# In situ observation on azobenzene isomerization along with photo-induced swelling of cross-linked vesicles by laser-trapping Raman spectroscopy

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## Synthesis of PNIPAM-PAzPy6

#### Monomer of 6-[4-(4-Pyridyazo)phenoxy]hexyl Methacrylates

The azopyridine monomer was synthesized following a previously described

procedure[ L. Cui, Y. Zhao, Chem. Mater. 2004, 16, 2076; M. Millaruelo, L. S.

Chinelatto, L. Oriol, M. Pinol, J.-L. Serrano, R. M. Tejedor, Macromol. Chem. Phys.

2006, 207, 2112].

#### Macro-CTA of N,N-Isopropylacrylamide

The chain transition agent (CTA) of 2-(dodecylthiocarbonothioylthio)-2methylpropanoic acid (DTCMA) was synthesized based on a reported method (J. T. Lai, D. Filla, R. Shea, Macromolecules 2002, 35, 6754). 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.

### **Azopyridine 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  $70^{\circ}$ 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.



Figure S1. GPC curves of PNIPAM macroinitiator and PNIPAM-b-PAzPy6 copolymers. The polydispersity indexes of PNIPAM macroinitiator and PNIPAM-b-PAzPy6 are 1.10 and 1.29, individually, given by GPC.



Figure S2. The <sup>1</sup>H NMR spectrum of PNIPAM-*b*-PAzPy6 in CDC13. The composition of the block copolymer was determined from the ratio of the integrals of the peak around 1.1 ppm and 4.0 ppm of PNIPAM to the peak at about 8.7ppm of PAzPy. The average numbers of repeat units were estimated by combining  $M_n$ =15000 (GPC) for the PNIPAM macroinitiator and the composition determined from the <sup>1</sup>H NMR spectrum, resulting in PNIPAM<sub>135</sub>-*b*-PAzPy<sub>54</sub>





Figure S3. The cis-trans LTRS of one single vesicle with cross-linking degree of 0% (a), 18.7%(b), and 30.5%(c)

Wavenumber(cm-1)	Assignment
3432	N-H stretching (bonding)
3310	N-H stretching (free)
3069	N-H
2968	asymmetric C-H stretching of
	-C(CH3)2
2936	symmetric CH2 stretching
2876	symmetric C-H stretching of
	-C(CH3)2
1725	C=O stretching of COOC
1646	C=O stretching of CONC
1602	Phenyl ring stretching
1584	Pyridine ring stretching
1546	N-H bending
1500	CH2 scissoring + C-H bending
	in plane
1457	CH2 scissoring in chain
	+symmetric
	deformation of -C(CH3)2
1454	CH2 scissoring in chain
1420	ring stretching + C-H bend
1404	CH2 scissoring
1388	asymmetric deformation of
	-C(CH3)2+
	CH2 bending in chain, in chain
	Direction
1368	asymmetric deformation of
1	

Table S1 Observed IR Frequencies (in cm-1) Assignments of PNIPAM-b-PAzPy6

	-C(CH3)2
1316	CH2 bending in chain, in chain
	direction
1256	ring stretching + CH2 bend in
	chain
1177	symmetric CH2 wag in chain
1141	C-O stretching
1020	CH2-CH2 stretch in chain, in
	chain
	direction
842	C-H out of plane
796	C-C=C bend
561	C-H out of plane