

How Can Photoisomerization of Azobenzene Induce a Large Cloud Point Temperature Shift of PNIPAM?

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Figure S1(a) presents the UV-vis spectra of P(NIPAM_{100-co}-MAzo₂) in a diluted aqueous solution (0.1 mg/mL) upon time-dependent irradiation with UV light 365 nm (90 mW cm⁻²). The *trans* to *cis* isomerization of azobenzene is obvious due to the continuous decrease of the initial absorption maximum of *trans* azobenzene at ~320 nm and the simultaneous increase of *cis* azobenzene at ~425 nm. The *trans-cis* isomerization is completed within 60 s under the experimental conditions. The transition of the *cis* isomer back to the *trans* form was also relatively fast (within 60 s) upon irradiation with visible light 400~500 nm (data not shown here). Nevertheless, the *cis* isomers are rather stable in the dark and the thermal *cis-trans* isomerization without visible light would take more than 20 hrs, which is thus stable enough to complete other measurements. By the incorporation of azobenzene, it is expected that the CPT of the present polymer will be influenced by photo-isomerization. As shown in Figure S1 (b), the transmittance of 2 mg/mL of P(NIPAM_{100-co}-MAzo₂) in aqueous solution was recorded as a function of temperature before and after UV irradiation. The abrupt decrease of transmittance above 17 °C corresponds to the hydration to de-hydration transition as the polymer becomes insoluble. Due to the hydrophobicity of azobenzene units, the CPT was lower compared to that of PNIPAM at ~32 °C. Subsequently, the polymer solution was exposed to 365 nm UV light. After the full *trans-cis* isomerization, the transmittance of *cis*-rich polymer solution was recorded with the same procedure. However, an identical transmittance versus temperature curve was present and the CPT shift induced by the *trans-cis* isomerization was within 2 °C. The CPT of 2 mg/mL of the polymer in the mixed solvent of water and dioxane (50:50, vol) is displayed in Figure S1(c). Surprisingly, the CPT of P(NIPAM_{100-co}-MAzo₂) was ~18 °C for *trans* isomers, while it increased to ~36 °C after exposure to UV (corresponding to a CPT shift of 18 °C). Moreover, the CPT shift of P(NIPAM_{100-co}-MAzo₂) caused by the isomerization of azobenzene should be reversible and tunable by different wavelengths of light similarly to BCP. The CPT shift of P(NIPAM-*co*-MAzo) is dependent on the amount of azobenzene. In the mixed solvent of H₂O and dioxane (50:50, vol), PNIPAM with 0.8 mol% only had a CPT shift ~5 °C by the isomerization. PNIPAM with 3.8 mol% azobenzene which had a CPT lower than 6 °C (beyond the limit of the temperature controller) showed a CPT shift >12 °C.

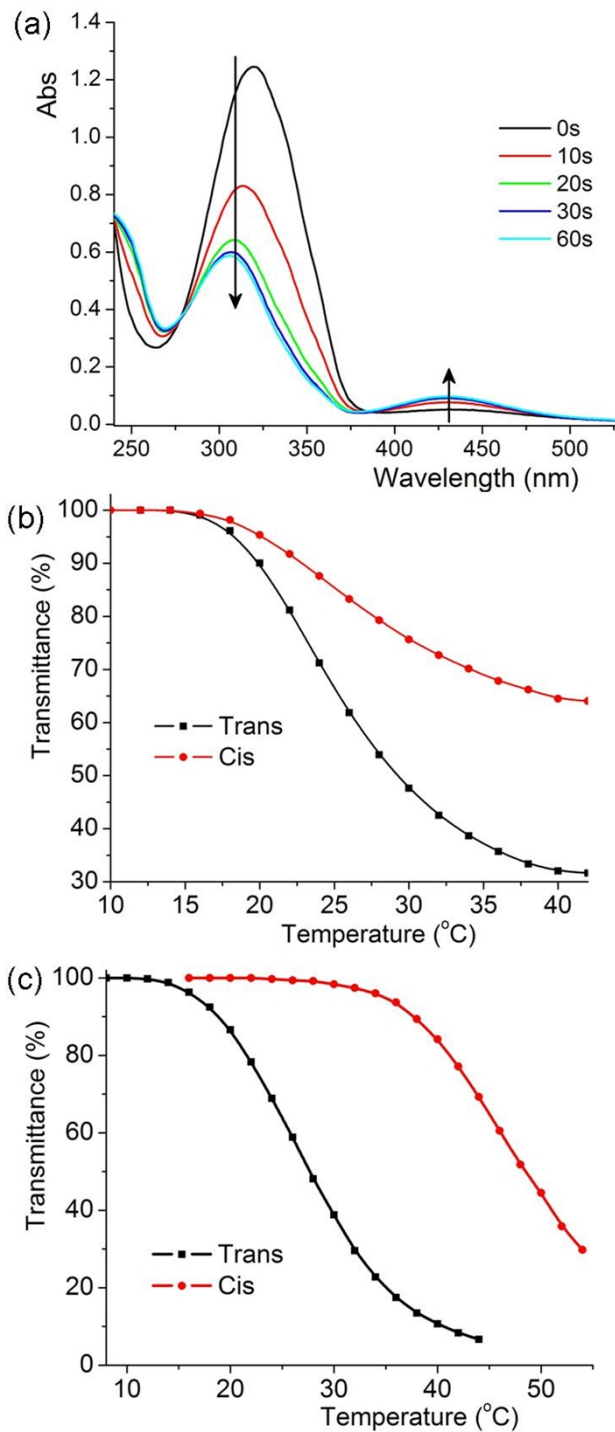


Figure S1. (a) UV-vis spectra of 0.1 mg/mL of P(NIPAM₁₀₀-co-MAZO₂) in water recorded at different UV (365nm) irradiation time; (b) Plot of the transmittance vs temperature for 2 mg/mL of P(NIPAM₁₀₀-co-MAZO₂) in H₂O before and after UV irradiation; (c) Plot of the transmittance vs temperature for 2 mg/mL of P(NIPAM₁₀₀-co-MAZO₂) in a mixed solvent of H₂O:dioxane =50:50 (vol%) before and after UV irradiation.