

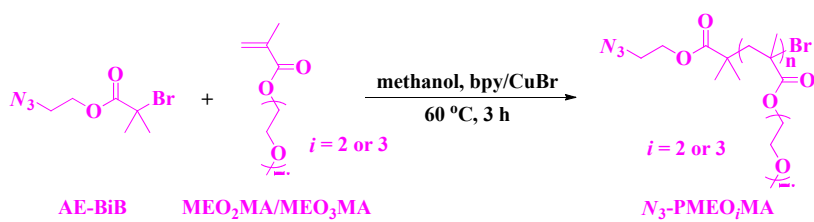
Electronic Supplementary Information

Thermo-responsive hybrid “hairy-rod” polypeptides for smart antitumor drug delivery

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Scheme S1 Synthetic route to N_3 -PMEO $_i$ MA.

Table S1 Characterizations of N_3 -PMEO_{*i*}MA.

Entry	Feeding Molar Ratio of MEO ₂ MA, MEO ₃ MA/Br	DP of MEO ₂ MA/ MEO ₃ MA ^{<i>a</i>}	M_n^a (g mol ⁻¹)	M_n^b (g mol ⁻¹)	PDI ^{<i>b</i>}
N_3 -PMEO ₂ MA ₂₇	50, 0	27/0	5300	5900	1.18
N_3 -P(MEO ₂ MA ₁₈ - <i>co</i> -MEO ₃ MA ₉)	35, 15	18/9	5700	6300	1.20
N_3 -P(MEO ₂ MA ₁₃ - <i>co</i> -MEO ₃ MA ₁₃)	25, 25	13/13	5700	6000	1.19
N_3 -P(MEO ₂ MA ₇ - <i>co</i> -MEO ₃ MA ₁₈)	15, 35	7/18	5700	6200	1.23
N_3 -PMEO ₃ MA ₂₆	0, 50	0/26	6300	6800	1.19
^{<i>a</i>} Determined by ¹ H NMR. ^{<i>b</i>} Determined by GPC.					

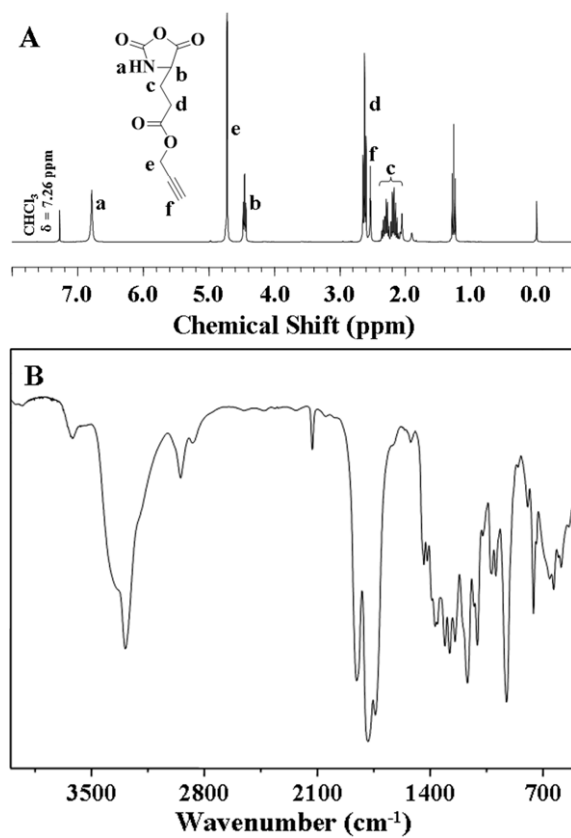


Fig. S1 ^1H NMR (in CDCl_3) (A) and FT-IR (B) spectra of PLG NCA.

