Supporting Information

Branched and crosslinked supracolloidal chains with diblock copolymer micelles having well-defined three patches

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Experimental Section

Materials

Commercially available chemicals were used as received unless otherwise stated. CaH_2 (90~95%), benzyl dithiobenzoate (BDTB) (96%), n-hexane (96%), N,N-dimethylformamide (DMF) (99.8%), N,N-dimethylacetamide (DMAc) (99.8%), γ-butyrolactone (>99%), 1,4-Dioxane (99.8%) were purchased from Aldrich. 2.2'-azoisobutyronitrile (AIBN) (95%) was acquired from Merck. AIBN was recrystallized with diethylether. Styrene (> 99%) and 4-vinylpyridine (4VP) (> 95%) were obtained from Aldrich. These monomers were passed through basic alumina columns to remove inhibitors and acidic impurities. Then, CaH_2 was added to the monomers, which were stirred overnight to eliminate traces of water. Monomers were further vacuum-distillated before polymerization. Polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP) in Table S1 were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization as described in the literature (*J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 1636), except PS(51k)-*b*-P4VP(18k), PS(41k)-*b*-P4VP(24k), PS(25k)-*b*-P4VP(7k), PS(27k)-*b*-P4VP(7k), PS(48k)-*b*-P4VP(21k), and PS(33k)-*b*-P4VP(8k) which were purchased from Polymer Source and used without further purification. The number in the parenthesis is a number-average molecular weight in g/mol.

Synthesis of PS-b-P4VP diblock copolymers

We first synthesized the P4VP block by RAFT polymerization and then it was used as a macro chain transfer agent (CTA) to synthesize the additional PS block. A representative polymerization procedure is described below in the case of PS(21k)-*b*-P4VP(13k). A mixture of 4VP (10.0 g), BDTB (95 mg), AIBN (13 mg), and DMF (5.0 g) were added into a 50 mL Schlenk tube. This solution was degassed by three freeze-evacuate-thaw cycles and the tube was filled with nitrogen gas. The reaction tube was subsequently immersed in an oil bath at 65 ^{o}C for 8 h and then placed in an ice bath to stop the polymerization. The resulting mixture was diluted with THF (20 g). Then, this solution was slowly poured into an excess of n-hexane (500 g) to precipitate the polymer which was collected by filtration and then dried in a vacuum oven at room temperature for 48 h. We obtained P4VP (4.0 g) which was used as a macro CTA for the synthesis of the second PS block. We basically repeated the above procedure of RAFT polymerization for PS(21k)-*b*-P4VP(13k). We prepared a mixture solution of styrene (5.0 g), macro CTA of P4VP (0.46 g), AIBN (0.2 mg), and DMF (5.0 g). The polymerization was proceeded at 85 ^{o}C for 12 h. The polymerized mixture was diluted with DMF (5.0 g), instead of THF, before precipitation in n-hexane. After precipitation, filtration, and drying, we obtained PS(21k)-*b*-P4VP(13k) (1.5 g) in light pink.

Formation of PS-b-P4VP micelles

We first dissolved PS-*b*-P4VP copolymers (10.0 mg) in chloroform (1.0 g), a good solvent for both PS and P4VP blocks, to yield a 1.0 wt% solution. Then, we slowly added toluene (1.0 g), a selective solvent for the PS block, to the solution by a syringe pump at a rate of 30 ml/h. After mixing, chloroform was completely evaporated at 45 ^{o}C to obtain a 1.0 wt% toluene solution of PS-*b*-P4VP micelles. The same procedure was applied to all PS-*b*-P4VP in Table S1. To crosslink the P4VP core, 1,4-dibromobutane (DBB) (3.9 mg) was added to a toluene solution (1.0 g) containing the copolymer (0.01 g), yielding a molar ratio of DBB to 4VP equal to 0.5, which can fully quarternize the 4VP units in the copolymer, followed by stirring at 45 ^{o}C for 48 h. The amounts described in the parentheses are representative values for PS(21k)-*b*-P4VP(13k).

