Supporting Information for

Asymmetrical Vesicles: Convenient In Situ RAFT Synthesis and Controllable Structure Determination

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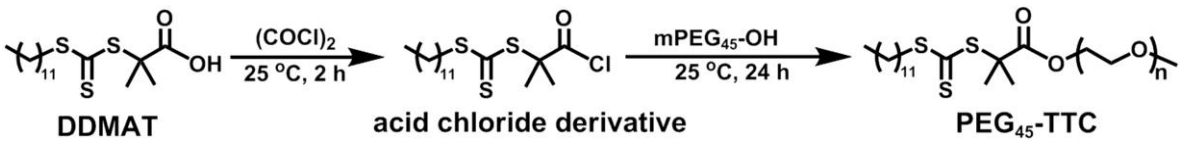
1 Synthesis of mPEG$_{45}$-TTC

Into a dry 100 mL flask, DDMAT (1.46 g, 4.00 mmol) and DCM (20.0 mL) were added, and subsequently dripping addition of oxalyl chloride [$(COCl)_2$, 1.7 mL, 20.0 mmol] dissolved in DCM (10.0 mL) in 10 min under nitrogen atmosphere was followed. The mixture was magnetically stirred under nitrogen atmosphere at 25 ^{0}C for about 2 h until the gas evolution stopped. The solvent and the excess oxalyl chloride were removed by rotary evaporation. Into the flask, *m*PEG$_{45}$-OH (4.00 g, 2.00 mmol) dissolved in DCM (20.0 mL) was added, and the reaction was allowed to proceed for 24 h at 25 ^{0}C with magnetically stirring under nitrogen atmosphere. The solution was concentrated under reduced pressure, and the polymer was precipitated in *n*-hexane and dried in a vacuum oven at room temperature to afford the desired macro-RAFT agent of PEG$_{45}$-TTC (4.6 g, 97% yield).



Scheme S1. Synthesis of PEG$_{45}$-TTC.

2 Tables

Table S1. Experimental details and summary of the P4VP macro-RAFT agents.

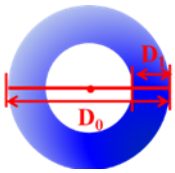
Macro-RAFT	$[M]_0$:$[CTA]_0$:$[I]_0$	Time (h)	Conv. (%)[a]	M_n (kg/mol)			PDI[e]
				$M_{n,th}$[b]	$M_{n,GPC}$[c]	$M_{n,NMR}$[d]	
$P4VP_{29}$-TTC	120:4:1	12	96	3.4	2.9	3.6	1.18
$P4VP_{46}$-TTC	200:4:1	12	92	5.2	4.8	5.5	1.14
$P4VP_{66}$-TTC	300:4:1	12	88	7.3	7.0	7.8	1.15
$P4VP_{93}$-TTC	400:4:1	12	93	10.1	9.8	10.9	1.16

[a] The monomer conversion determined by ^{1}H NMR analysis. [b] Theoretical molecular weight determined by monomer conversion. [c] The molecular weight determined by GPC analysis. [d] The molecular weight determined by ^{1}H NMR analysis. [e] The PDI (M_w/M_n) value determined by GPC analysis.

3 Equations

$$M_{n,NMR} = \frac{9I_{3.64}}{2I_{1.1-1.45}} \times 44 + 364 \quad \text{(S1)}$$

$$M_{n,NMR} = \frac{3I_{8.30}}{2I_{0.88}} \times M_{n,4VP} + M_{n,RAFT} \quad \text{(S2)}$$



$$S_{out}/S_{in} = \frac{4\pi(\frac{D_0}{2})^2}{4\pi[\frac{(D_0-2D_1)}{2}]^2} = \frac{{D_0}^2}{(D_0-2D_1)^2} \quad \text{(S3)}$$

