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ELECTRONIC SUPPLEMENTARY INFORMATION

A_3B-type miktoarm star polymer nanoassemblies prepared by reversible addition-fragmentation chain transfer (RAFT) dispersion polymerization

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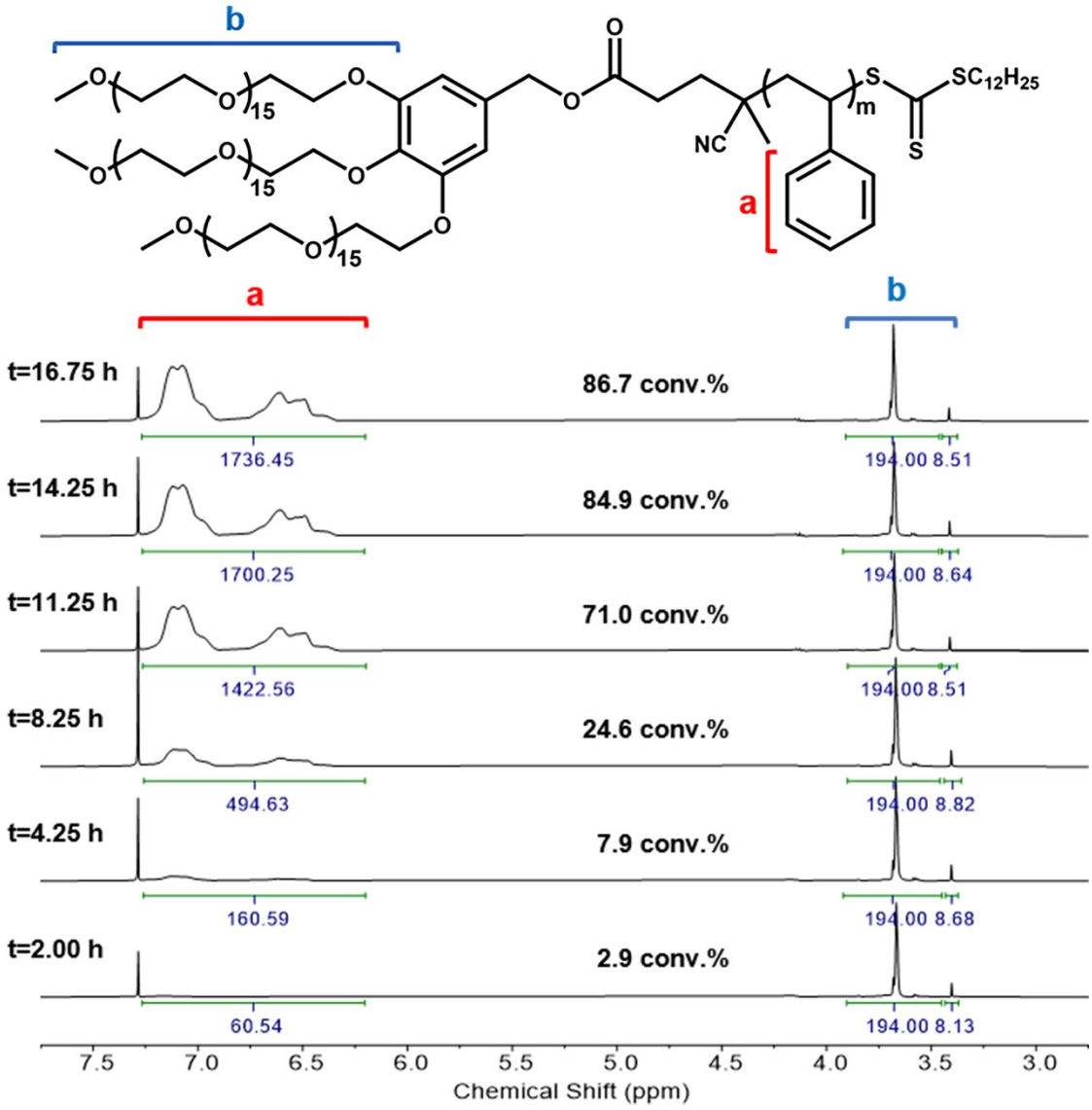


Figure S1 ^{1}H NMR spectra for the kinetic study of $(mPEG750)_3$-CDPA mediated RAFT dispersion polymerization of St ($CDCl_3$). [CTA]/[AIBN] = 3/1, MeOH/H_2O = 4/1 (w/w), 70 °C, 48 h.

$$Conversion\% = \frac{(S_a - 2)/5}{DP_{design}}$$

Equation S1 Calculation of conversion by ^{1}H NMR.

$$M_{n,NMR} = M_{styrene} \times \frac{S_a - 2}{5} + M_{CTA}$$

Equation S2 Calculation of $M_{n,NMR}$ by ^{1}H NMR.

