

Supporting Information

Synthesis and properties of heterografted toothbrushlike copolymers with alternating PEG and PCL grafts and tunable RAFT-generated segments

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Table S1 Solubility of (A-*g*-D)(B-*alt*-C)_mD (A = PDMA, B = PEG, C = PCL) toothbrushlike copolymers in different solvents

Sample	D	hexane	toluene	ether	methanol	acetone	water	THF	chloroform	dioxane	DMSO
T5	PNIPAM	–	+	–	–	+	–	+	+	+	+
T6	PNIPAM	–	±	–	–	±	–	±	+	±	+
T7	PNIPAM	–	+	–	–	+	±	+	+	+	+
T8	PMMA	–	+	–	–	+	–	+	+	+	+
T9	PSt	–	+	–	–	+	–	+	+	+	+
T10	PMA	–	+	–	–	+	–	+	+	+	+

Solubility: +, soluble; ±, partly soluble; –, insoluble.

Table S2 DSC results of various toothbrushlike copolymers and their precursors

sample	T_g (°C)	$T_{m,PEG}$ (°C)	$T_{m,PCL}$ (°C)	$f_{w,PEG}^a$	$f_{w,PCL}^a$	$\Delta H_{m,PEG}$ (J/g) ^b	$\Delta H_{m,PCL}$ (J/g) ^b	$X_{c,PEG}$ (%) ^c	$X_{c,PCL}$ (%) ^c
St-PEG	—	29.5	—	0.878	—	93.5	—	49.8	—
MI-PCL	-59.5	—	39.9, 47.9	0	0.924	—	75.7	—	60.2
PDMA	17.9	—	—	—	—	—	—	—	—
T1	-59.6	24.0	41.1	0.247	0.545	19.9	16.5	37.7	22.2
T6	-57.5, 109.4	22.1	42.5	0.125	0.276	5.06	0.29	18.9	0.77
T8	-49.8, 66.6	—	—	0.131	0.288	0	0	0	0
T9	-63.6, 85.2	25.8	42.0	0.102	0.225	1.40	1.07	6.42	3.49
T10	-57.4, -5.8	—	38.5	0.110	0.243	0	3.21	0	9.71

^a Weight content of PEG and PCL determined by ¹H NMR analysis. ^b Crystallization enthalpy of PEG and PCL segments determined by DSC. ^c Degree of crystallinity of PEG and PCL segments, where $X_{c,PEG} = \Delta H_{m,PEG} / (213.7 \times f_{w,PEG})$, $X_{c,PCL} = \Delta H_{m,PCL} / (136.1 \times f_{w,PCL})$.

Table S3 Dependence of apparent drug-release rate (K), cumulative release (CR) and increment of cumulative release (ICR) at 48 h on additives (1.0 mM α -CD or 10 mM DTT) during in vitro DOX release from various aggregates

Aggregates	T (°C)	α -CD	DTT	K (h ⁻¹)	CR (%)	ICR (%)
T6	25	none	none	0.0536	25.2	0
T6	25	yes	none	0.0684	33.8	34.1
T6	25	none	yes	0.0806	35.5	40.9
T6	37	none	none	0.121	42.5	68.7
T6	37	yes	none	0.133	50.6	101
T6	37	none	yes	0.145	53.8	113
T6-SH	25	none	none	0.0910	35.7	0
T6-SH	25	none	yes	0.118	40.7	14.0
T6-SH	37	none	none	0.122	44.2	23.8
T6-SH	37	none	yes	0.151	46.6	30.5

