Supporting Information for:

Macro-RAFT agent mediated dispersion copolymerization: a small amount of solvophilic co-monomer leads to a great change

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1. The ^{1}H NMR spectra of the polymerization solution and the equations

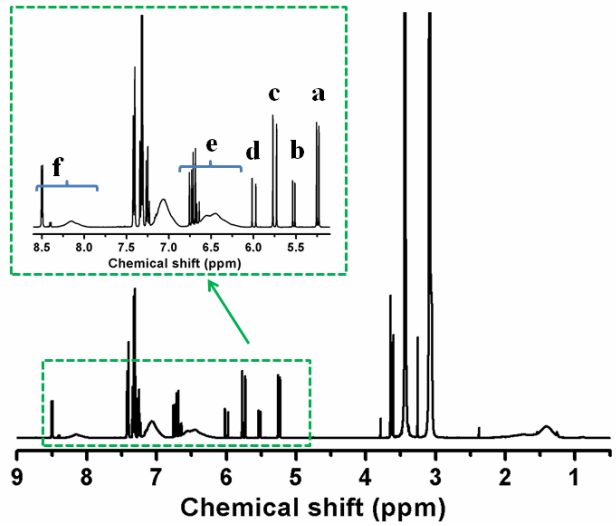

Figure S1. The ^{1}H NMR spectra of the polymerization solution after the RAFT dispersion polymerization of 4VP and St.

$$Conversion_{4VP}\% = \frac{I_{7.90\sim8.60} - 2I_{5.50\sim5.55}}{I_{7.90\sim8.60}} \times 100\% \quad \text{(S1)}$$

$$Conversion_{St}\% = \frac{2I_{6.10\sim6.80} - I_{7.90\sim8.60} - I_{5.20\sim5.30}}{2I_{6.10\sim6.80} - I_{7.90\sim8.60}} \times 100\% \quad \text{(S2)}$$

$$Conversion_{St/4VP}\% = \frac{n_{st} \times Conversion_{St} + n_{4VP} \times Conversion_{4VP}}{n_{St} + n_{4VP}} \times 100\% \quad \text{(S3)}$$

in which, n_{St} and n_{4VP} are the initial molar quantity of the feeding styrene and 4-vinylpyridine, respectively.

2. Summary of the synthesized polymers

Table S1. Summary of the synthesized polymers.

