

Supporting Information

Effects of the Photo-induced Proton Generation on the Assembly Formation of Dual-Temperature and pH Responsive Block Copolymers

Yohei Kotsuchibashi,^a Tomomi Takiguchi,^{bc} Mitsuhiro Ebara^{bcd} and Takao Aoyagi*^{bc}

^a*International Center for Young Scientists (ICYs) and International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

^b*Biomaterials Unit, WPI-MANA, NIMS, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

^c*Department of Materials Engineering, Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan*

^d*Graduate School of Industrial Science and Technology, Tokyo University of Science, 6-3-1 Niijuku, Katsushika, Tokyo 125-8585, Japan*

E-mail: aoyagi.takao@nihon-u.ac.jp; Fax: +81-3-3293-7572; Tel: +81-3-3259-0433

FIGURE LEGENDS

Scheme S1. Synthesis of (A) P(NIPAAm-*co*-CIPAAm) (macro-CTA) and (B) P(NIPAAm-*co*-CIPAAm)-*b*-P(NIPAAm-*co*-BMAAm) by RAFT polymerization.

Figure S1. ^1H NMR spectra of P(NIPAAm-*co*-CIPAAm) in DMSO-d₆ at room temperature.

Figure S2. (A) Transmittance change of 0.1 w/v% aqueous solution of Red line: P(NIPAAm₈₈-*co*-CIPAAm₅), Blue line: P(NIPAAm₈₅-*co*-CIPAAm₇), Green line: P(NIPAAm₅₉-*co*-CIPAAm₁₅) at (A) pH 2 and (B) 12 as a function of temperature.

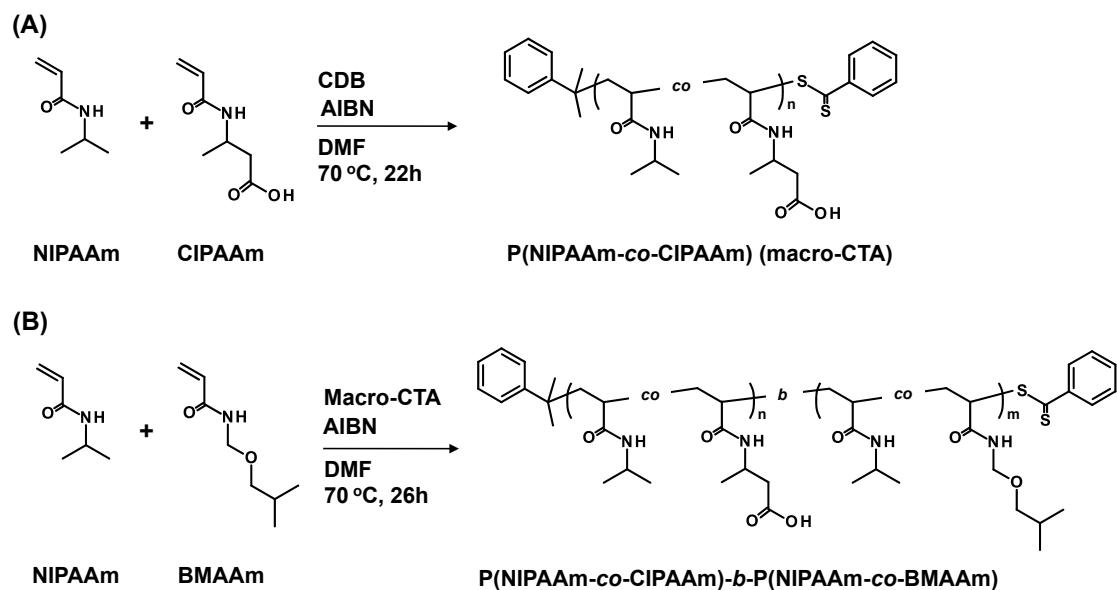
Figure S3. PH change of micelle solutions (P(NIPAAm₈₈-*co*-CIPAAm₅)-*b*-P(NIPAAm₅₈-*co*-BMAAm₇)) (○) NBA loaded micelle, (△) mixture solution of micelle and NBA, and (□) adding 1mM HCl to micelle solution.

