Supporting Information for

One-pot preparation of BAB triblock copolymer nano-objects through bifunctional macromolecular RAFT agent mediated dispersion polymerization

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1. TEM sampling of the stained PS_{273}-*b*-$P4VP_{48}$-*b*-PS_{273} triblock copolymer nano-objects

Preparation of the CH_3I-stained PS_{273}-*b*-$P4VP_{48}$-*b*-PS_{273} nano-objects. Into a flask, the methanol dispersion of PS_{273}-*b*-$P4VP_{48}$-*b*-PS_{273} triblock copolymer nano-objects (1.00 g, 0.2 wt%) and the methanol solution of CH_3I (1.43 g, 0.03 wt%) were added, in which the molar ratio of the pyridine ligand in PS_{273}-*b*-$P4VP_{48}$-*b*-PS_{273} to CH_3I was set at 1:2. This mixture was kept at room temperature with stirring for 3 days, and then the stained PS_{273}-*b*-$P4VP_{48}$-*b*-PS_{273} triblock copolymer nano-objects were checked by TEM.

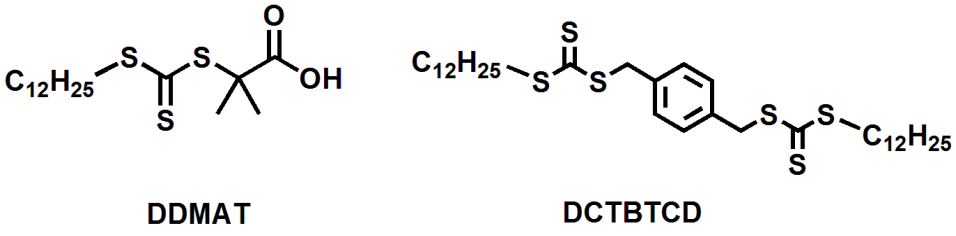
Preparation of the HCl-acidified PS_{273}-*b*-$P4VP_{48}$-*b*-PS_{273} nano-objects. Into HCl aqueous solution (1.00 g, pH = 1), the methanol dispersion of PS_{273}-*b*-$P4VP_{48}$-*b*-PS_{273} triblock copolymer nano-objects (0.02 mL, 5.30 wt%) was added. This mixture was kept at room temperature with stirring for 3 days, and then the acidified PS_{273}-*b*-$P4VP_{48}$-*b*-PS_{273} triblock copolymer nano-objects were checked by TEM.

2. Table S1

polymer	M_n (kg/mol)			$Đ_1$[d]	$Đ_2$[e]
	$M_{n,th}$[a]	$M_{n,GPC1}$[b]	$M_{n,GPC2}$[c]		
TTC-P4VP$_{48}$-TTC	5.7	7.1	18.5	1.31	1.29
PS$_{52}$-*b*-P4VP$_{48}$-*b*-PS$_{52}$	16.6	9.0	24.8	1.34	1.31
PS$_{273}$-*b*-P4VP$_{48}$-*b*-PS$_{273}$	62.6	52.8	67.8	1.36	1.35

[a] The theoretical molecular weight determined by monomer conversion according to eqn 1. [b] The molecular weight determined by GPC analysis using PMMA as calibration standard. [c] The molecular weight determined by GPC analysis using PS as calibration standard. [d] The $Đ$ (M_w/M_n) values determined by GPC analysis using PMMA as calibration standard. [e] The $Đ$ (M_w/M_n) values determined by GPC analysis using PS as calibration standard.

3. Scheme S1



Scheme S1. The chemical structures of the monofunctional RAFT agent of DDMAT and the bifunctional RAFT agent of DCTBTCD.

4 Equation

$$M_{n,NMR} = \frac{(I_{7.22\sim6.26} - I_{8.30})\times 2}{I_{8.30}\times 5} \times DP_{4VP} \times M_{n,St} + M_{n,TTC-P4VP-TTC} \qquad (S1)$$

