

## Supporting Information

### Light-Responsive Block Copolymer Vesicles Based on a Photo-Softening Effect

Bin Yan, Xia Tong, Patrick Ayotte, Yue Zhao\*

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

#### 1. Synthesis

##### Materials

All reagents were purchased from Aldrich at the highest purity available and used as received unless otherwise stated. 2, 2'-Azobis(isobutyronitrile)(AIBN) (Polyscience) was recrystallized twice from ethanol before use. The azobenzene monomer, 6-[4-(4-methoxyphenylazo)phenoxy]hexyl acrylate (Azo),<sup>1</sup> and the monomer displaying a biphenyl group, 6-[4-(4-cyanophenyl)phenoxy]hexyl acrylate (BiPA),<sup>2</sup> were synthesized according to literature methods. The chain transfer agent (CTA), 2-dodecylsulfanylthiocarbonylsulfanyl-2-methyl propionic acid, was synthesized as previously described.<sup>3</sup>

##### Synthesis of Diblock Copolymers PDMA-*b*-P(BiPA-*co*-Azo)

The macro-CTA, PDMA<sub>37</sub>-CTA, was synthesized using a method taken from the literature<sup>3</sup> and the details will thus not be repeated here. However, the synthesis of one BCP is briefly described below. BiPA (0.4236 g, 1.2 mmol), Azo (0.056 g, 0.5 mmol), macro-CTA (0.09 g, 0.03 mmol), and AIBN (1.4 mg, 0.009 mmol) were added into a 5 mL one-necked (?) flask. Then, dimethylsulfoxide (0.5 mL) was added to dissolve the mixture. After purging 15 min with nitrogen, the flask was sealed and placed in an oil bath preheated to 80 °C for 2 hr. The solution was then diluted with THF and dripped into anhydrous ethyl ether for precipitation of the BCP. The purification was repeated three times before the sample was collected and dried in a vacuum oven at room temperature for 24 h. Yield: 50 %. In this case, the sample obtained was PDMA<sub>37</sub>-*b*-Poly (BiPA<sub>50</sub>-*co*-AZO<sub>6</sub>).

##### Synthesis of Diblock Copolymers PAA-*b*-P(BiPA-*co*-Azo)

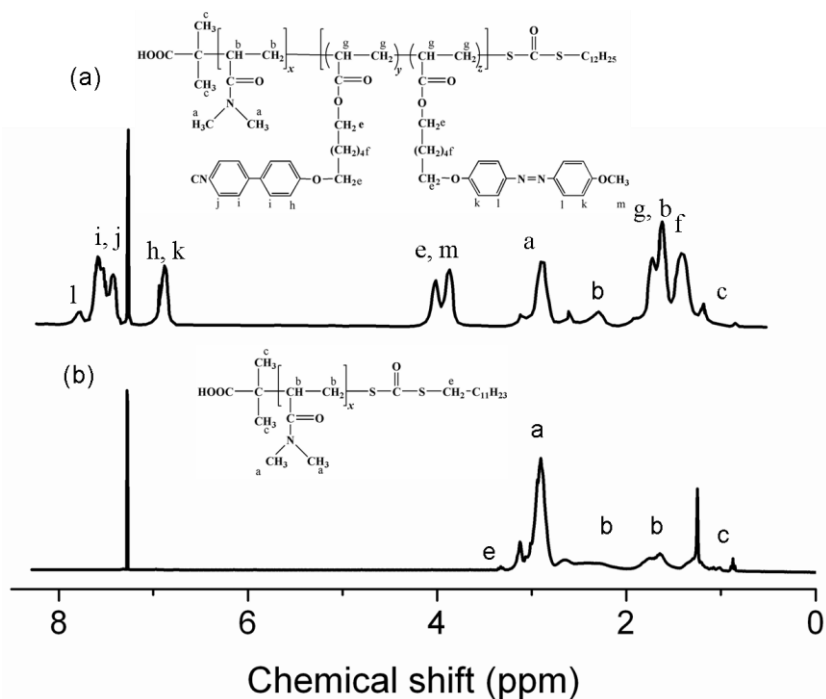
The synthesis of the macro-CTA, PtBA<sub>40</sub>-CTA, followed a procedure taken from the literature<sup>4</sup> and will thus not be repeated. An example of the BCP synthesis is detailed here. BiPA (0.2824 g, 8 mmol), Azo (0.03 g, 0.8 mmol), PtBA<sub>40</sub>-CTA (0.08 g, 0.02 mmol), AIBN (0.8 mg, 0.009 mmol) were added into a 5 mL one-necked flask. They were then dissolved in dimethylsulfoxide (0.7 mL). After 15 min nitrogen purge, the flask was sealed and placed in a preheated oil bath at 80 °C for 2 h. The reaction solution was diluted with THF and dripped into cold anhydrous ethyl ether for precipitation of the sample. The purification was repeated three times, and the sample was collected and at room temperature for 24 h in a vacuum oven. The diblock copolymer obtained was PtBA<sub>25</sub>-*b*-P(BiPA<sub>50</sub>-*co*-AZO<sub>4</sub>) (P9 in Table 1), which was then used to prepare PAA<sub>25</sub>-*b*-P(BiPA<sub>50</sub>-*co*-AZO<sub>4</sub>) through hydrolysis. In a typical reaction, PtBA<sub>25</sub>-*b*-P(BiPA<sub>50</sub>-*co*-AZO<sub>4</sub>) (223 mg) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) followed by the addition of a 5-fold molar excess of trifluoroacetic acid (with respect to the amount of *t*-butyl groups in the copolymer) (0.5 g). The reaction mixture was stirred at room temperature for 24 h. After purification by precipitation in ether, the BCP of PAA-*b*-P(BiPA-*co*-Azo) was collected and dried in a vacuum

