Supporting Information

A Unique Fabrication Strategy of Hierarchical Morphologies: Combination of Multi-Step Self-Assembling and Morphology Transition

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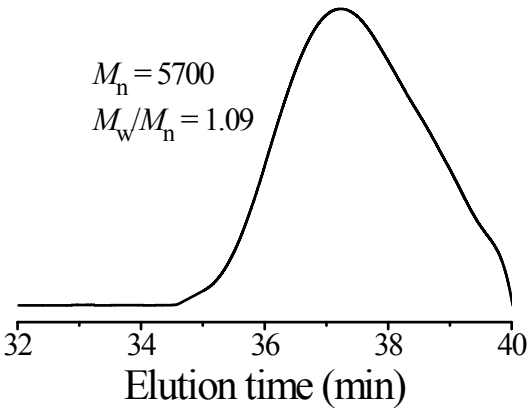


Figure S1. GPC trace of P4VP-TC in DMF.

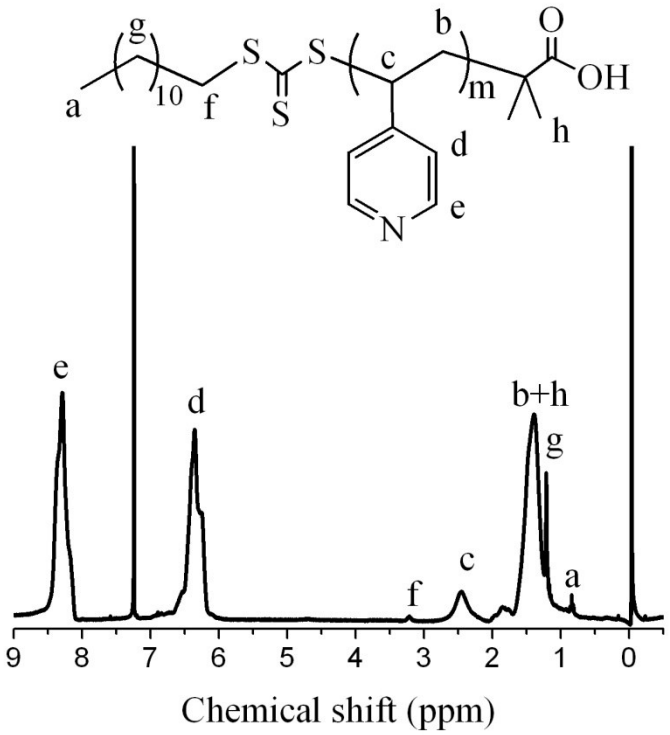
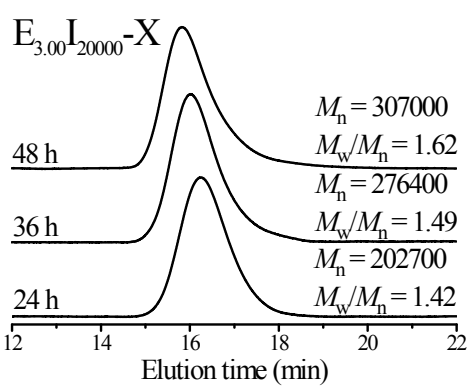
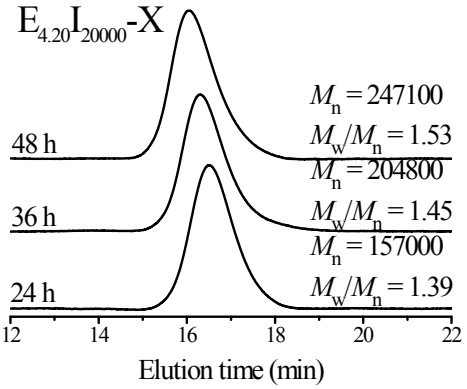
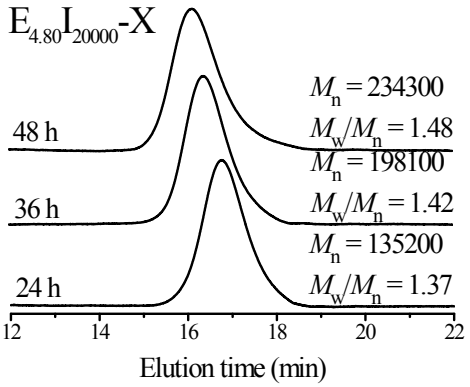
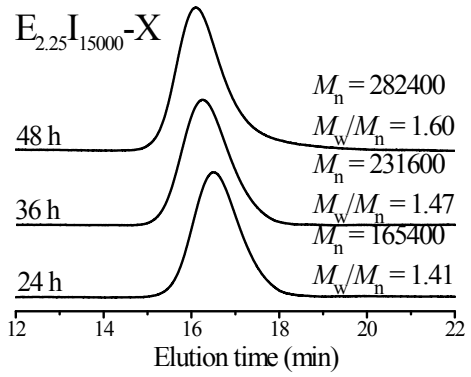


