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Photoinduced Fusion of Micro-Vesicles Self-Assembled from Azobenzene-Containing Amphiphilic Diblock Copolymers

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Experimental Section

Materials

Chain transfer agent (CTA), 2-phenylprop-2-yl dithiobenzoate (PPDTB), was synthesized by Grignard/addition reactions based on the reported method.[1] The azobenzene monomer 6-[4-(4-methylphenyl-azo)phenoxy]hexyl acrylate(AzoM) was synthesized according to the procedure similar to the published method.[2] Tetrahydrofuran (THF) was refluxed over sodium for 24 h, and then distilled prior to use. N-isopropylacrylamide (NIPAM) was purified by recrystallization in a benzene/n-hexane (v/v=35/65) mixture. Azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol. Other chemicals were used without further purification unless otherwise indicated.

Synthesis of Poly(N-isopropylacrylamide) Capped with Dithiobenzoate (PNIPAM-SC(S)Ph)
A THF solution of NIPAM (2 g, 1.8×10⁻² mol), AIBN (3 mg, 1.8×10⁻⁵ mol) and PPDTB (48 mg, 1.8×10⁻⁴ mol) in a glass tube was degassed by three freeze-pump-thaw cycles, sealed off under vacuum, and heated at 70 °C for 24 h. After three times solution in THF and precipitation in diethyl ether, there was isolated a polymer PNIPAM capped with dithiobenzoate group (PNIPAM-SC(S)Ph), which, according to the NMR spectra, had 83 repeating units and was used as macro-CTA in the following block copolymerization of azobenzene monomer. PNIPAM-CTA: 

\[ {^1}H \text{ NMR (300MHz, CDCl}_3\), \delta : 5.8-7.1, 4.0, 2.2, 1.8, 1.6, 1.4, 1.1. \]

The molecular weight and molecular weight distribution of the PNIPAM homopolymer were determined by gel permeation chromatography (GPC) using THF as eluents: \( M_n=8900 \) and \( M_w/M_n=1.05 \).

**Synthesis of PNIPAM-b-PAzoM Diblock Copolymers**

A mixture of azobenzene monomer (2.0 g, 5.5×10⁻³ mol), PNIPAM-CTA (1.0 g, 1.1×10⁻⁴ mol) and AIBN (3.3 mg, 2.0×10⁻⁵ mol) was dissolved in 10mL THF, and the mixture solution was treated by the same degassing process above, the resulting solution was heated to 70 °C for 24 h. Afterward, the reaction mixture was dissolved in THF and precipitated in diethyl ether for three times, and the collected copolymer was dried in a vacuum oven for 24 h at room temperature. The molecular weight and molecular weight distribution of PNIPAM-b-PAzoM were characterized by GPC: \( M_n=14300 \) and \( M_w/M_n=1.06 \). The number of the repeating units for PAzoM block was determined to be 20 by \( {^1}H \) NMR. Copolymer PNIPAM_{83}-b-PAzoM_{20} (composition determined by \( {^1}H \) NMR) was synthesized using PNIPAM_{83} as macro-RAFT agent. The \( {^1}H \) NMR spectrum of the copolymer is given in Figure 1. \( T_g: 43 \) °C and \( T_{ni}: 97 \) °C. UV-vis (THF): \( \lambda_{max}=350 \) nm (trans \( \pi-\pi^* \) transition).

**Measurements**
$^1$H NMR spectra were obtained on a Bruker 300 MHz FT-NMR spectrometer. The transition temperatures were recorded using a Perkin-Elmer PYRIS diamond differential scanning calorimeter (DSC) (heating and cooling rates: 10 °C/min). UV-vis spectra were recorded on a SHIMADZU UV-2501PC spectrophotometer, which was also used for turbidity measurement. The instrument was set at the transmittance mode, and measurements were performed varying with different water content, at $\lambda=700$ nm. The molecular weights and their distributions of PNIPAM and PNIPAM-$b$-PAzoM were determined by GPC utilizing a Waters model 1515 pump and a model 2414 differential refractive index detector with three Styrage columns HT2, HT3, and HT4 connected in a serial fashion. THF was used as the eluent at a flow rate of 1.0 mL/min.