Table S4 Dependence of hydrodynamic diameter (D), peak size (D_{peak}) and particle size distribution (PD) of aggregates formed from (PDMA-*g*-PNIPAM)(PEG-*alt*-PCL)_mPNIPAM (T6) toothbrushlike copolymer ($c = 0.50$ mg/mL) in PBS solution (50 mM, pH 7.4) on temperature, additive and time

run	T (°C)	additive	t (h)	D (nm)	D_{peak} (nm)	PD
1	25	none	0	144	145	0.128
2	25	none	48	148	156	0.132
3	25	DTT	2	215	39.2/264	0.385
4	25	DTT	5	219	235	0.115
5	25	DTT	10	256	291	0.536
6	25	DTT	24	178	36.7/212	0.460
7	25	α -CD	2	311	329	0.219
8	25	α -CD	5	305	317	0.155
9	25	α -CD	10	255	71.4/283	0.434
10	25	α -CD	24	239	251	0.229
11	37	none	0	125	135	0.195
12	37	none	48	122	131	0.204
13	37	DTT	2	205	228	0.135
14	37	DTT	5	248	261	0.126
15	37	DTT	10	204	48.5/229	0.475
16	37	DTT	24	296	315	0.136
17	37	α -CD	2	362	377	0.168
18	37	α -CD	5	370	381	0.180
19	37	α -CD	10	393	69.4/431	0.462
20	37	α -CD	24	501	176/642	0.663

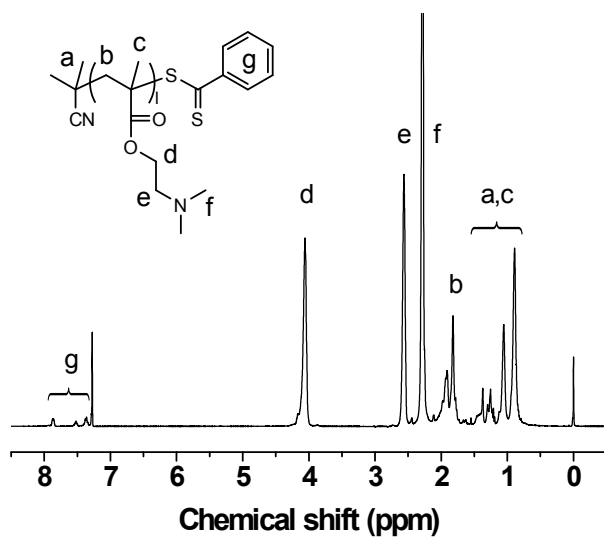


Fig. S1 ^1H NMR spectrum of PDMA (DP = 27.6).

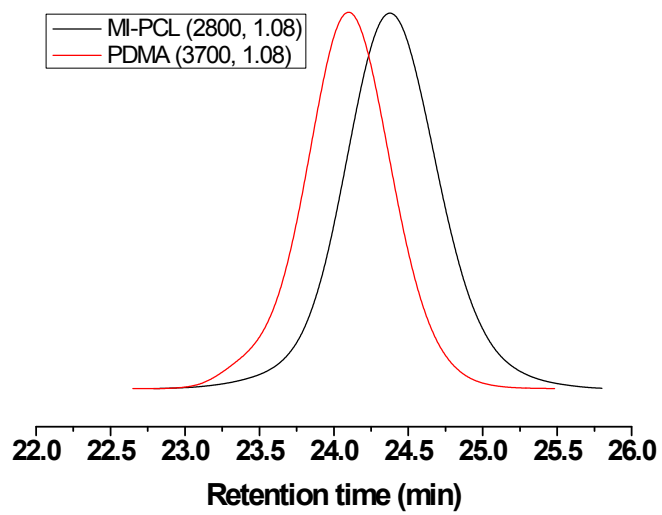


Fig. S2 GPC traces of MI-PCL and PDMA.