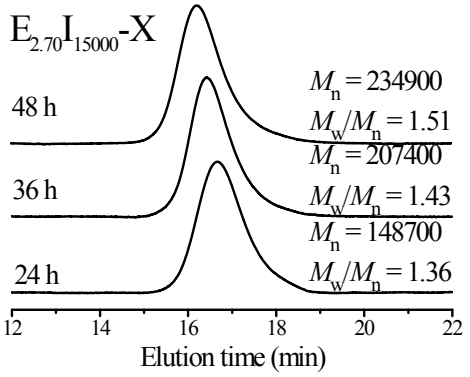
Figure S2. ^{1}H NMR spectrum of P4VP-TC in $CDCl_3$.

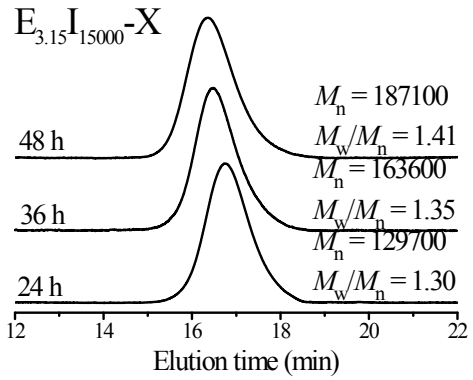