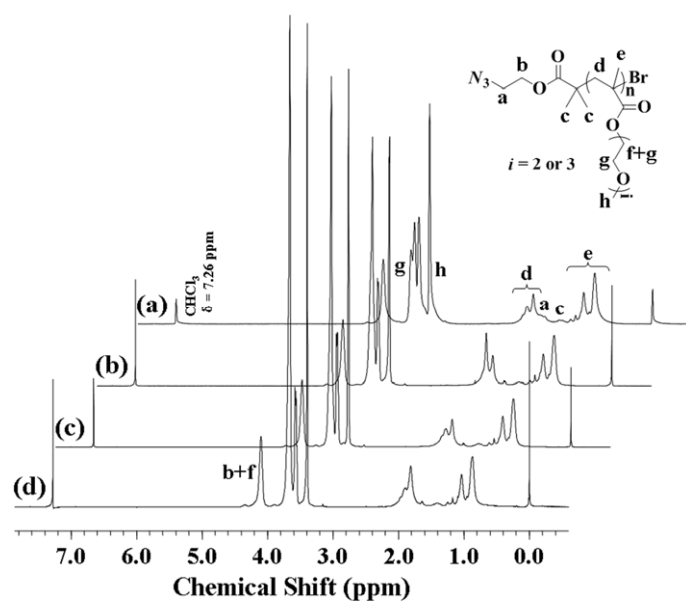


Fig. S2 ^1H NMR spectra of $N_3\text{-PMEO}_2\text{MA}_{27}$ (a), $N_3\text{-P}(\text{MEO}_2\text{MA}_{18}\text{-co-MEO}_3\text{MA}_9)$ (b), $N_3\text{-P}(\text{MEO}_2\text{MA}_7\text{-co-MEO}_3\text{MA}_{18})$ (c) and $N_3\text{-PMEO}_3\text{MA}_{26}$ (d) (in CDCl_3).

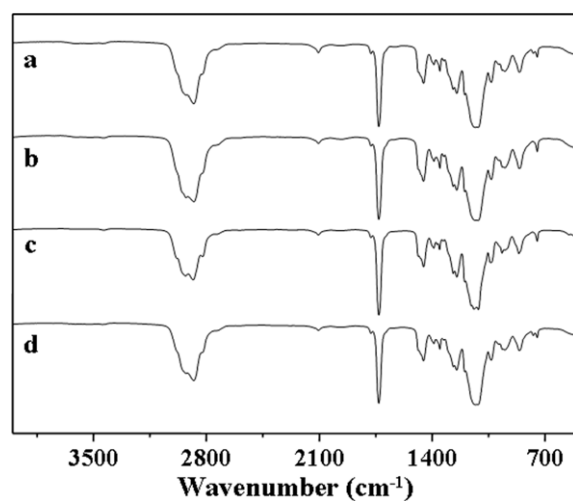


Fig. S3 FT-IR spectra of N_3 -PMEO₂MA₂₇ (a), N_3 -P(MEO₂MA₁₈-*co*-MEO₃MA₉) (b), N_3 -P(MEO₂MA₇-*co*-MEO₃MA₁₈) (c) and N_3 -PMEO₃MA₂₆ (d).

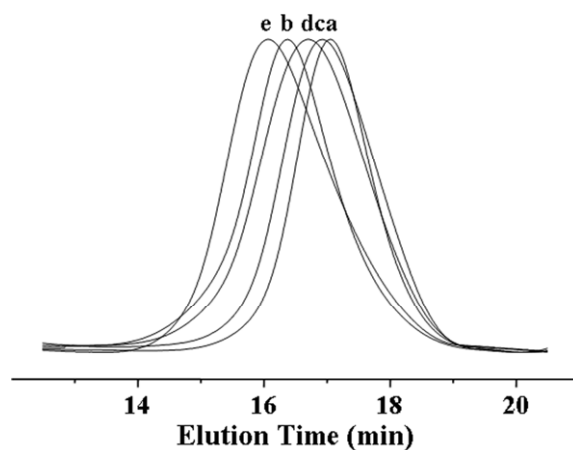


Fig. S4 GPC chromatograms of N_3 -PMEO₂MA₂₇ (a), N_3 -P(MEO₂MA₁₈-*co*-MEO₃MA₉) (b), N_3 -P(MEO₂MA₁₃-*co*-MEO₃MA₁₃) (c), N_3 -P(MEO₂MA₇-*co*-MEO₃MA₁₈) (d) and N_3 -PMEO₃MA₂₆ (e) with THF as eluent.