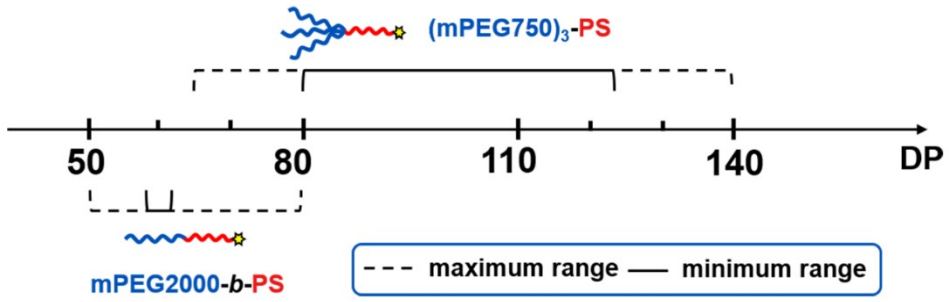
Figure S2 Digital images of the withdrawn samples from the RAFT dispersion polymerization of St mediated by $(mPEG750)_3$-CDPA. Polymerization conditions: $[St]_0$:[CTA]:[AIBN] = 1200:3:1, 15 wt% soilds, MeOH/H_2O = 4/1 (w/w), 70 °C. 1-6 correspond to 4.25, 8.25, 11.25, 14.25, 16.75, and 19.75 h.

Table S1 Polymerization results of RAFT-PISA mediated by $(mPEG750)_3$-CDPA and mPEG2000-CDPA at 25% solids

macro-CTA	$[M]_0$: $[CTA]_0$: $[I]_0$[a]	Conv%[b]	M_n (g/mol)		$Đ$[e]	Morphology
			$M_{n,GPC}$[c]	$M_{n,NMR}$[d]		
$(mPEG750)_3$-CDPA	180:3:1	66.6	8100	6900	1.18	—
	225:3:1	85.3	9700	9400	1.18	S
	270:3:1	80.5	11200	10200	1.06	S, W
	300:3:1	92.4	15800	12300	1.08	W, V
	420:3:1	87.7	17500	15500	1.11	V
	480:3:1	99.0	20700	19300	1.10	V
	660:3:1	99.0	25800	25700	1.12	V
	840:3:1	98.5	32300	31400	1.15	V
	1020:3:1	97.9	35000	37300	1.15	V
	1200:3:1	70.8	31300	32200	1.14	V
mPEG2000-CDPA	180:3:1	66.6	8600	6600	1.12	—
	225:3:1	80.4	9600	8700	1.13	S, W
	270:3:1	89.0	12200	10700	1.17	S, V
	300:3:1	99.0	16100	12800	1.16	V
	480:3:1	96.9	19700	19000	1.18	V
	660:3:1	91.8	24600	24200	1.15	V
	840:3:1	88.2	29300	26800	1.25	V
	1020:3:1	92.4	36300	34100	1.14	V
	1200:3:1	57.7	22100	26400	1.18	V

[a]molar ratio of reactant; [b]conversion calculated by ^{1}H NMR; [c]number average molecular weight by GPC; [d]number average molecular weight calculated by ^{1}H NMR; [e]polydispersity index by GPC. ("—" means no assembly occurred, "W" means worms-like micelle, "S" means sphere-like micelle, "V" means vesicle, "OV" means oversized-vesicle, "CV" means columnar vesicle, "MLV" means multi-lamellar vesicle.

Scheme S1 DP_{PS} range of the worm-like micelle of $(mPEG750)_3$-PS and mPEG2000-*b*-PS at 25% solids.