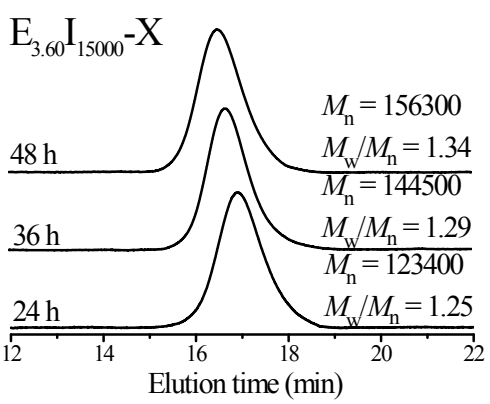


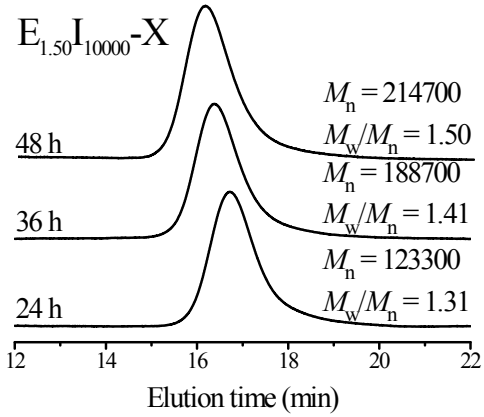












