Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting Information

Room Temperature Synthesis of Block Copolymer Nano-Objects with Different Morphologies via Ultrasound Initiated RAFT Polymerization-Induced Self-Assembly (Sono-RAFT-PISA)

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Thermal initiator radical species concentration

Radical species generated from decomposition of azo compound initiator. Thus,

$$\frac{d[R]}{dt} = -2f\frac{d[I]}{dt} = 2fk_d[I],\ k_d = ln2/t_{1/2}$$

$$[R] = 2f([I]_0 - [I]) = 2f[I]_0(1 - e^{-k_d t})$$

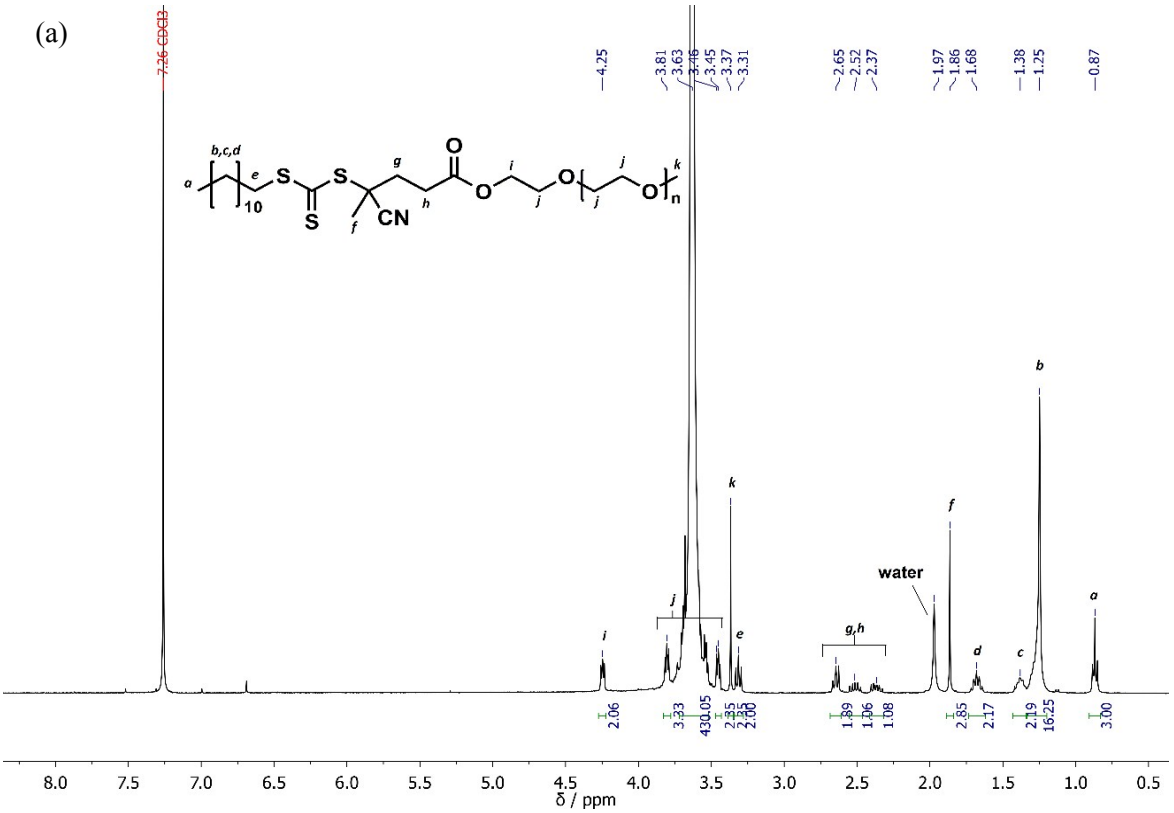
$[R]$= radical concentration, $[I]$= initiator concentration, k_d = decomposition rate constant, $t_{1/2}$= half-life of initiator, f = initiator efficiency.

For this study, taking PEG_{113}-$PHPMA_{400}$ thermal-PISA as example, initial initiator concentration $[I]_0$ = 0.5 mM. At 50 °C, $t_{1/2}$ of VA-044 = 250 min, $k_d = 2.772 \times 10^{-3} min^{-1}$. Initiator efficiency is not considered when estimating radical species concentration during ultrasound irradiation, thus thermal initiator f is ignored for comparison. For maximum radical generation, f=1. At end of thermal-PISA (4 hr), t= 240 min, $[R]$=0.49 mM.

Disassembly/reassembly after sono-PISA

100 µL Suspension of PEG_{113}-$PHPMA_{400}$ prepared via sono-PISA (10% w/w) was lyophilized overnight to obtain ~ 10 mg dried polymer. Tetrahydrofuran (THF) was added to the dried polymer to make 10 mg polymer/mL THF solution. The solution was stirred for 4hr to ensure polymer is well dissolved. Take 0.1 mL 10 mg/mL THF solution into a small vial with stirrer bar, add 0.9 mL DI water to THF solution drop by drop with constant stirring (100 rpm) to make a cloudy solution with concentration of 1 mg polymer/ mL (water: THF=9:1). The cloudy solution was dialysed against DI water using 2 kDa dialysis membrane for 24 hr to remove THF. The dialysed solution was used to prepare TEM sample without further dilution.

