

Supporting Information

Preparation and Characterization of a pH-Responsive Nanogel Based on a Photo-Cross-linked Micelle Formed From Block Copolymers with Controlled Structure

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Synthesis of PEG Based Chain Transfer Agent (PEG-CTA). PEG-CTA was synthesized according to a modified literature procedure.¹ A CH₂Cl₂ solution (100 mL) of *N,N'*-dicyclohexylcarbodiimide (DCC, 5.66 g, 27.4 mmol) was added dropwise to a CH₂Cl₂ solution (100 mL) of MeOPEG (M_n _{NMR} = 2110, 27.4g, 13.0 mmol), CPD (4.60 g, 16.5 mmol), and a trace of 4-(dimethylamino)pyridine over a period of 30 min. After the reaction mixture stirred for 20 h at 40 °C, it was filtrated to remove dicyclohexylurea. The solvent was removed, and the crude product was purified by silica gel column chromatography using a mixture of CHCl₃ and methanol (95/5, v/v) as eluent afforded 14.0 g of PEG-CTA as a red powder: yield 44.8 % ; mp 55.5–57.8 °C; ¹H NMR (CDCl₃) δ (ppm): 2.17 (s, 3H), 2.40–2.74 (m, 4H), 3.38 (s, 3H), 3.45–4.25 (m, 188H), 4.27 (t, 2H), 7.40 (t, 2H), 7.57 (t, 1H), 7.90 (d, 2H).

Kinetic Study of Block Copolymerization. To investigate relationship between polymerization time and conversion, predetermined amounts of neutralized DEAEMA, HEA, PEG-CTA and initiator were dissolved in D₂O. This stock solution was transferred to several NMR tubes and deoxygenated by purging with Ar gas for 30 min. After deoxygenation, the cap was sealed and the solutions were heated at 70 °C in an oil bath for varying lengths of time. Conversion and M_n were characterized by ¹H NMR and GPC, respectively.

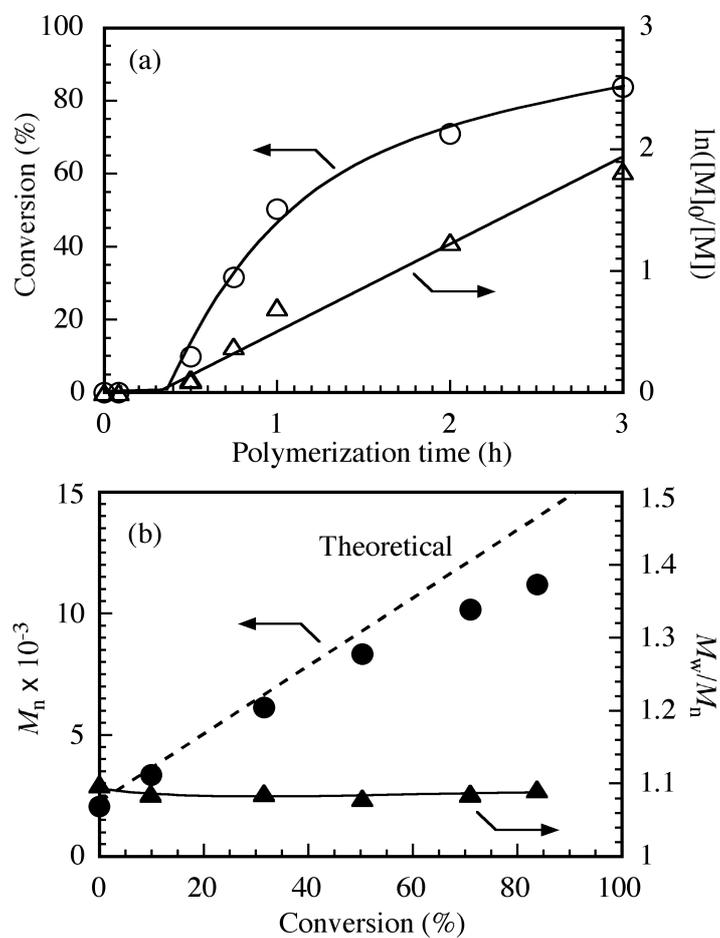


Figure S1. (a) Time–conversion (○) and the first-order kinetic plots (Δ) for the polymerization of DEAEMA and HEA in the presence of PEG-CTA in D₂O at 70 °C. (b) Dependence of M_n (●) and M_w/M_n (▲) on the average monomer conversion in the polymerization of DEAEMA and HEA in the presence of PEG-CTA. The dotted line represents theoretical line.

We prepared PEG-*b*-P(DEAEMA/HEA), a precursor of photo-cross-linkable PEG-*b*-P(DEAEMA/CEA), by random copolymerization of DEAEMA and HEA in the presence of PEG-CTA ($M_{n,NMR} = 2370$, $M_w/M_n = 1.02$) by RAFT radical polymerization in water. Figure S1a shows a relationship between polymerization time and the average monomer conversion of DEAEMA and HEA along with the pseudo first-order plot. The consumption of DEAEMA and HEA was monitored by ^1H NMR as a function of polymerization time. After an induction period of ca. 20 min, the conversion increases with increasing polymerization time. The conversion of 84 % was reached within 3 h. The linear increase in the first-order plot implies a constant concentration of propagating radicals during the polymerization.