5. Figures

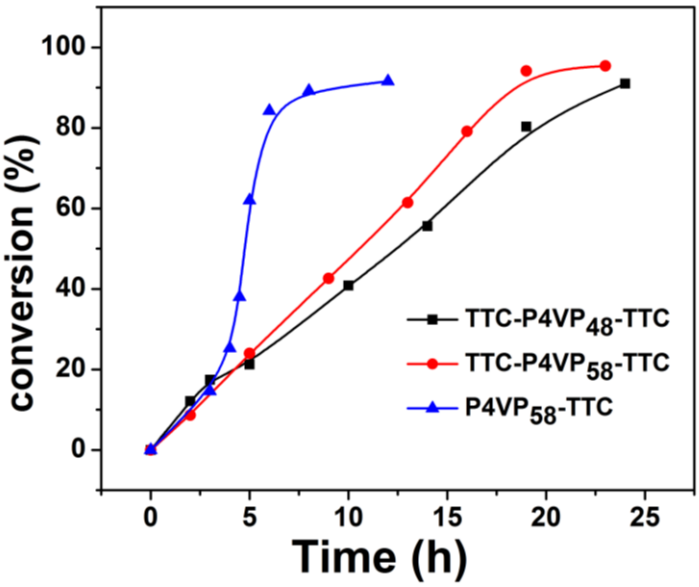


Fig S1. The monomer conversion-time plot for the dispersion RAFT polymerization of styrene in the presence of TTC-P4VP$_{48}$-TTC, TTC-P4VP$_{58}$-TTC and P4VP$_{58}$-TTC respectively. Polymerization conditions for the P4VP$_{58}$-TTC macro-RAFT agent mediated dispersion polymerization: [St]$_0$:[P4VP$_{58}$-TTC]$_0$:[AIBN]$_0$ = 600:1:/1/6, 70 ^{o}C, the fed St monomer concentration being at 28 wt%. The polymerization conditions for the TTC-P4VP$_{48}$-TTC or TTC-P4VP$_{58}$-TTC bifunctional macro-RAFT agent mediated dispersion polymerization can be found in Figure 3.

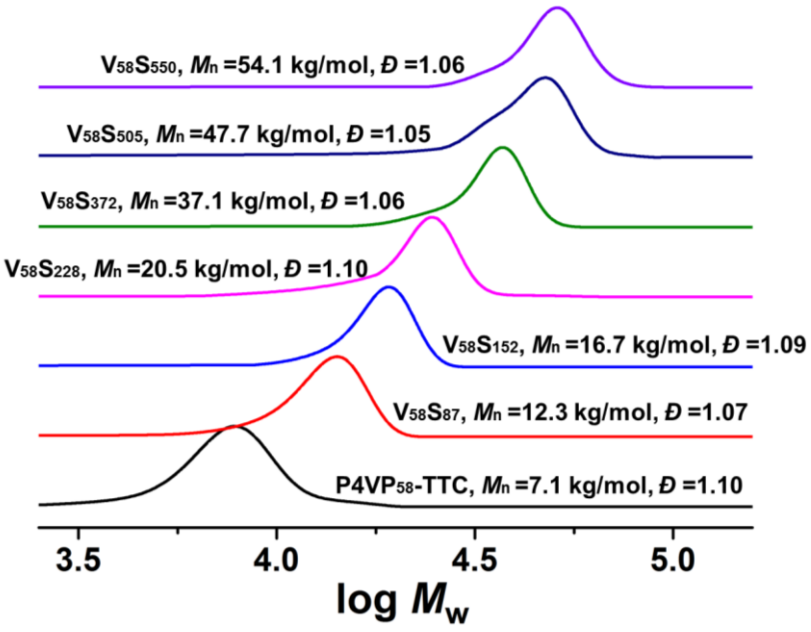


Fig S2. The GPC traces of the P4VP-*b*-PS diblock copolymers prepared through the monofunctional P4VP$_{58}$-TTC macro-RAFT agent mediated dispersion polymerization

(P4VP-*b*-PS is briefly called VS, in which S represents the PS block and V represents the P4VP block).

