Supporting Information

Promotion of morphology transition of di-block copolymer nano-objects via RAFT dispersion copolymerization

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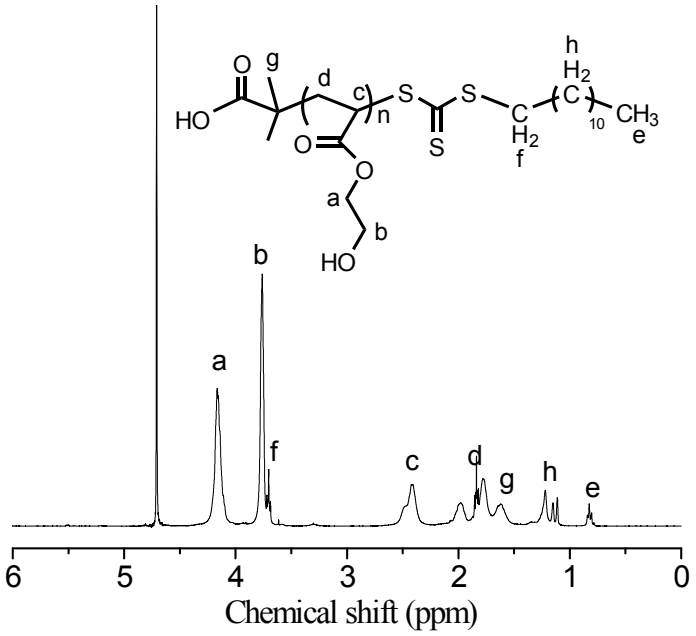

Figure S1.[1]H NMR spectrum of PHEA in D_2O.

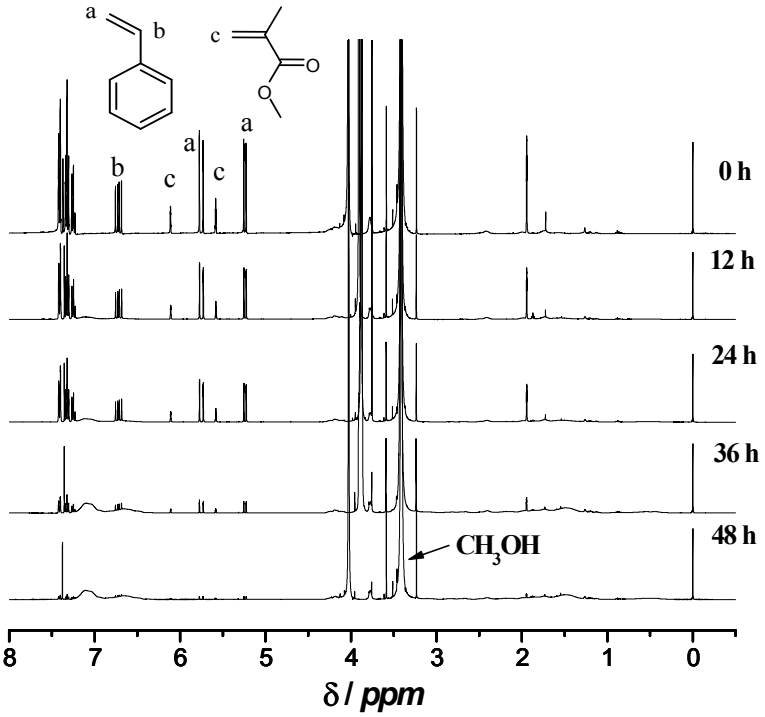

Figure S2.[1]H NMR spectra (in $CDCl_3$) of the RAFT dispersion copolymerization system at different polymerization time. The polymerization was conducted with a molar ratio of $[St\&MMA]_0/[PHEA_{21}]_0/[AIBN]_0$ = 300/3/1 in methanol at 70 °C (St/MMA = 4/1, total solids concentration = 20%).

