Facile synthesis, sequence-tuned thermoresponsive behaviours and reaction-induced reorganization of water-soluble keto-polymers

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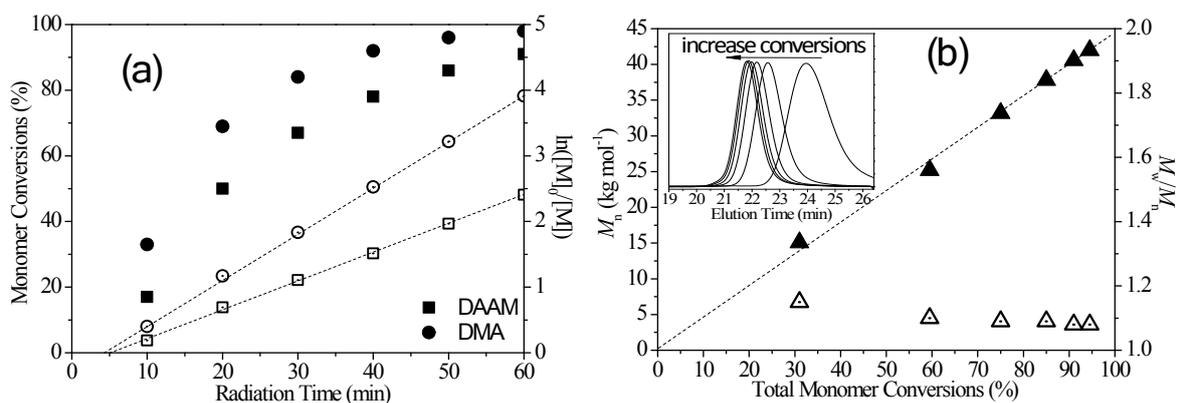
Electronic Supplementary Information

Figure S1. (a) The kinetic curves of RAFT copolymerization at a $[DAAM]_0:[DMA]_0:[EDMAT]_0:[TPO]_0 = 100:100:1:0.25$ in 50 wt% methanol under visible light irradiation at 25 °C; **(b)** M_n and M_w/M_n *vs.* total monomer conversions (*Insert:* GPC traces).

Table S1. Structure Parameters of Purified Copolymers that were obtained at Different Monomer Conversions on Copolymerization at a $[DMA]_0:[DAAM]_0:[EDMAT]_0:[TPO]_0 = 300:300:1:0.25$.

Irradiation (min)	X_{DAAM} (%) [a]	X_{DMA} (%) [a]	X_{DAAM}/X_{DMA}	DAAM/DMA[a]	$M_{n, GPC}$ (kg mol^{-1})	M_w/M_n
14	42	69	0.61	127/205 (0.62)	72.9	1.09
25	63	85	0.74	191/252 (0.76)	90.2	1.11
45	94	98	0.96	280/294 (0.95)	110.7	1.12