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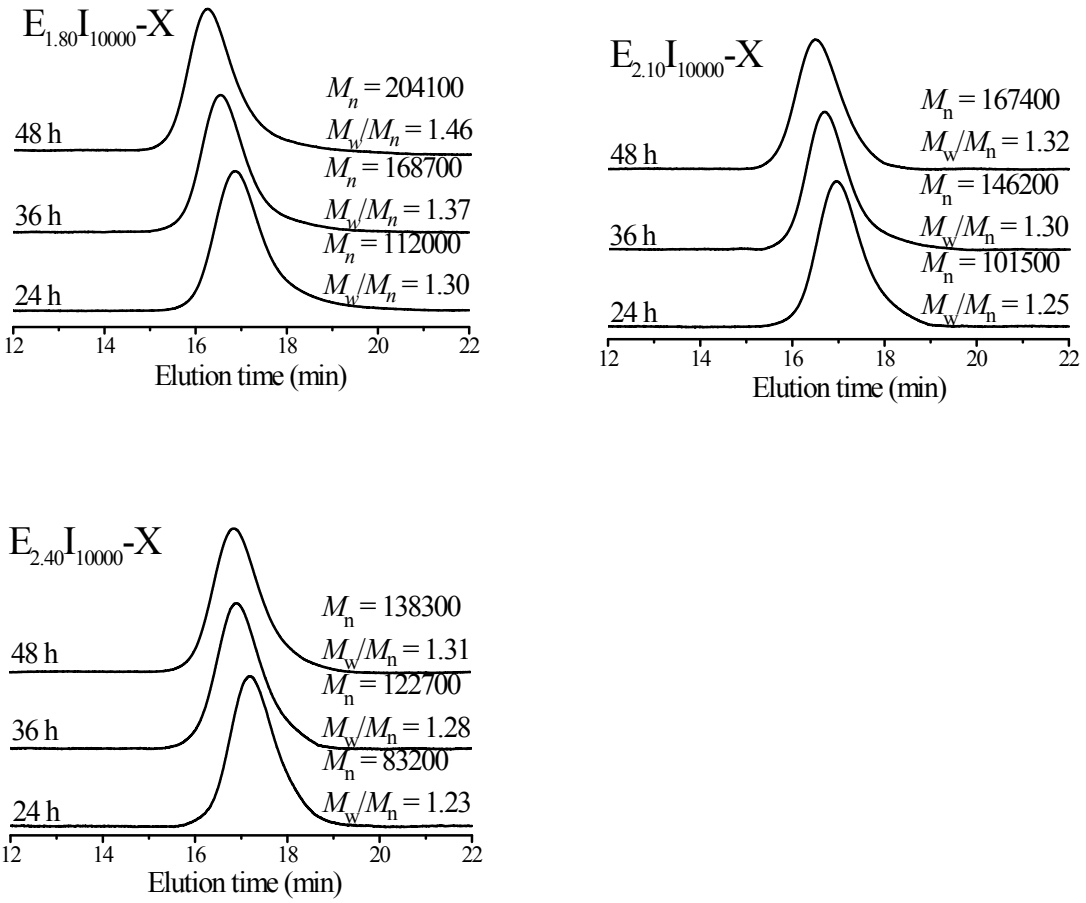
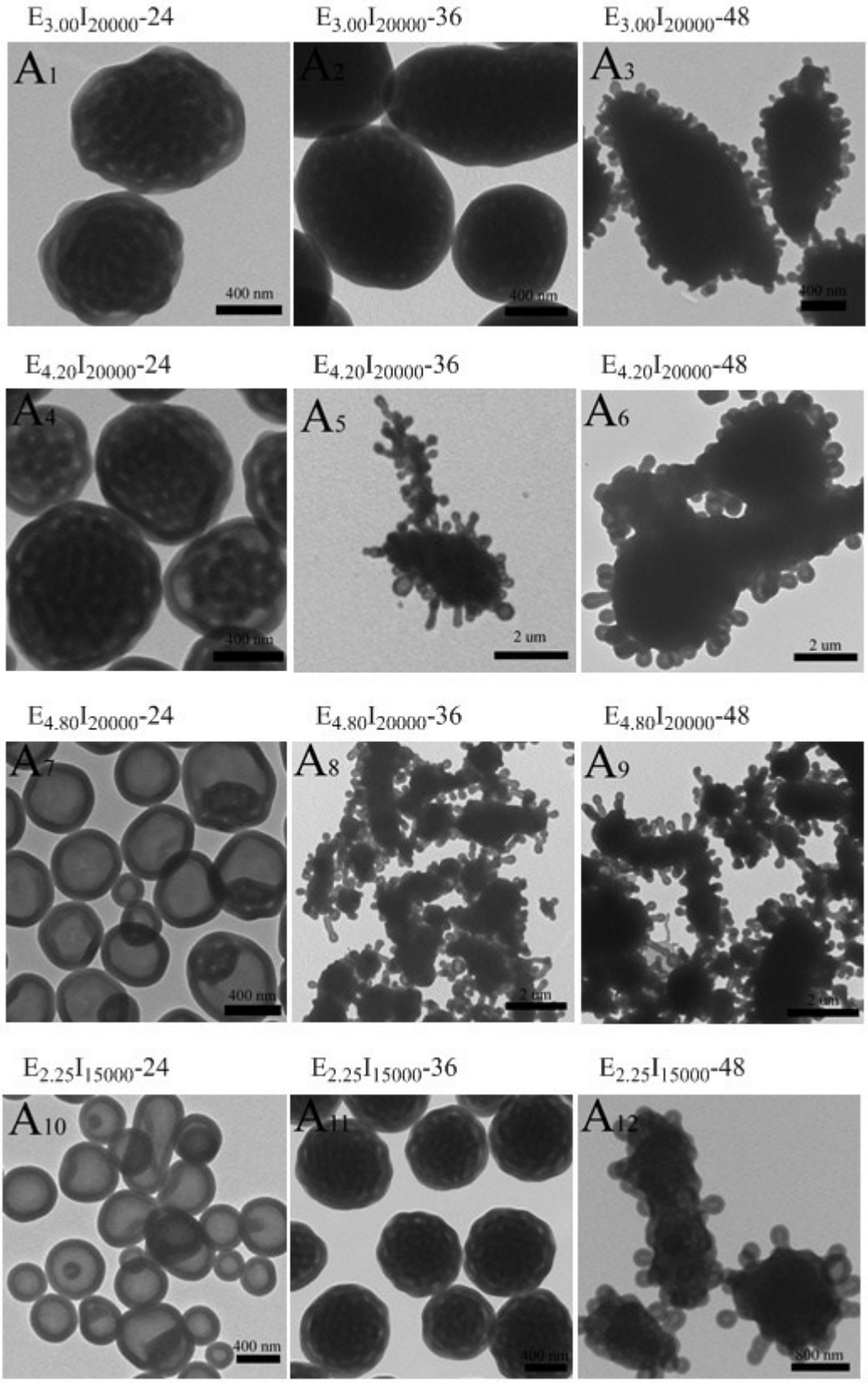