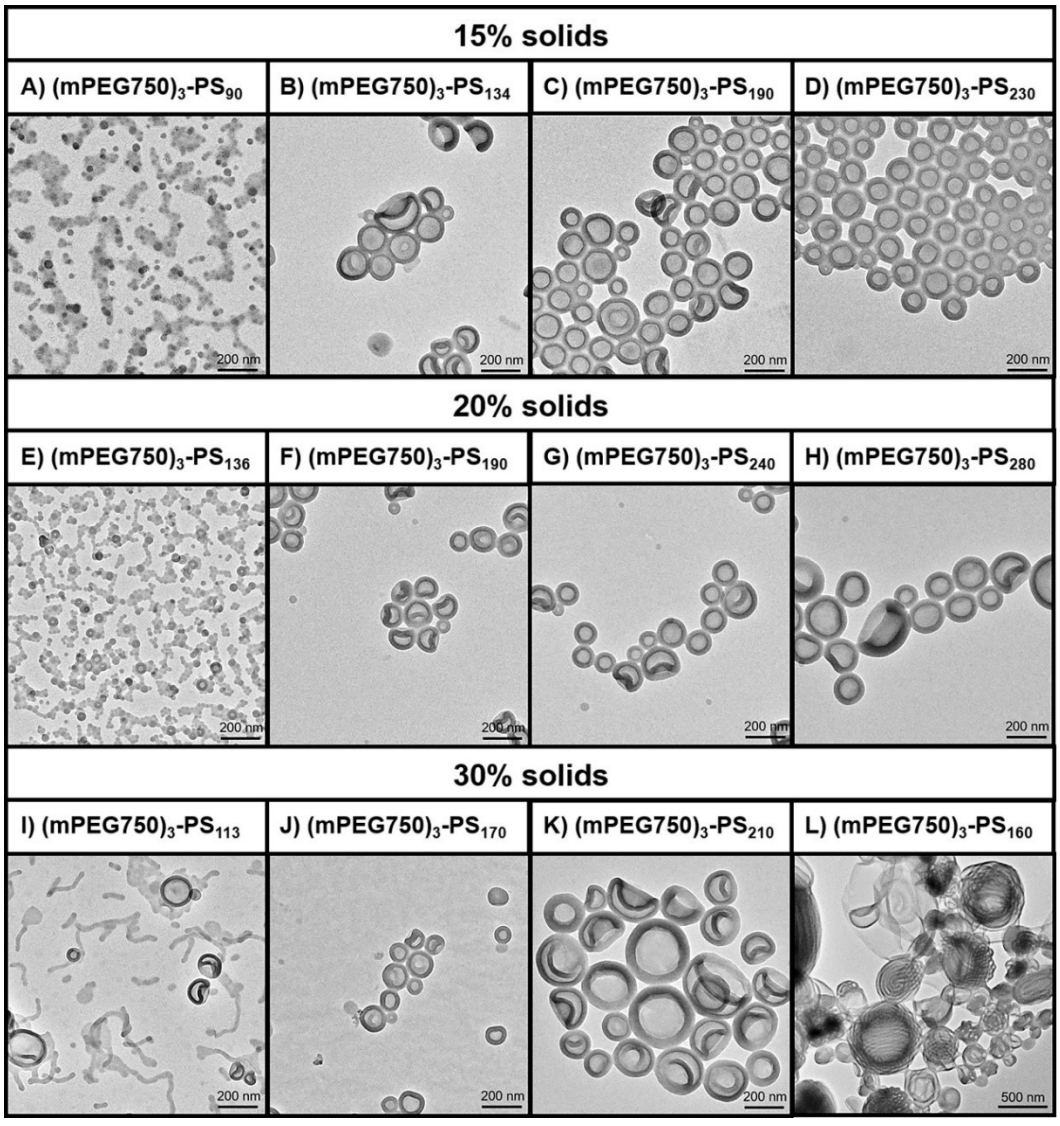


Figure S3 The TEM micrographs of $(mPEG750)_3$-PS at 15, 20, and 30 wt% solids. [CTA]/[AIBN] = 3/1, MeOH/H_2O = 4/1 (w/w), 70 °C, 48 h.

Table S2 Polymerization results of $(mPEG550)_3$-CDPA mediated RAFT polymerization of St at 10-30% solids

Solid content	$[M]_0$:$[CTA]_0$:$[I]_0$[a]	Conv%[b]	M_n (g/mol)		$Đ$[e]	Morphology
			$M_{n,GPC}$[c]	$M_{n,NMR}$[d]		
10%	150:3:1	74.4	6500	6000	1.10	—
	210:3:1	71.4	8100	7300	1.13	V
	270:3:1	73.3	9500	9000	1.12	V
	360:3:1	50.8	12000	8500	1.04	V
	480:3:1	66.3	15100	13200	1.05	V
	600:3:1	71.5	17000	17000	1.05	V
	720:3:1	80.8	22700	22300	1.07	V
	840:3:1	65.3	22700	21200	1.05	V
	1080:3:1	41.2	23400	22300	1.10	V
	1320:3:1	66.3	31100	29800	1.10	V
15%	120:3:1	70.5	5100	5100	1.11	—
	240:3:1	69.8	9800	8000	1.05	—
	360:3:1	75.8	13300	11600	1.07	V
	480:3:1	74.1	15900	14500	1.06	V
	600:3:1	82.1	19900	19200	1.10	V
	720:3:1	75.7	22400	21100	1.14	OV
	840:3:1	67.4	24600	21800	1.11	OV
	960:3:1	25.2	13600	10600	1.11	—
	1080:3:1	29.0	15500	13000	1.08	—
20%	180:3:1	72.0	7400	6700	1.06	—
	240:3:1	71.0	8900	8100	1.07	—
	360:3:1	75.7	12000	11600	1.10	V
	480:3:1	83.2	15300	16000	1.10	V
	600:3:1	67.5	15100	16200	1.16	V
	720:3:1	28.7	10300	9300	1.16	—
25%	180:3:1	36.3	8000	4400	1.06	—
	240:3:1	54.5	9500	6700	1.06	—
	360:3:1	66.3	13000	10500	1.10	V
	480:3:1	74.0	16200	14500	1.12	V
	600:3:1	29.3	10300	8300	1.08	—
	720:3:1	26.0	10300	8700	1.07	—
30%	180:3:1	74.7	8500	6800	1.06	—
	300:3:1	77.8	11800	10300	1.10	—
	420:3:1	83.0	14500	14300	1.11	V, CV, MLV
	600:3:1	40.5	12100	10600	1.08	—