Supplementary Figures



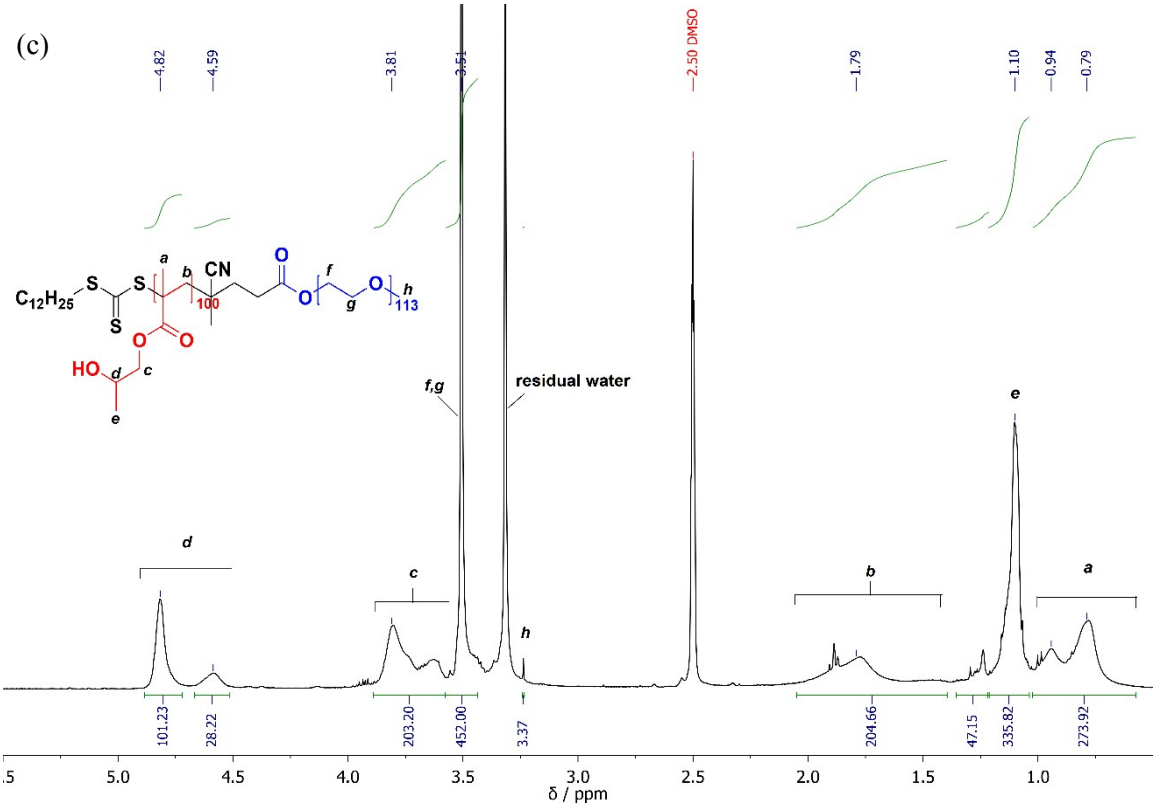


Fig. S1 (a) ^{1}H NMR spectrum (400 MHz, $CDCl_3$) and (b) ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of PEG_{113}-CDTPA synthesized (c) ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of PEG_{113}-$PHPMA_{103}$ synthesized via sono-RAFT-PISA (multiple polymer peak due to monomer HPMA is mixture of 2-hydroxypropyl methacrylate and 2-hydroxyisopropyl methacrylate).

