

Supporting Information

Synthesis and properties of stimuli-sensitive heterografted toothbrushlike terpolymers with linear handle and two types of V-shaped grafts

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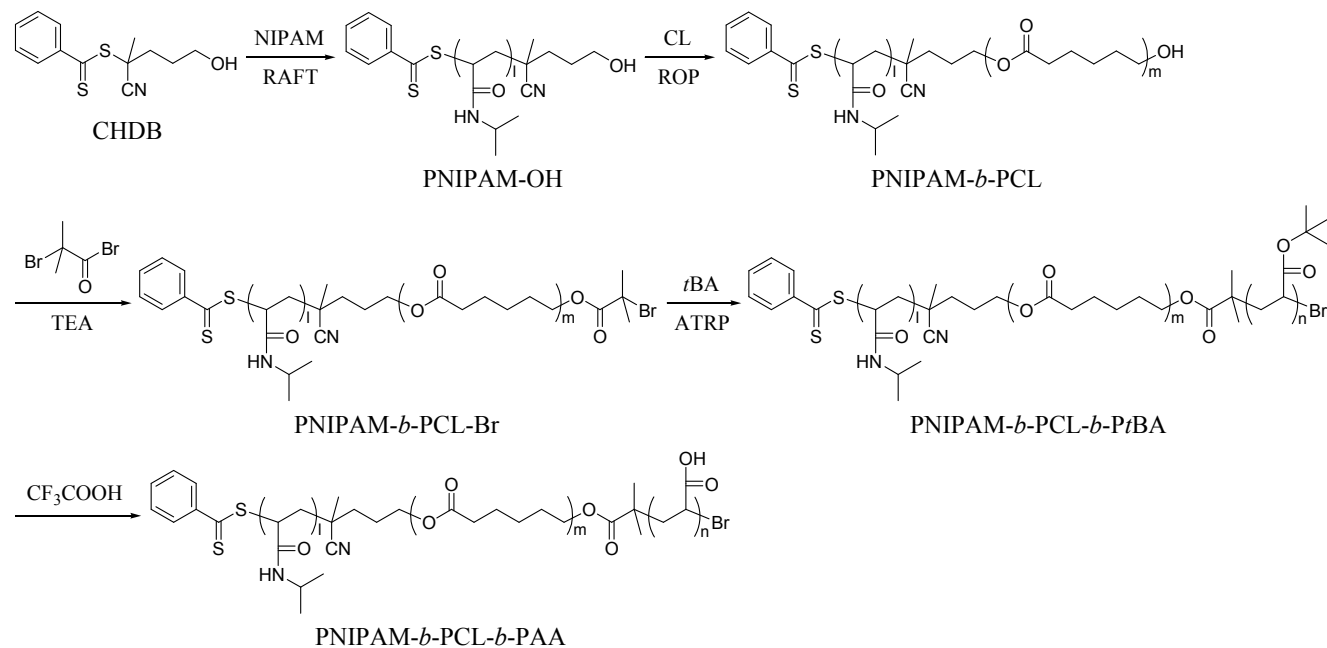
Table S1. Results for synthesis of PNIPAM-OH (run 1), PNIPAM-*b*-PCL (run 2) and PNIPAM-*b*-PCL-*b*-PtBA (run 3)^a

run	I ^b	M	T (°C)	t (h)	C% ^c	M _{n,th} ^d	M _{n,GPC} ^e	PDI ^e	M _{n,NMR} ^f	DP _{PM} ^f
1	CHDB	NIPAM	70	18	50.5	4830	4950	1.09	4810	40.2
2	PNIPAM-OH	CL	110	20	97.2	10400	13200	1.08	10300	48.3
3	PNIPAM- <i>b</i> -PCL-Br	<i>t</i> BA	80	12	49.0	18000	19600	1.11	17800	56.9

^a Reaction conditions: [NIPAM]₀: [CHDB]₀: [AIBN]₀ = 80:1:0.1, [M]₀ = 3.0 mol L⁻¹, in dioxane (run 1); [CL]₀: [PNIPAM]₀: [Sn(Oct)₂]₀ = 50:1:0.2, [M]₀ = 1.9 mol L⁻¹, in toluene, and then the isolated PNIPAM-*b*-PCL copolymer was further reacted with 2-bromoisobutyryl bromide to generate PNIPAM-*b*-PCL-Br (run 2); [*t*BA]₀: [AB-Br]₀: [CuBr]₀: [PMDETA]₀ = 120:1:1:1, [M]₀ = 1.5 mol L⁻¹, in acetone (run 3). ^b Functional RAFT agent (run 1) and macroinitiator (runs 2 and 3). ^c Monomer conversion determined by gravimetry. ^d Theoretical molecular weight. ^e Number-average molecular weight and polydispersity estimated by GPC. ^f Number-average molecular weight (M_{n,NMR}) and polymerization degree of PM segment (DP_{PM}) determined by ¹H NMR analysis.