[a]molar ratio of reactant; [b]conversion calculated by ^{1}H NMR; [c]number average molecular weight by GPC; [d]number average molecular weight calculated by ^{1}H NMR；[e]polydispersity index by GPC. (“—” means no assembly occurred, “V” means vesicle, “OV” means oversized-vesicle, “CV” means columnar vesicle, “MLV” means multi-lamellar vesicle.)

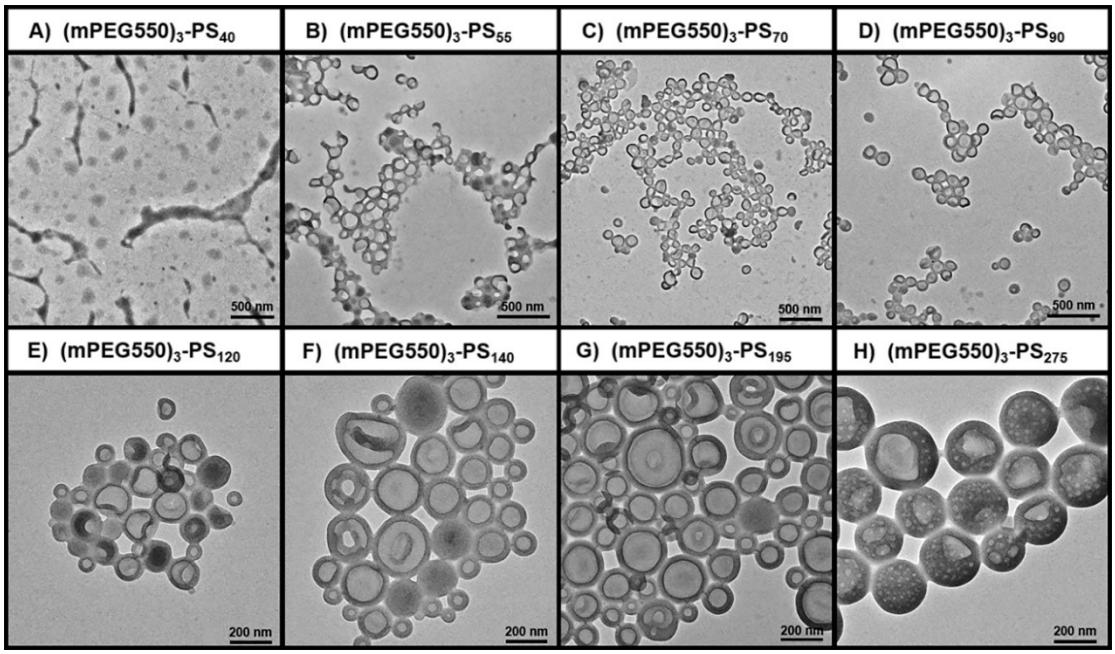


Figure S4 TEM micrographs of $(mPEG550)_3$-PS at 10% solids. [CTA]/[AIBN] = 3/1, MeOH/H_2O = 4/1 (w/w), 70 °C, 48 h.

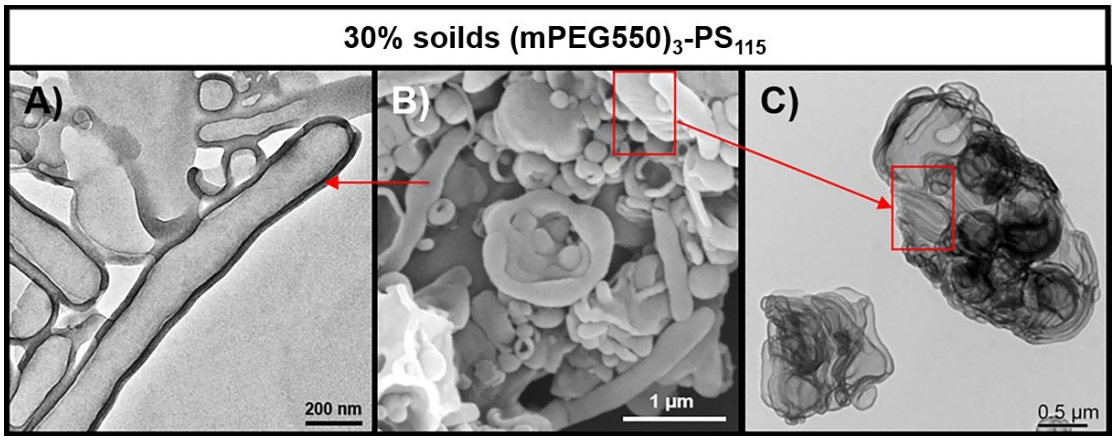


Figure S5 TEM (A, C) and SEM (B) micrographs of $(mPEG550)_3$-PS_{115}. [CTA]/[AIBN] = 3/1, MeOH/H_2O = 4/1 (w/w), 70 °C, 48 h.

