Electronic Supplementary Material (ESI) for Polymer Chemistry.
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# Supporting Information

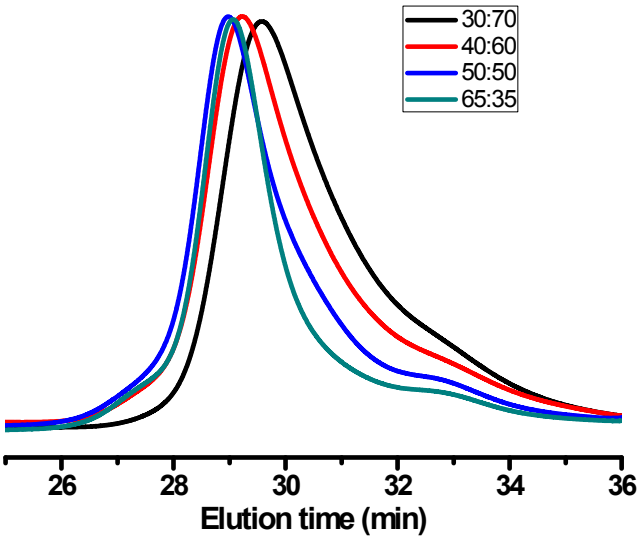


**Fig. S1**. GPC traces of PDMA-*b*-PNIPAM copolymers synthesized in different water-methanol mixtures, [$PDMA_{64}$ ]:[NIPAM]:[V-50] = 1:200:0.05, 70 °C, 4 h, solid content 5% w/v. (Macromolecular parameters are shown in Table S1).

**Table S1. Synthetic results of PDMA-*b*-PNIPAM copolymers prepared in water/methanol solution.**[a]

| Water/Methanol (v:v)[b] | 30:70 | 40:60 | 50:50 | 65:35 |
|---|---|---|---|---|
| $M_n$[c] | 26070 | 27700 | 28050 | 27900 |
| $Đ$[c] | 1.32 | 1.29 | 1.25 | 1.23 |

[a]Synthetic conditions: [$PDMA_{64}$]:[NIPAM]:[V-50]=1:200:0.05, solid content=5% w/v, water-methanol solution, 70 °C, 4 h. [b]Volumetric ratio. [c]GPC results vs PMMA standard.

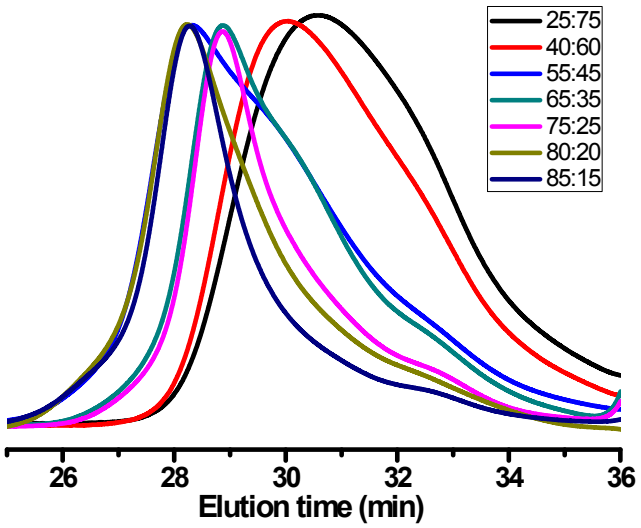


**Fig. S2**. GPC traces of PDMA-*b*-PNIPAM copolymers synthesized in different water-ethanol mixtures, [$PDMA_{64}$]:[NIPAM]:[V-50] = 1:200:0.05, 70 °C, 4 h, solid content 5% w/v. (Macromolecular parameters are shown in Table S2).

**Table S2. Synthetic results of PDMA-*b*-PNIPAM copolymers prepared in water/ethanol solution.**[a]

| Water/Ethanol[b] | 25:75 | 40:60 | 55:45 | 65:35 | 75:25 | 80:20 | 85:15 |
|---|---|---|---|---|---|---|---|
| $M_n$[c] | 23900 | 24500 | 27600 | 26800 | 27200 | 28100 | 28600 |
| $Đ$[c] | 1.42 | 1.39 | 1.50 | 1.30 | 1.26 | 1.31 | 1.27 |

[a]Synthetic conditions: [$PDMA_{64}$]:[NIPAM]:[V-50]=1:200:0.05, solid content=5% w/v, water-ethanol solution, 70 °C, 4 h. [b]Volumetric ratio. [c]GPC results vs PMMA standard.

