Supporting Information

Synthesis and Single-Chain Folding of Amphiphilic Random Copolymers in Water

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Figure S1. Time-conversion curves in Ru-catalyzed living radical copolymerization of PEGMA and RMA [(a-e) DMA, (f) MMA, (g) nBMA, (h) tBMA, (i) OcMA, (j) AdMA, (k) CDMA, (l) ODMA] for PEGMA/RMA random copolymers [(a) 2, (b) 4, (c) 5, (d) 6, (e) 7, (f) 8, (g) 9, (h) 10, (i) 11, (j) 12, (k) 13, (l) 14]: (a-e) [PEGMA]_0+[DMA]_0/[ECPA]_0/[Ru(Ind)Cl(PPh_3)_2]_0/[n-Bu_3N]_0 = (a) 450+50, (b) 300+200, (c) 250+250, (d) 200+300/2.1/1.0/10 mM, (e) 400+100/4.2/2.0/20 mM in toluene at 80 °C; (f-l)[PEGMA]_0+[RMA]_0/[ECPA]_0/[Ru(Ind)Cl(PPh_3)_2]_0/[n-Bu_3N]_0 = 400+100 /2.1/1.0/10 mM in toluene at 80 °C.



Figure S2. Effects of temperature on R_h for a PEGMA/RMA (160/40) copolymer (**3**) in H₂O at 25 - 80 °C: [polymer] = 10 mg/mL.

Code	PEGMA/DMA	$R_{ m h}^{\ a}$	$R_{ m h}^{\ a}$	$R_{ m h}^{\ a}$
	(<i>m</i> / <i>n</i>)	(CH_2Cl_2)	(DMF)	(H ₂ O)
1	200/0	8.0	6.9	7.7
2	180/20	9.2	6.5	7.6
3	160/40	9.0	7.1	5.8
4	120/80	8.9	7.0	5.0
5	100/100	8.7	7.2	7.9
6	80/120	9.5	5.8	11.1
7	80/20	6.0	5.6	4.6

Table S1. Hydrodynamic radius of PEGMA/DMA (*m/n*) Random Copolymers^{*a*}

^{*a*} Determined by DLS in H₂O or CH₂Cl₂ at 25 °C: [polymer] = 10 mg/mL.



Figure S3. ¹H NMR spectra of **3** in CD₃OD/D₂O (0/100 - 100/0, v/v) at 25 °C.



Figure S4. ¹H NMR spectra of **3** in D_2O at 5 - 80 °C.



Figure S5. ¹H NMR spectra of 14 in D_2O at 5 – 80 °C.



Figure S6. ¹H NMR spectra of **1** in D_2O at 5 – 80 °C.



Figure S7. Half width of ¹H NMR peaks (c, d, e, h: see Figures S5 and S6) for (a) a PEGMA homopolymer (1) and (b) a PEGMA/ODMA random copolymer (14) in D₂O at 5-80 °C.



Figure S8. ¹H NMR spectra of Reichardt's dye (**RD**) in (a) acetone- d_6 or (b) D₂O/acetone (19/1, v/v) and (c) **RD** with a PEGMA/DMA (160/40) random copolymer (**3**) in D₂O/acetone (19/1, v/v) at 25 °C.



Figure S9. (a) Effects of temperature on λ_{max} of Reichardt's dye (**RD**) in the presence of a PEGMA/DMA (160/40) copolymer (3): [3]/[**RD**] = 0.09/0.45 mM in H₂O/acetone (19/1, v/v) at 25-80 °C. (b) λ_{max} of **RD** in the presence of PEGMA/RMA (160/40) copolymers [RMA = DMA (3), AdMA (12), CDMA (13)]: [polymer]/[**RD**] = 0.0045/0.45 - 0.09/0.45 mM in H₂O/acetone (19/1, v/v) at 25 °C.



Figure S10. Transmittance of aqueous solutions of PEGMA/DMA (m/n = 200/0 - 80/120) copolymers (1, 3-6) as a function of temperature (heating rate: 1 °C/min, from 40 to 95 °C): [polymers] = 4 mg/mL.

Entry	Code	RMA	PEGMA/RMA (<i>m</i> / <i>n</i>)	Cp^{a} (°C)
1	1	-	200/0	92
2	2	DMA	180/20	87
3	3	DMA	160/40	85
4	4	DMA	120/80	74
5	5	DMA	100/100	65
6	6	DMA	80/120	55
7	8	MMA	160/40	82
8	9	nBMA	160/40	79
9	10	tBMA	160/40	80
10	11	OcMA	160/40	83
11	12	AdMA	160/40	81
12	13	CDMA	160/40	84
13	14	ODMA	160/40	89

Table S2. Cloud Points of aqueous solutions of PEGMA/RMA Random Copolymers

^{*a*} Cloud point temperature: 50% transmittance for the aqueous polymer solutions (1-6, 7-14) that were heated from 40 to 95 °C (heating rate: 1 °C/min), monitored by UV-vis spectroscopy at 660 nm.