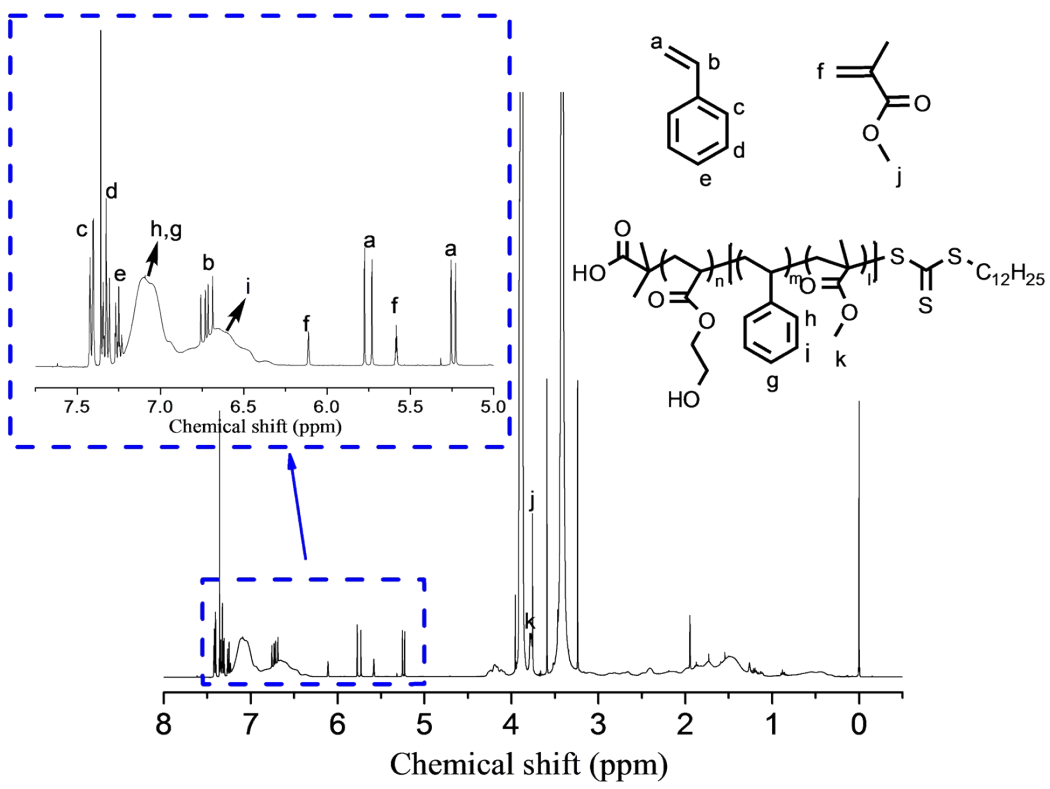

Figure S3.[1]H NMR spectrum of the RAFT dispersion copolymerization system of St and MMA.

$$Conversion_{St} = \frac{I_{6.30\sim7.35} + I_{7.38\sim7.45} - 6I_{5.70\sim5.80}}{I_{6.30\sim7.35} + I_{7.38\sim7.45} - I_{5.70\sim5.80}} \times 100\% \qquad (S1)$$

$$Conversion_{MMA} = \frac{I_{3.70\sim3.81} - 3I_{5.55\sim5.61}}{I_{3.70\sim3.81}} \times 100\% \qquad (S2)$$

$$Conversion_{St\&MMA} = \frac{n_{St} \times Conversion_{St} + n_{MMA} \times Conversion_{MMA}}{n_{St} + n_{MMA}} \times 100\% \qquad (S3)$$

n_{St} and n_{MMA} are the initial molar quantity of the feeding St and MMA, respectively.

Table S1. Polymerization time, monomer conversions, molecular weightsand morphology characterization of $PHEA_{21}$-b-P(St-co-MMA)$_x$ di-block copolymers synthesized by RAFT dispersion copolymerization

Entry	Polymerization time (h)	Conversion of St[a] (%)	Conversion of MMA[a] (%)	DP of P(St-co-MMA) block	M_n[b]	M_w/M_n[b]	TEM morphology
Figure 3	0	---	---	---	3000	1.13	---
	6	13	18	14	4100	1.07	n. d.
	12	22	29	24	5000	1.06	n. d.
	18	26	34	28	5900	1.07	n. d.
	24	34	41	35	7200	1.07	s
	30	49	54	50	10100	1.08	w, v
	36	83	81	82	19400	1.05	v
	42	94	92	93	22900	1.05	v
	48	96	94	96	24600	1.04	v
	54	97	96	97	24700	1.04	v

[a] The results were calculated based on ^{1}H NMR spectra in $CDCl_3$. [b] The number-average molecular weight and polydispersity of di-block copolymers were determined by GPC measurements.The polymerization was conducted with a molar ratio of $[St\&MMA]_0/[PHEA_{21}]_0/[AIBN]_0$ = 300/3/1 in methanol for different polymerization times (St/MMA = 4/1, solids concentration = 20%). Abbreviation: n.d. = not determined, s = spheres, w = nanowires, v = vesicles.

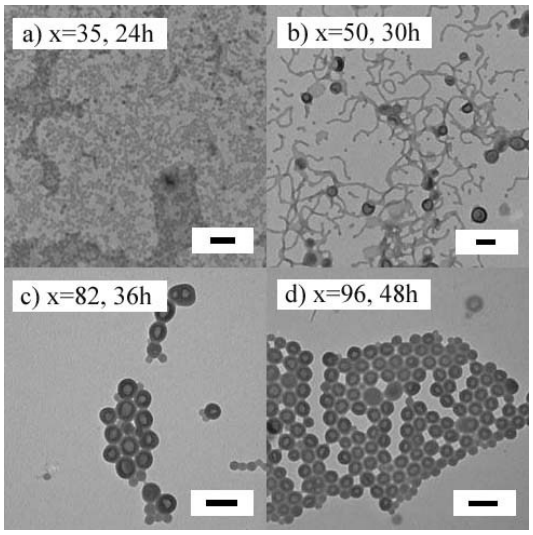

Figure S4. TEM images of $PHEA_{21}$-b-P(St-co-MMA)$_x$ nanoparticles fabricated by RAFT dispersion copolymerization of St and MMA at different polymerization times. The polymerization was conducted with a molar ratio of $[St\&MMA]_0/[PHEA_{21}]_0/[AIBN]_0$ = 300/3/1 in methanol at 70 °C (St/MMA = 4/1, total solids concentration = 20%). The values of x are determined to be 35 (a), 50 (b), 82 (c) and 96 (d), respectively. All scale bars are 200 nm.