4 Figures

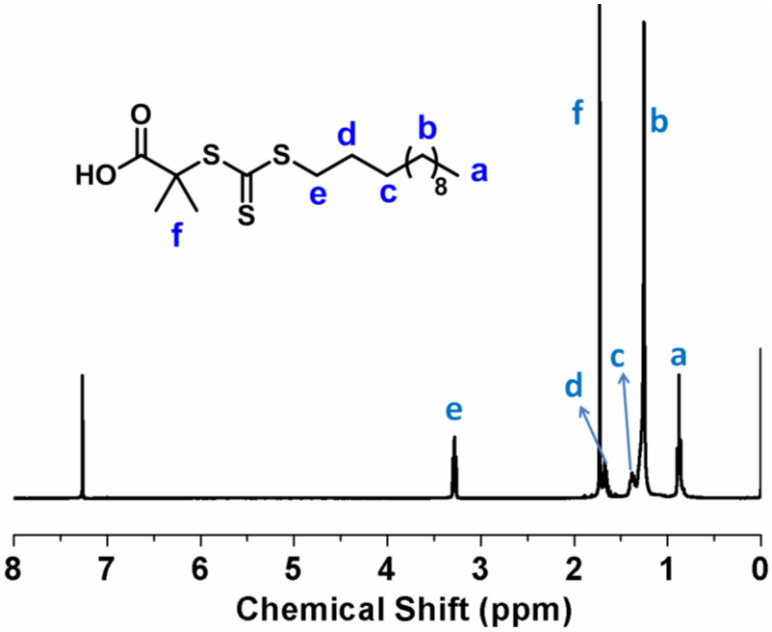


Figure S1. The ^{1}H NMR spectra of DDMAT.

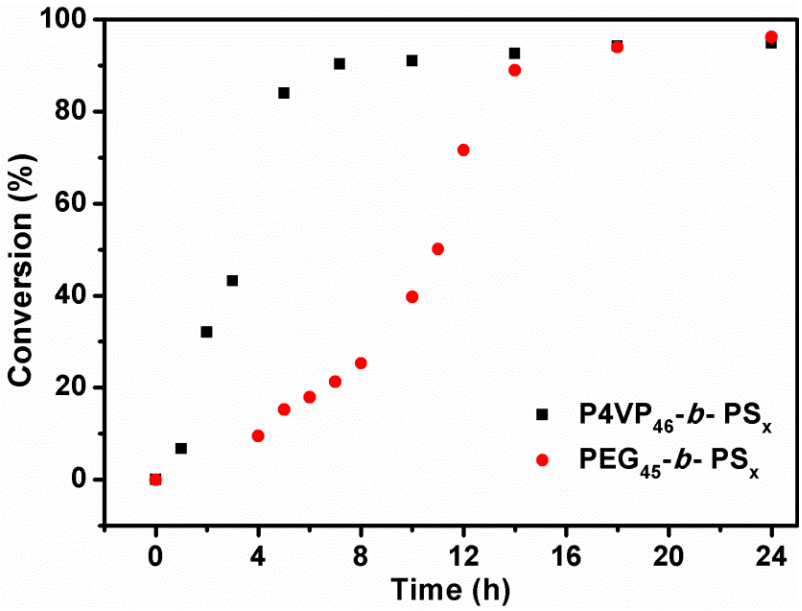


Figure S2. The time dependent monomer conversion in the individual macro-RAFT agent mediated polymerization in the presence of PEG_{45}-TTC or $P4VP_{46}$-TTC. Polymerization conditions: St (1.50 g, 14.4 mmol), the methanol/water mixture (9.25 g, 80/20 by weight), $[St]_0$:[macro-RAFT]:$[AIBN]_0$ = 300:1:1/3, 70 ^{o}C.