Entry		Polymer	$St]_0:[4VP]_0$	Time (h)	$Conv_{St\ and\ 4VP}$[a] (%)	$Conv_{St/4VP}$[b] (%)	M_n (kg/mol)			PDI[f]
							$M_{n,th}$[c]	$M_{n,GPC}$[d]	$M_{n,NMR}$[e]	
	1A	PEG_{45}-TTC	---	0	---	---	2.4	2.9	2.3	1.05
	1B	PEG_{45}-*b*-PS_{39}	6.0:0	2	9.9/---	9.9	6.4	9.2	6.5	1.08
	1C	PEG_{45}-*b*-PS_{54}	6.0:0	4	13.4/---	13.4	8.0	11.1	7.9	1.07
	1D	PEG_{45}-*b*-PS_{69}	6.0:0	6	17.4/---	17.4	9.5	12.3	9.2	1.18
	1E	PEG_{45}-*b*-PS_{92}	6.0:0	8	23.0/---	23.0	11.7	15.0	11.3	1.11
Fig S2-4	1F	PEG_{45}-*b*-PS_{128}	6.0:0	10	32.0/---	32.0	15.7	19.6	15.2	1.12
	1G	PEG_{45}-*b*-PS_{160}	6.0:0	12	40.1/---	40.1	19.0	22.5	18.5	1.11
	1H	PEG_{45}-*b*-PS_{250}	6.0:0	15	62.4/---	62.4	26.0	29.8	27.1	1.09
	1I	PEG_{45}-*b*-PS_{304}	6.0:0	18	76.0/---	76.0	34.0	38.2	35.3	1.11
	1J	PEG_{45}-*b*-PS_{373}	6.0:0	21	93.2/---	93.2	41.2	46.1	43.0	1.10
	1K	PEG_{45}-*b*-PS_{384}	6.0:0	24	96.6/---	96.6	42.3	50.3	47.3	1.12
	2A	PEG_{45}-*b*-PS_{384}	6.0:0	24	96.6/---	96.6	42.3	50.3	47.3	1.12
	2B	PEG_{45}-*b*-P($4VP_{57}$-*co*-St_{315})	5.0:1	36	94.5/85.9	93.1	41.2	45.7	42.2	1.10
	2C	PEG_{45}-*b*-P($4VP_{71}$-*co*-St_{305})	4.0:1	36	95.4/88.2	94.0	41.6	48.6	43.9	1.10
Fig 1-4	2D	PEG_{45}-*b*-P($4VP_{87}$-*co*-St_{282})	3.0:1	36	94.1/87.3	92.4	40.9	47.7	43.2	1.11
	2E	PEG_{45}-*b*-P($4VP_{98}$-*co*-St_{267})	2.5:1	36	93.5/85.4	91.2	40.6	46.6	42.9	1.18
	2F	PEG_{45}-*b*-P($4VP_{113}$-*co*-St_{247})	2.0:1	36	92.5/84.5	89.8	40.2	45.3	42.7	1.10
	2G	PEG_{45}-*b*-P($4VP_{133}$-*co*-St_{223})	1.5:1	36	93.0/83.4	89.2	40.1	49.5	45.5	1.23
	3A	PEG_{45}-TTC	---	0	---	---	2.4	2.9	2.3	1.05
	3B	PEG_{45}-*b*-P($4VP_{14}$-*co*-St_{41})	3.0:1	4	13.8/13.7	13.7	8.1	12.2	9.1	1.11
	3C	PEG_{45}-*b*-P($4VP_{25}$-*co*-St_{78})	3.0:1	7	26.0/24.8	25.7	13.1	17.9	14.7	1.12
	3D	PEG_{45}-*b*-P($4VP_{36}$-*co*-St_{115})	3.0:1	10	38.4/36.3	37.9	18.1	21.9	18.5	1.10
	3E	PEG_{45}-*b*-P($4VP_{50}$-*co*-St_{164})	3.0:1	13	54.8/49.7	53.5	24.7	29.4	25.5	1.11
Fig 5-7	3F	PEG_{45}-*b*-P($4VP_{62}$-*co*-St_{201})	3.0:1	16	67.1/62.0	65.8	29.8	33.7	30.2	1.12
	3G	PEG_{45}-*b*-P($4VP_{68}$-*co*-St_{221})	3.0:1	18	73.6/68.1	72.2	32.5	36.7	34.0	1.10
	3H	PEG_{45}-*b*-P($4VP_{73}$-*co*-St_{237})	3.0:1	20	78.9/72.7	77.3	34.7	39.2	36.2	1.09
	3I	PEG_{45}-*b*-P($4VP_{79}$-*co*-St_{259})	3.0:1	25	86.2/79.3	84.5	37.6	42.5	39.9	1.10
	3J	PEG_{45}-*b*-P($4VP_{84}$-*co*-St_{275})	3.0:1	30	91.6/84.1	89.7	39.8	44.7	41.9	1.10
	3K	PEG_{45}-*b*-P($4VP_{87}$-*co*-St_{282})	3.0:1	36	94.1/87.3	92.4	40.9	47.7	43.2	1.11
	4A	PEG_{45}-*b*-PS_{100}	6.0:0	24	99.9/---	99.9	12.8	14.5	13.4	1.18
	4B	PEG_{45}-*b*-PS_{200}	6.0:0	24	99.9/---	99.9	23.2	26.8	25.1	1.16
	4C	PEG_{45}-*b*-PS_{294}	6.0:0	24	98.2/---	98.2	33.0	38.9	36.7	1.15
Fig 8	4D	PEG_{45}-*b*-PS_{384}	6.0:0	24	96.6/---	96.6	42.3	50.3	47.3	1.12
	4E	PEG_{45}-*b*-P($4VP_{24}$-*co*-St_{74})	3.0:1	36	98.9/96.1	98.2	12.6	15.9	14.2	1.11
	4F	PEG_{45}-*b*-P($4VP_{47}$-*co*-St_{147})	3.0:1	36	98.3/94.6	97.4	22.6	28.7	26.4	1.17
	4G	PEG_{45}-*b*-P($4VP_{68}$-*co*-St_{220})	3.0:1	36	97.6/91.1	96.0	32.4	38.6	36.1	1.12
	4H	PEG_{45}-*b*-P($4VP_{87}$-*co*-St_{282})	3.0:1	36	94.1/87.3	92.4	40.9	47.7	43.2	1.11

[a] The conversion of the St and 4VP monomers determined by ^{1}H NMR analysis. [b] The

St/4VP conversion calculated by equation S3. [c] Theoretical molecular weight determined by monomer conversion. [d] The molecular weight determined by GPC analysis. [e] The molecular weight determined by ^{1}H NMR analysis. [f] The PDI (M_w/M_n) value determined by GPC analysis.

