Electronic Supplementary Information

Thermoresponsive Property of Polymer Hydrogels Induced by Copolymerization of Hydrophilic and Hydrophobic Monomers: Comprehensive Study from Monomer Sequence and Water Affinity

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Determination of Copolymerization Reactivity Ratio

The copolymerization reactivity ratios were determined by the Kelen-Tüdõs method. Radical random copolymerization of various combinations of hydrophilic monomer and hydrophobic monomer, and the monomer consumption behavior was monitored using ^{1}H NMR spectroscopy. When M_1 and M_2 denote a hydrophilic monomer and a hydrophobic monomer, respectively, the following four cross-propagation reactions proceed in a radical copolymerization of M_1 and M_2:

$$\sim M_1 \cdot + M_1 \rightarrow \sim M_1M_1 \cdot \quad (k_{11})$$

$$\sim M_1 \cdot + M_2 \rightarrow \sim M_1M_2 \cdot \quad (k_{12})$$

$$\sim M_2 \cdot + M_1 \rightarrow \sim M_2M_1 \cdot \quad (k_{21})$$

$$\sim M_2 \cdot + M_2 \rightarrow \sim M_2M_2 \cdot \quad (k_{22})$$

where k_{11}, k_{12}, k_{21} and k_{22} stand for the rate constant for each reaction. The reactivity ratios for M_1 and M_2, or r_1 and r_2, are defined as $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$.

The parameters H and G are calculated as below (Eq. S1 and S2) using monomer feed ratio, F (= $[M_1]/[M_2]$), and composition ratio in the polymer produced at the early stage of a polymerization reaction, f (= $d[M_1]/d[M_2]$).

$$H = \frac{F^2}{f} \qquad (S1)$$

$$G = \frac{F(f-1)}{f} \qquad (S2)$$

The copolymerization reactivity ratios are determined by Eq. S3:

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \qquad (S3)$$

where

$$\eta = \frac{G}{\alpha + H} \qquad (S4)$$

$$\xi = \frac{H}{\alpha + H} \qquad (S5)$$

$$\alpha = (H_{min} \times H_{max})^{\frac{1}{2}} \qquad (S6)$$

α is determined by the maximum and minimum H among the experimental values. The η is plotted against ξ, and r_1 and r_2 are obtained from the slope and the intercept (Tables S1 ~ S6 and Fig. S1).

Table S1. Parameters for Kelen-Tüdõs plots of copolymerization of HEAAm and tBAAm.[a]

	[HEAAm] : [tBAAm]				
	1 : 9	3 : 7	5 : 5	7 : 3	9 : 1
F	0.110	0.429	1.00	2.34	8.97
f	0.150	0.506	1.02	3.09	13.9
H	0.0806	0.363	0.983	1.76	5.80
G	–0.623	–0.418	0.017	1.58	8.32
ξ	0.105	0.347	0.590	0.721	0.895
η	–0.814	–0.400	0.0104	0.646	1.28

[a] Reaction condition: see the caption of Fig. 3. $\alpha = 0.684$.

Table S2. Parameters for Kelen-Tüdõs plots of copolymerization of HEA and tBAAm.[a]

	[HEA] : [tBAAm]				
	1 : 9	3 : 7	5 : 5	7 : 3	9 : 1
F	0.114	0.435	1.03	2.36	8.85
f	0.135	0.689	1.50	2.51	9.70
H	0.0961	0.274	0.704	2.23	8.08
G	–0.729	–0.196	0.341	1.42	7.94
ξ	0.097	0.234	0.440	0.713	0.902
η	–0.735	–0.167	0.213	0.455	0.886

[a] Reaction condition: see the caption of Fig. 3. $\alpha = 0.896$.

Table S3. Parameters for Kelen-Tüdõs plots of copolymerization of HEAAm and tBA.[a]

	[HEAAm] : [tBA]				
	1 : 9	3 : 7	5 : 5	7 : 3	9 : 1
F	0.111	0.442	1.03	2.36	9.14
f	0.062	0.370	0.713	1.85	7.16
H	0.198	0.528	1.48	3.02	11.66
G	–1.68	–0.753	–0.414	1.08	7.87
ξ	0.115	0.258	0.493	0.665	0.885
η	–0.978	–0.368	–0.138	0.238	0.597

[a] Reaction condition: see the caption of Fig. 3. $\alpha = 1.52$.

Table S4. Parameters for Kelen-Tüdõs plots of copolymerization of HEA and tBA.[a]

	[HEA] : [tBA]				
	1 : 9	3 : 7	5 : 5	7 : 3	9 : 1
F	0.101	0.423	1.04	2.38	9.23
f	0.087	0.382	0.788	1.96	12.4
H	0.116	0.469	1.37	2.89	6.85
G	–1.05	–0.685	–0.279	1.17	8.49
ξ	0.115	0.345	0.605	0.764	0.885
η	–1.04	–0.503	–0.124	0.309	1.10

[a] Reaction condition: see the caption of Fig. 3. $\alpha = 0.892$.

