

Supporting Information

UV and visible light induced fission of azobenzene-containing polymer vesicles

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Materials

N,N-isopropylacrylamide was recrystallized twice from hexanes prior to use. Meanwhile, α,α' -azobisisobutyronitrile (AIBN) was recrystallized from ethanol and stored at low temperature. THF was refluxed over sodium and distilled while triethylamine was refluxed with potassium hydroxide and distilled. As for 4-(decyloxy)benzoic acid, it was prepared according to a method established in the literature.^[1] The other chemicals were used without further purification.

Monomer of 6-[4-(4-methoxyphenylazo)phenoxy]hexyl methacrylate

The azobenzene monomer was synthesized following a previously described procedure.^[2]

Macro-CTA of N,N-Isopropylacrylamide

The chain transition agent (CTA) of 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid (DTCMA) was synthesized based on a reported method.^[3] A distilled tetrahydrofuran (THF) solution of NIPAM (1 g), AIBN (3 mg) and DTCMA (60 mg) in a glass tube was degassed through three freeze-pump-thaw cycles, sealed off under a vacuum, and heated at 70 °C for 24 h. The solution in THF was then precipitated in ethyl ether. Afterwards,

PNIPAM

capped with trithiobenzoate groups (PNIPAM-SC(S)SR) was obtained. The polymer was purified by dissolution in THF and precipitation in ethyl ether three times. Finally, the

collected macro-CTA was dried at 50 °C under a vacuum.

Azobenzene diblock copolymer

A mixture of azo monomer (0.5 g), PNIPAM-SC(S)SR (0.3 g) and AIBN (0.5 mg) was dissolved in 5 mL of THF. It was then subjected to the same handling process described above. The resulting solution was then heated to 70 °C for 36 h. The product of the reaction was purified by dissolution in THF and precipitation in ethyl ether three times. Lastly, the collected polymer was dried at 50 °C for 24 h under a vacuum.

Characterization of PNIPAM-b-PAZO

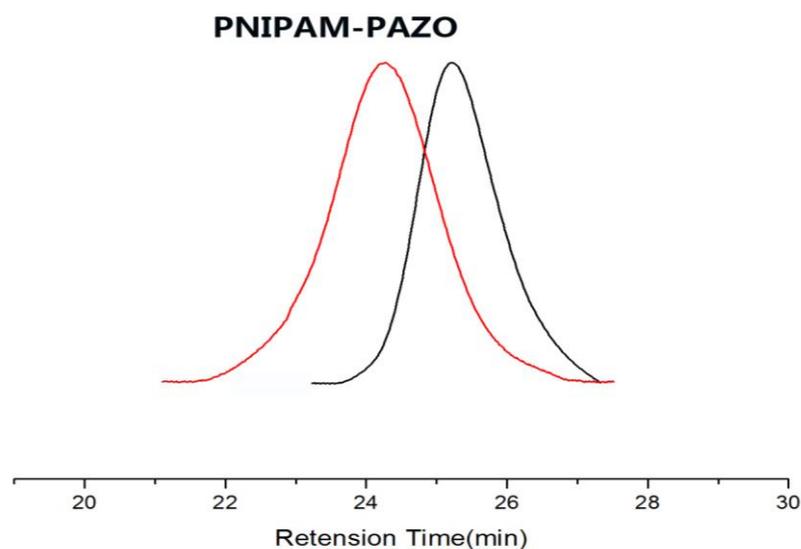


Figure S1. GPC curves of PNIPAM macroinitiator and PNIPAM-b-PAZO copolymers.

The polydispersity indexes of PNIPAM macroinitiator and PNIPAM-b-PAZO are 1.06 and 1.27, individually, given by GPC in THF using polystyrene calibration. In addition, the molecule weight of two polymers was also obtained: \overline{Mn} = 14153 (PNIPAM), \overline{Mn} = 34200 (PNIPAM-b-PAZO). The average numbers of repeat units were estimated by comparing the molecular weight of polymer block with that of monomers, resulting in PNIPAM₁₂₃-b-PAZO₅₀.

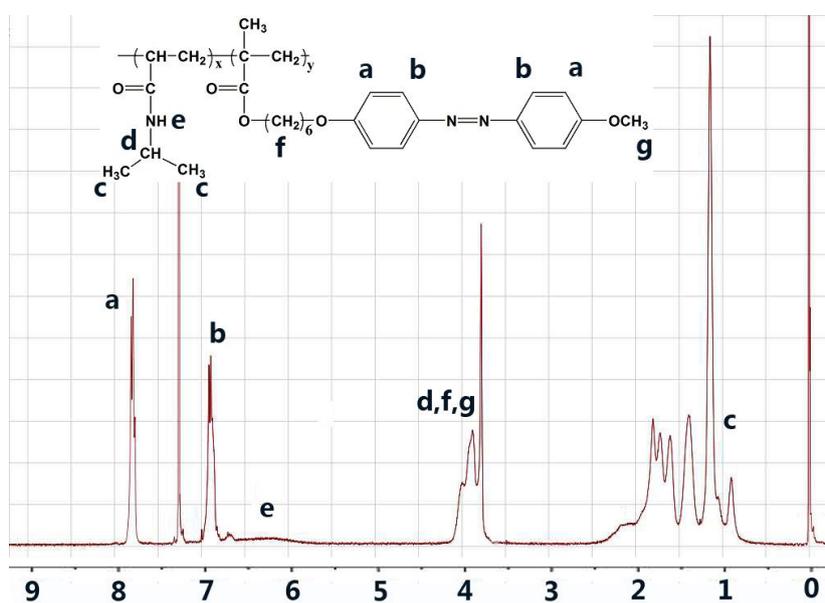


Figure S2. The ¹H NMR spectrum of PNIPAM-b-PAZO in CDCl₃.