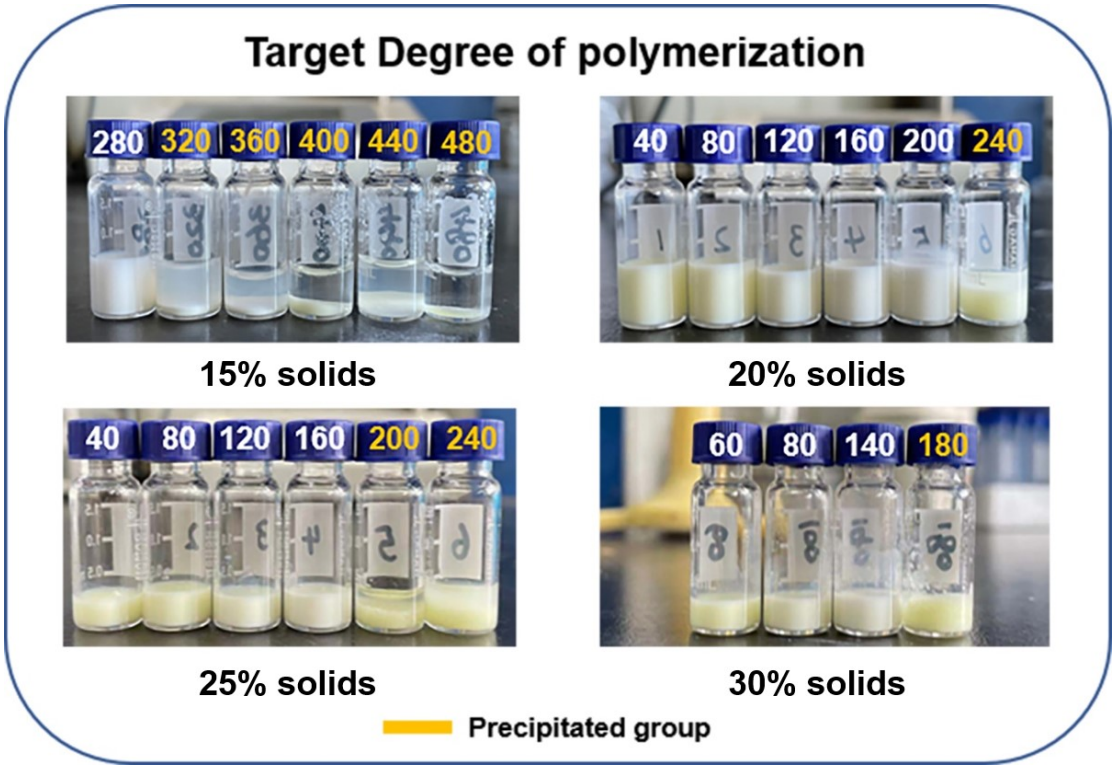


Figure S6 Digital images of the polymerization system of $(mPEG550)_3$-PS at different solids. [CTA]/[AIBN] = 3/1, MeOH/H_2O = 4/1 (w/w), 70 °C, 48 h.

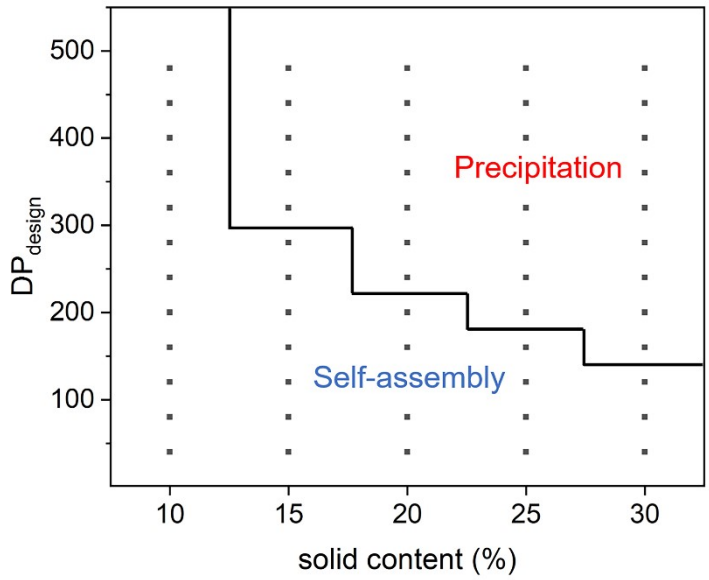


Figure S7 Phase diagram of the self-assembly and precipitation of $(mPEG550)_3$-CDPA mediated RAFT dispersion polymerization of St.