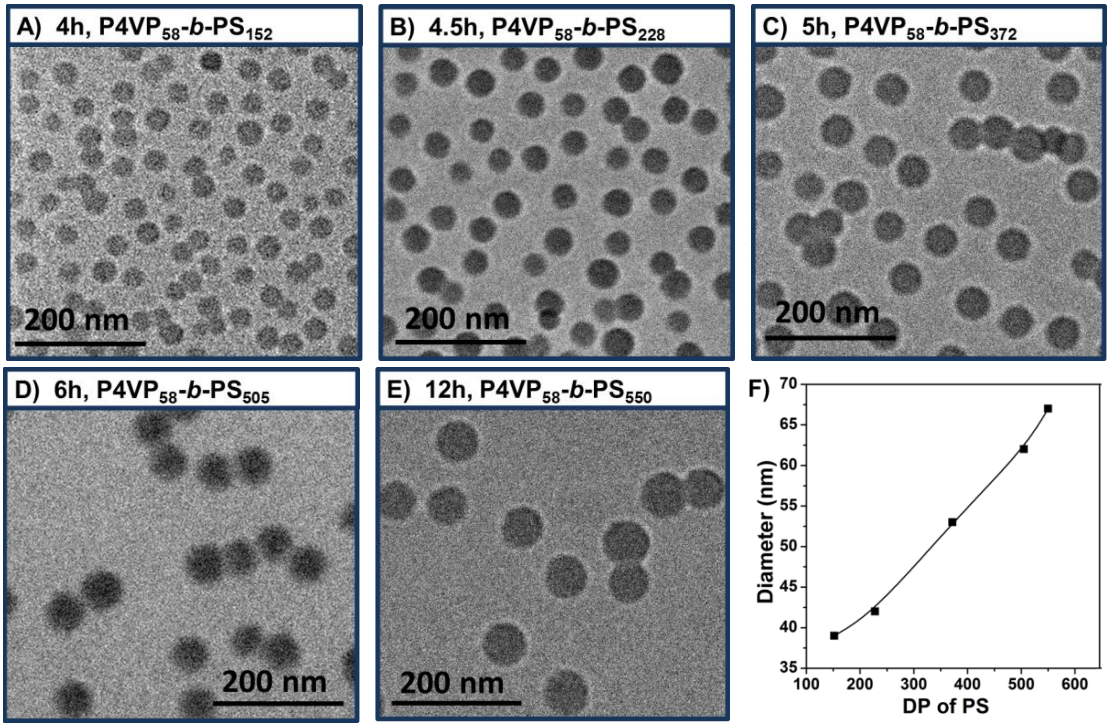


Fig S3. TEM images and the average size of the P4VP-*b*-PS diblock copolymers prepared through the monofunctional $P4VP_{58}$-TTC macro-RAFT agent mediated dispersion polymerization.

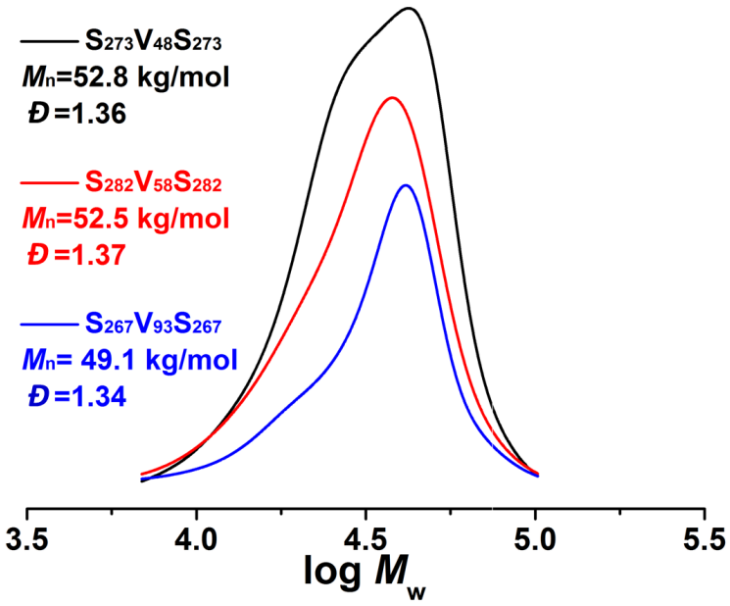


Fig S4. The GPC traces of the PS-*b*-P4VP-*b*-PS triblock copolymers of $S_{273}V_{48}S_{273}$, $S_{282}V_{58}S_{282}$, $S_{267}V_{93}S_{267}$ (PS-*b*-P4VP-*b*-PS is briefly called SVS, in which S represents the PS block and V represents the P4VP block).