Table S5. Parameters for Kelen-Tüdõs plots of copolymerization of HEAAm and MA.[a]

	[HEAAm] : [MA]				
	1 : 9	3 : 7	5 : 5	7 : 3	9 : 1
F	0.109	0.416	0.970	2.19	7.56
f	0.0801	0.312	0.614	1.01	6.21
H	0.148	0.556	1.53	4.72	9.21
G	–1.25	–0.919	–0.611	0.032	6.34
ξ	0.113	0.322	0.567	0.802	0.887
η	–0.951	–0.533	–0.226	0.00543	0.611

[a] Reaction condition: see the caption of Fig. 3. $\alpha = 1.17$.

Table S6. Parameters for Kelen-Tüdõs plots of copolymerization of HEA and MA.[a]

	[HEA] : [MA]				
	1 : 9	3 : 7	5 : 5	7 : 3	9 : 1
F	0.113	0.433	1.00	2.43	7.51
f	0.0891	0.413	0.874	2.28	5.06
H	0.143	0.454	1.14	2.58	11.14
G	–1.16	–0.615	–0.145	1.36	6.03
ξ	0.102	0.264	0.475	0.671	0.898
η	–0.821	–0.358	–0.0601	0.355	0.486

[a] Reaction condition: see the caption of Fig. 3. $\alpha = 1.26$.

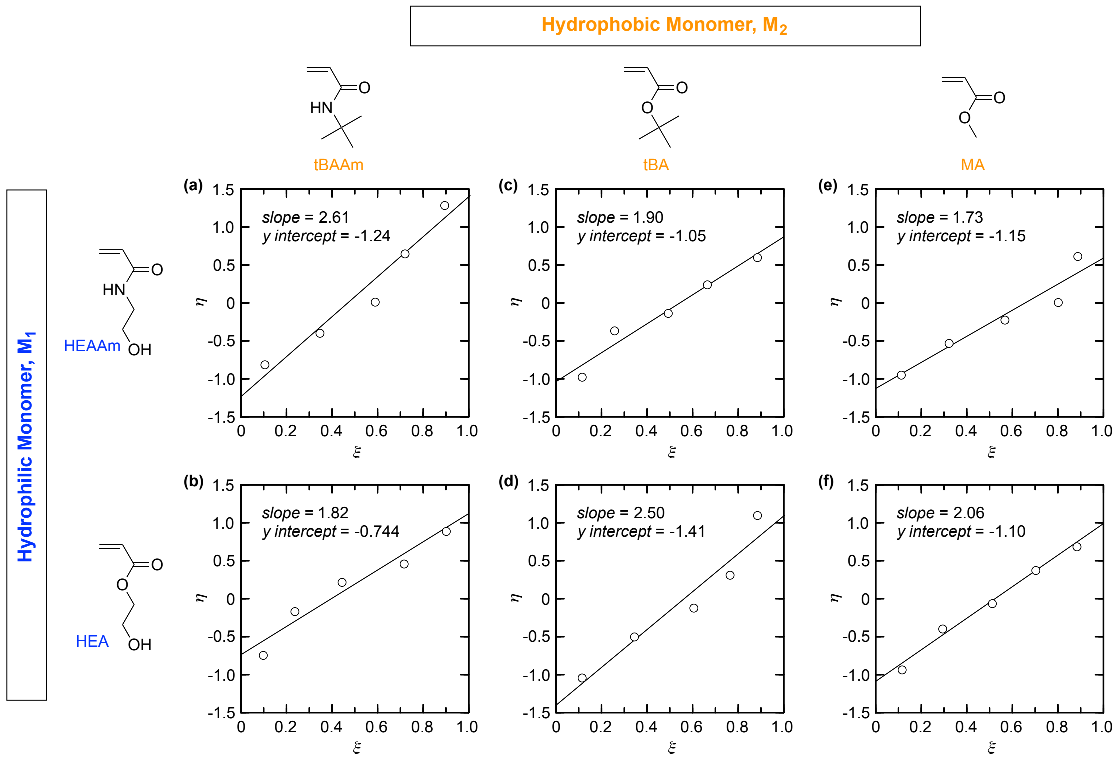

Fig. S1 Kelen-Tüdõs plots for radical copolymerization of hydrophilic and hydrophobic monomers: (a) HEAAm/tBAAm, (b) HEA/tBAAm, (c) HEAAm/tBA, (d) HEA/tBA, (e) HEAAm/MA, and (f) HEA/MA.

Table S7. Water/octanol partition coefficient of the monomers.

Monomer	Value
HEAAm	–0.63 [a]
HEA	–0.21 [a]
tBAAm	1.45 [b]
tBA	2.09 [c]
MA	0.80 [a]

[a] Obtained from safety data sheet (SDS) published by Tokyo Chemical Industry. [b] Obtained from data shown in the website of European Chemicals Agency. [c] Obtained from SDS published by Fujifilm Wako Pure Chemicals.