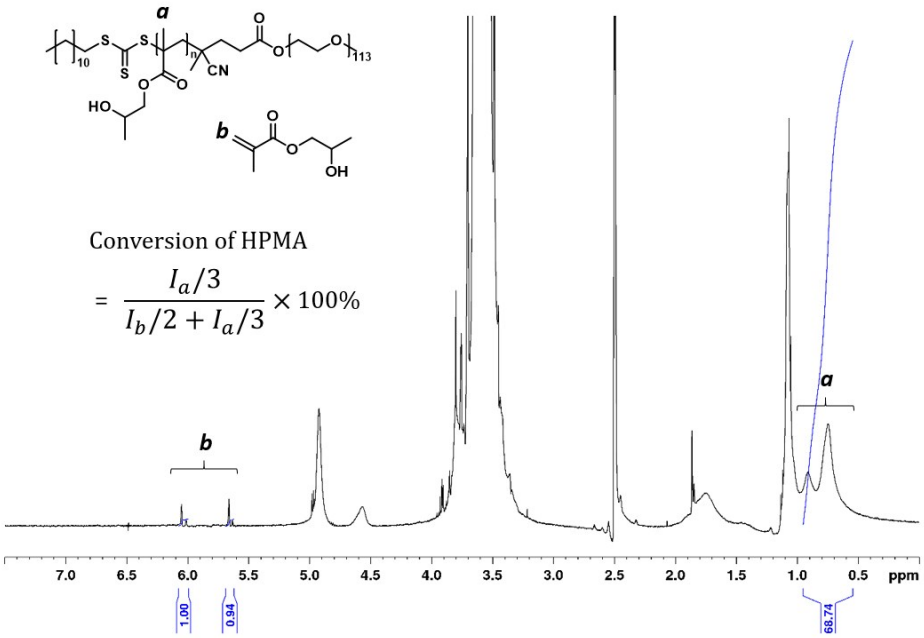


Fig. S2 Exemplary ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of PEG_{113}-$PHPMA_x$ crude (target DP 400) synthesized via sono-RAFT-PISA showing monomer conversion calculation.
Conversion=(68.74/3)/[(1.00+0.94)/2+68.74/3]×100%=95.9%.

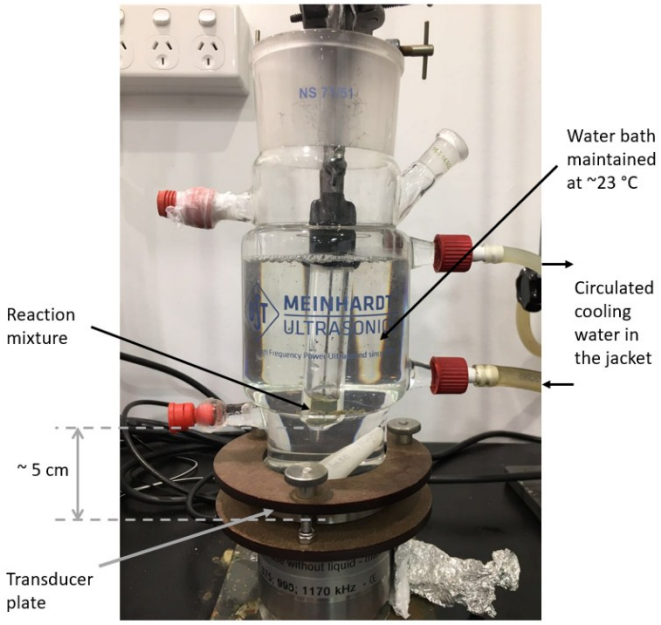


Fig. S3 Experimental setup of ultrasound transducer and reaction vessel for PEG_{113}-$PHPMA_{103}$ sono-RAFT-PISA experiment at room temperature, water batch temperature measured 23.8 °C at the end of polymerization (ultrasound amplifier and water circulation pump not shown).

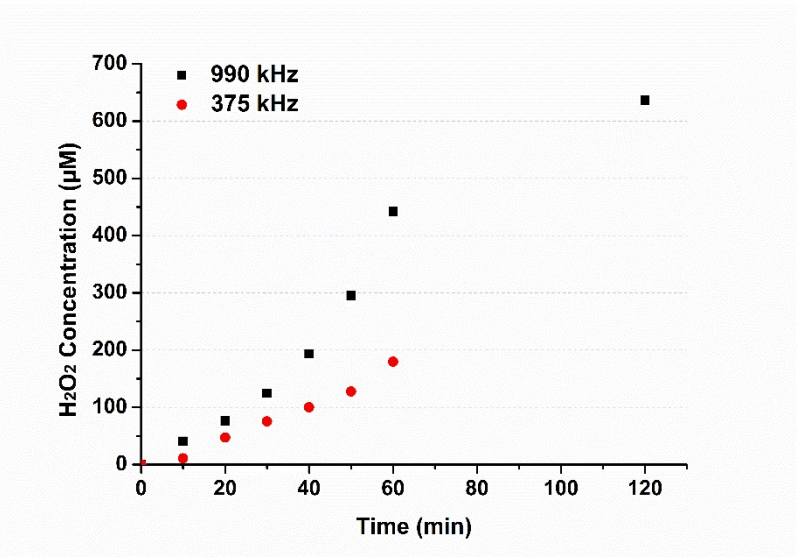


Fig. S4 Quantification of H_2O_2 (and indirectly, $HO^{\cdot}$) generated ultrasonically at 375 kHz and 990 kHz.

