Electronic Supplementary Material (ESI) for Polymer Chemistry

Precise evaluation of the block copolymer nanoparticle growth through polymerization-induced self-assembly under dispersion conditions

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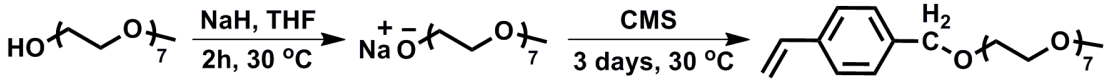
1. Synthesis of mPEGV



Scheme S1. Schematic synthesis of the mPEGV macromonomer.

2. The ^{1}H NMR spectrum of mPEGV

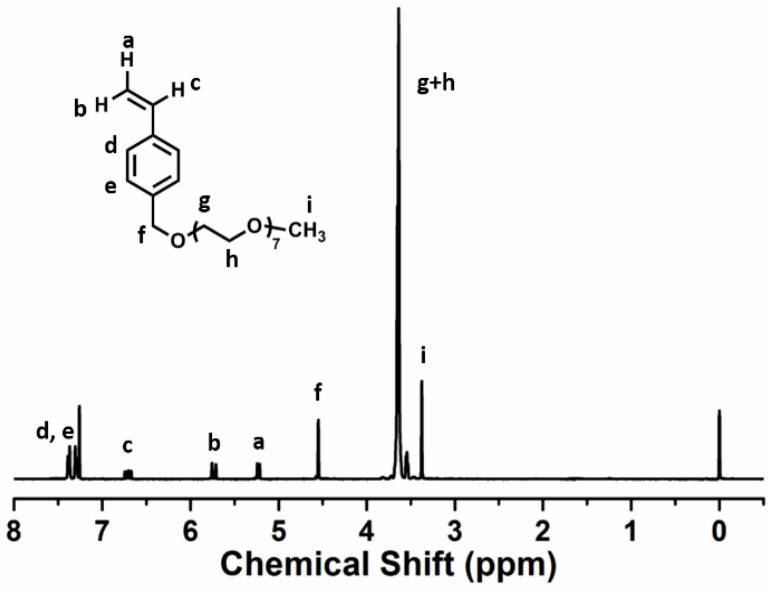


Figure S1. ^{1}H NMR spectrum of mPEGV.

3. Summary of the brush-linear PmPEGV-*b*-PS and the linear-linear PDMA-*b*-PS block copolymers

Table S1. Summary of the PmPEGV-*b*-PS block copolymers synthesized through the dispersion RAFT polymerization.

No	polymer	Time (h)	Conv. (%)	M_n (kg/mol)			PDI	D (nm)	D_h (nm)
				$M_{n,th}$	$M_{n,NMR}$	$M_{n,GPC}$			
1	$P(mPEGV)_9$	10	75.6	4.6	4.6	6.6	1.26	-	-
2	$P(mPEGV)_9$-*b*-PS_{54}	4	15.3	9.4	10.2	9.9	1.17	-	-
3	$P(mPEGV)_9$-*b*-PS_{117}	8	26.7	12.9	16.8	14.0	1.13	-	-
4	$P(mPEGV)_9$-*b*-PS_{180}	10	43.1	18.1	23.3	19.4	1.21	23	31
5	$P(mPEGV)_9$-*b*-PS_{270}	12	63.0	24.3	32.7	25.3	1.28	28	43
6	$P(mPEGV)_9$-*b*-PS_{342}	14	80.0	29.6	40.2	31.0	1.22	34	48
7	$P(mPEGV)_9$-*b*-PS_{369}	16	86.5	31.6	43.0	31.9	1.21	37	50
8	$P(mPEGV)_9$-*b*-PS_{387}	18	90.6	32.9	44.9	32.0	1.26	38	53
9	$P(mPEGV)_9$-*b*-PS_{405}	20	94.3	34.1	46.8	32.6	1.27	39	54
10	$P(mPEGV)_9$-*b*-PS_{405}	24	95.5	34.4	46.8	32.9	1.28	40	55

Table S2. Summary of the PDMA-*b*-PS block copolymers synthesized through the dispersion RAFT polymerization.