oven at room temperature.

## 2. Characterizations

$^1\text{H}$  NMR spectra were obtained with a Bruker Spectrometer (300 MHz, AC 300). Gel permeation chromatography (GPC) measurements were performed using a Waters system equipped with a refractive index and a photodiode array detector; THF was used as eluent, and flowed at a rate of 0.5 mL/min, while polystyrene (PS) standards were used for calibration. A Perking-Elmer DSC-7 differential scanning calorimeter (DSC) was used to investigate the phase transition behaviors. Indium was used as the calibration standard while heating or cooling rates were set to 10 °C /min. Polarizing optical microscopic (POM) observations were conducted on a Leitz DMR-P microscope equipped with an Instec hot stage. UV-vis spectra were recorded with a Varian 50 Bio spectrophotometer. Transmission electron microscopy (TEM) observations were carried out using a Hitachi H-7500 microscope at an acceleration voltage of 80 kV. For sample preparation, 5  $\mu\text{L}$  of a given vesicle solution was deposited on a TEM copper grid and dried at room temperature. UV and visible lights used for irradiation of vesicle solutions were generated by a spot curing system (Novacure 2100) combined with a UV filter (centered at 365 nm) and a visible light filter (in the 400-500 nm region).

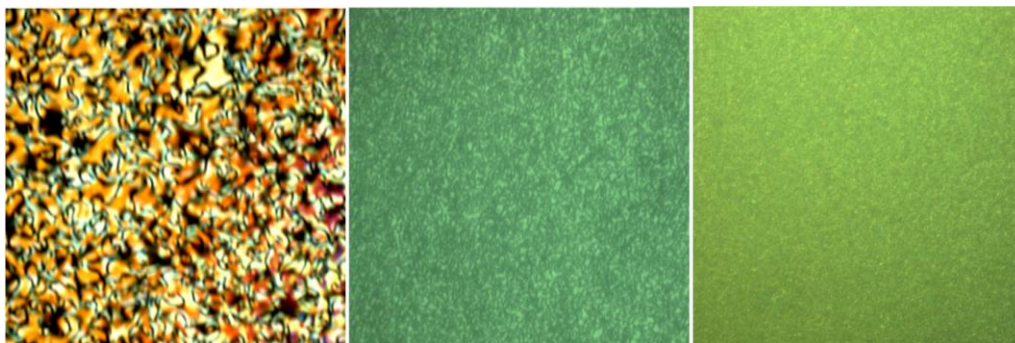
Figure S1 shows the  $^1\text{H}$  NMR spectra of PDMA<sub>37</sub>-CTA and PDMA<sub>37</sub>-*b*-P(BiPA<sub>50</sub>-*co*-Azo<sub>6</sub>) (samples P0 and P2 in Table 1 respectively). The BCP composition could be determined by comparing the integrals of the resonance peaks of azobenzene at ~ 7.83 ppm, of biphenyl group at 7.40-7.72 ppm, of PDMA methyl groups at 2.9-3.2 ppm and of PtBA methyl groups at 1.5 ppm.