3. Polymerization kinetics of the dispersion RAFT polymerization of St

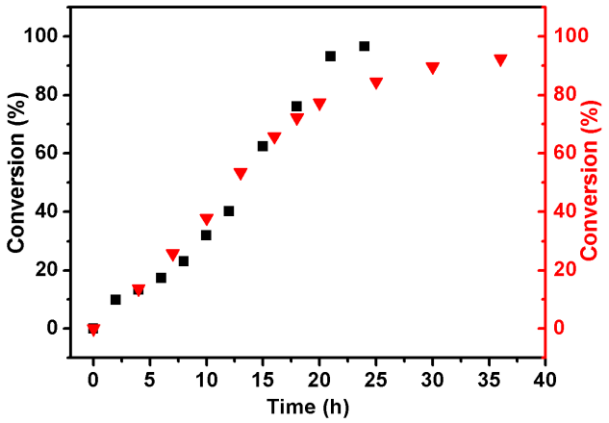

Figure S2. The monomer conversion-time plot for the dispersion RAFT polymerization of St (■) and the dispersion RAFT copolymerization of St/4VP (▼). Polymerization conditions: $[St]_0$: $[PEG_{45}\text{-TTC}]_0$:$[AIBN]_0$ = 1200: 3:1 or $[St]_0$:$[4VP]_0$:$[PEG_{45}\text{-TTC}]_0$:$[AIBN]_0$ = 900:300:3:1, 70 ℃. Note: the St/4VP conversion is defined by eq S3.

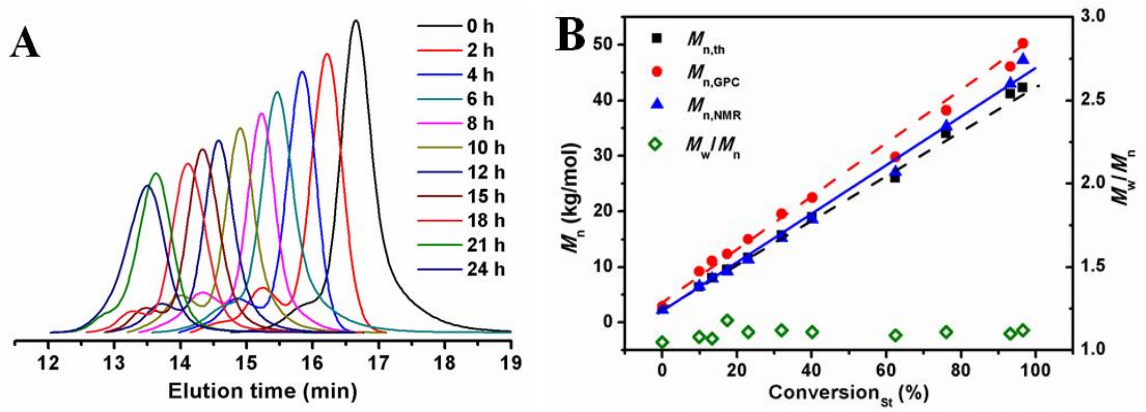

Figure S3. The GPC traces (A) and evolution of the molecular weight and the PDI (M_w/M_n) value (B) of the E-*b*-S diblock copolymer synthesized through the dispersion RAFT polymerization of St. Polymerization conditions can be found in the caption for Figure S2.

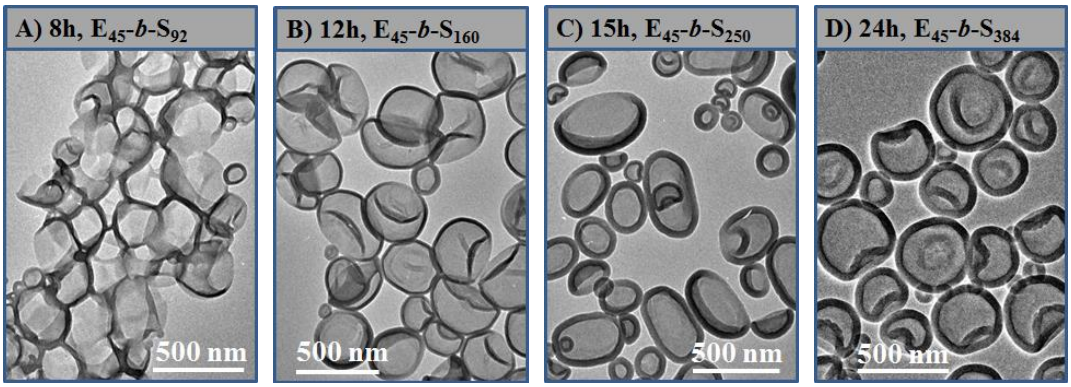

Figure S4. TEM images of the synthesized E-*b*-S diblock copolymer nano-objects prepared at the polymerization times. Polymerization conditions can be found in the caption for Figure S2.