Figure S4. Absorbance of micelle of P(NIPAAm₈₈-*co*-CIPAAm₅)-*b*-P(NIPAAm₅₈-*co*-BMAAm₇) and NBA suspension by UV irradiation.

Figure S5. Transmittance change of 0.1 w/v% aqueous solution of P(NIPAAm₅₉-*co*-CIPAAm₁₅)-*b*-P(NIPAAm₄₃-*co*-BMAAm₁₀) at pH 2 and 12 as a function of temperature.

Figure S6. Transmittance change of 0.1 w/v% aqueous solution of P(NIPAAm₈₈-*co*-CIPAAm₅)-*b*-P(NIPAAm₅₈-*co*-BMAAm₇) at various pH solutions as a function of temperature.

Figure S7. Size distribution histogram for P(NIPAAm₅₉-*co*-CIPAAm₁₅)-*b*-P(NIPAAm₄₃-*co*-BMAAm₁₀) at 25 °C in pH 12.



Scheme S1. Synthesis of (A) P(NIPAAm-co-CIPAAm) (macro-CTA) and (B) P(NIPAAm-co-CIPAAm)-b-P(NIPAAm-co-BMAAm) by RAFT polymerization.

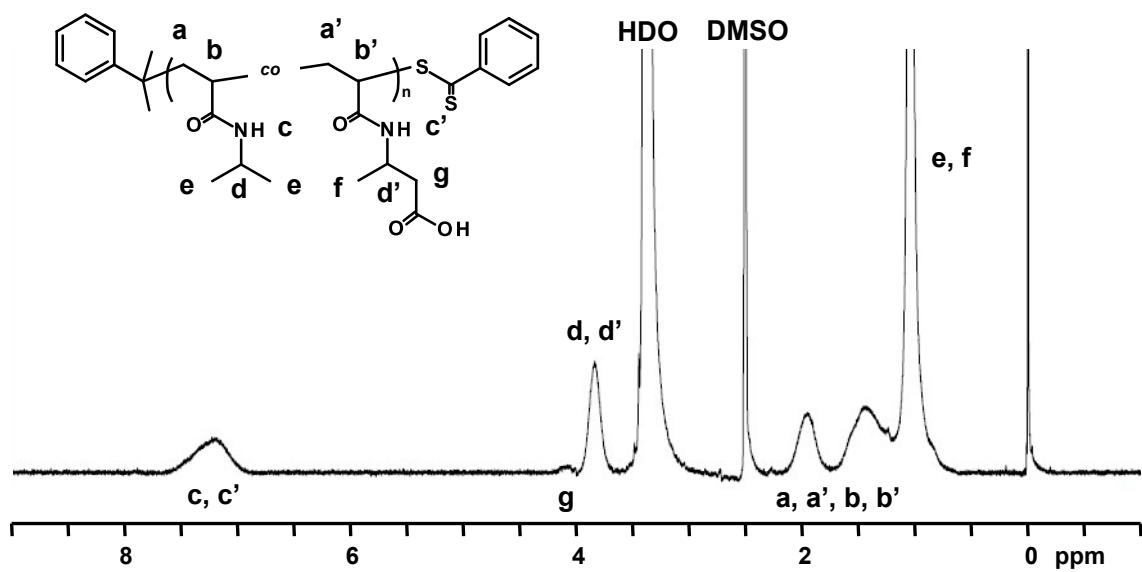


Figure S1. ^1H NMR spectra of P(NIPAAm-*co*-CIPAAm) in DMSO-d₆ at room temperature.

