Supplementary Material

Preparation of pendant group-functionalized diblock copolymers with adjustable thermogelling behavior

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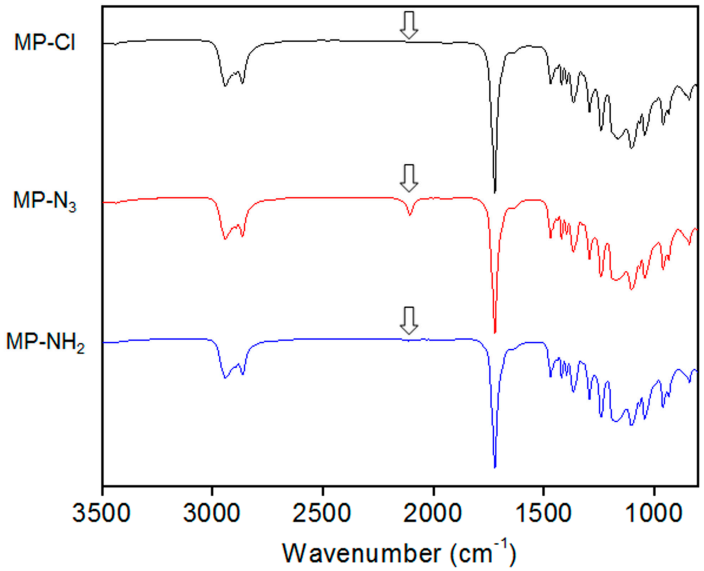

Figure S1. FT-IR spectra of MP-Cl, MP-N_3, and MP-NH_2 diblock copolymers.

Table S1. Synthesis of MP-Cl, MP-N_3, and MP-NH_2 diblock copolymers.

No	[CL]/[fCL] molar ratio	$M_{n,\ calcd}$ MPEG-polyester (g/mol)	$M_{n,\ NMR}$ [a] MPEG-polyester (g/mol)	Yield (%)	M_w/M_n [b]
MP	100/0	750-2400	750-2410	96	1.2
MP–Cl–97/3		750-2410	750-2380	91	1.4
MP–N_3–97/3	97/3	750-2420	750-2410	81	1.4
MP–N_3–97/3		750-2380	750-2400	72	1.8
MP–Cl–95/5		750-2430	750-2540	94	1.4
MP–N_3–95/5	95/5	750-2570	750-2550	87	1.6
MP–N_3–95/5		750-2540	750-2540	68	1.7
MP–Cl–90/10		750-2480	750-2610	94	1.3
MP–N_3–90/10	90/10	750-2660	750-2630	84	1.3
MP–N_3–90/10		750-2600	750-2670	74	1.5
MP–Cl–85/15		750-2420	750-2430	96	1.3
MP–N_3–85/15	85/15	750-2515	750-2520	89	1.3
MP–N_3–85/15		750-2440	750-2440	80	1.6

[a] Determined from ^{1}H NMR spectra.

[b] Measured by means of gel-permeation chromatography (based on standard polystyrene).

Table S2. Elementary analysis of MP-N3 and MP-NH2 diblock copolymers.

	97/3		95/5		90/10		85/15	
	MP-N_3	MP-NH_2	MP-N_3	MP-NH_2	MP-N_3	MP-NH_2	MP-N_3	MP-NH_2
Calc. C	61.02	61.50	60.99	60.15	60.01	60.08	59.13	61.68
Mea. C	60.96	61.28	60.66	60.72	59.96	60.05	58.73	62.47
Calc. H	8.90	8.98	8.44	8.52	8.66	8.73	8.13	8.65
Mea. H	8.78	9.01	9.01	8.91	8.9	8.92	8.64	8.23
Calc. N	0.61	0.21	1.07	0.35	1.42	0.47	3.47	1.2
Mea. N	0.63	0.27	0.83	0.28	1.21	0.31	3.36	0.82

Table S3. Thermogelling properties of MP-Cl, MP-N_3, and MP-NH_2 diblock copolymers.

No	pH [a]	Emulsion formation Time (min)	Phase Transition [b]	Gelation time [c] (s)	Gelation time [d] (s)
MP	4.6±0.1	< 20	O	~10	<1
MP–Cl–97/3	5.4±0.1	< 15	O	~30	<1
MP–N_3–97/3	6.1±0.0$_2$	< 10	X	X	X
MP–NH_2–97/3	4.6±0.1	~10	O	~20	<1
MP–Cl–95/5	4.9±0.1	~ 10	O	~30	<1
MP–N_3–95/5	5.0±0.1	< 5	X	X	X
MP–NH_2–95/5	4.2±0.1	< 5	O	~30	<1
MP–Cl–90/10	3.7±0.0$_3$	< 5	X	X	X
MP–N_3–90/10	3.8±0.1	< 5	X	X	X
MP–NH_2–90/10	3.6±0.1	< 5	O	~50	~184
MP–Cl–85/15	3.5±0.0$_2$	< 3	X	X	X
MP–N_3–85/15	3.7±0.0$_4$	< 2	X	X	X
MP–NH_2–85/15	3.4±0.1	< 3	X	X	X

[a] Measured by pH meter (Orion 3-Star, Thermo Scientific, USA).

[b] Solution-to-hydrogel phase transition at 37 °C.

[c] Measured by tilting experiment.

[d] Measured by Anton Paar Viscometer MCR 102.

Table S4. Thermal properties of MP-Cl, MP-N3, and MP-NH2 diblock copolymers.

No	[CL]/[fCL] molar ratio	Bulk state			Aqueous solution		χ_c [b]
		T_m (°C)	ΔH_m (J/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	
MP	100/0	56.4	70.1	-65.5	47.6	10.9	37
MP–Cl–97/3	97/3	47.2	52.6	-61.3	41.5	5.1	32
MP–N_3–97/3		47.3	50.2	-55.2	45.2	2.7	30
MP–NH_2–97/3		48.4	51.9	-	44.2	33.1	31
MP–Cl–95/5	95/5	44.8	49.7	-43.4	44.9	3.7	29
MP–N_3–95/5		46.0	49.2	-36.5	44.6	2.5	26
MP–NH_2–95/5		48.5	67.8	-	42.1	14.0	33
MP–Cl–90/10	90/10	43.1	48.8	-41.3	43.9	1.7	28
MP–N_3–90/10		46.1	44.2	-35.4	45.2	1.4	25
MP–NH_2–90/10		52.2	76.6	-	45.8	3.1	36
MP–Cl–85/15	85/15	43.0	18.4	-33.2	-	-	17
MP–N_3–85/15		45.0	33.6	-18.5	-	-	23
MP–NH_2–85/15		35.4	33.1	-52.6	38.7	0.1	22

[a] Measured by DSC.

[b] χc was calculated as the ratio of the crystalline peak areas to the total areas under the scattering curve.