Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Dual-Temperature and pH Responsive (Ethylene Glycol)-Based Nanogels via Structural Design

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Preparation of (ethylene glycol)-based nanogels (NGs)

NG1 and 2

Macro-CTA of P(MEO_2MA_{38}-*co*-$OEGMA_{10}$) (40 mg, 3.3×10^{-3} mmol), MEO_2MA (149.1 mg, 0.79 mmol), cross-linker (CL) of di(ethylene glycol) dimethacrylate (48.0 mg, 0.20 mmol), and VA-044 (4.27×10^{-1} mg, 1.32×10^{-3} mmol) ($[MEO_2MA]_0/[CL]_0/[\text{Macro-CTA}]_0/[\text{VA-044}]_0$ = 240/60/1/0.4) were dissolved in a 5 mL water/2-propanol (1/4 (mL) = **NG1**, 4/1 (mL) = **NG2**) solution at 0 °C. After degassing with nitrogen gas for 30 min at 0 °C, the mixture was allowed to polymerize for 20 h at 37 °C. The polymerization container was soaked into liquid nitrogen to stop the reactions. NG was purified by dialysis (MWCO: 12~14 kDa) in distilled water for 3 days at 4 °C and was collected by freeze-drying.

NG3 and 4

Macro-CTA of P(MEO_2MA_{38}-*co*-$OEGMA_{10}$) (40 mg, 3.3×10^{-3} mmol), MEO_2MA (177.0 mg, 0.94 mmol), CL (12.0 mg, 5.0×10^{-2} mmol), and VA-044 (4.27×10^{-1} mg, 1.32×10^{-3} mmol) ($[MEO_2MA]_0/[CL]_0/[\text{Macro-CTA}]_0/[\text{VA-044}]_0$ = 285/15/1/0.4) were dissolved in a 5 mL water/2-propanol (1/4 (mL) = **NG3**, 4/1 (mL) = **NG4**) solution at 0

°C. The NGs were prepared and purified by same condition with above NGs.

NG5~8

Macro-CTA of P(MEO_2MA_{66}-*co*-$OEGMA_{17}$) (83 mg, 4.0×10^{-3} mmol), MEO_2MA (**NG5**: 179.0 mg, 0.95 mmol, **NG6**: 201.4 mg, 1.07 mmol, **NG7**: 119.3 mg, 0.63 mmol, and **NG8**: 134.2 mg, 0.71 mmol), CL (**NG5**: 57.6 mg, 0.24 mmol, **NG6**: 28.8 mg, 0.12 mmol, **NG7**: 38.4 mg, 0.16 mmol, and **NG8**: 19.2 mg, 7.9×10^{-2} mmol), and VA-044 (4.27×10^{-1} mg, 1.32×10^{-3} mmol) ($[MEO_2MA]_0/[CL]_0/[\text{Macro-CTA}]_0/[\text{VA-044}]_0$ = 240/60/1/0.33 (**NG5**), 270/30/1/0.33 (**NG6**), 160/40/1/0.33 (**NG7**), and 180/20/1/0.33 (**NG8**)) were dissolved in a 5 mL water/2-propanol (1/4 (mL)) solution at 0 °C. The NGs were prepared and purified by same condition with above NGs.

NG9~11

Macro-CTA of P(MEO_2MA_{92}-*co*-$OEGMA_{24}$) (114 mg, 4.0×10^{-3} mmol), MEO_2MA (**NG9**: 179.0 mg, 0.95 mmol, **NG10**: 201.4 mg, 1.07 mmol), CL (**NG9**: 57.6 mg, 0.24 mmol, **NG10**: 28.8 mg, 0.12 mmol), and VA-044 (4.27×10^{-1} mg, 1.32×10^{-3} mmol) ($[MEO_2MA]_0/[CL]_0/[\text{Macro-CTA}]_0/[\text{VA-044}]_0$ = 240/60/1/0.33 (**NG9**), 270/30/1/0.33

(**NG10**)) were dissolved in a 5 mL water/2-propanol (1/4 (mL)) solution at 0 °C. The NGs were prepared and purified by same condition with above NGs. The preparation method of **NG11** was shown in experimental part in this paper.