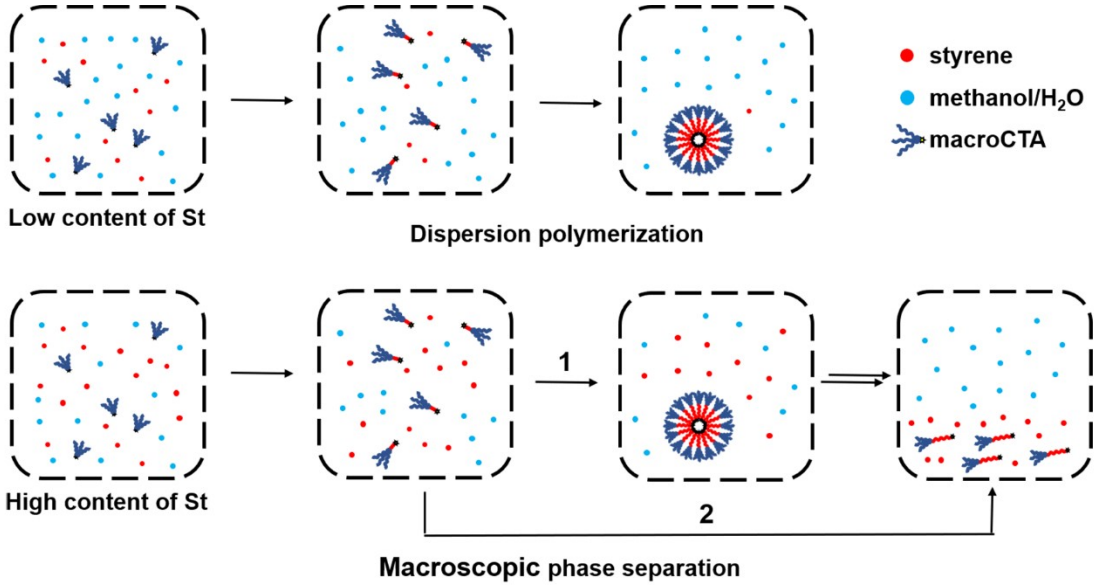


Figure S8 Possible process of dispersion polymerization and macroscopic phase separation in $(mPEG550)_3$-CDPA mediated RAFT polymerization of St. Process 1 occurs at relatively low solids and targeted DP_{PS}, while process 2 occurs at relatively high solids and targeted DP_{PS}.

Table S3 Polymerization results of $(mPEG1000)_3$-CDPA mediated RAFT polymerization of St at 15-25% solids

Solid content	$[M]_0$: $[CTA]_0$: $[I]_0$[a]	Conv%[b]	M_n (g/mol)		$Đ$[e]	Morphology
			$M_{n,GPC}$[c]	$M_{n,NMR}$[d]		
15%	600:3:1	80.6	24900	20300	1.26	S
	900:3:1	78.9	34100	28100	1.29	S
	1200:3:1	71.6	50800	33300	1.20	S
	1500:3:1	78.9	51800	44500	1.19	S
	1800:3:1	81.9	58800	54600	1.23	S
	2100:3:1	81.7	65800	63000	1.25	S
	2400:3:1	77.1	60600	67600	1.29	S
20%	600:3:1	69.0	20800	17800	1.08	S
	900:3:1	69.1	28000	25000	1.11	S
	1200:3:1	62.2	38900	29400	1.09	S
	1500:3:1	68.3	45100	39000	1.13	S, V
	1800:3:1	62.8	48200	42700	1.15	S, V
	2100:3:1	60.9	54400	47900	1.16	S, V
	2400:3:1	63.1	57900	56000	1.20	S, V
25%	600:3:1	77.7	22000	19700	1.08	S
	900:3:1	75.9	28900	27200	1.10	S, V
	1200:3:1	79.5	39000	36600	1.14	V
	1500:3:1	70.7	41900	40200	1.13	V
	1800:3:1	68.6	47700	46300	1.14	V
	2100:3:1	71.2	54200	55300	1.18	V
	2400:3:1	59.8	53700	53200	1.17	V

[a]molar ratio of reactant; [b]conversion calculated by ^{1}H NMR; [c]number average molecular weight by GPC; [d]number average molecular weight calculated by ^{1}H NMR; [e]polydispersity index by GPC ("S" means sphere-like micelle, "V" means vesicle).