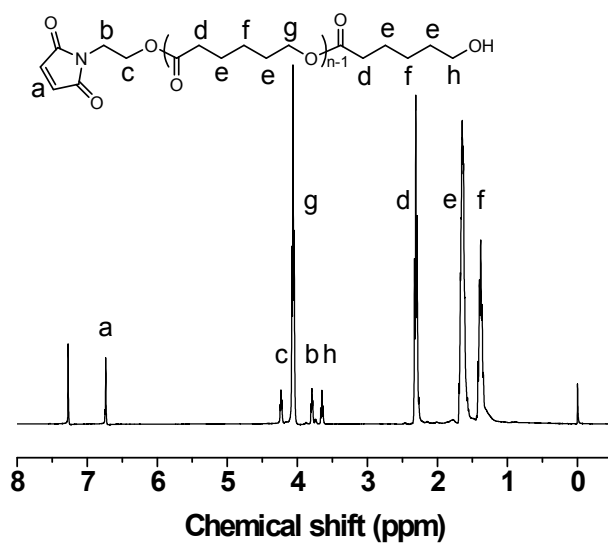


Fig. S3 ^1H NMR spectrum of MI-PCL (DP = 15.0).

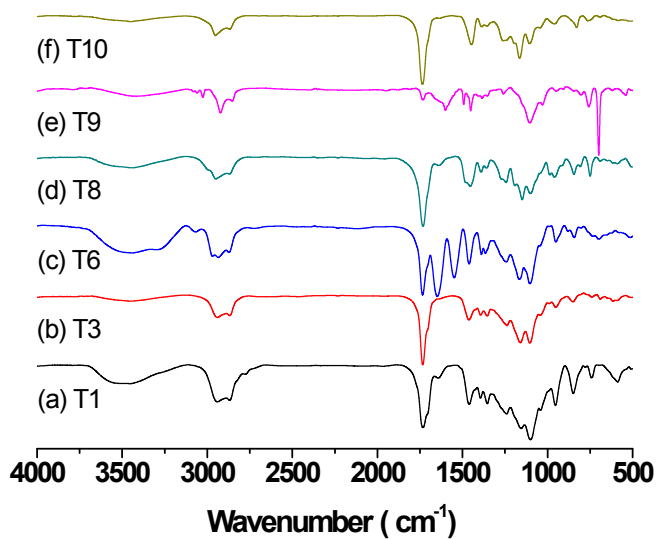


Fig. S4 IR spectra of various toothbrushlike copolymers.

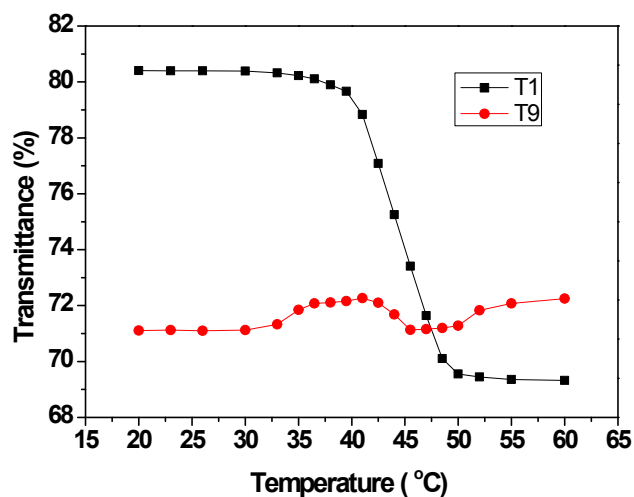


Fig. S5 Dependence of transmittance of copolymer aggregates ($c = 1.0$ mg/mL) on temperature.