[a] Monomer conversions (X_{DAAM}, X_{DMA}) and unit ratios (DAAM/DMA) were assessed by ^{1}H NMR.
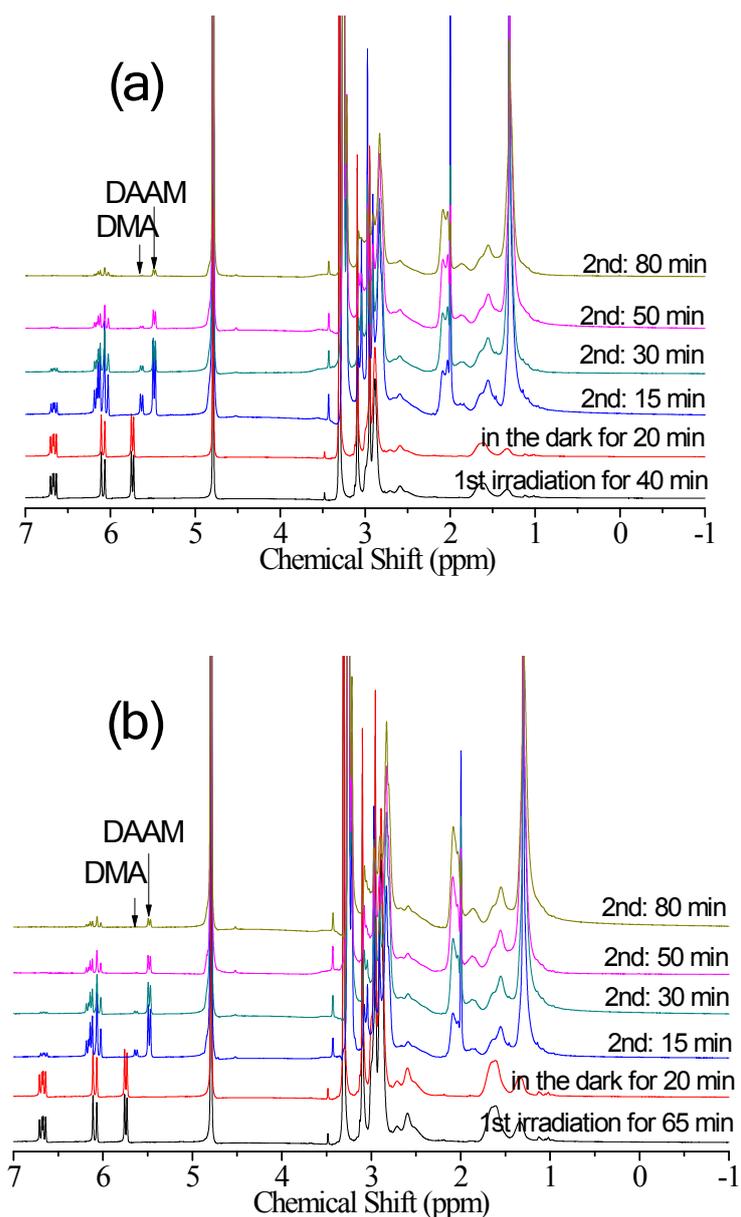
Figure S2. ^{1}H NMR spectrum evolution of the solution in which (*from bottom to upper*) after (**a**) 51% or (**b**) 75% DMA monomer has been polymerized on irradiated with visible light at a $[DMA]_0:[EDMAT]_0:[TPO]_0=120:1:0.25$ in 50 wt% methanol at 25 ^{o}C, visible light was turned off and the solution was kept in the dark for 20 min. Thereafter, the argon-gas-saturated DAAM ($[DMA]_0:[DAAM]_0=120:100$, 50 wt% in methanol) was added in the dark and then irradiated with visible light at 25 ^{o}C.
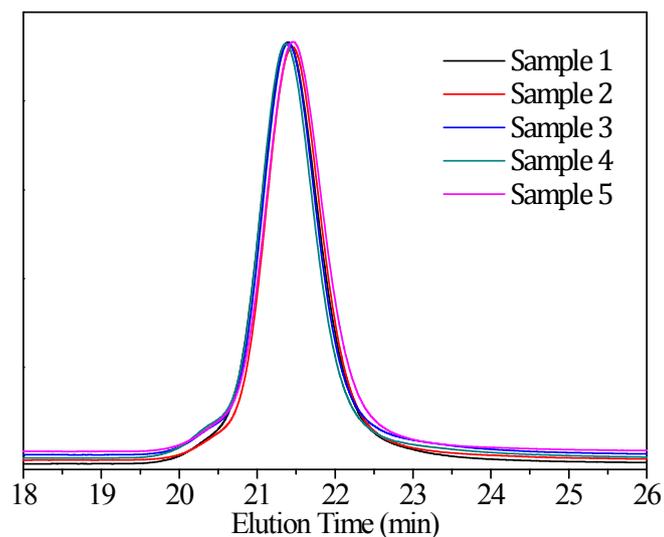
Figure S3. GPC traces of P(DMA-*co*-DAAM) copolymers (Table 4 in Main Text) that were selected to illustrate the sequence regulation on the thermo-responsive behavior and reaction-induced reorganization.
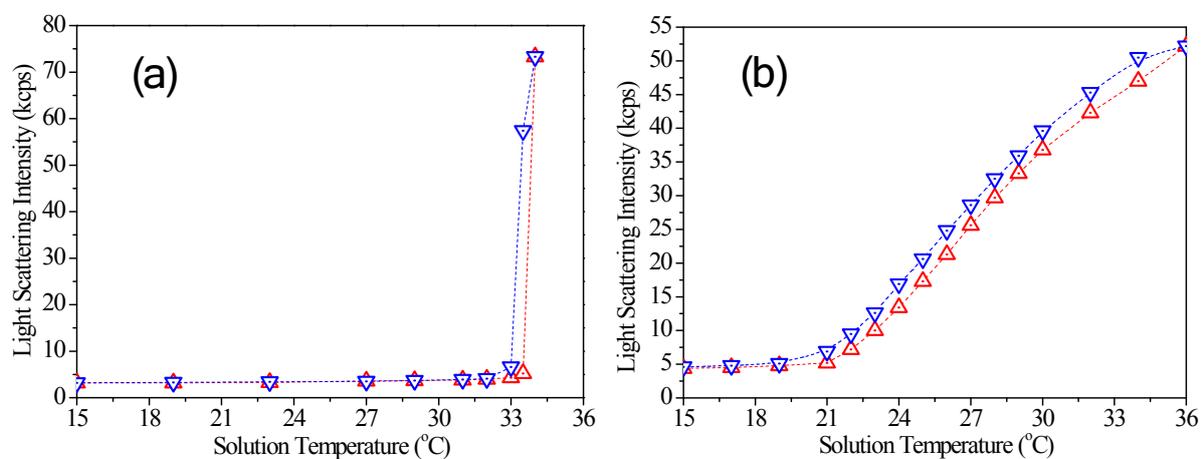

Figure S4. The variation of light scattering intensity of 4.0 mg mL^{-1} of (**a**) P(DAAM$_{94}$- *grad*-DMA$_{113}$) or (**b**) PDMA$_{37}$-*b*-P(DAAM$_{92}$-*grad*-DMA$_{79}$) in water on cycling the heating (up-triangle) and cooling (down-triangle).