**Figure S1.** Examples of  $^1\text{H}$  NMR spectra of polymers: (a) P2; and (b) P0 (Table 1)

### 3. Polarizing Optical Microscope Images

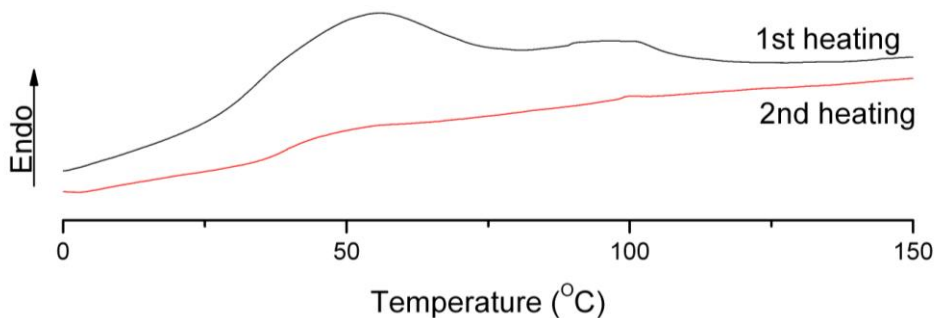
Figure S2 shows polarized optical micrographs of three BCP samples: PDMA<sub>37</sub>-*b*-P(BiPA<sub>50</sub>-*co*-Azo<sub>6</sub>) (P2); PtBA<sub>40</sub>-*b*-P(BiPA<sub>36</sub>-*co*-Azo<sub>12</sub>) (P11); and PAA<sub>40</sub>-*b*-P(BiPA<sub>36</sub>-*co*-Azo<sub>12</sub>) (P12). The micrographs were recorded at 60 °C upon cooling the BCP thin films from the isotropic phase and into the LC phase. The apparently different textures should be a reflection of the influence of the hydrophilic block on the LC domain development in the solid state.



**Figure S2.** Polarizing optical micrographs of liquid crystal block copolymers: (a) P2; (b) P11; (c) P12. All of them were annealed at 60 °C (Picture area: 81 μm × 81 μm). (put a, b, and c on pictures)

### 4. DSC of BCP Vesicles

Vesicles of P2 were collected by freeze-drying of an aqueous solution yielding a powder sample. Figure S3 shows the DSC heating curves of the freeze-dried vesicles. A large enthalpy relaxation endotherm is observed around 50 °C on the first heating scan, which is not unusual for polymer samples prepared by freeze-drying (i.e., unrelaxed); a LC-isotropic transition can also be noticed near 100 °C. This observation suggests the presence of a LC phase within the vesicle membrane. After cooling from the isotropic phase, the second scan shows T<sub>g</sub> and LC-isotropic transitions similar to those observed in bulk samples of P2.



**Figure S3.** DSC curves of the P2 vesicle powder

### References:

1. Ringsdorf, H.; Schmidt, H. W. *Makromol. Chem.* **1984**, *185*, 1327.
2. Portugall, M.; Ringsdorf, H.; Zentel, R. *Makromol. Chem.* **1982**, *183*, 2311.
3. Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754.
4. Qi, B.; Tong, X.; Zhao, Y.; Zhao, Y. *Macromolecules* **2008**, *41*, 3562.
5. Yu, S. Y.; Azzam, T.; Rouiller, I.; Eisenberg, A. *J. Am. Chem. Soc.* **2009**, *131*, 10557.
6. Lakowicz, J. *Principle of Fluorescence Spectroscopy*, 3<sup>rd</sup> Ed. Springer, 2006.
7. Wu, J.; Eisenberg, A. *J. Am. Chem. Soc.* **2006**, *128*, 2880.