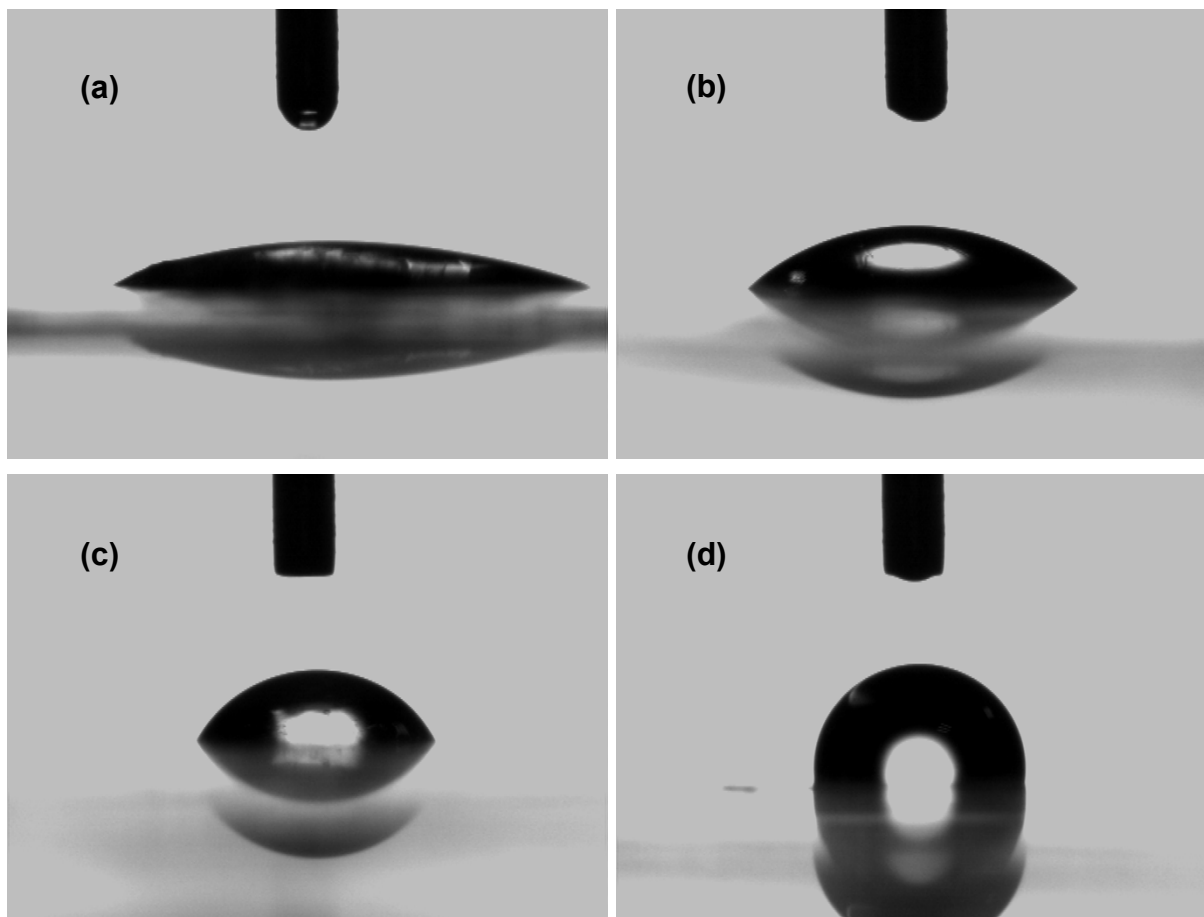


Fig. S6 Water contact angle photographs of polymer films casted from THF solution of $A(B\text{-}alt\text{-}C)_m$ (T1, a and b) and $(A\text{-}g\text{-}PSt)(B\text{-}alt\text{-}C)_mPSt$ (T9, c and d) copolymers at 25 (a, c) and 40 °C (b, d), in which A, B and C were PDMA, PEG and PCL, respectively.