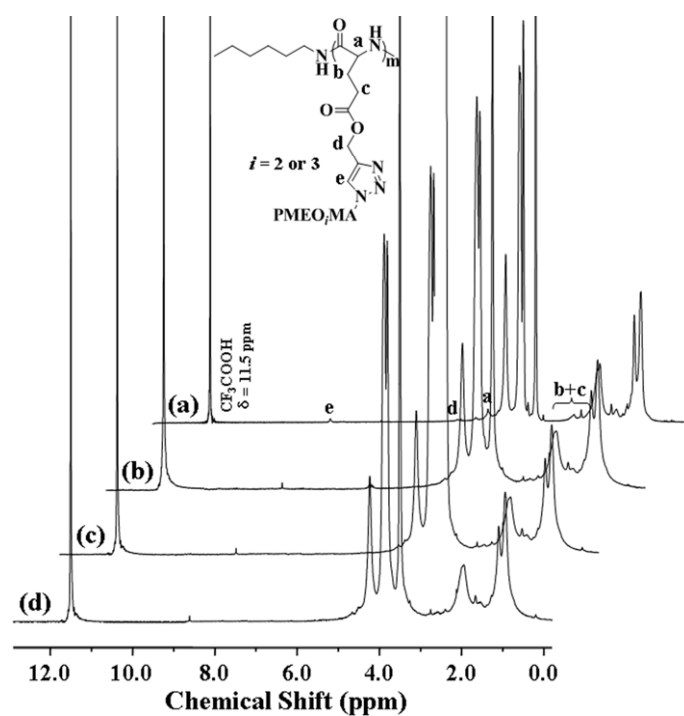


Fig. S5 ^1H NMR spectra of **P1** (a), **P2** (b), **P4** (c) and **P5** (d) (in CF_3COOD).

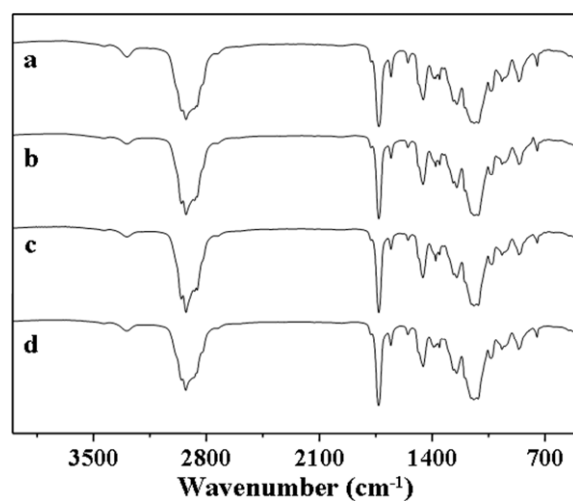


Fig. S6 FT-IR spectra of **P1** (a), **P2** (b), **P4** (c) and **P5** (d).

