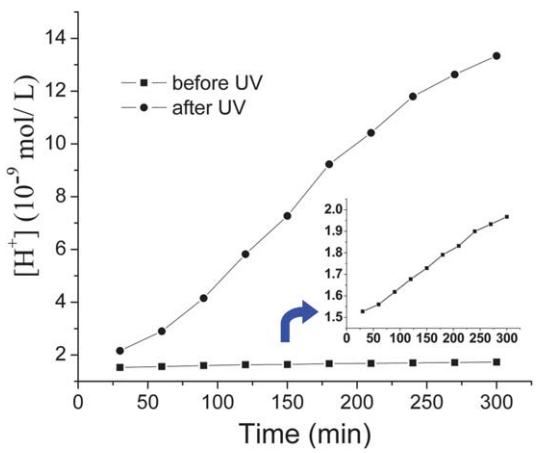


**Fig. 11** Plot of proton concentration [H+] (calculated from the excitation spectra of HPTS) *vs.* time for a vesicle solution of $PDMA_{37}$-*b*-P($BiPA_{50}$-*co*-$Azo_6$) with a pH gradient at 40 °C. The inset is the rescaled result obtained with the solution without UV irradiation.

## Conclusions

We synthesized two series of amphiphilic BCPs, PDMA-*b*-P(BiPA-*co*-Azo) and PAA-*b*-P(BiPA-*co*-Azo), which differ in the hydrophilic block but have the same SCLCP hydrophobic block containing biphenyl mesogens in majority and a small amount of azobenzene mesogens. Both BCPs could form large vesicles in aqueous solution with a SCLCP membrane. The BCPs were designed for investigation of the photoinduced order–disorder transition of the mesogens confined within the vesicle membrane as a result of the *trans-cis* photoisomerization of azobenzene and the LC cooperativity. Photo-optical measurements on a vesicle solution provided evidence that a photoinduced LC order-disorder transition within the vesicle membrane occurred in aqueous solution. Using pH-sensitive HPTS as a fluorescent probe, we found a photo-softening effect on the vesicle membrane. Similar to plasticization of the vesicle membrane by adding a good solvent in aqueous solution, the photoinduced softening results in an increase in the rate of proton diffusion from the interior to outside of the vesicle through the SCLCP membrane.

## Acknowledgements

We acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and le Fonds québécois de la recherche sur la nature et les technologies of Québec (FQRNT). YZ is a member of the FQRNT-funded Center for Self-Assembled Chemical Structures. BY also thanks the China Scholarship Council for a scholarship supporting his studies in Canada.

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