Preparation of patchy micelles

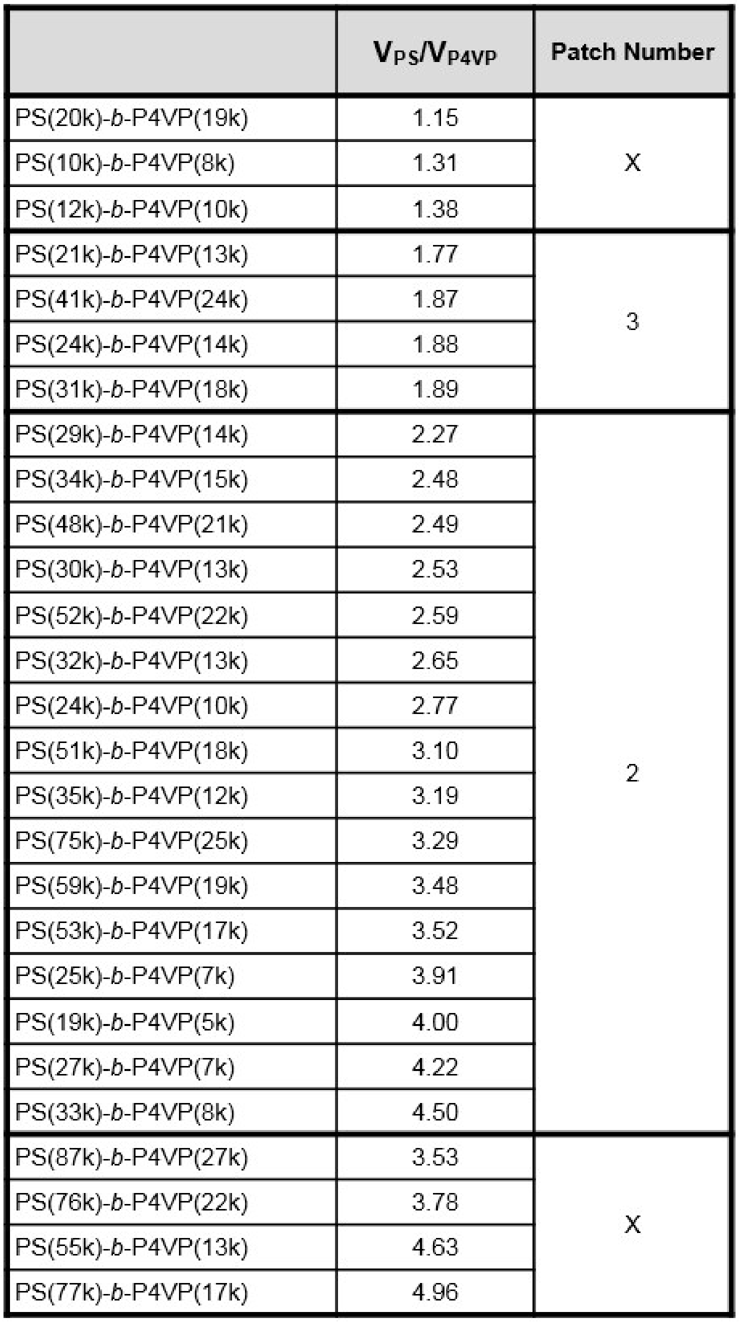
To produce colloidal monomers of patchy micelles, we changed the polarity of the solvent by adding DMF (9.9 g) to a 1.0 wt% toluene solution (0.1 g) of crosslinked PS-*b*-P4VP micelles by a syringe pump at a rate of 50 ml/h, resulting in a 0.01 wt% solution of patchy micelles of PS-*b*-P4VP. The same procedure was used for all PS-*b*-P4VP in Table S1

Supracolloidal polymerization of patchy micelles

We further increased the polarity of the solvent to synthesize supracolloidal chains of patchy micelles by dropping a mixture (1.0 ml for the period of 60 s) of DI water and anhydrous DMF (2.5 : 7.5 w/w) to yield 12.5 wt% water in the final solution. The solution was kept without stirring at 30 ^{o}C up to 48 h. For branched and crosslinked supracolloidal chains, we added 5% trifunctional micelles of PS(41k)-*b*-P4VP(24k) to a solution of patchy micelles of PS(51k)-*b*-P4VP(18k) and then followed the same procedure described above.