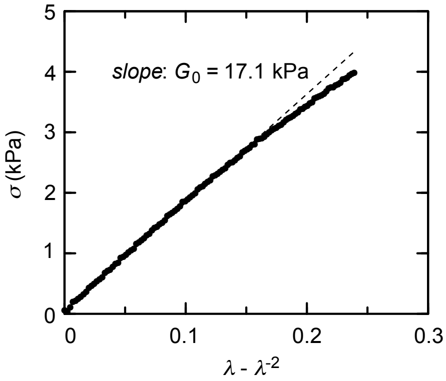

Fig. S2 σ vs $\lambda - \lambda^{-2}$ plot for HEAAm/tBAAm copolymerization gel (HEAAm : tBAAm = 4 : 6). The initial slope corresponds to shear modulus, G_0 (= v_0kT).

Table S8. v_0 and ϕ_0 of the copolymerization gels.[a]

Entry	Monomer		Composition	v_0 (mol/m^3)	ϕ_0
	Hydrophilic	Hydrophobic			
1	HEAAm	tBAAm	8 : 2	8.07	0.130
2			5 : 5	8.43	0.136
3			4 : 6	6.91	0.156
4	HEA	tBAAm	9 : 1	7.34	0.130
5			8 : 2	8.77	0.136
6	HEA	tBA	9 : 1	7.86	0.134
7	HEAAm	-	10 : 0	12.6	0.126
8	HEA	-	10 : 0	6.04	0.128

[a] v_0 was obtained from the results of the uniaxial tensile test, and ϕ_0 was obtained from the weight measurement of the methanol solution of the corresponding linear polymers in a predetermined volume, or calculation from the density of the monomer and feed composition.

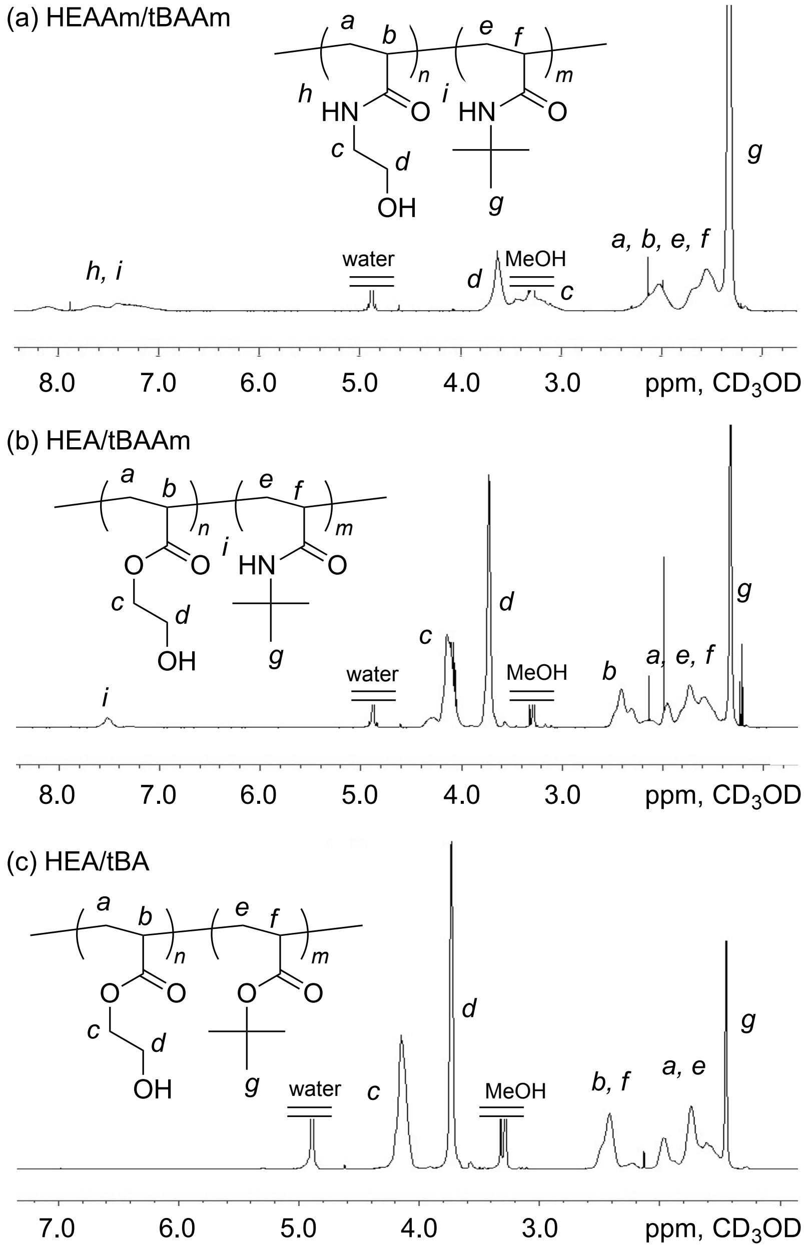

Fig. S3 ^{1}H NMR spectra of hydrophilic/hydrophobic copolymers: (a) HEAAm/tBAAm (4 : 6), (b) HEA/tBAAm (8 : 2), and (c) HEAAm/tBA (9 : 1).