Table S2. Glass transition temperature (T_g), melting peak (T_m) and degree of crystallinity (X_c) of various samples

sample	T_g (°C)	T_m (°C)	X_c (%)	$f_{w,PCL}$
PNIPAM	135.9	—	—	—
PNSM	121.2	—	—	—
T1	49.5, 113.9	—	—	—
T2	-44.5, 117.1	49.7	13.3	0.203
T3	-45.2, 115.0	49.6	32.3	0.306
T4	-50.5, 106.4	50.4	44.8	0.478
T5	-58.7, 85.3, 112.7	48.0, 56.4	24.4	0.252
T6	-59.6, 85.1, 110.4	45.5, 54.4	37.6	0.368
T7	-61.0, 88.6, 112.4	49.8	52.6	0.550



Scheme S1 Synthetic routes to PNIPAM-*b*-PCL-*b*-PAA triblock copolymer.

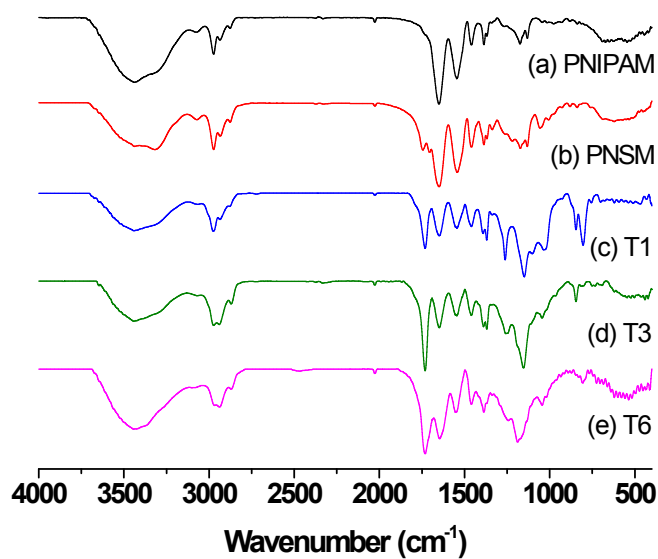


Fig. S1 IR spectra of typical toothbrushlike terpolymers and their precursors.

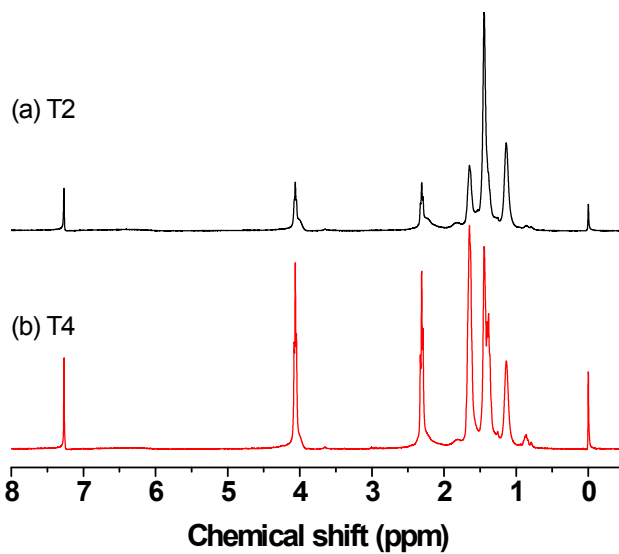


Fig. S2 ¹H NMR spectra of PNIPAM(*Pt*BA)_{2m}(PCL)_{2m} copolymers.

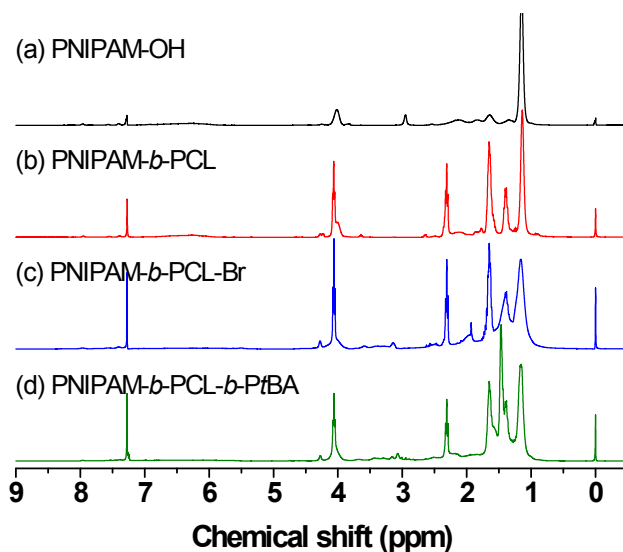


Fig. S3 ^1H NMR spectra of PNIPAM-*b*-PCL-*b*-PtBA triblock copolymer and its precursors.