FIGURE LEGENDS

Figure S1. Transmittance change of 0.5 w/v% (A) P(MEO_2MA_{38}-*co*-$OEGMA_{10}$), (B) P(MEO_2MA_{66}-*st*-$OEGMA_{10}$), and (C) P(MEO_2MA_{92}-*st*-$OEGMA_{24}$) in water.

Figure S2. Size distribution histogram of 0.1 wt% NG 9 in water at (A) 15 and (B) 37 ^oC.

Figure S3. Transmittance change of P(MEO_2MA_{92}-*st*-$OEGMA_{24}$) in pH 2 $HCl_{aq.}$ at different concentrations.

Figure S4. Transmittance change of 0.1 wt% P(MEO_2MA_{92}-*st*-$OEGMA_{24}$) in pH 2 $HCl_{aq.}$ and 10 mM $NaCl_{aq.}$.

Figure S5. Size distribution histogram of 0.1 wt% NG 9 in pH 2 $HCl_{aq.}$ at (A) 15 and (B) 37 ^oC and in 10 mM $NaCl_{aq.}$ at (C) 15 and (D) 37 ^oC.

Figure S6. Transmittance change of 0.1 wt% NG9 in 50 mM $NaCl_{aq}$.

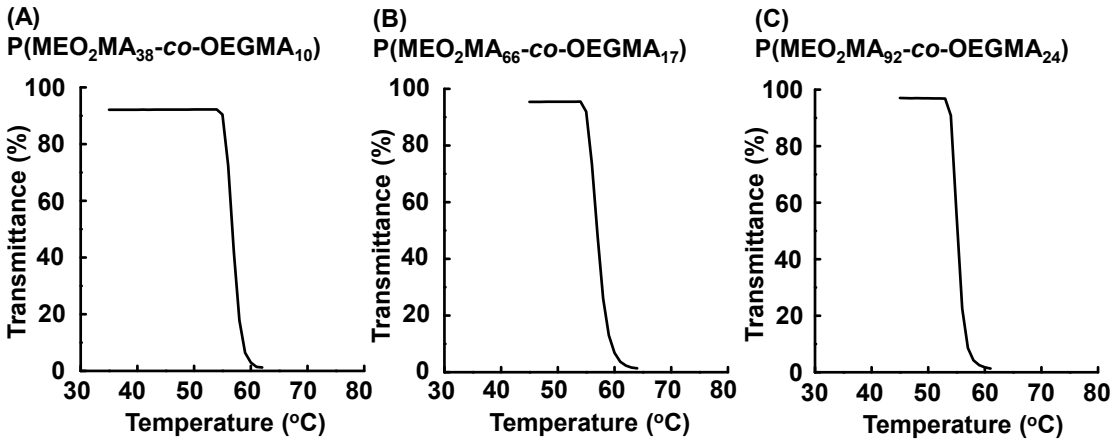

Figure S1. Transmittance change of 0.5 w/v% (A) P(MEO_2MA_{38}-*co*-$OEGMA_{10}$), (B) P(MEO_2MA_{66}-*st*-$OEGMA_{10}$), and (C) P(MEO_2MA_{92}-*st*-$OEGMA_{24}$) in water.