Characterizations

NMR spectra were obtained on a Varian NMR System (500 MHz). Gel permeation chromatography (GPC) was carried out on a Waters system (1515 pump, 2414 refractive index detector) with a Shodex GPC LF-804 column. Transmission electron microscopy (TEM) was performed on a Hitachi 7600 operating at 100 kV. A TEM sample was prepared by dropping a solution of micelles or supracolloidal chains on a carbon-coated TEM grid with removal of excess solvent by a filter paper. After drying in air, the TEM sample was exposed to I_2 and RuO_4 which stained P4VP and PS, respectively. Field-emission scanning electron microscopy (SEM) was performed on a Carl Zeiss SIGMA operating at 15 kV. Dynamic light scattering (DLS) analysis was carried out with an ALV/CGS-3 compact goniometer system.



	V_{PS}/V_{P4VP}	Patch Number
PS(20k)-*b*-P4VP(19k)	1.15	X
PS(10k)-*b*-P4VP(8k)	1.31	
PS(12k)-*b*-P4VP(10k)	1.38	
PS(21k)-*b*-P4VP(13k)	1.77	3
PS(41k)-*b*-P4VP(24k)	1.87	
PS(24k)-*b*-P4VP(14k)	1.88	
PS(31k)-*b*-P4VP(18k)	1.89	
PS(29k)-*b*-P4VP(14k)	2.27	2
PS(34k)-*b*-P4VP(15k)	2.48	
PS(48k)-*b*-P4VP(21k)	2.49	
PS(30k)-*b*-P4VP(13k)	2.53	
PS(52k)-*b*-P4VP(22k)	2.59	
PS(32k)-*b*-P4VP(13k)	2.65	
PS(24k)-*b*-P4VP(10k)	2.77	
PS(51k)-*b*-P4VP(18k)	3.10	
PS(35k)-*b*-P4VP(12k)	3.19	
PS(75k)-*b*-P4VP(25k)	3.29	
PS(59k)-*b*-P4VP(19k)	3.48	
PS(53k)-*b*-P4VP(17k)	3.52	
PS(25k)-*b*-P4VP(7k)	3.91	
PS(19k)-*b*-P4VP(5k)	4.00	
PS(27k)-*b*-P4VP(7k)	4.22	
PS(33k)-*b*-P4VP(8k)	4.50	
PS(87k)-*b*-P4VP(27k)	3.53	X
PS(76k)-*b*-P4VP(22k)	3.78	
PS(55k)-*b*-P4VP(13k)	4.63	
PS(77k)-*b*-P4VP(17k)	4.96	

Table S1. List of PS-*b*-P4VP with volume ratios of PS to P4VP and patch numbers. The number in the parentheses is a molecular weight in g/mol.