Table S2. Monomers conversions, number-average molecular weight and polydispersity, and TEM morphology of $PHEA_{21}$-b-P(St-co-MMA)$_x$ di-block copolymers synthesized by RAFT dispersion copolymerization in methanol.

Entry	Molar ratio of St/MMA	Target DP of P(St-co-MMA)	Solids (wt %)	Conversion[a]	Actual DP of P(St-co-MMA)	M_n[b]	M_w/M_n[b]	Morphology[c]
	7/3	50	20%	73%	38	9500	1.05	S
	7/3	60	20%	72%	44	10200	1.06	S
	7/3	70	20%	70%	49	11900	1.06	S&W
	7/3	80	20%	80%	63	13500	1.06	W&V
	7/3	90	20%	80%	72	19300	1.04	V
	7/3	100	20%	87%	86	22300	1.04	V
	7/3	50	30%	95%	47	10600	1.09	S&W
	7/3	60	30%	90%	53	13500	1.08	W&V
	7/3	70	30%	97%	68	14500	1.07	W&V
Figure 4A	7/3	80	30%	96%	76	18300	1.05	V
	7/3	90	30%	98%	88	20000	1.06	V
	7/3	100	30%	94%	94	20400	1.06	V
	7/3	50	40%	98%	49	10100	1.09	S&W
	7/3	60	40%	98%	59	13000	1.10	S&W&V
	7/3	70	40%	99%	70	15800	1.10	V
	7/3	80	40%	99%	79	18200	1.09	V
	7/3	90	40%	98%	88	20400	1.08	V
	7/3	100	40%	98%	98	22100	1.07	V
	4/1	50	20%	83%	42	9800	1.05	S
	4/1	60	20%	89%	54	13600	1.05	S
	4/1	70	20%	95%	66	15600	1.04	S
	4/1	80	20%	97%	77	18400	1.03	S&V
	4/1	90	20%	98%	88	21400	1.03	S&V
	4/1	100	20%	97%	96	24500	1.04	V
	4/1	50	30%	98%	49	9800	1.08	S
	4/1	60	30%	99%	60	12300	1.08	S
Figure 4B	4/1	70	30%	99%	69	14700	1.07	S&V
	4/1	80	30%	99%	79	18100	1.05	V

	4/1	90	30%	99%	89	19500	1.05	V
	4/1	100	30%	99%	99	22600	1.04	V
	4/1	50	40%	99%	50	10100	1.10	S
	4/1	60	40%	99%	50	12100	1.10	S&W&V
	4/1	70	40%	100%	70	14600	1.09	S&W&V
	4/1	80	40%	99%	79	16400	1.07	V
	4/1	90	40%	100%	90	21400	1.05	V
	4/1	100	40%	100%	100	23900	1.04	V
	9/1	50	20%	96%	48	10600	1.04	S
	9/1	60	20%	96%	58	13200	1.04	S
	9/1	70	20%	97%	68	16100	1.04	S
	9/1	80	20%	96%	77	19900	1.03	S
	9/1	90	20%	97%	88	21700	1.03	S
	9/1	100	20%	98%	98	23200	1.03	S
	9/1	50	30%	99%	50	11800	1.06	S
	9/1	60	30%	99%	59	14700	1.05	S
	9/1	70	30%	99%	69	18000	1.06	S
Figure 4C	9/1	80	30%	99%	79	19500	1.04	S&V
	9/1	90	30%	99%	89	20600	1.05	S&V
	9/1	100	30%	99%	99	24200	1.05	S&V
	9/1	50	40%	100%	50	11700	1.08	S
	9/1	60	40%	100%	60	14300	1.08	S& V
	9/1	70	40%	100%	70	17300	1.05	S&V
	9/1	80	40%	100%	80	18100	1.08	S&V
	9/1	90	40%	100%	90	20600	1.05	V
	9/1	100	40%	100%	100	24600	1.05	V

[a] The results were calculated based on ^{1}H NMR spectra in $CDCl_3$. [b] The number-average molecular weight and polydispersity of di-block copolymers were determined by GPC measurements. [c] The morphologies formed in methanol were identified by TEM. Abbreviation: S = spheres, W = nanowires, V = vesicles.