No	polymer	Time (h)	Conv. (%)	M_n (kg/mol)			PDI	D (nm)	D_h (nm)
				$M_{n,th}$	$M_{n,NMR}$	$M_{n,GPC}$			
1	$PDMA_{67}$	1	65.9	6.9	7.0	5.4	1.15	-	-
2	$PDMA_{67}$-*b*-PS_{43}	4	15.0	11.6	11.5	9.9	1.29	-	-
3	$PDMA_{67}$-*b*-PS_{113}	6	27.5	15.5	18.8	13.8	1.15	-	-
4	$PDMA_{67}$-*b*-PS_{206}	8	49.1	22.2	28.5	21.2	1.08	24	32
5	$PDMA_{67}$-*b*-PS_{287}	10	71.1	29.1	36.9	25.8	1.08	28	34
6	$PDMA_{67}$-*b*-PS_{330}	12	81.1	32.2	41.3	27.8	1.12	31	36
7	$PDMA_{67}$-*b*-PS_{335}	14	88.0	34.4	41.9	30.7	1.12	32	37
8	$PDMA_{67}$-*b*-PS_{337}	16	90.8	35.2	42.1	31.4	1.12	32	38
9	$PDMA_{67}$-*b*-PS_{339}	18	91.8	35.5	42.3	32.4	1.14	33	39
10	$PDMA_{67}$-*b*-PS_{341}	24	92.2	35.7	42.5	33.0	1.08	33	40

4. Evolution of N_p and N_{agg} of the PDMA-*b*-PS block copolymer nanoparticles during the dispersion RAFT polymerization

The N_p and N_{agg} values of the PDMA-*b*-PS block copolymer nanoparticles during the dispersion RAFT polymerization are calculated according to equations S1-S4, in which $D_{h\text{-core}}$ is the core-size of the core-shell micelles of PDMA-*b*-PS containing a

PS core and a PDMA shell calculated by equation S1, n is the DP of the PDMA block, $L_{\text{max-PDMA}}$ is the length of the fully extended PDMA chains calculated by equation S2, τ is the mass of the PS block in per gram of ethanol/water mixture (g/g) at a given monomer conversion, and d_p represents the density of the PS core approximately at 1.0 g/cm^3, N_a is the Avogadro's constant, and $M_{\text{PS,NMR}}$ is the molecular weight of the PS block in the PDMA-*b*-PS block copolymer determined by ^{1}H NMR analysis, respectively. The N_p and N_{agg} values are summarized in Figure S2.

$$D_{h-core} = D_h - 2L_{\text{max-PDMA}} \quad \text{(S1)}$$

$$L_{\text{max}} = \left(\frac{2}{3}\right)^{\frac{1}{2}} nl = \left(\frac{2}{3}\right)^{\frac{1}{2}} n \times 1.54\ \text{Å} \quad \text{(S2)}$$

$$N_p = \frac{6\tau}{\pi D_{h-core}{}^3 d_p} \quad \text{(S3)}$$

$$N_{agg} = \frac{\pi D_{h-core}{}^3 d_p N_A}{6M_{\text{PS,NMR}}} \quad \text{(S4)}$$

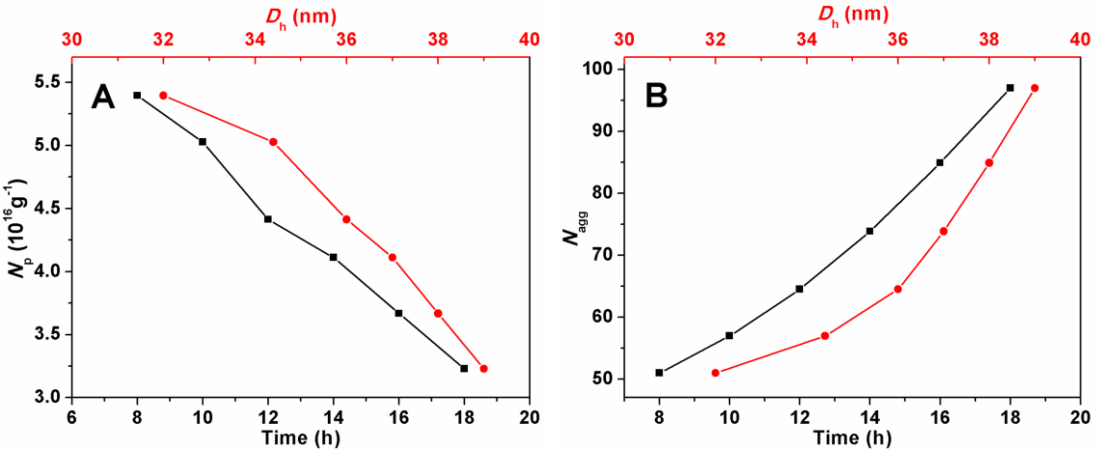


Figure S2. The correlation of the polymerization time or the D_h of the PDMA-*b*-PS block copolymer nanoparticles with the number (N_p) of the total block copolymer nanoparticles (A) and the aggregation number (N_{agg}) of the single block copolymer nanoparticles (B).