Figure S1b shows the dependence of M_n and M_w/M_n on the average monomer conversion. The polymerization system yields low polydispersity products, and M_n increases with the monomer conversion, which indicates that the polymerization can be controlled. Apparent deviation of the relationship between the average conversion and M_n from the theoretical line may come from some complex kinetic effect and an unexpected interaction of the GPC column with the polymers or from a difference between the polymer and standard poly(2-vinylpyridine) samples.

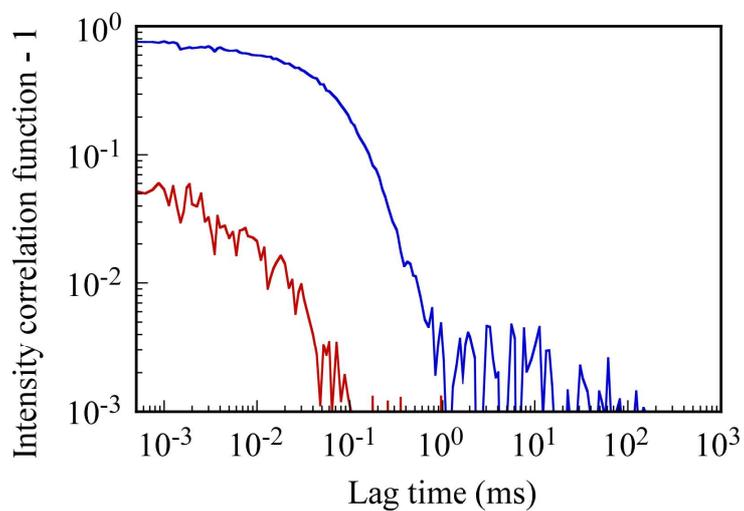


Figure S2. Intensity correlation functions for PEG-*b*-P(DEAEMA/CEA) in 0.1 M NaCl aqueous solutions at pH 3 (—) and 10 (—).

The results of the R_h distribution are based on a non-linear regularization analysis (REPES); this type of inverse Laplace transformation is known to be an ill-posed problem and it is poor to separate relaxation modes that are close to each other.

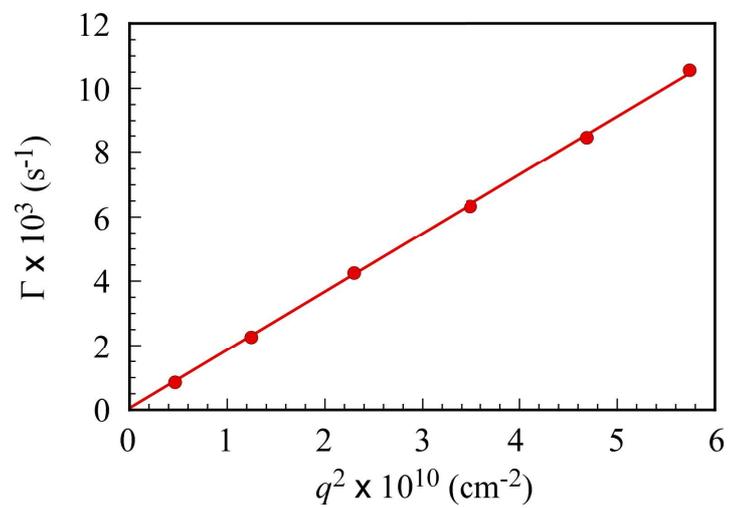


Figure S3. Relationship between relaxation rate (Γ) and the square of the scattering vector (q^2) for PEG-*b*-P(DEAEMA/CEA) in 0.1 M NaCl aqueous solutions at pH 10.

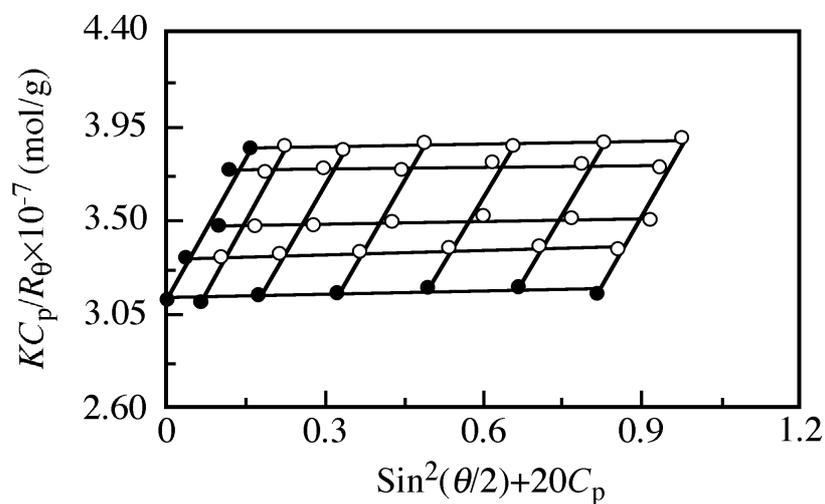


Figure S4. Zimm plots for the uncross-linked polymer micelle formed from PEG-*b*-P(DEAEMA/CEA) in 0.1 M NaCl aqueous solutions at pH 10. The angle was varies from 30 to 130° with 20° increment, and the polymer concentration was varied from 2.0 to 8.0 g/L. The Rayleigh ratio (R_θ) was determined by subtracting the solvent scattering from the total scattering of the solutions.

References

- (1) Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071-2074.