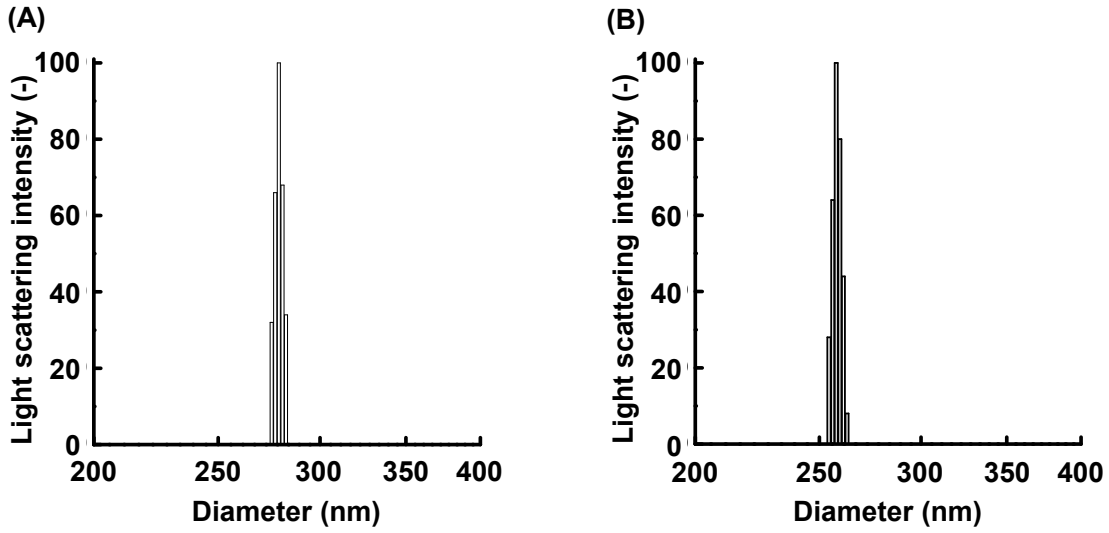

Figure S2. Size distribution histogram of 0.1 wt% NG 9 in water at (A) 15 and (B) 37 ^{o}C.

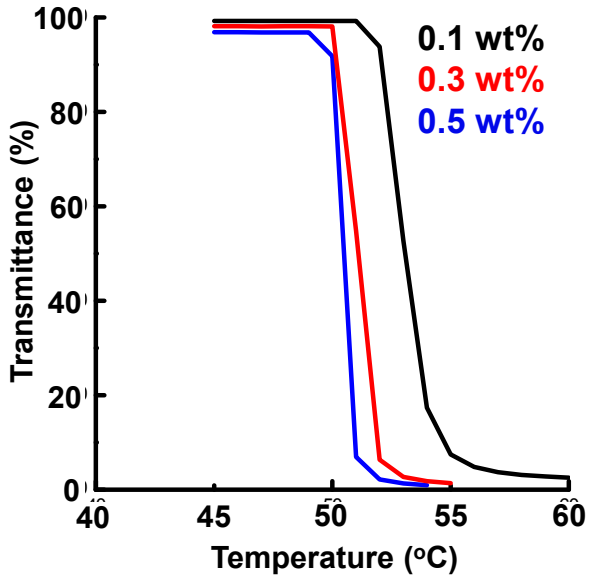

Figure S3. Transmittance change of P(MEO_2MA_{92}-*st*-$OEGMA_{24}$) in pH 2 $HCl_{aq.}$ at different concentrations.

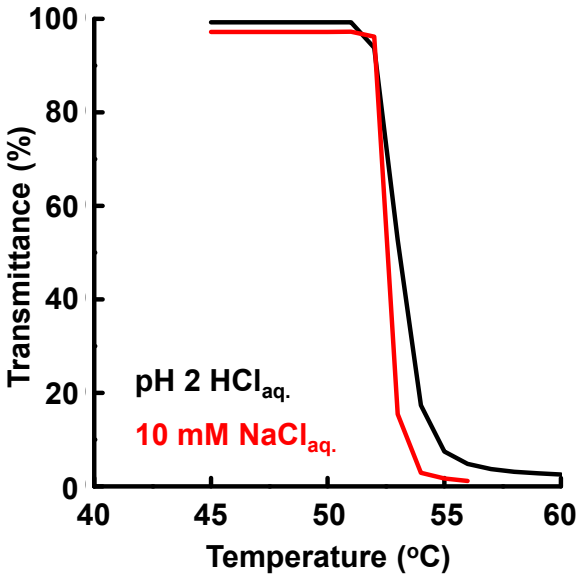

Figure S4. Transmittance change of 0.1 wt% P(MEO_2MA_{92}-*st*-$OEGMA_{24}$) in pH 2 $HCl_{aq.}$ and 10 mM $NaCl_{aq.}$.