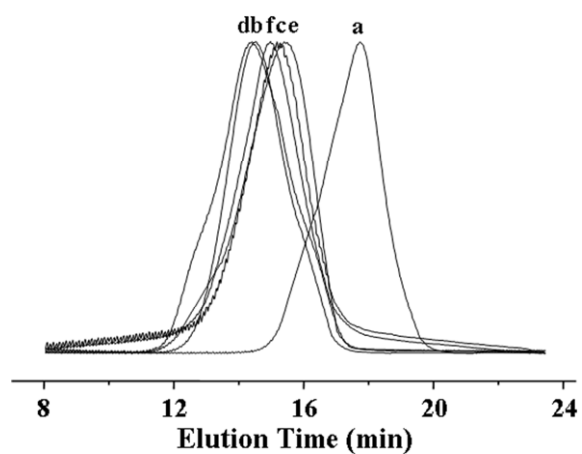


Fig. S7 GPC chromatograms of PPLG₄₀ (a), **P1** (b), **P2** (c), **P3** (d), **P4** (e) and **P5** (f) with DMF as eluent.

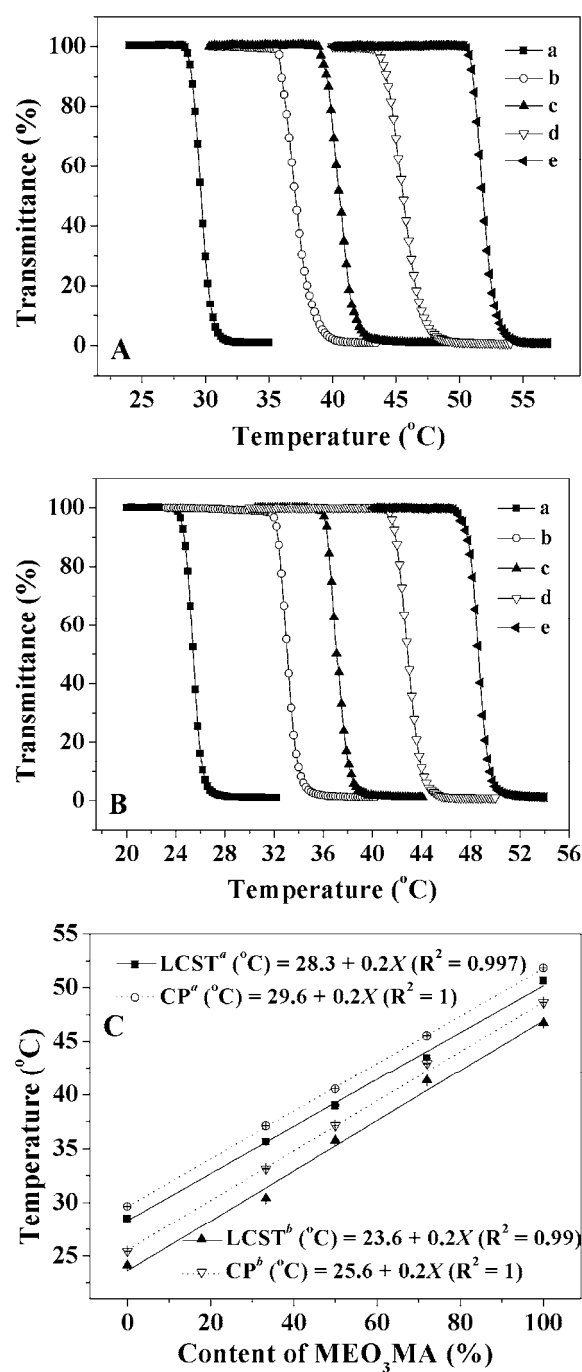


Fig. S8 Thermo-responsive behaviors of *N*₃-PMEO₂MA₂₇ (a), *N*₃-P(MEO₂MA₁₈-*co*-MEO₃MA₉) (b), *N*₃-P(MEO₂MA₁₃-*co*-MEO₃MA₁₃) (c), *N*₃-P(MEO₂MA₇-*co*-MEO₃MA₁₈) (d) and *N*₃-PMEO₃MA₂₆ (e) in deionized water (A) and physiological saline (B), and LCST and CP as a function of MEO₃MA content in deionized water (a) and physiological saline (b) (C).