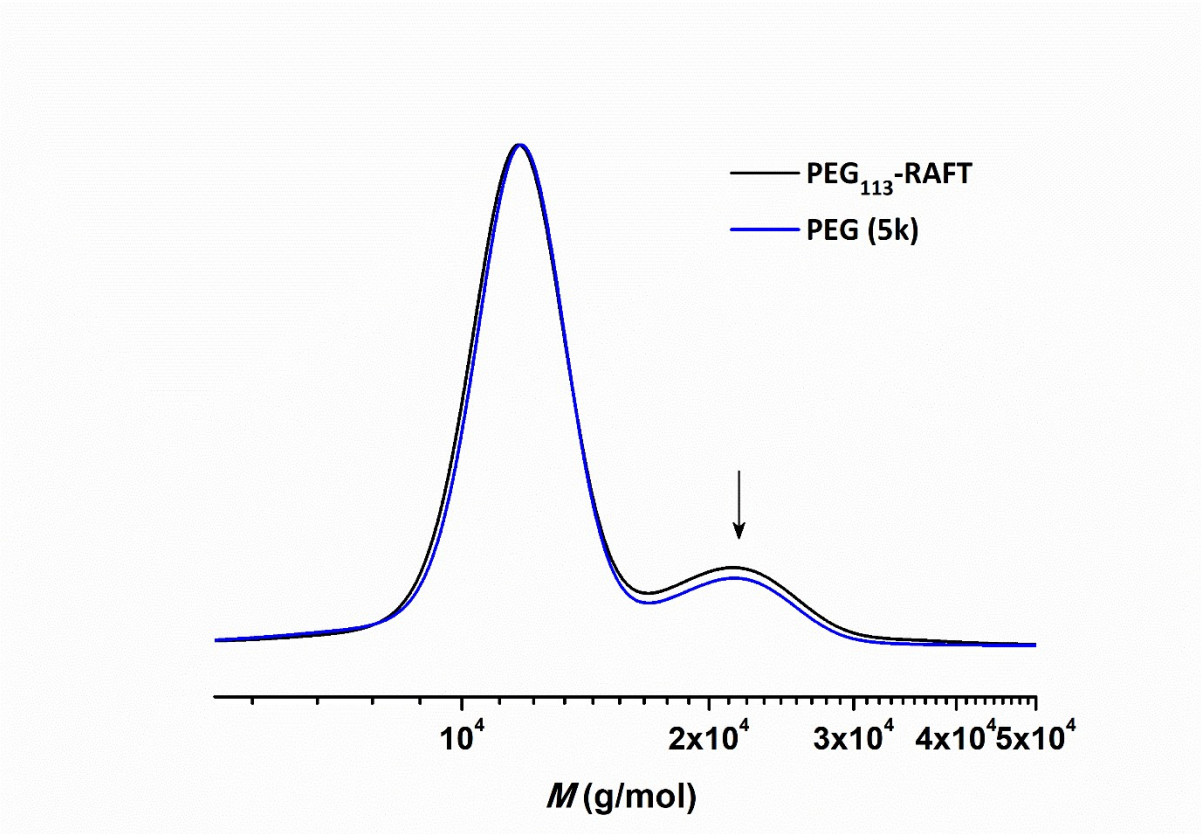


Fig. S5 GPC traces of poly(ethylene glycol) methyl ether (PEG (5k), average M_n 5,000) and synthesized PEG_{113}-RAFT.

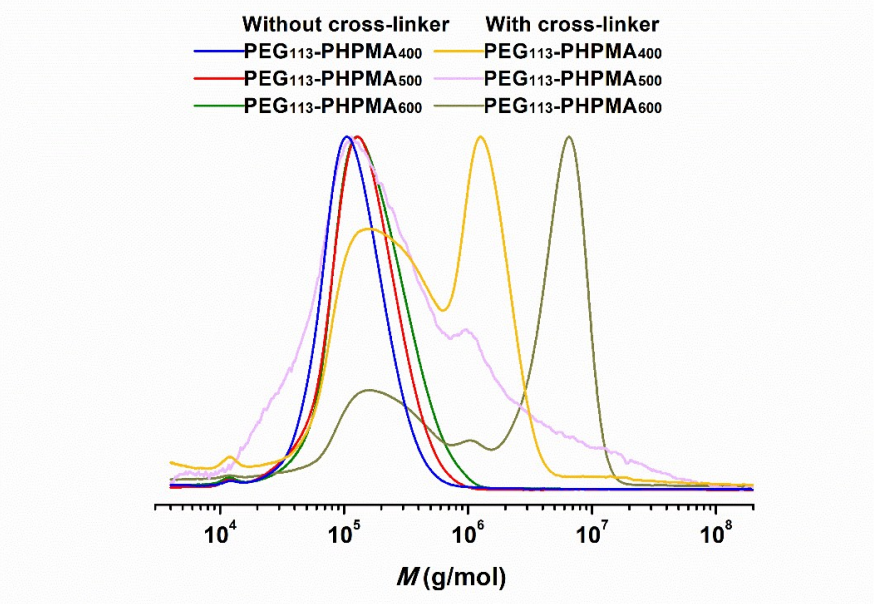


Fig. S6 GPC traces of a series of PEG_{113}-$PHPMA_x$ block copolymers with or without crosslinker (dimethacrylate impurity).