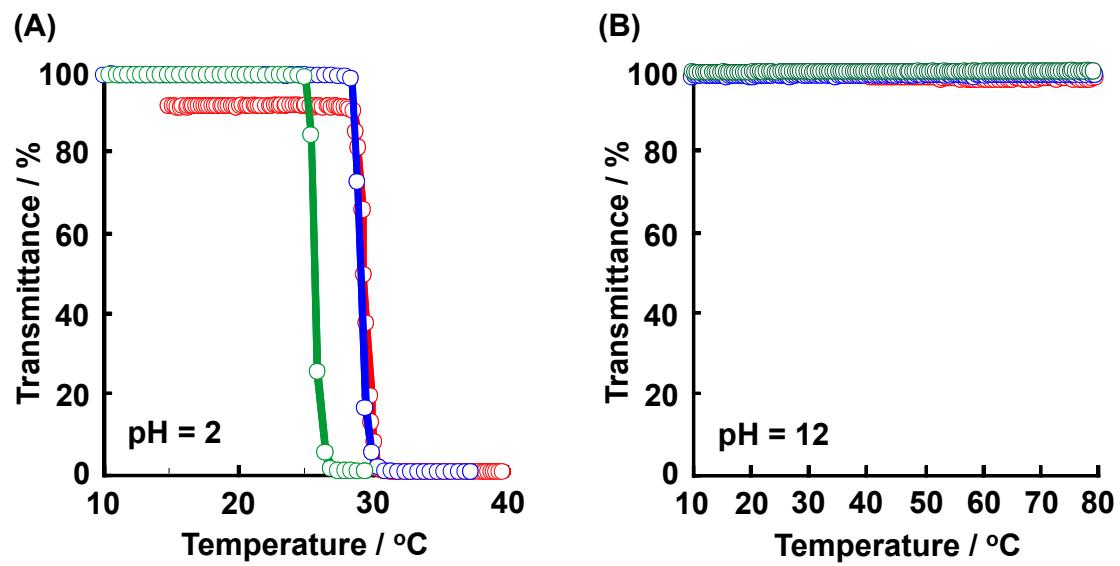


Figure S2. (A) Transmittance change of 0.1 w/v% aqueous solution of Red line: P(NIPAAm₈₈-co-CIPAAm₅), Blue line: P(NIPAAm₈₅-co-CIPAAm₇), Green line: P(NIPAAm₅₉-co-CIPAAm₁₅) at (A) pH 2 and (B) 12 as a function of temperature.

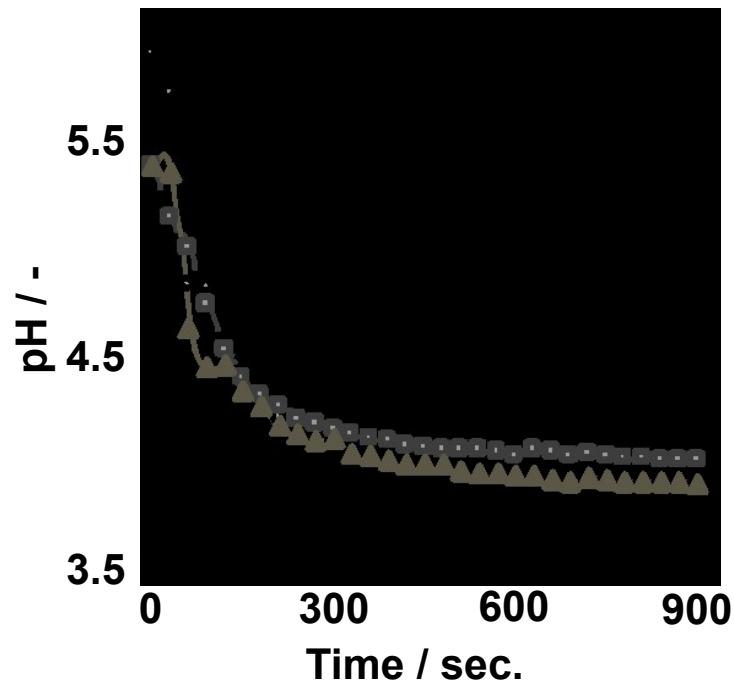


Figure S3. PH change of micelle solutions (P(NIPAAm₈₈-*co*-CIPAAm₅)-*b*-P(NIPAAm₅₈-*co*-BMAAm₇)) (○) NBA loaded micelle, (△) mixture solution of micelle and NBA, and (□) adding 1mM HCl to micelle solution.