The composition of the block copolymer was determined from the ratio of peak integrals around 1.1 ppm and 4.0 ppm of PNIPAM to the peak at approximately 7.8 ppm of PAZO.

It agrees with the structure analyzed by GPC .

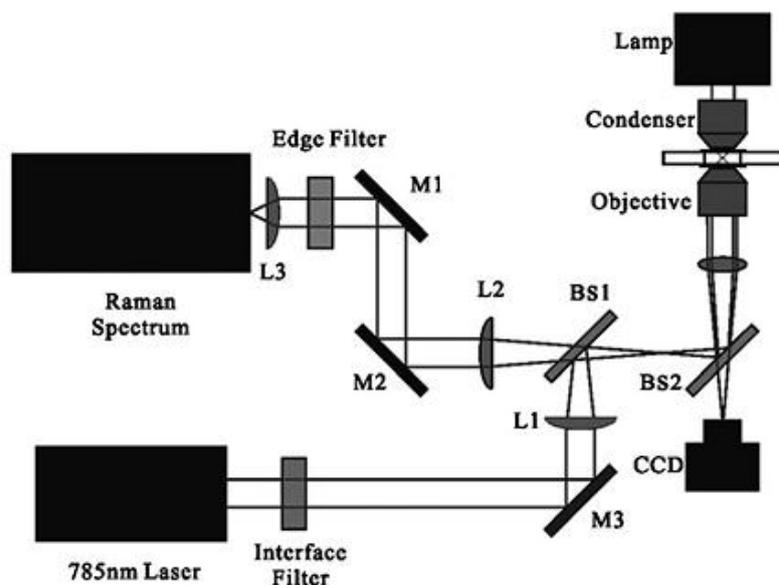


Figure S3. Layout of the LTRS instrument.

The system composes of microscope, a spectrometer and a continuous-wave diode-pumped solid-state laser, in which the 785 nm laser beam is used as both a trap beam and a Raman excitation beam. The Raman spectrum excited from the sample is collected by liquid nitrogen cooled CCD and stored on a computer for analysis. Videos were taken by CCD camera and recorded on a computer. The 785 nm laser beam from an diode laser (120 mW Crystalaser) is focused by a high NA oil-immersion objective (100 \times , NA1.35, OLYMPUS) to a spot in the specimen plane. This spot which is able to hold small particles creates optical tweezer. With a interface filter blocks the plasma line, the beam can also be used for Raman spectrum excitation. The Raman spectrum excited from the sample is collected by a liquid nitrogen cooled CCD and stored on a computer for analysis. The high pressure Mercury is an accessory of the microscope with output of 150 mW \cdot cm⁻², which serves as a light source for irradiation experiment. Videos are taken by CCD camera and recorded on a computer.

M: mirror, L: lens, BS: beam splitter.

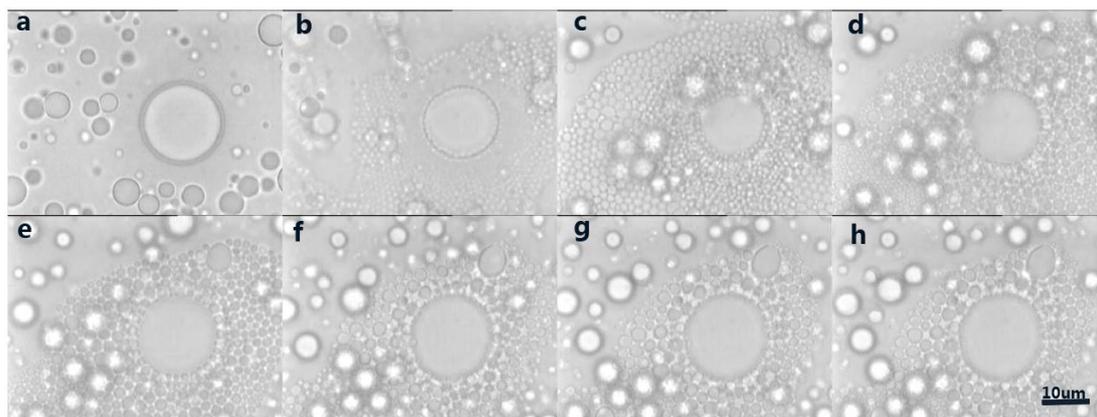


Figure S4. Optical micrographs of the PNIPAM-PAZO vesicles in 50 vol.-% H₂O/THF solution before (a) and after irradiation of light (435 nm, 1.5 mW · cm⁻²) for 10 second (b), 40 second (c) and then exposed to visible light(532 nm,1.5 mW · cm⁻²), 50 second (d), 70 second(e), 260 second(f), 300 second(g), 370 second (h).

Video

The fission of a single vesicle under the irradiation of UV light (365 nm, 1.5 mW · cm⁻²).

References

- [1] D. Lacey, H. N. Beattie, G. R. Mitchellb, J. A. Pople, *J. Mater.Chem.* 1998, 8, 53.
- [2] Ringsdorf, H.; Schmidt, H. W. *Makromol. Chem.* 1984, 185,1327.
- [3] J. T. Lai, D. Filla, R. Shea, *Macromolecules* 2002, 35, 6754.