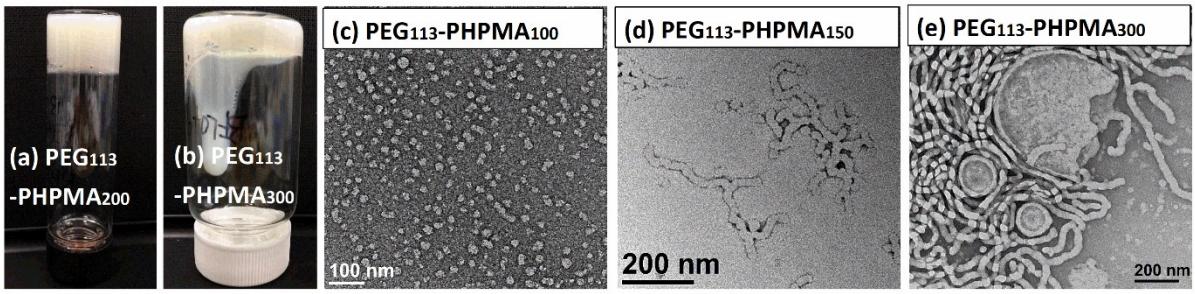


Fig. S7 Digital photos of standing-free gel dispersion of (a) PEG_{113}-$PHPMA_{200}$ and (b) PEG_{113}-$PHPMA_{300}$ prepared by thermal-PISA and (c-e) TEM images of nano-objects prepared by thermal-PISA.

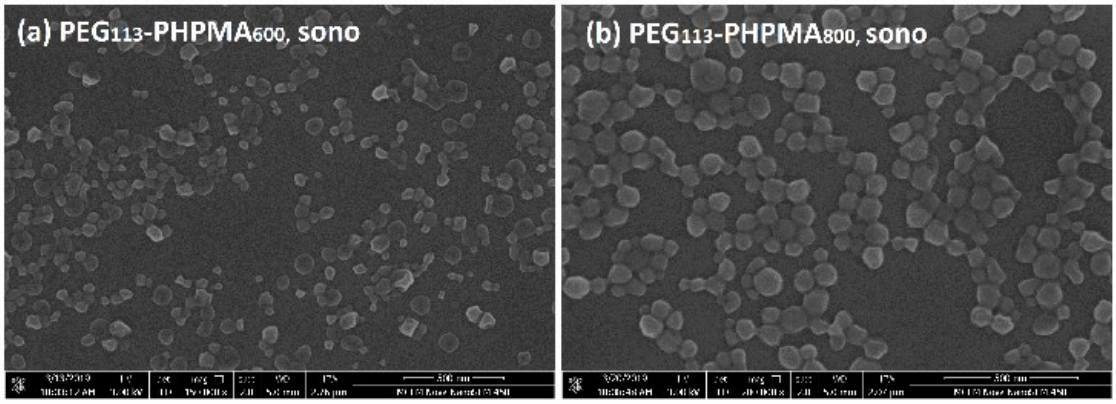


Fig. S8 Representative SEM images of (a) PEG_{113}-$PHPMA_{600}$ and (b) PEG_{113}-$PHPMA_{800}$ synthesized by sono-RAFT-PISA (10.0 % w/w solid content).

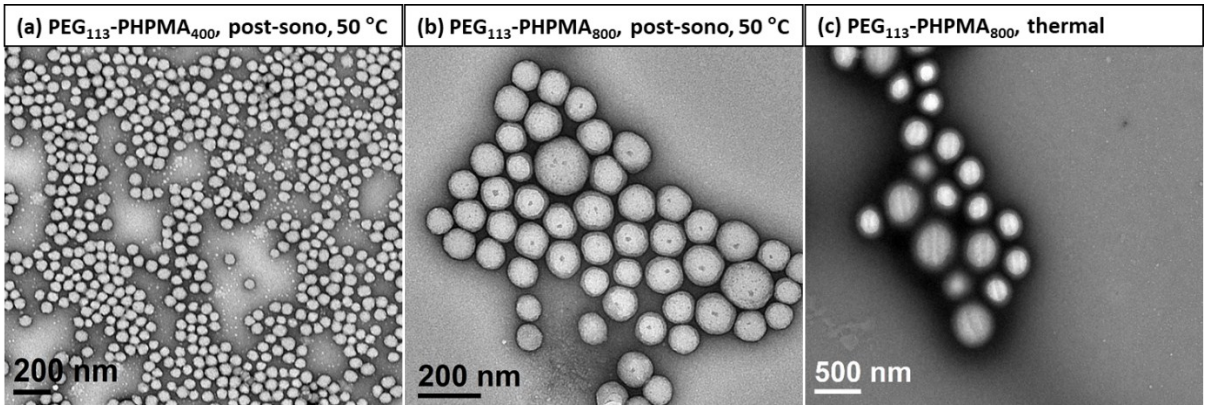


Fig. S9 Representative TEM images of (a) PEG_{113}-$PHPMA_{400}$, (b) PEG_{113}-$PHPMA_{800}$ synthesized by sono-RAFT-PISA and warmed up to 50 °C for 24 hr. (c) PEG_{113}-$PHPMA_{800}$ synthesized by thermal-PISA (10.0 % w/w solid content). TEM sample preparation protocol was modified in order to investigate the effect of temperature change on morphology. The warmed sample was diluted to 0.10 % w/v using DI water pre-warmed to 50 °C. The TEM sample was prepared immediately after dilution by proceeding the normal procedure.