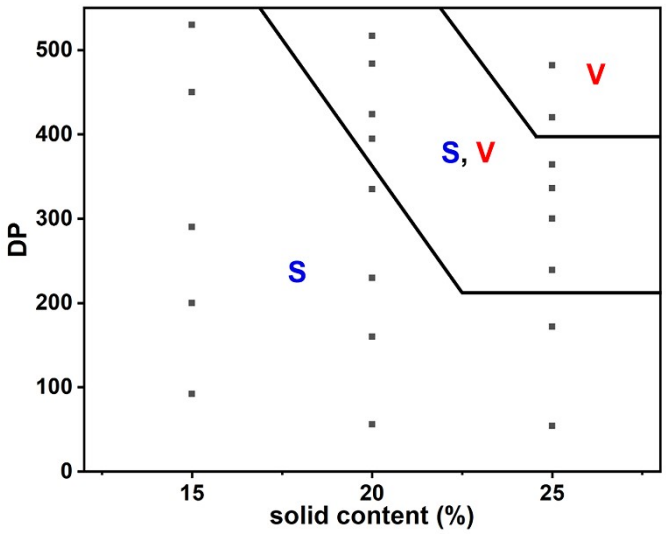


Figure S9 Phase diagram of $(mPEG1000)_3$-PS at different solids and DP_{PS}.

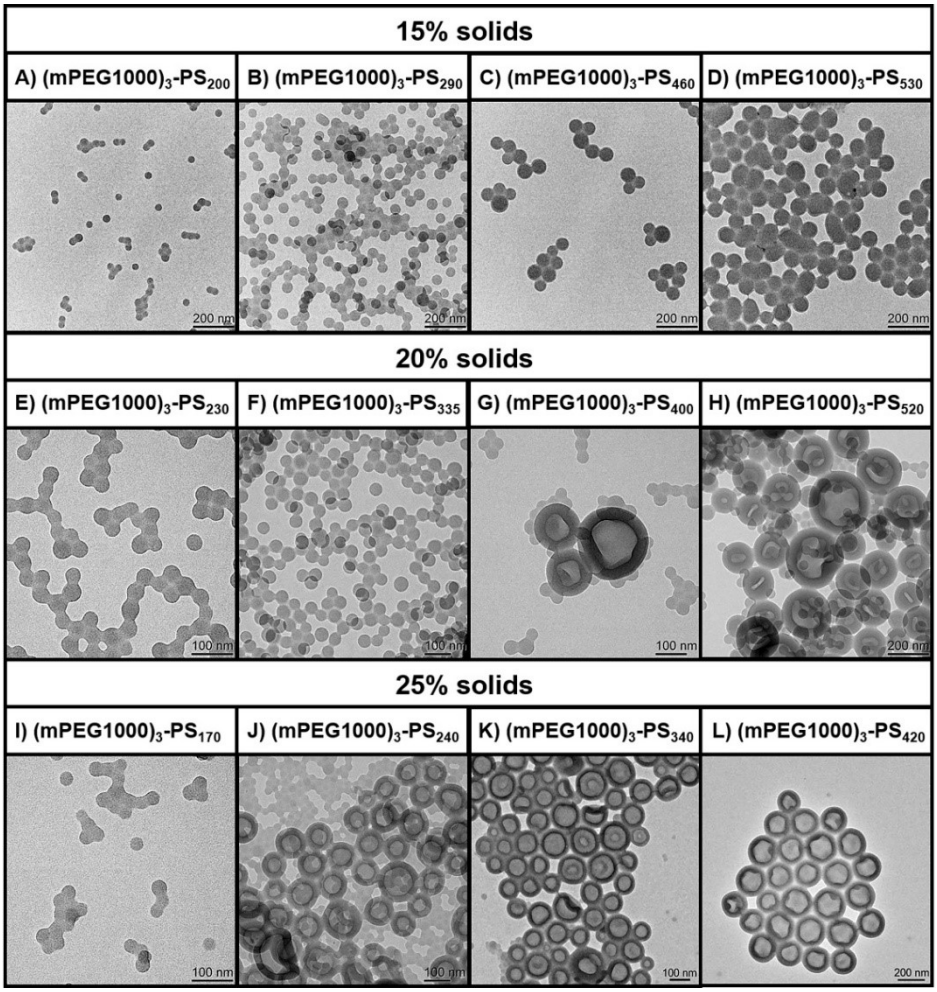


Figure S10 TEM micrographs of $(mPEG1000)_3$-PS at 15%-25% solids. [CTA]/[AIBN] = 3/1, MeOH/H_2O = 4/1 (w/w), 70 °C, 48 h.