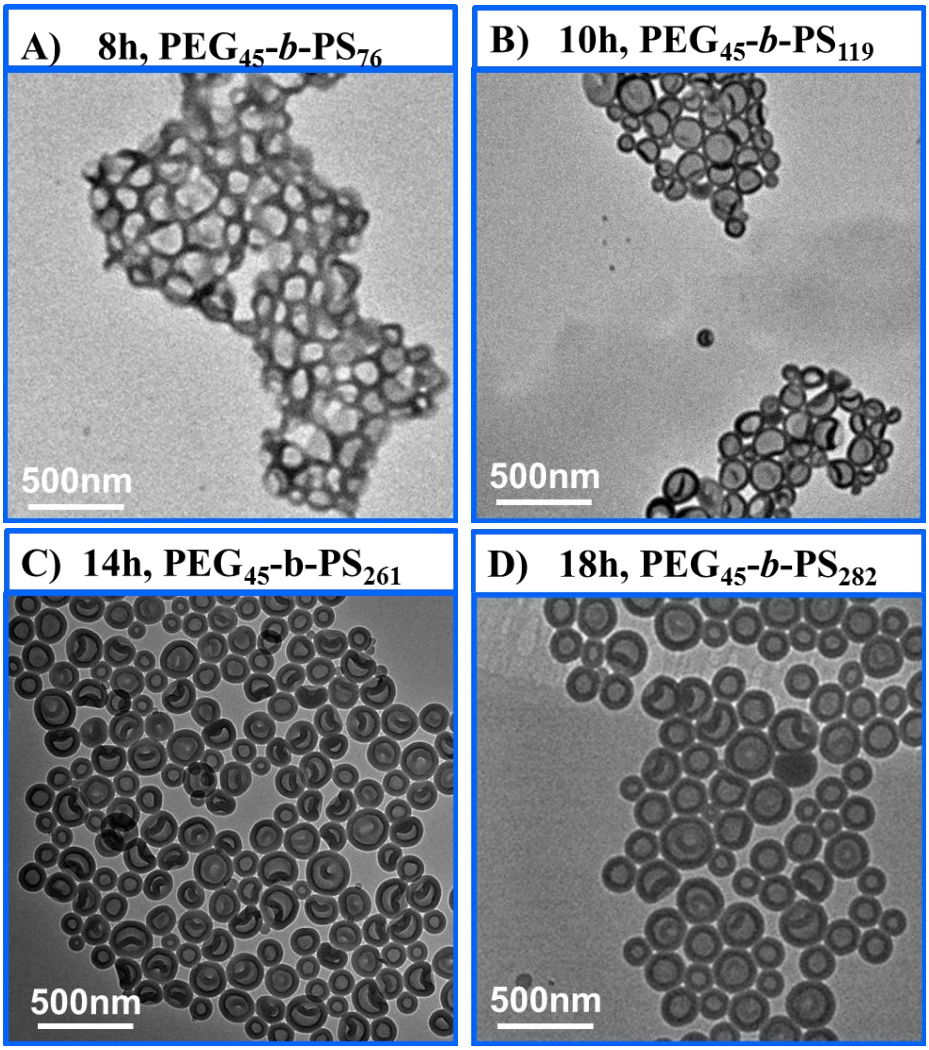


Figure S3. The TEM images of the PEG_{45}-*b*-PS nano-objects prepared through the PEG_{45}-TTC macro-RAFT agents mediated dispersion polymerization at different polymerization times. Polymerization conditions: St (1.50 g, 14.4 mmol), the methanol/water mixture (9.25 g, 80/20 by weight), $[St]_0$:$[PEG_{45}\text{-TTC}]$:$[AIBN]_0$ = 300:1:1/3, 70 ^{o}C. Note: the TEM samples are not stained.