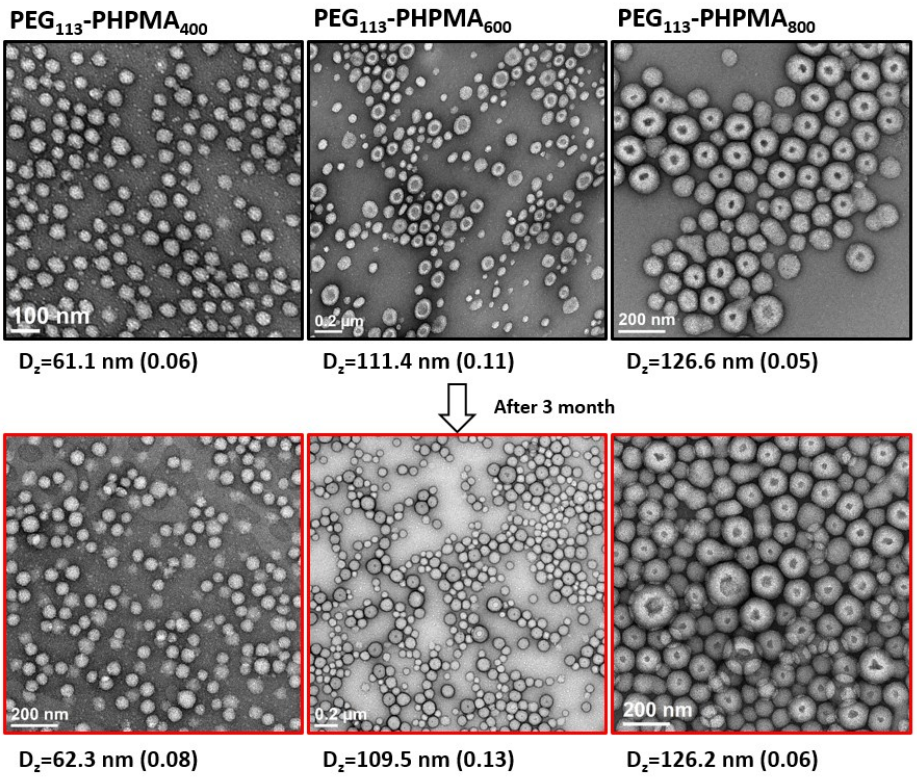


Fig. S10 DLS size distribution data and representative TEM images of PEG_{113}-$PHPMA_{800}$ synthesized by sono-PISA and after 3 months standing at room tempearture.

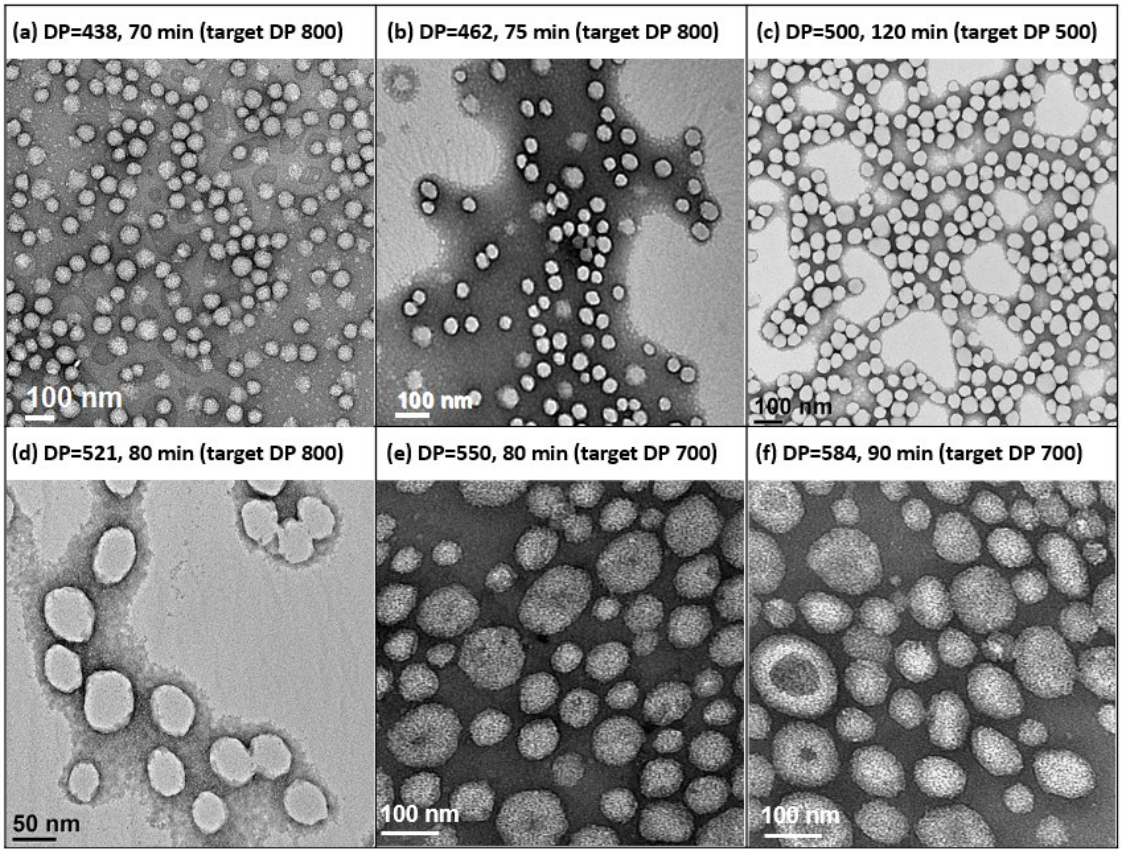


Fig. S11 TEM images of PEG_{113}-$PHPMA_X$ prepared via sono-PISA by varying target DP and sampling at certain time points during polymerization (focused on DP 400~600).