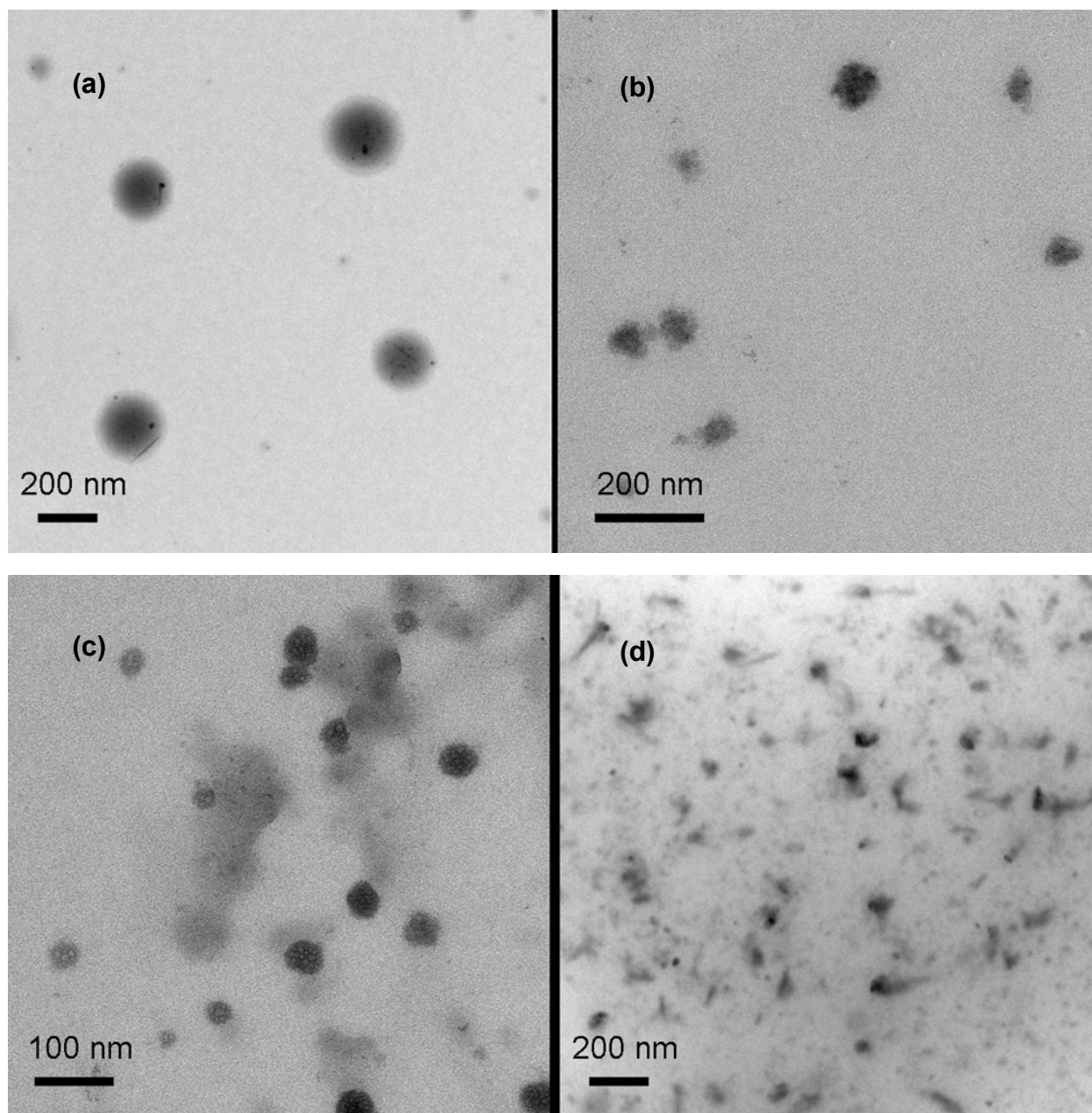


Fig. S7 TEM images of various aggregates ($c = 0.50$ mg/mL) formed in PBS solution (pH 7.4, 50 mM) at 37 °C: (a) T1; (b) T8; (c) T9; (d) T10.