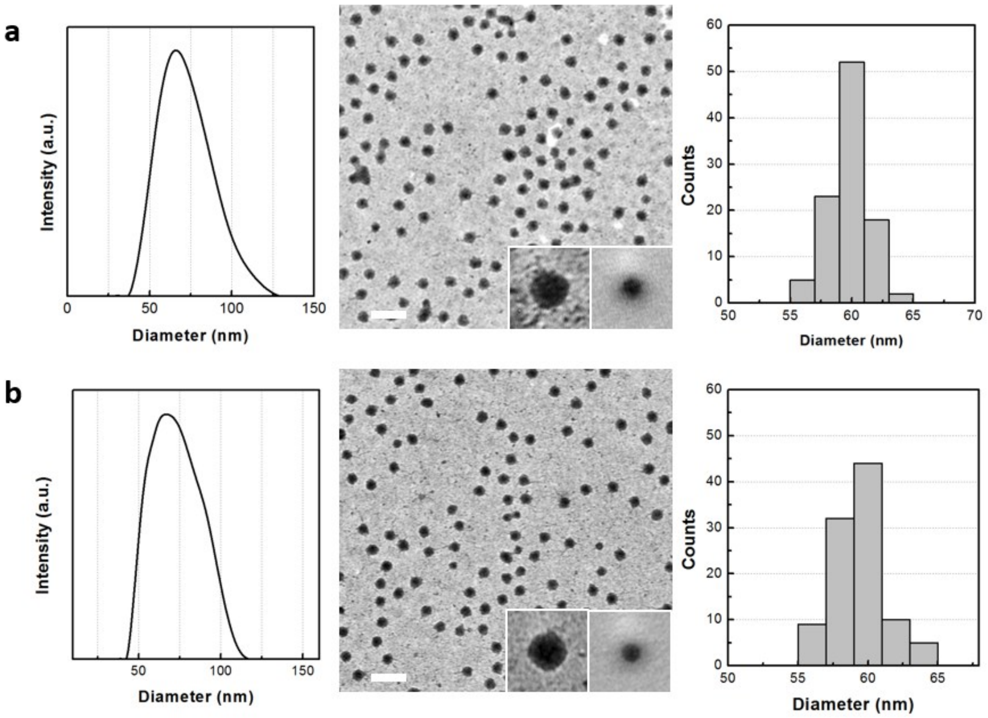


Figure S1. Spherical micelles of (a) PS(41k)-*b*-P4VP(24k) and (b) PS(51k)-*b*-P4VP(18k): (left column) diameter distributions by DLS; (center column) TEM images after RuO_4 staining; (right column) diameter histograms from TEM images. The scale bars in the TEM images are 200 nm. The insets are enlarged images (100 nm × 100 nm) of micelles stained with RuO_4 (left) and I_2 (right).

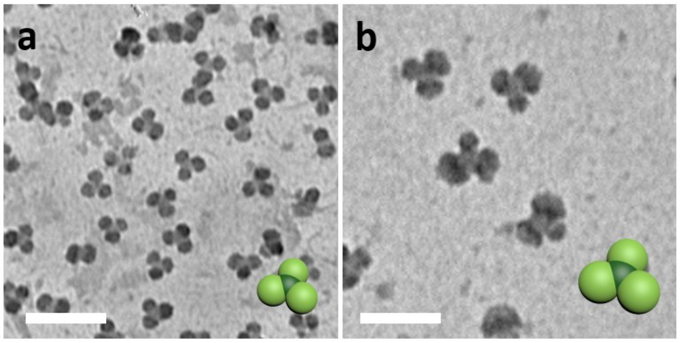


Figure S2. TEM images of small and large micelles having three patches: (a) PS(21k)-*b*-P4VP(13k); (b) PS(41k)-*b*-P4VP(24k). PS patches were stained with RuO_4. The scale bars are 100 nm.