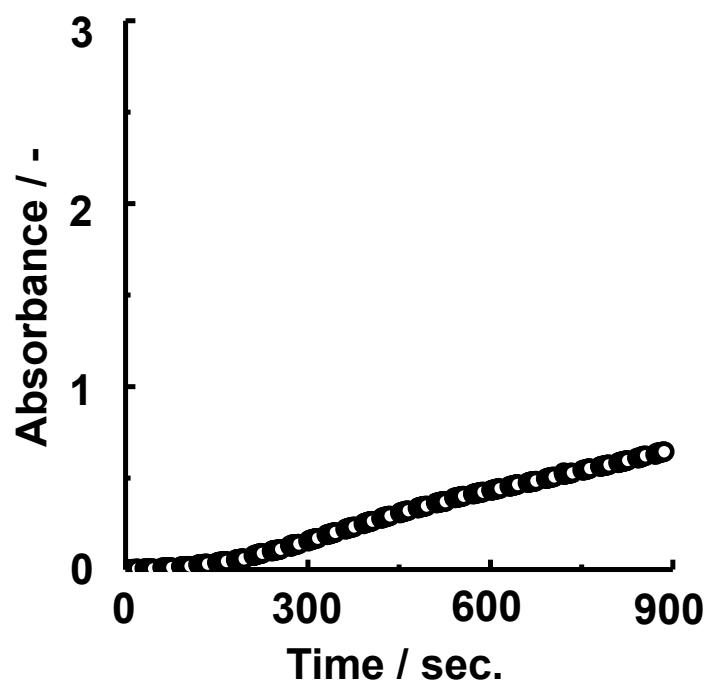


Figure S4. Absorbance of micelle of P(NIPAAm₈₈-*co*-CIPAAm₅)-*b*-P(NIPAAm₅₈-*co*-BMAAm₇) and NBA suspension by UV irradiation.

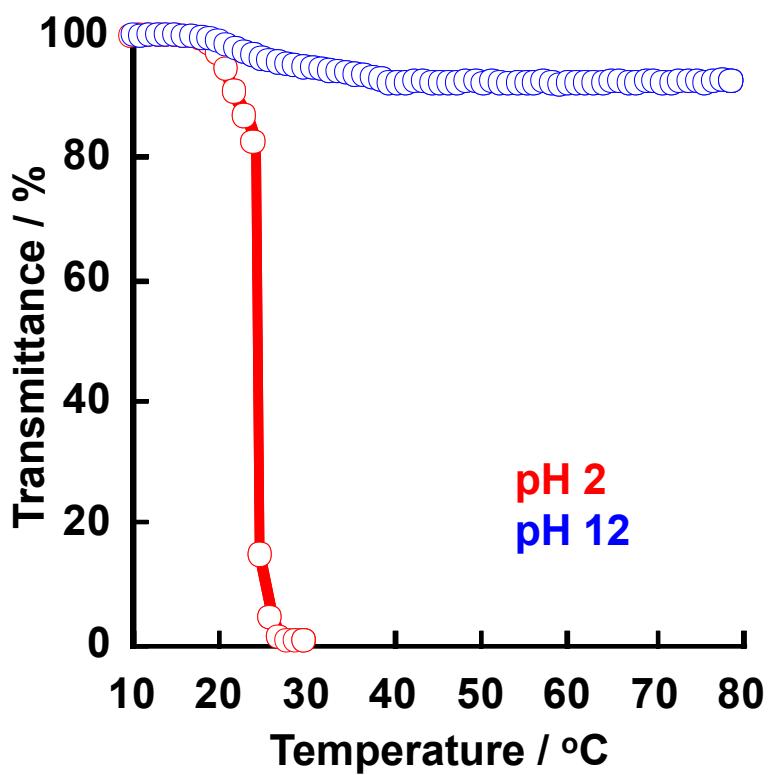


Figure S5. Transmittance change of 0.1 w/v% aqueous solution of P(NIPAAm₅₉-*co*-CIPAAm₁₅)-*b*-P(NIPAAm₄₃-*co*-BMAAm₁₀) at pH 2 and 12 as a function of temperature.