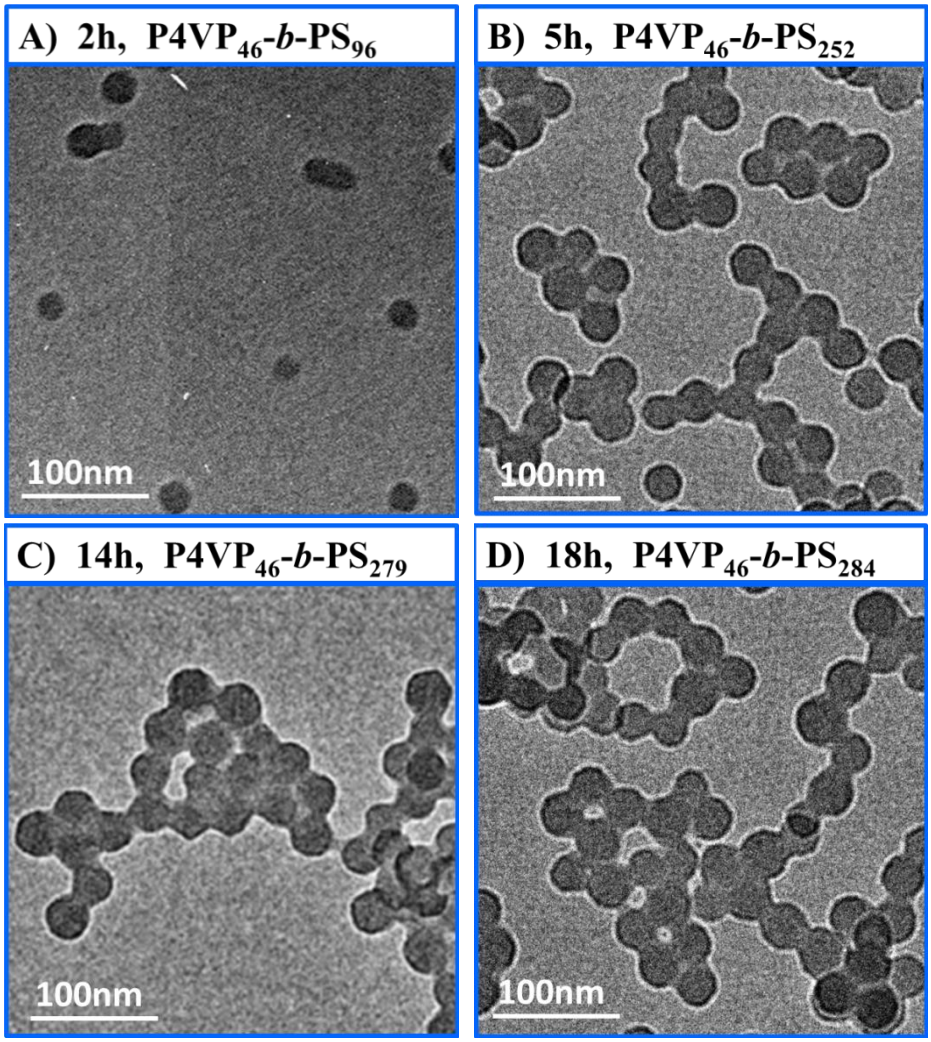


Figure S4. The TEM images of the P4VP$_{46}$-*b*-PS nano-objects prepared through the P4VP$_{46}$-TTC macro-RAFT agents mediated dispersion polymerization at different polymerization times. Polymerization conditions: St (1.50 g, 14.4 mmol), the methanol/water mixture (9.25 g, 80/20 by weight), [St]$_0$:[P4VP$_{46}$-TTC]:[AIBN]$_0$ = 300:1:1/3, 70 ^{o}C. Note: the TEM samples are not stained.

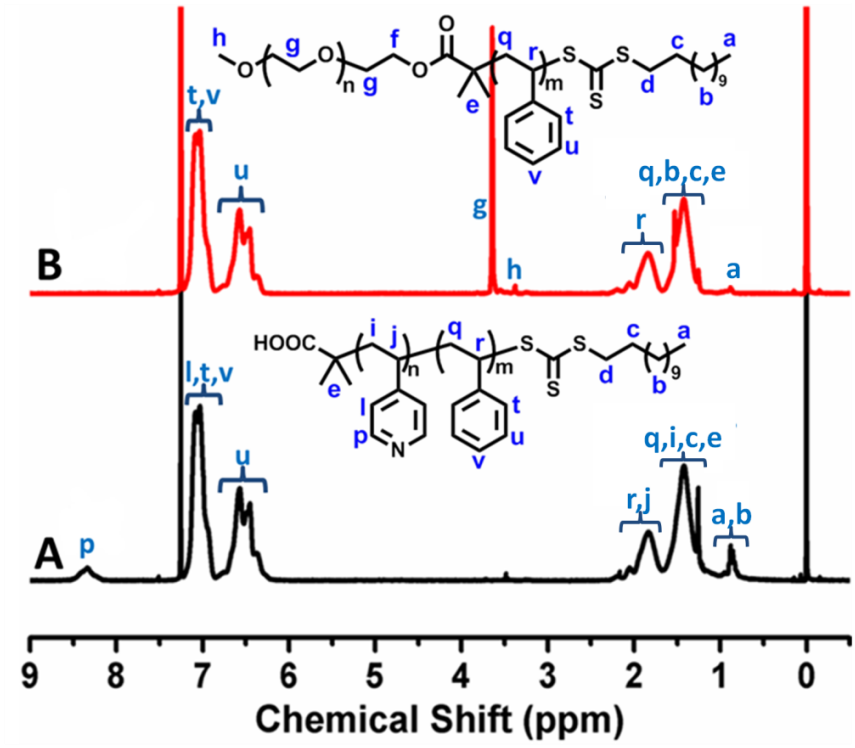


Figure S5. The ^{1}H NMR spectra of PEG_{45}-*b*-PS_{261} (A) and $P4VP_{46}$-*b*-PS_{279} (B) prepared through the individual macro-RAFT agent mediated dispersion polymerization at 14 h. Note: the polymerization conditions can be found in the Captions for Figures S3 and S4.