Figure S3. GPC traces of the $P4VP_{39}$-PS_m block copolymers obtained from RAFT dispersion polymerization with various molar ratios of St/P4VP-TC/AIBN at 80°C for different polymerization times. E_aI_b-X: X denotes polymerization time (h); I_{20000}, I_{15000} and I_{10000} respectively refer to initial feed molar ratios of St/P4VP/AIBN = 20000/1/0.1, 15000/1/0.1 and 10000/1/0.1; E_a refers to weight (g) of the ethanol mixed with 5.2 g of St for I_{20000}, 3.9 g of St for I_{15000}, and 2.6 g of St for I_{10000}.



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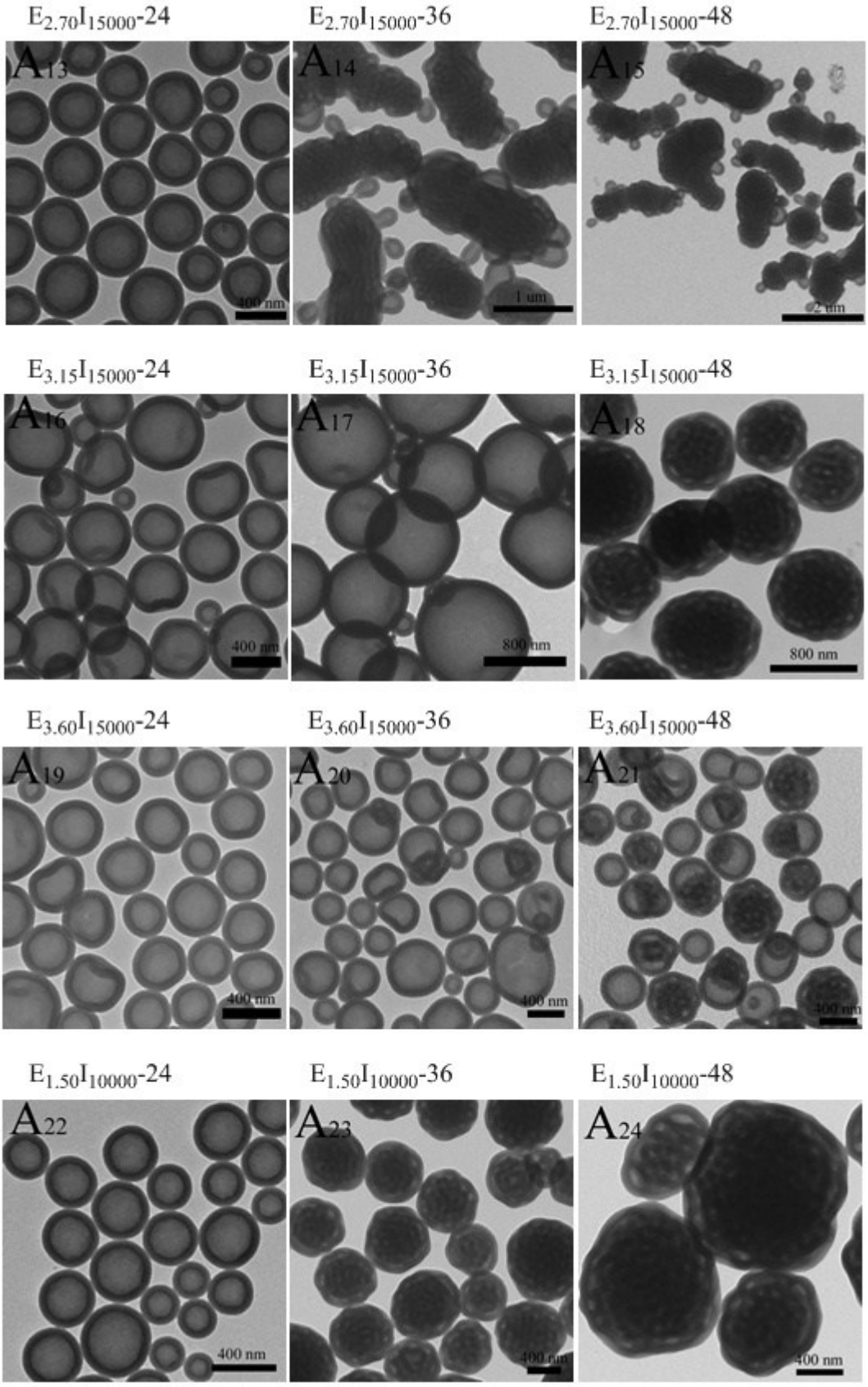