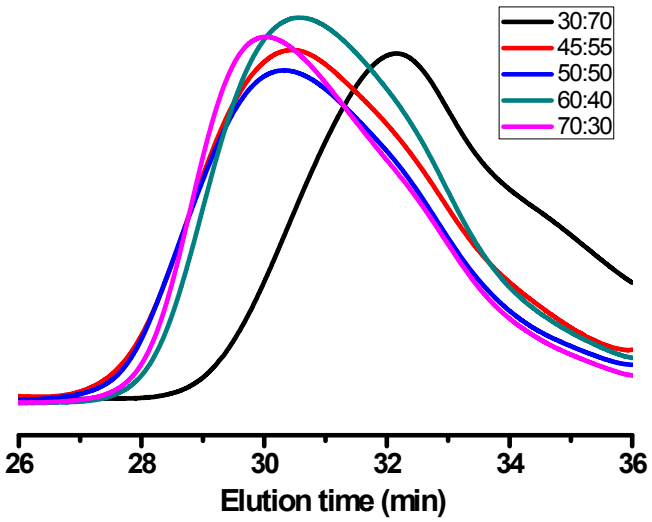


**Fig. S3**. GPC traces of PDMA-*b*-PNIPAM copolymers synthesized in different water-isopropanol mixtures: [$PDMA_{64}$ ]:[NIPAM]:[V-50] = 1:200:0.2, 70 °C, 4 h, solid content 5% w/v. (Macromolecular parameters are shown in Table S3).

**Table S3. Synthetic results of PDMA-*b*-PNIPAM copolymers prepared in water/isopropanol solution.**[a]

| Water/ Isopropanol[b] | 30:70 | 45:55 | 50:50 | 60:40 | 70:30 |
|---|---|---|---|---|---|
| $M_n$[c] | 22400 | 26100 | 26400 | 25500 | 25800 |
| $Đ$[c] | 1.48 | 1.43 | 1.41 | 1.43 | 1.42 |

[a]Synthetic conditions: [$PDMA_{64}$]:[NIPAM]:[V-50]=1:200:0.2, solid content=5% w/v, water-isopropanol solution, 70 °C, 4 h. [b]Volumetric ratio. [c]GPC results vs PMMA standard.

**Table S4. Summary of RAFT dispersion copolymerization for the synthesis of PDMA$_{64}$-*b*-P(NIPAM-*co*-HEAM) nanogels.[a]**

| entry | [PDMA$_{64}$]:[NIPAM]:[HEAM]:[BIS][b] | $D_h$ (nm)[c] | PDI[c] | $D'_h$ (nm)[d] | PDI'[d] | NIPAM conv. (%)[e] | HEAM conv. (%)[e] |
|---|---|---|---|---|---|---|---|
| 1 | 1:200:0:5 | 40 | 0.05 | 83 | 0.09 | 90 | - |
| 2 | 1:190:10:5 | 52 | 0.05 | 89 | 0.07 | 97 | 100 |
| 3 | 1:180:20:5 | 67 | 0.12 | 102 | 0.17 | 95 | 100 |
| 4 | 1:170:30:5 | 77 | 0.15 | 112 | 0.18 | 96 | 100 |

[a]Synthetic conditions: [PDMA$_{64}$]:[V-50]=1:0.05, solid content=10% w/v, water-ethanol (75:25, v:v), 70 °C, 2 h. [b]Molar ratio relative to PDMA. [c]DLS results measured in water-ethanol (75:25, v:v) cononsolvent at 25 °C. [d]DLS results measured in water at 25 °C. [e]Monomer conversion determined by $^1$H NMR in DMSO-d$_6$.