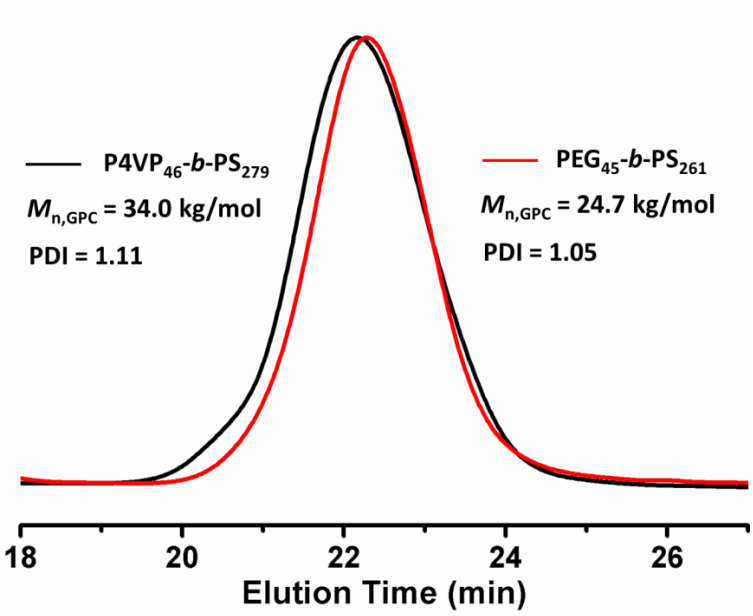


Figure S6. The GPC traces of PEG_{45}-*b*-PS_{261} and $P4VP_{46}$-*b*-PS_{279}. prepared through the individual macro-RAFT agent mediated dispersion polymerization at 14 h. Note: the polymerization conditions can be found in the Captions for Figures S3 and S4.

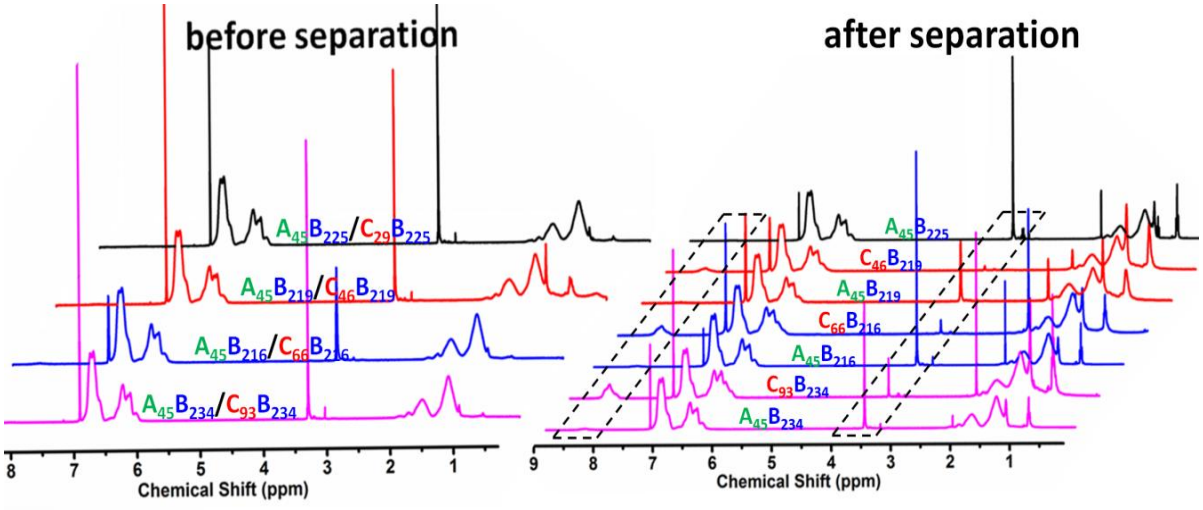


Figure S7. The ^{1}H NMR spectra of the PEG-*b*-PS/P4VP-*b*-PS mixture before and after separation. Note: in the separated $P4VP_{46}$-*b*-PS_{219}, $P4VP_{66}$-*b*-PS_{216} and $P4VP_{93}$-*b*-PS_{234}, about part of the PEG_{45}-*b*-PS diblock copolymer at about 7%, 11% and 13.7% was immerged. For the PEG_{45}-*b*-PS_{225}/$P4VP_{29}$-*b*-PS_{225} mixture, part of PEG_{45}-*b*-PS_{225} was separated and its NMR spectra as indicated by the black plot were shown in Figure S7, whereas the separation of $P4VP_{29}$-*b*-PS_{225} was not achieved.