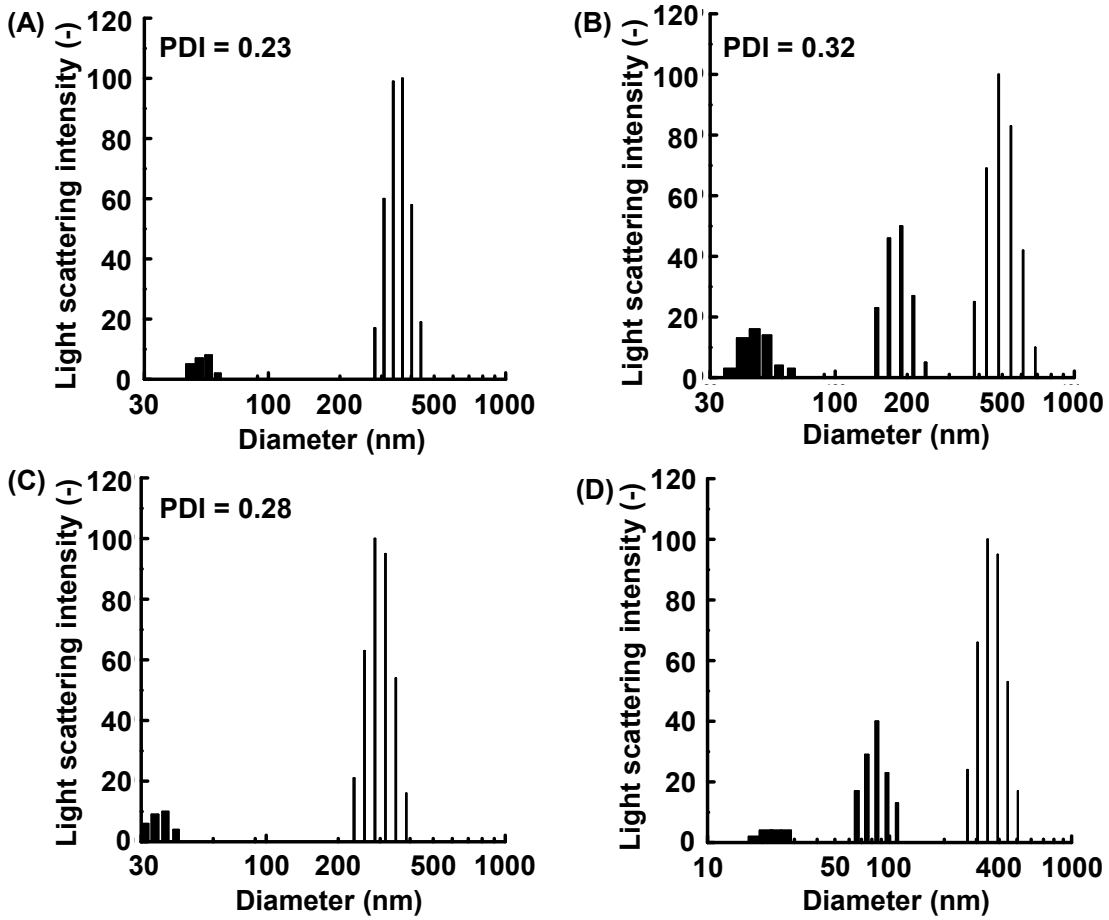

Figure S5. Size distribution histogram of 0.1 wt% NG 9 in pH 2 $HCl_{aq.}$ at (A) 15 and (B) 37 ^{o}C and in 10 mM $NaCl_{aq.}$ at (C) 15 and (D) 37 ^{o}C.

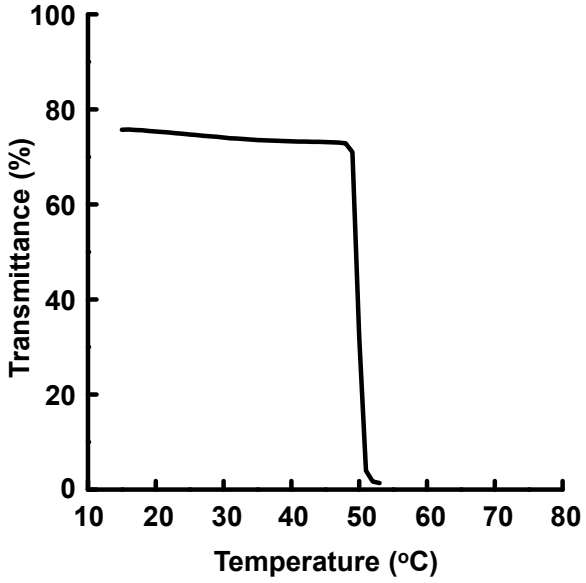

Figure S6. Transmittance change of 0.1 wt% NG9 in 50 mM $NaCl_{aq}$.