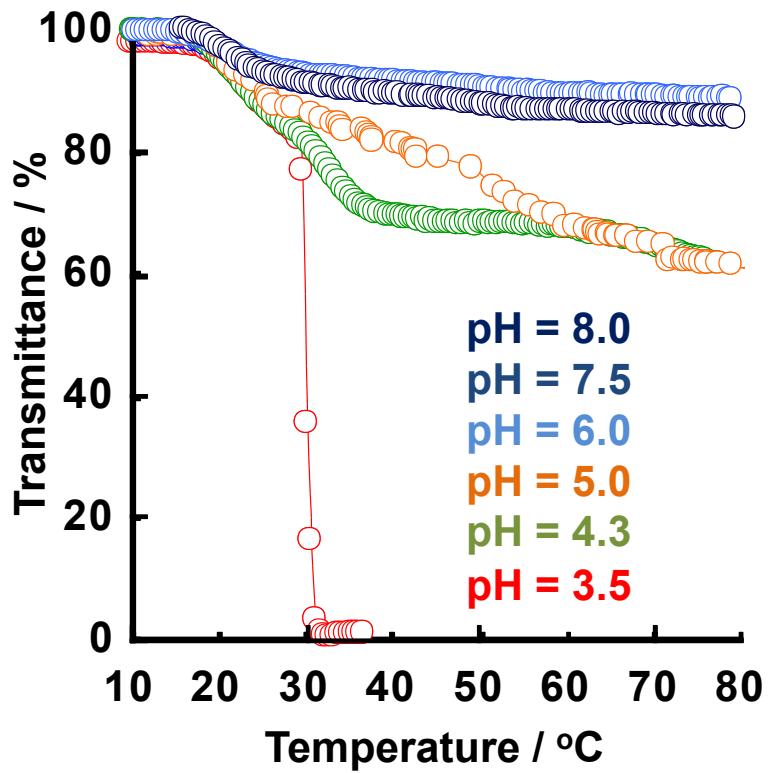


Figure S6. Transmittance change of 0.1 w/v% aqueous solution of P(NIPAAm₈₈-co-CIPAAm₅)-b-P(NIPAAm₅₈-co-BMAAm₇) at various pH solutions as a function of temperature.

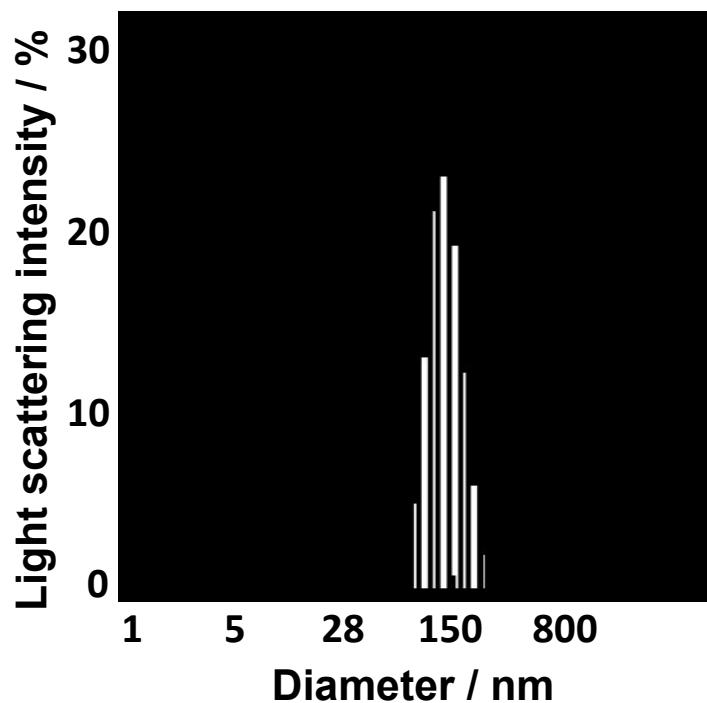


Figure S7. Size distribution histogram for P(NIPAAm₅₉-*co*-CIPAAm₁₅)-*b*-P(NIPAAm₄₃-*co*-BMAAm₁₀) at 25 °C in pH 12.