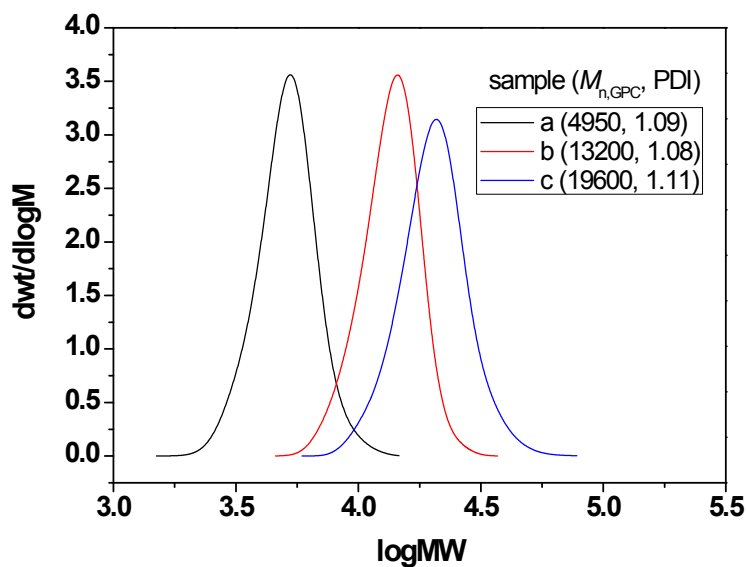


Fig. S4 GPC traces of PNIPAM-OH (a), PNIPAM-*b*-PCL (b) and PNIPAM-*b*-PCL-*b*-PtBA (c).

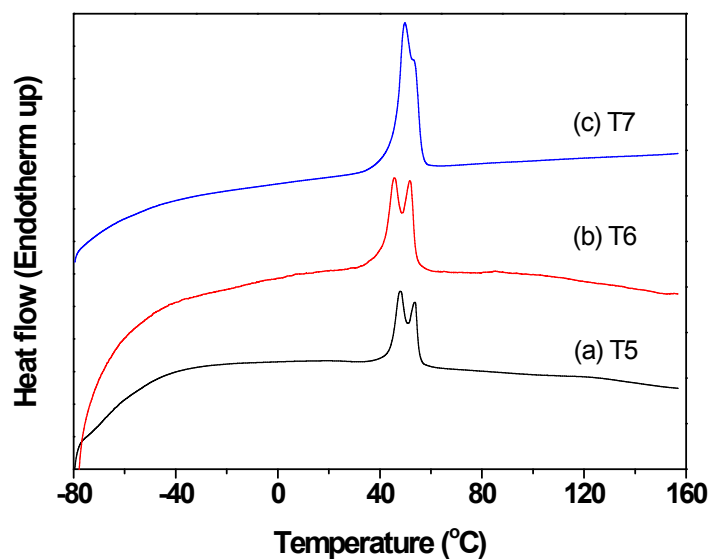


Fig. S5 DSC curves of PNIPAM(PAA)_{2m}(PCL)_{2m} copolymers.

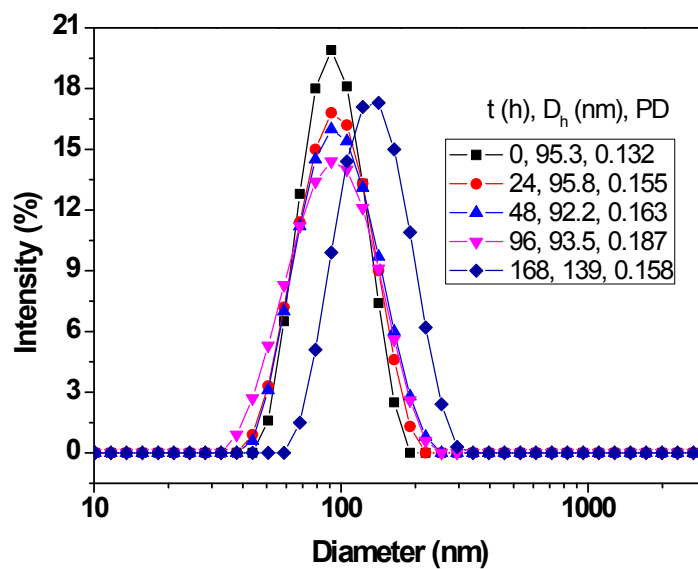


Fig. S6 Influence of storage time on DLS plots of T6 aggregates ($c = 0.50 \text{ mg mL}^{-1}$) formed in PBS solution (50 mM) at 37 °C.