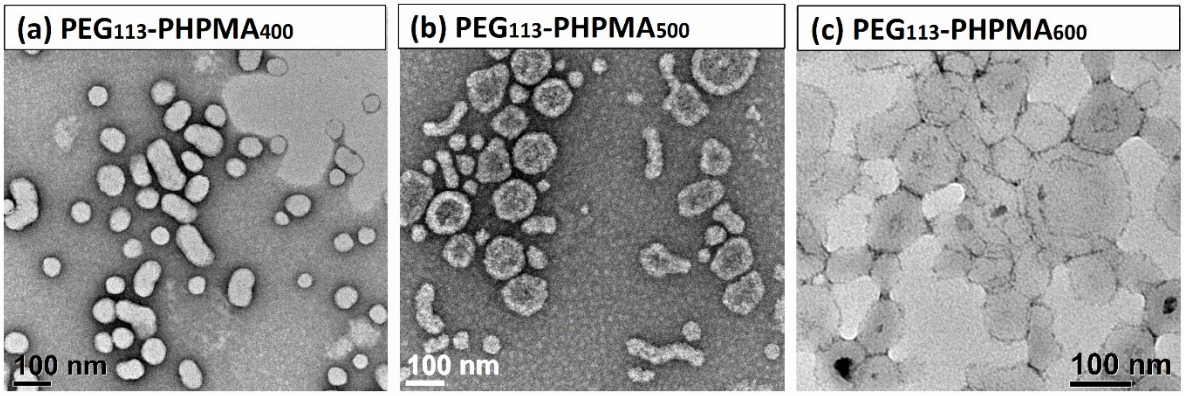


Fig. S12 Representative TEM images of (a) PEG_{113}-$PHPMA_{400}$, (b) PEG_{113}-$PHPMA_{500}$ and (c) PEG_{113}-$PHPMA_{600}$ synthesized by sono-RAFT-PISA using unpurified monomer HPMA (10.0 % w/w solid content).

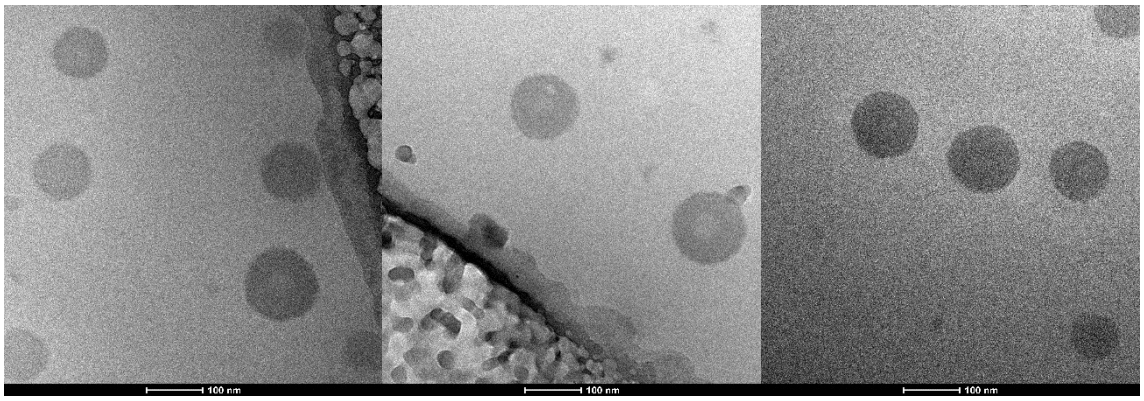


Fig. S13 Supplementary cyro-TEM images of PEG_{113}-$PHPMA_{800}$ vesicles synthesized by sono-PISA.