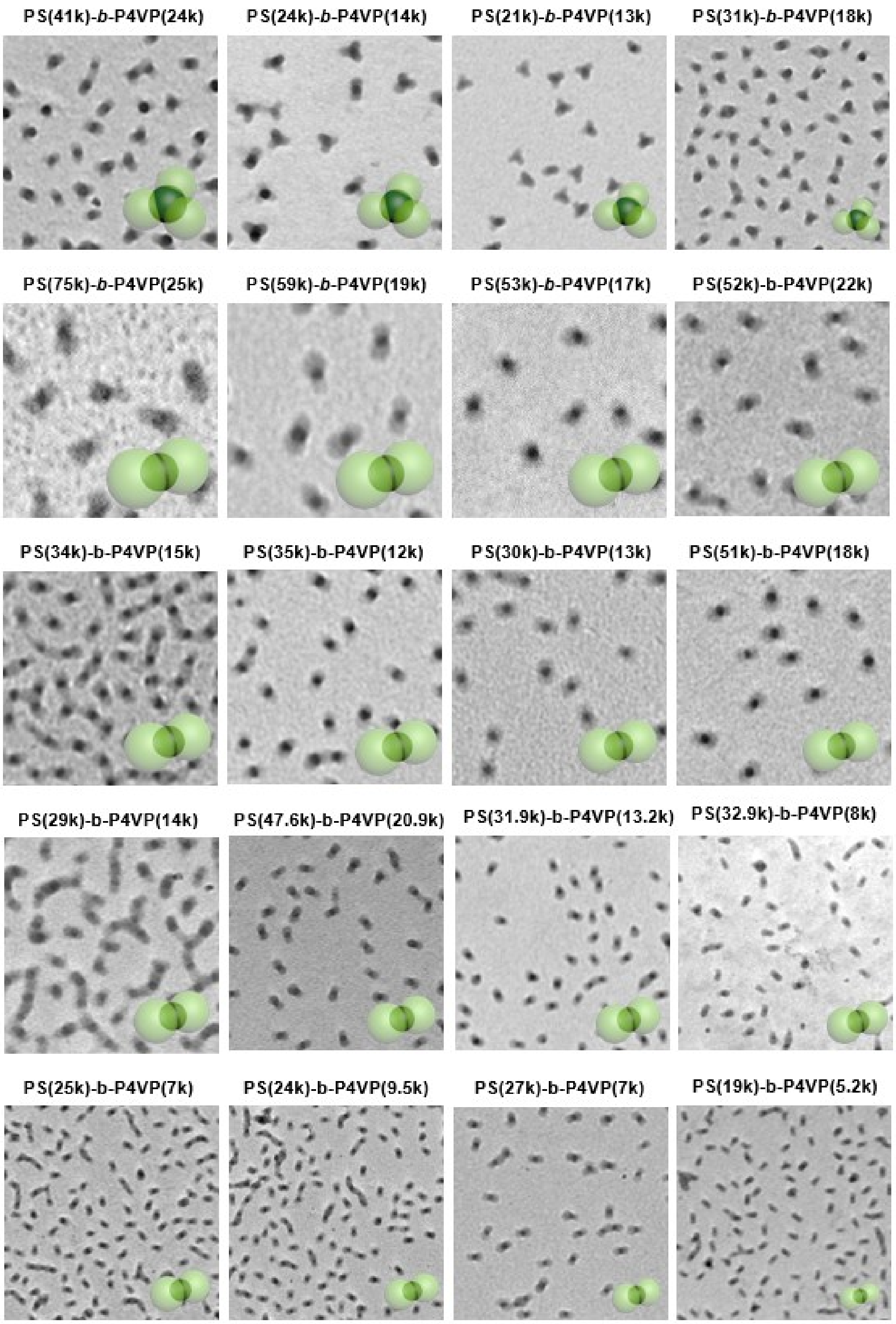


Figure S3. TEM images of micelles having two and three patches. The size of each image is 450 nm × 450 nm. P4VP cores were stained with I_2.

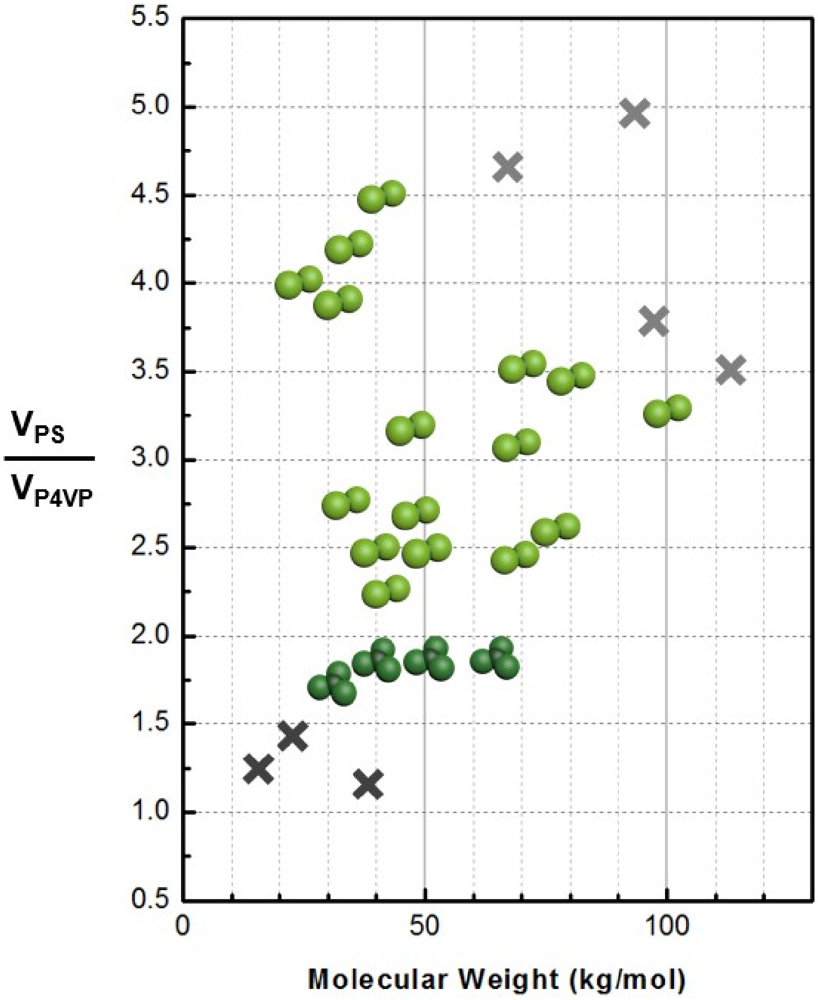


Figure S4. Micelles with two and three patches depending on the total molecular weight and the volume ratio of PS to P4VP.