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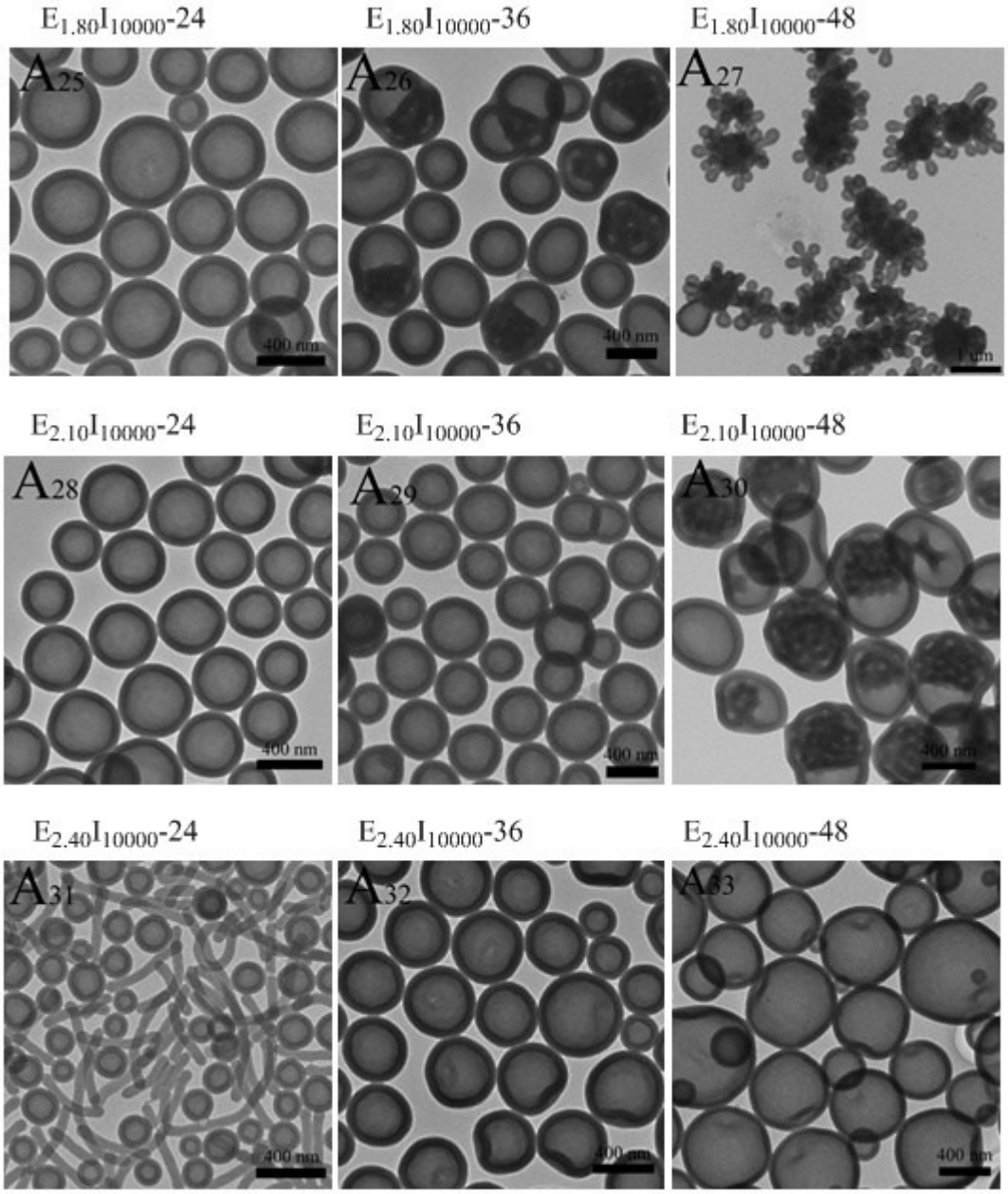

Figure S4. TEM images of the resultant aggregates obtained from RAFT dispersion polymerization in ethanol at 80°C for different polymerization times. E_aI_b-X, X denotes polymerization time (h); I_{20000}, I_{15000} and I_{10000} refer to initial feed molar ratio of St/P4VP/AIBN = 20000/1/0.1, 15000/1/0.1 and 10000/1/0.1, respectively; E_a refers to weights (g) of the ethanol mixed with 5.2 g of St for I_{20000}, 3.9 g of St for I_{15000}, and 2.6 g of St for I_{10000}.