**Polymer Structure Characterization**

The $^1$H NMR spectrum of PNIPAM in CDCl$_3$ reveals the presence of signals characteristic of PNIPAM at $\delta$: =5.8-7.1 (for NH), 4.0 (for CH connected to NH), and 1.1 ppm (for CH$_3$) and the presence of signals at $\delta$=7.9, 7.6, and 7.4 ppm, which are ascribed to the dithiobenzoyl groups located at the PNIPAM chain end.$^{[3]}$ According to the NMR spectrum, the degrees of polymerization (DP) of the PNIPAM homopolymer were determined to be 83 and the molecular weight was calculated to be 9300. The PNIPAM-CTA is synthesized and the molecular weight distribution is characterized by GPC in THF using polystyrene calibration. Narrow distributed PNIPAM homopolymer is obtained: $M_n=8900$ and $M_w/M_n=1.05$. Comparing with the molecular weight determined by $^1$H NMR, lower molecular weights of PNIPAM and the copolymer of PNIPAM-$b$-PAzoM were found by GPC measurement, as shown in Table S1.

The $^1$H NMR spectrum of PNIPAM-$b$-PAzoM in CDCl$_3$ is shown in Figure S1 and the correspondences are presented. It agrees well with the proposed structure. The molecular weight and the molecular weight distribution are also characterized by GPC in THF using polystyrene
calibration: $M_n$=14300 and $M_w/M_n$=1.06. Figure S2 shows the GPC traces of PNIPAM$_{83}$ and the final block copolymer PNIPAM$_{83}$-b-PAzoM$_{20}$. The $M_w/M_n$ preserved narrow distribution in the copolymerization of PNIPAM-CTA with azobenzene monomers. The number of repeating units of AzoM in the copolymer is determined to be 20 in terms of $^1$H NMR analysis.

**Liquid Crystalline Property of PNIPAM-b-PAzoM**

Polymer film was coated from THF solution (2 wt%) onto a quartz surface. Nematic marbled and *Schlieren* textures were observed for PNIPAM$_{83}$-b-PAzoM$_{20}$ diblock copolymer under annealing condition at 90 °C for 12 h, which is shown in Figure S3.


Table S1. Synthesis of copolymer based on N-isopropylacrylamide (NIPAM) and azobenzene monomer (AzoM) by RAFT polymerization

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>T °C</th>
<th>Time h</th>
<th>CTA</th>
<th>[AIBN] mol/L×10⁻³</th>
<th>[Monomer] mol/L</th>
<th>[CTA] mol/L×10⁻²</th>
<th>Mₙ,exp a g/mol</th>
<th>Mₙ,exp b g/mol</th>
<th>Mₘ/Mₙ b</th>
</tr>
</thead>
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<tr>
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<td>24</td>
<td>PPDTB</td>
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<td>1.8</td>
<td>1.8</td>
<td>9300</td>
<td>8900</td>
<td>1.05</td>
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<tr>
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<td>PNIPAM-b-PAzoM</td>
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<td>24</td>
<td>PNIPAM</td>
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<td>1.1</td>
<td>16600</td>
<td>14300</td>
<td>1.06</td>
</tr>
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</table>

a) Determined by $^1$H NMR in CDCl₃.

b) Determined by GPC (THF, calibration with polystyrene standards).

Figure S1. $^1$H NMR spectrum of PNIPAM-b-PAzoM in CDCl₃.
**Figure S2.** GPC traces of PNIPAM$_{83}$ macro-RAFT agent and PNIPAM$_{83}$-b-PAzoM$_{20}$.

**Figure S3.** Polarizing optical micrograph (POM) of PNIPAM$_{83}$-b-PAzoM$_{20}$ film (480×).

**Figure S4.** Relationship between T% of the dispersion and the water content.
Figure S5. Photomicrographs of the self-assembled vesicles in the H2O/THF mixture with different water content (vol.-%): (a) 33% (b) 50% (c) 75%.

Figure S6. UV-vis spectra of PNIPAM-b-PAzoM dissolved in THF solution (solid line), and self-assembling into micro-vesicles in a 50% (vol.-%) H2O/THF mixture before UV irradiation (dash line) and after UV irradiation (dot line).