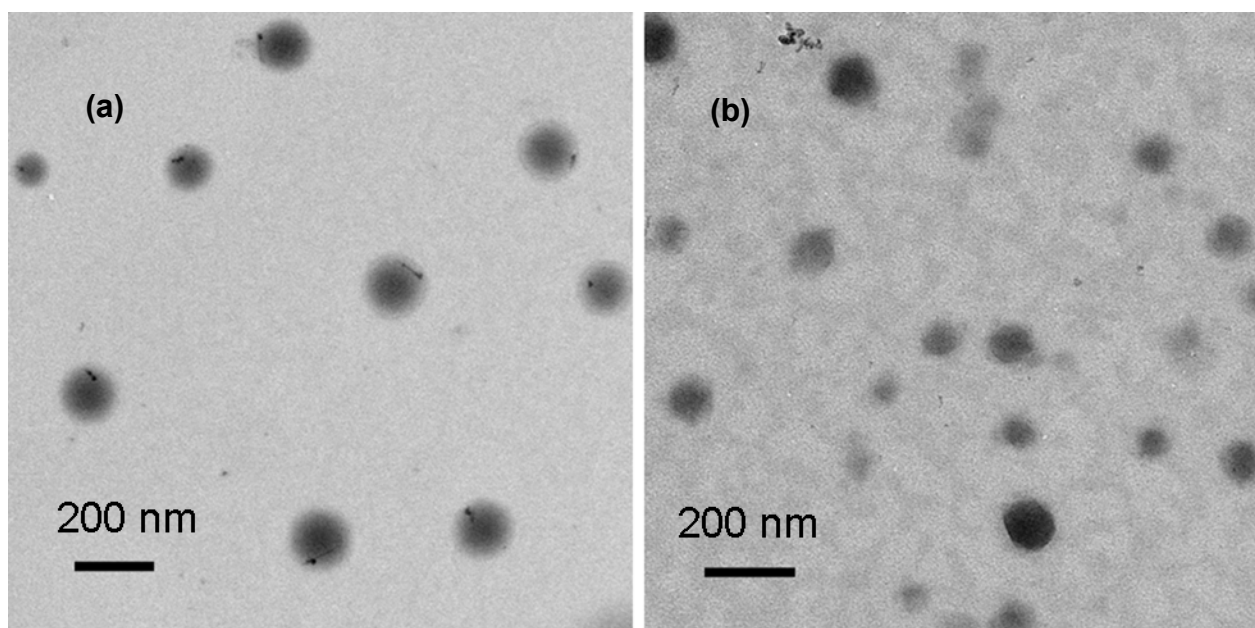


Fig. S8 TEM images of T6 aggregates ($c = 0.50$ mg/mL) formed in PBS solution (pH 7.4, 50 mM) at 25 (a) and 37 °C (b).

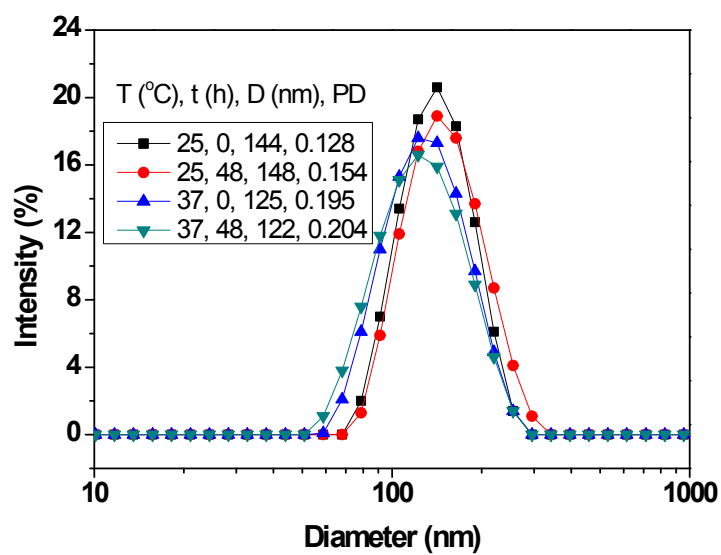


Fig. S9 DLS plots of T6 aggregates ($c = 0.50$ mg/mL) in PBS solution (50 mM, pH 7.4) at 25 or 37 °C for different time periods ($t = 0$ and 48 h).