We note that the corona seemed to be divided into several tiny patches with V_{PS}/V_{P4VP} lower than 1.5. However, they were not clearly discernible in TEM images so that we do not have enough evidences of patchy formation in this case.

We investigated the effect of solvent quality on the formation of patchy micelles with the solubility parameter δ as a probing factor for preference of a solvent to each block. Based on the δ values (unit of $MPa^{1/2}$),[30] toluene (18.2) is a good solvent for PS (18.6) but a non-solvent for P4VP (22.2) so that a spherical micelle consisting of the PS corona and the P4VP core formed in toluene. By adding 1,4-dioxane (20.5), which has a slightly larger δ than toluene, into a toluene solution of micelles, spherical micelles remained, regardless of the amount of 1,4-dioaxane (Table S2). However, by the addition of DMF (24.8), which is a good solvent for P4VP but a poor solvent for PS, patchy micelles were obtained above ~65 wt% DMF by rearranging the PS corona into segregated patches with the central P4VP directly exposed to DMF. Patchy micelles were also produced with a polar solvent having δ close to that of DMF such as DMAc (22.7), γ-butyrolactone (26.3), and DMSO (26.7). TEM images of observed micelles are summarized in Table S2. In the same solvent quality, micelles of PS(51k)-*b*-P4VP(18k) and PS(41k)-*b*-P4VP(24k) generated two and three patches, respectively. We note that precipitation was observed in high contents of γ-butyrolactone and DMSO, presumably because the PS block became insoluble. It is noted that the crosslinked P4VP would have a higher δ than that of pure P4VP due to ionic charges by the crosslinking agent.

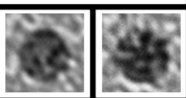
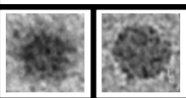
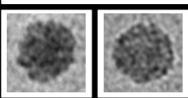
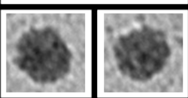
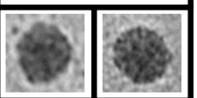
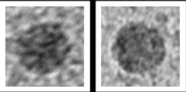
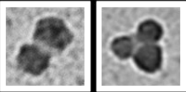
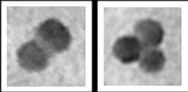
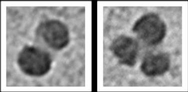
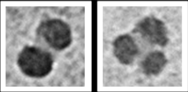
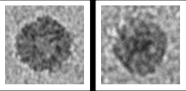
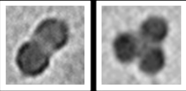
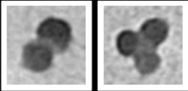
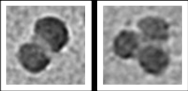
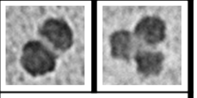
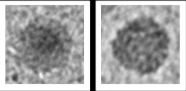
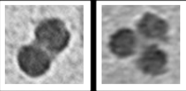
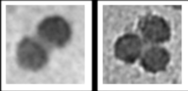
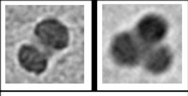
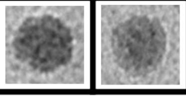
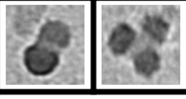
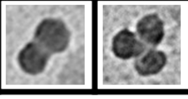
Solvent	1,4-Dioxane	DMAc (N,N-Dimethylacetamide)	DMF (N,N-Dimethylformamide)	γ-Butyrolactone	DMSO (Dimethylsulfoxide)
δ (MPa$^{1/2}$)	**20.5**	**22.7**	**24.8**	**26.3**	**26.7**
50 wt%					
67 wt%					
80 wt%					
89 wt%					*precipitated*
99 wt%				*precipitated*	*precipitated*

Table S2. Micelles of PS(51k)-*b*-P4VP(18k) (left) and PS(41k)-*b*-P4VP(24k) (right) in toluene mixed with polar solvents having various solubility parameters (δs). The size of each TEM image is 80 nm × 80 nm. Micelles were stained with RuO_4. Each polar solvent was added to a 0.1 wt% toluene solution (0.1 g) of crosslinked micelles by a syringe pump at a rate of 50 ml/h.