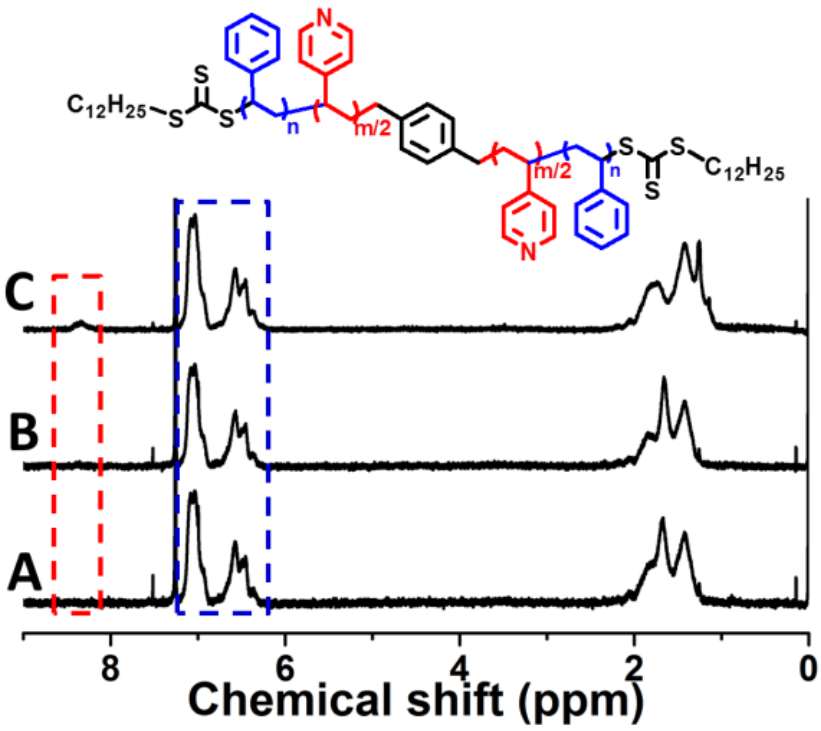


Fig S5. The ^{1}H NMR spectra of the triblock copolymers of PS_{273}-*b*-$P4VP_{48}$-*b*-PS_{273} (A), PS_{282}-*b*-$P4VP_{58}$-*b*-PS_{282} (B), PS_{267}-*b*-$P4VP_{93}$-*b*-PS_{267} (C).

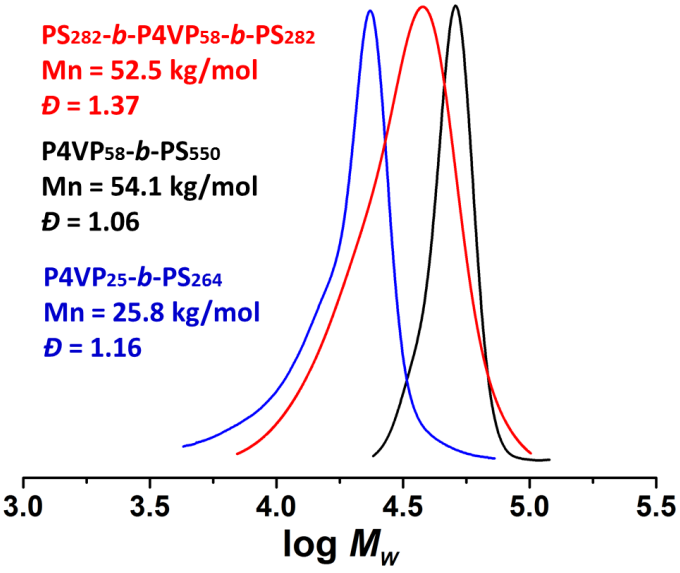


Fig S6. The GPC traces of PS_{282}-*b*-$P4VP_{58}$-*b*-PS_{282}, $P4VP_{58}$-*b*-PS_{550} and $P4VP_{25}$-*b*-PS_{264}.

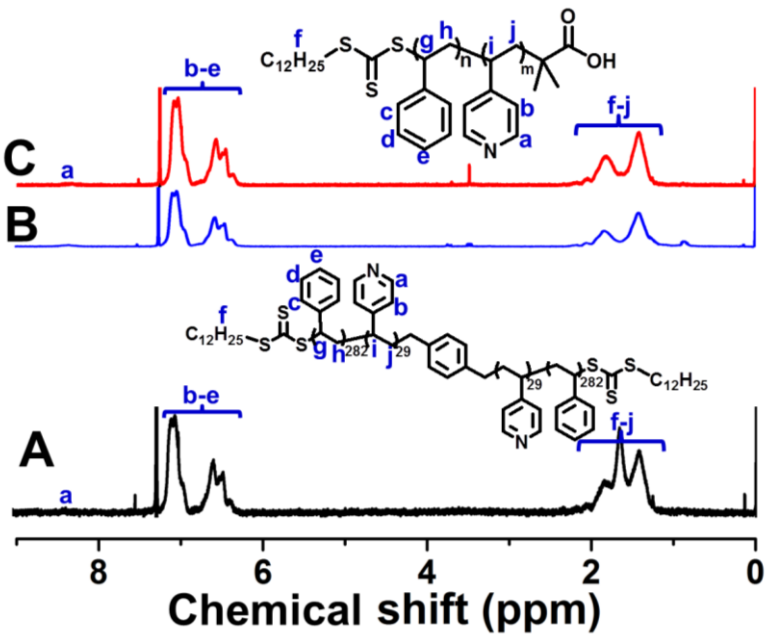


Fig S7. The ^{1}H NMR spectra of PS_{282}-*b*-$P4VP_{58}$-*b*-PS_{282} (A), $P4VP_{25}$-*b*-PS_{264} (B) and $P4VP_{58}$-*b*-PS_{550} (C).