Table S4 Polymerization results of $(mPEG2000)_3$-CDPA mediated RAFT polymerization of St at 20% and 30% solids

Solid content	$[M]_0$: $[CTA]_0$: $[I]_0$[a]	Conv%[b]	M_n (g/mol)		$Đ$[e]	Morphology
			$M_{n,GPC}$[c]	$M_{n,NMR}$[d]		
20%	900:3:1	85	32900	33100	1.22	S
	1500:3:1	93.4	58300	55100	1.14	S
	2100:3:1	93.9	75200	74900	1.18	S
	2700:3:1	91.0	92000	91600	1.20	S
	3300:3:1	82.1	95300	100400	1.21	S
	3900:3:1	94.6	112200	134500	1.29	S
30%	900:3:1	99.7	38300	37700	1.10	S
	1500:3:1	97.0	57200	57000	1.13	S
	2100:3:1	99.1	75000	78700	1.16	S
	2700:3:1	98.0	93400	98300	1.20	S
	3300:3:1	93.8	101000	113900	1.19	S
	3900:3:1	96.1	115400	136400	1.20	S

[a]molar ratio of reactant; [b]conversion calculated by ^{1}H NMR; [c]number average molecular weight by GPC; [d]number average molecular weight calculated by ^{1}H NMR；[e]polydispersity index by GPC. (“S” means sphere-like micelle)

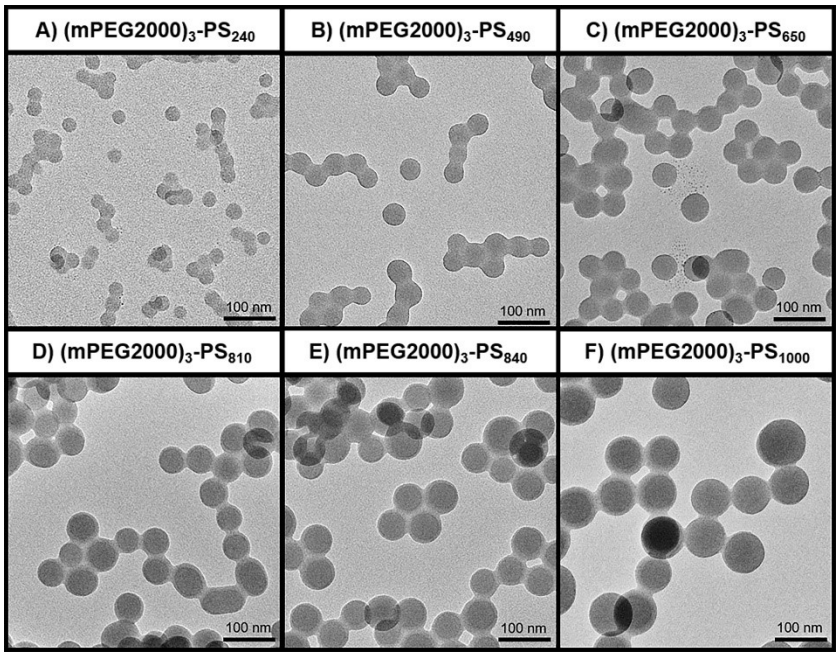


Figure S11 TEM micrographs of $(mPEG2000)_3$-PS at 20% solids. [CTA]/[AIBN] = 3/1, MeOH/H_2O = 4/1 (w/w), 70 °C, 48 h.

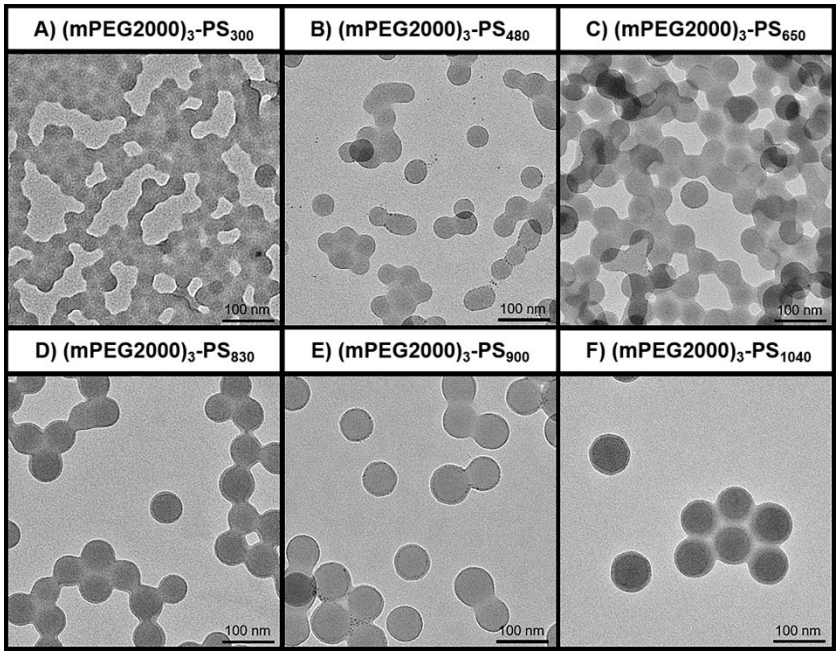


Figure S12 TEM micrographs of $(mPEG2000)_3$-PS at 30% solids. [CTA]/[AIBN] = 3/1, MeOH/H_2O = 4/1 (w/w), 70 °C, 48 h.