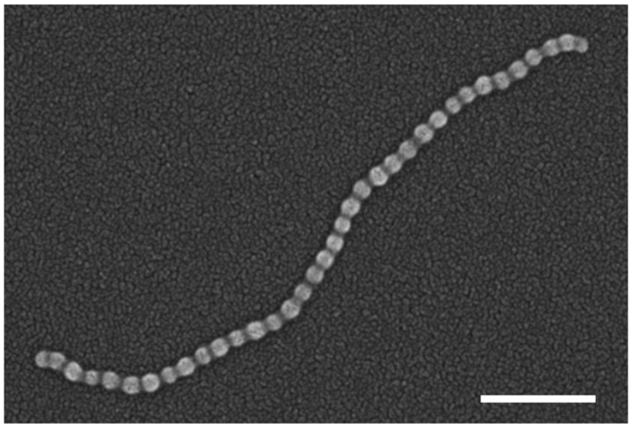


Figure S5. SEM image of a linear supracolloidal chain of PS(51k)-*b*-P4VP(18k). The scale bar is 200 nm.

Chains were also induced by the addition of 10~30 wt% water (Figure S6). However, precipitation was observed with a large amount of water (> 30 wt%) and polymerization was not induced with a small amount of water (< 10 wt%). By adding 12.5 wt% methanol ($\delta = 29.6$ MPa$^{1/2}$) or ethylene glycol ($\delta = 33.0$ MPa$^{1/2}$), instead of water ($\delta = 47.8$ MPa$^{1/2}$),[30] polymerization of patchy micelles was also initiated (Figure S7).

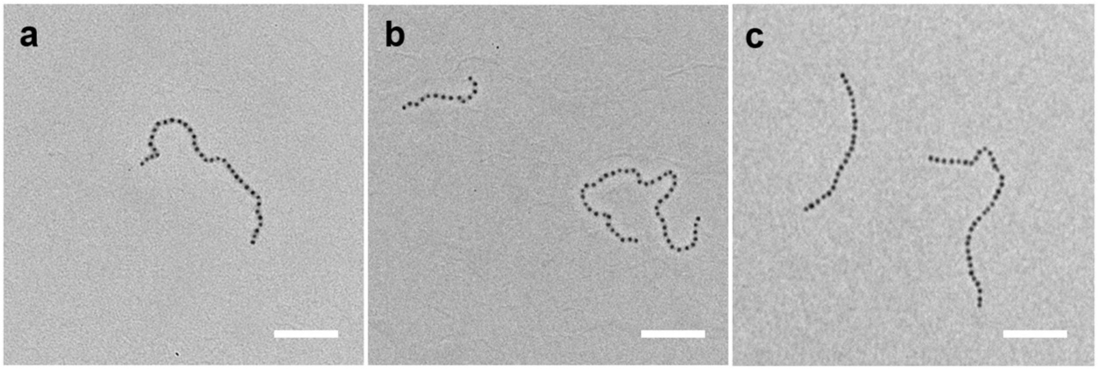


Figure S6. TEM images after 12 h supracolloidal polymerization of patchy micelles of PS(51k)-*b*-P4VP(18k) by adding different amounts of water: (a) 12.5 wt%; (b) 20.0 wt%; (c) 27.5 wt%. The P4VP block was stained with I_2. The scales bars are 300 nm.

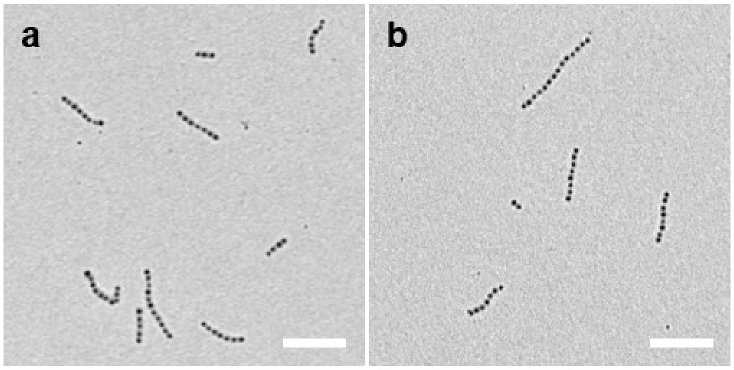


Figure S7. TEM image after 12 h supracolloidal polymerization of patchy micelles of PS(51k)-b-P4VP(18k) by adding 12.5 wt% polar solvent instead of water: (a) methanol; (b) ethylene glycol. The P4VP block was stained with I_2. The scales bars are 300 nm.