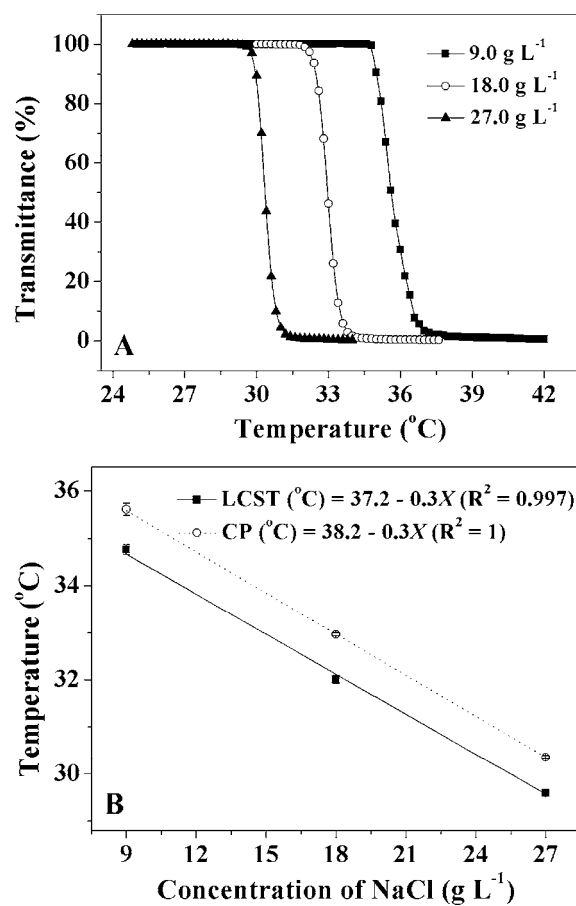


Fig. S9 Thermo-responsive behaviors of **P4** in 9.0, 18.0 and 27.0 g L⁻¹ aqueous sodium chloride (NaCl) (A), and LCST and CP as a function of NaCl concentration (B).

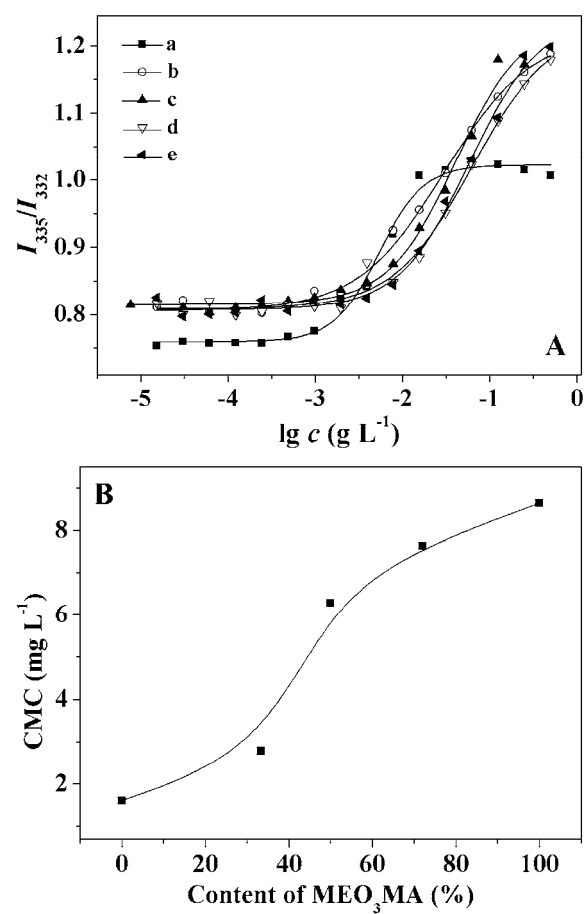


Fig. S10 The intensity ratio (I_{335}/I_{332}) as a function of logarithm of **P1** (a), **P2** (b), **P3** (c), **P4** (d) or **P5** concentration (e) (A), and CMC value as a function of MEO₃MA content in PBS (B).