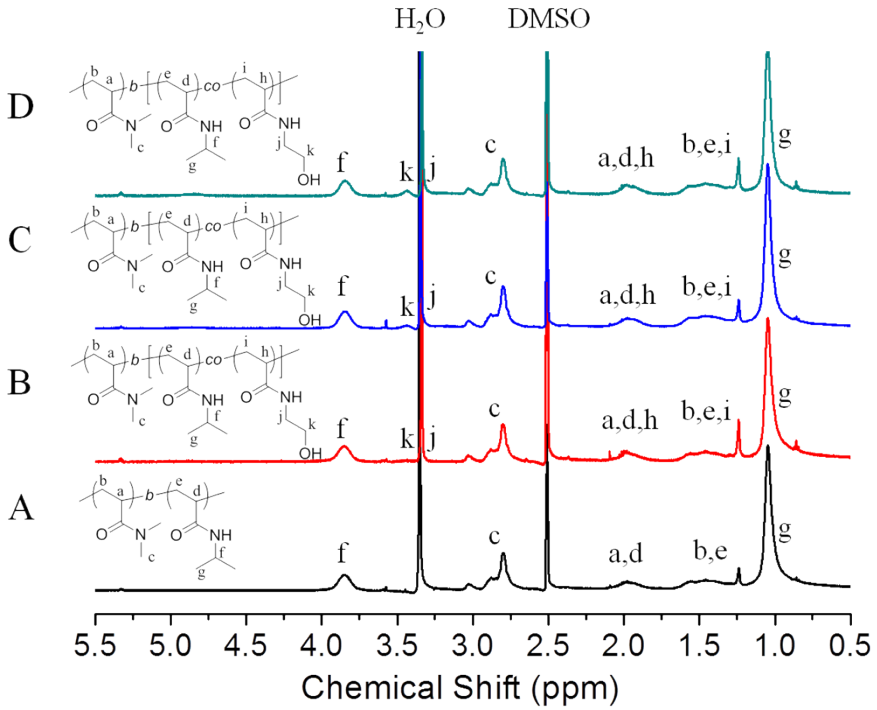


**Fig. S4.** $^1$H NMR spectra in DMSO-d$_6$ of PDMA$_{64}$-*b*-P(NIPAM$_{181}$-*co*-BIS$_5$) nanogel (A), PDMA$_{64}$-*b*-P(NIPAM$_{184}$-*co*-HEAM$_{10}$-*co*-BIS$_5$) nanogel (B), PDMA$_{64}$-*b*-P(NIPAM$_{170}$-*co*-HEAM$_{20}$-*co*-BIS$_5$) nanogel (C), and PDMA$_{64}$-*b*-P(NIPAM$_{163}$-*co*-

$HEAM_{30}$-*co*-$BIS_5$) nanogel (D). BIS is omitted in the structures due to its negligible composition.