Table S1. Characterizations of $P4VP_{39}$-PS_x Diblock Copolymers and Morphologies Prepared by RAFT Dispersion Polymerization in ethanol at 80°C

Sample code[a]	N_{PS}[b]	R[b]	M_n[c] (g/mol)	M_w/M_n[c]	Morphology[d]
$E_{3.00}I_{20000}$-24	2434	62.4	202700	1.42	lcv
$E_{3.00}I_{20000}$-36	3226	82.7	276400	1.49	lcv
$E_{3.00}I_{20000}$-48	3637	93.3	307000	1.62	SHM
$E_{3.60}I_{20000}$-12	970	24.9	99300	1.36	v
$E_{3.60}I_{20000}$-24	2220	56.9	189000	1.40	v + lcv
$E_{3.60}I_{20000}$-30	2790	71.5	231100	1.46	lcv
$E_{3.60}I_{20000}$-36	3021	77.5	261900	1.52	SHM
$E_{3.60}I_{20000}$-48	3420	87.7	289100	1.59	SHM
$E_{4.20}I_{20000}$-24	1864	47.8	157000	1.39	lcv
$E_{4.20}I_{20000}$-36	2488	63.8	204800	1.45	SHM
$E_{4.20}I_{20000}$-48	2907	74.5	247100	1.53	SHM
$E_{4.80}I_{20000}$-24	1539	39.5	135200	1.37	v
$E_{4.80}I_{20000}$-36	2285	58.6	198100	1.42	SHM
$E_{4.80}I_{20000}$-48	2850	73.1	234300	1.48	SHM
$E_{2.25}I_{15000}$-24	1904	48.8	165400	1.41	v
$E_{2.25}I_{15000}$-36	2411	61.8	231600	1.47	lcv
$E_{2.25}I_{15000}$-48	2742	70.3	282400	1.60	SHM
$E_{2.70}I_{15000}$-24	1653	42.4	148700	1.36	v
$E_{2.70}I_{15000}$-36	2143	54.9	207400	1.43	SHM
$E_{2.70}I_{15000}$-48	2536	65.0	234900	1.51	SHM
$E_{3.15}I_{15000}$-24	1476	37.8	129700	1.30	v
$E_{3.15}I_{15000}$-36	1910	49.0	163600	1.35	v
$E_{3.15}I_{15000}$-48	2086	53.5	187100	1.41	lcv
$E_{3.60}I_{15000}$-24	1352	34.7	123400	1.25	v
$E_{3.60}I_{15000}$-36	1677	43.0	144500	1.29	v
$E_{3.60}I_{15000}$-48	1813	46.5	156300	1.34	v + lcv
$E_{1.50}I_{10000}$-24	1524	39.1	123300	1.31	v
$E_{1.50}I_{10000}$-36	2207	56.6	188700	1.41	lcv
$E_{1.50}I_{10000}$-48	2394	61.4	214700	1.50	lcv
$E_{1.80}I_{10000}$-24	1368	35.1	112000	1.30	v
$E_{1.80}I_{10000}$-36	1881	48.2	168700	1.37	v + lcv
$E_{1.80}I_{10000}$-48	2105	54.0	204100	1.46	SHM
$E_{2.10}I_{10000}$-24	1251	32.1	101500	1.25	v
$E_{2.10}I_{10000}$-36	1660	42.6	146200	1.30	v
$E_{2.10}I_{10000}$-48	1858	47.6	167400	1.32	v + lcv
$E_{2.40}I_{10000}$-24	1047	26.8	83200	1.23	v + nr
$E_{2.40}I_{10000}$-36	1334	34.2	122700	1.28	v
$E_{2.40}I_{10000}$-48	1452	37.2	138300	1.31	v

[a]Note: E_aI_b-X, where E stands for ethanol, "a" denotes initial weight (g) of ethanol mixed with 5.2 g of St for I_{20000}, 3.9 g of St for I_{15000}, and 2.6 g of St for I_{10000}; I_b is the initial molar ratio of the St/P4VP-TC, X is polymerization time (h). [b] N_{PS} is DP of PS and *R* is chain length ratio of the PS block to P4VP block, which were calculated according to ^{1}H NMR data. [c]Number-average molecular weights (M_n) and M_w/M_n of P4VP-PS_m obtained by GPC. [d]The copolymer morphology is identified by TEM, where nr = nanorods, v = vesicles, lcv = large compound vesicles, SHM = sea cucumber-like hierarchical microstructures.