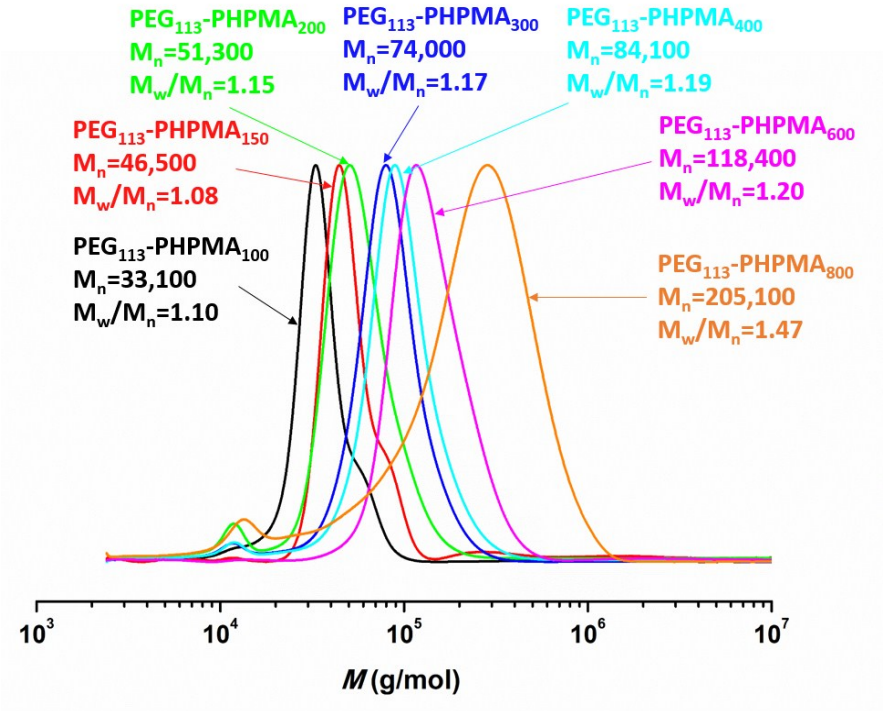


Fig. S14 Gel permeation chromatography traces (PMMA standards) obtained for PEG_{113}-$PHPMA_X$ (target DP x=150-800) copolymers synthesized via thermal-PISA at 50 °C (Table S1 entry 12-18).

Entry[a]	Target PHPMA DP	Preparation method[b]	$M_{n,th}$[c] (conv.%)	GPC		DLS		Morphology[e]	Note
				$M_{n,GPC}$[d]	M_w/M_n	Z_a (nm)	PDI		
1	104	US	18,900 (90.0)	31,500	1.24	28.7 ± 1.4	0.11 ± 0.09	S	[f]
2	174	US	30,000 (98.0)	63,000	1.35	45.3 ± 0.6	0.07 ± 0.01	S	[f]
3	200	US	34,200 (>99.0)	44,100	1.13	44.9 ± 0.3	0.08 ± 0.01	S	
4	400	US	60,700 (95.9)	98,400	1.34	61.1 ± 0.8	0.06 ± 0.01	S	
5	500	US	75,800 (97.6)	109,600	1.47	72.0 ± 0.6	0.13 ± 0.01	S	
6	600	US	90,200 (98.0)	124,800	1.50	111.4 ± 1.5	0.11 ± 0.07	S/V	
7	800	US	116,100 (96.0)	158,500	1.61	126.6 ± 1.1	0.05 ± 0.03	V	
8	400	US	62,200 (99.2)	1,200,000; 148,300	1.15; 1.48	77.8 ± 0.4	0.09 ± 0.01	S/C	[f]
9	500	US	74,500 (95.9)	1,222,500; 86,900	1.24; 1.99	94.2 ± 1.0	0.10 ± 0.01	S/W/V	[f]
10	600	US	90,700 (99.0)	5,331,900; 160,300	1.16; 1.47	126.7 ± 1.0	0.11 ± 0.02	V	[f]
11	800	US	118,000 (98.0)	5,193,100; 181,900	1.07; 1.43	153.5 ± 2.8	0.09 ± 0.03	V	[f]
12	100	T	19,800 (>99.0)	33,100	1.10	31.8 ± 0.8	0.13 ± 0.02	S	
13	150	T	27,000 (>99.0)	46,500	1.08	90.5 ± 0.8	0.20 ± 0.02	W	
14	200	T	34,200 (>99.0)	51,300	1.15	593.9 ± 29.6	0.33 ± 0.01	W/V	
15	300	T	48,600 (>99.0)	74,000	1.17	359.2 ± 6.6	0.25 ± 0.02	W/V	
16	400	T	63,000 (>99.0)	84,100	1.19	587.2 ± 22.8	0.19 ± 0.05	V	
17	600	T	91,900 (>99.0)	118,400	1.20	142.8 ± 2.3	0.18 ± 0.01	S	
18	800	T	120,700 (>99.0)	205,100	1.47	581.6 ± 26.2	0.19 ± 0.03	S	

[a] All entries conducted at 10 % w/w solid content. [b] Preparation method: US: sono-PISA, T: thermal-PISA. [c] Monomer conversion calculated based on ^{1}H NMR spectra. $M_{n,th}$ =conversion × target HPMA DP × MW(HPMA)+MW(PEG_{113}-RAFT). [d] DMF eluent, PEG standards. [e] S=spheres, V= vesicles, W=worms, C=cylinders. [f] Bimodal or broad GPC chromatography resulted by the cross-linking due to dimethacrylate impurity in HPMA monomer.

Table S1 Characterization data of PEG_{113}-$PHPMA_x$ copolymer nano-objects by sono-PISA and thermal-PISA.