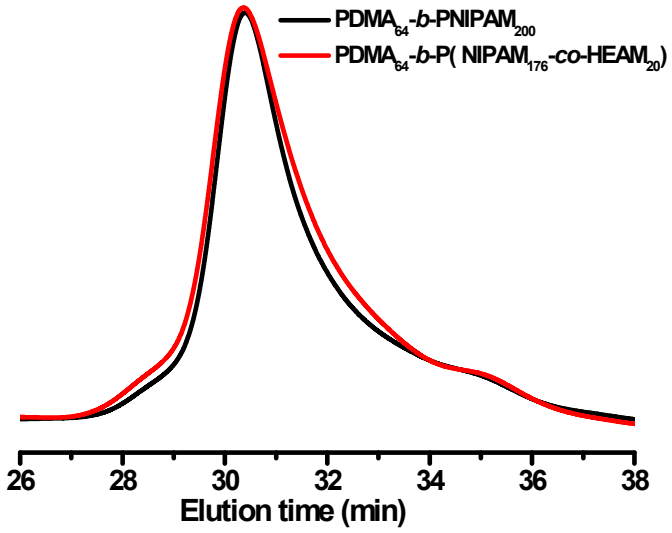


**Fig. S5.** GPC traces of $PDMA_{64}$-*b*-$PNIPAM_{200}$ and $PDMA_{64}$-*b*-P($NIPAM_{178}$-*co*-$HEAM_{20}$).

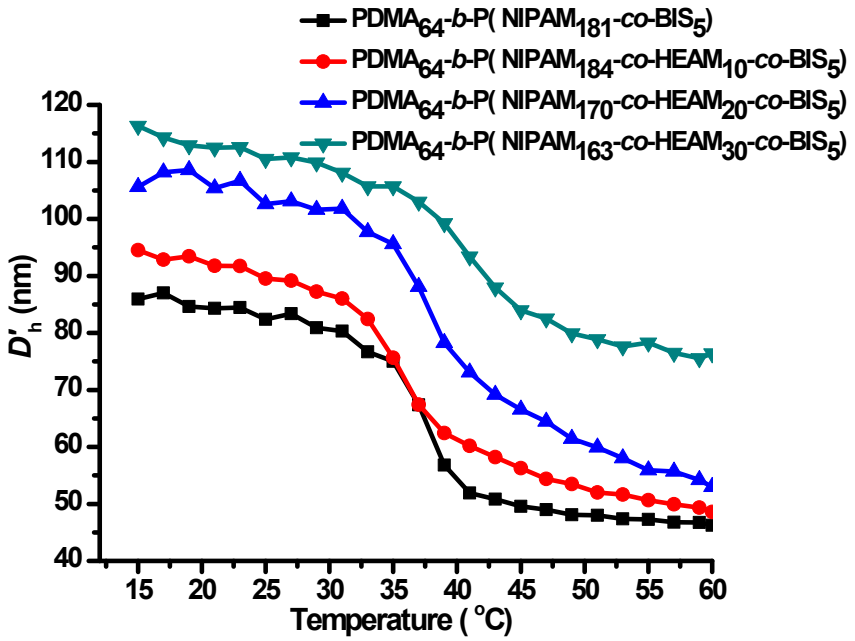


**Fig. S6.** Thermal profiles for nanogels with different molar fractions of HEAM, measured in water.

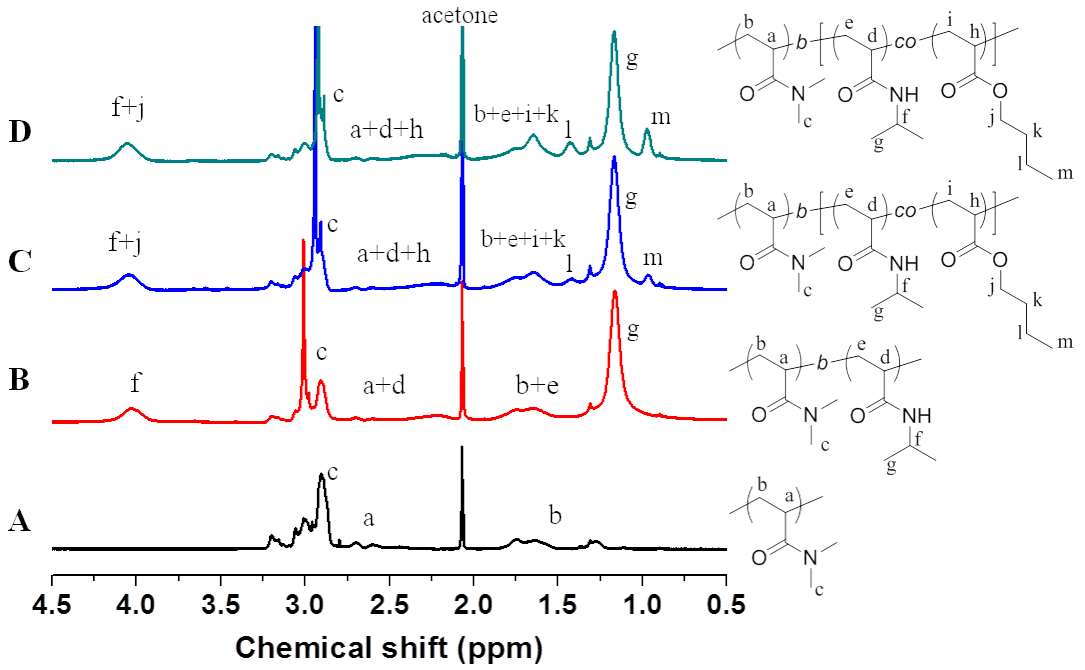


**Fig. S7.** $^{1}$H NMR spectra in acetone-$d_6$ of $PDMA_{64}$ (A), $PDMA_{64}$-*b*-P($NIPAM_{181}$-*co*-$BIS_5$) nanogel (B), $PDMA_{64}$-*b*-P($NIPAM_{173}$-*co*-$BA_{20}$-*co*-$BIS_5$) nanogel (C), and $PDMA_{64}$-*b*-P($NIPAM_{144}$-*co*-$BA_{40}$-*co*-$BIS_5$) nanogel (D). BIS is omitted in the structures due to its negligible composition.

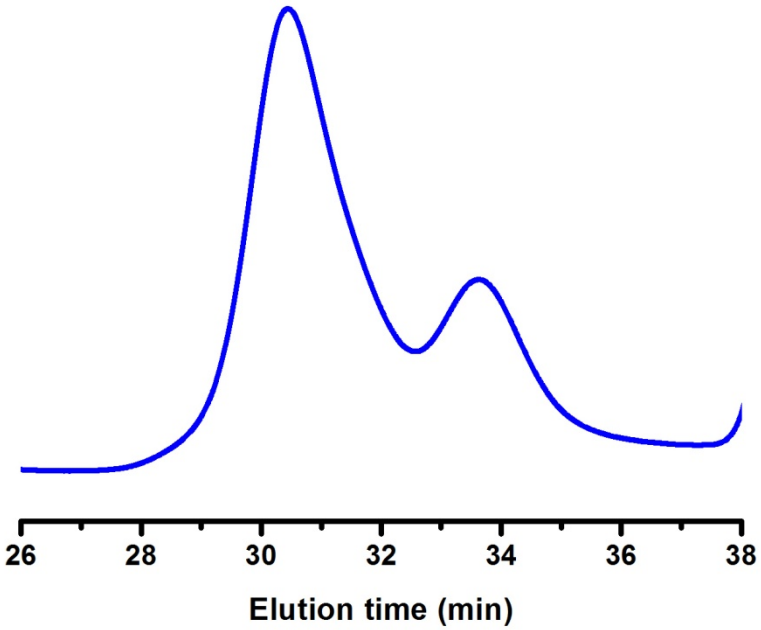


**Fig. S8.** GPC trace of $PDMA_{64}$-*b*-$PBA_{30}$-*b*-$PNIPAM_{160}$ before purification.