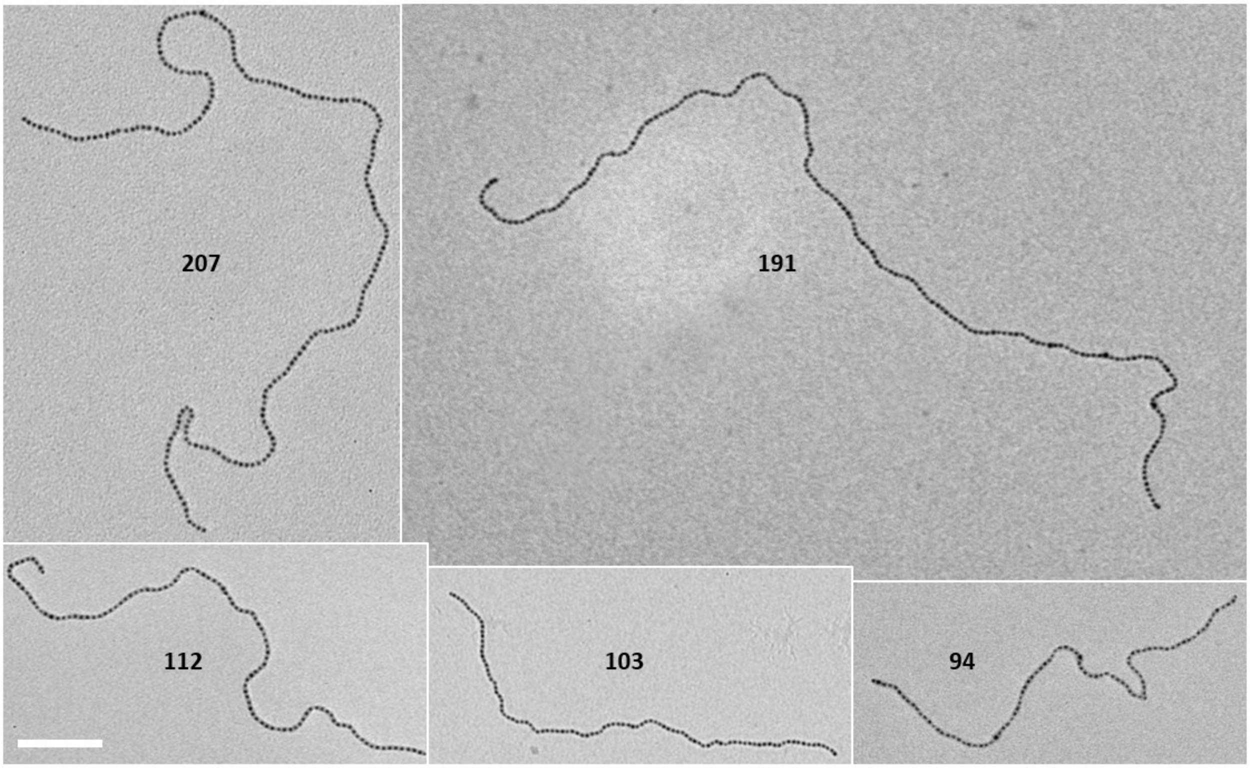


Figure S8. TEM images of long linear supracolloidal chains of bifunctional micelles with various DPs. The number with each chain is the DP of the chain. The scale bar is 500 nm.

It is noted that supracolloidal polymerization of bifunctional micelles apparently followed the kinetics of catalyzed step-growth polymerization,[22] i.e., a linear increase of the size with respect to the polymerization time, when dynamic light scattering measurements were employed (Figure S9). To confirm the kinetics, however, precise analysis on time-dependent DPs of chains in TEM images is necessary, which is one of our current research topics.

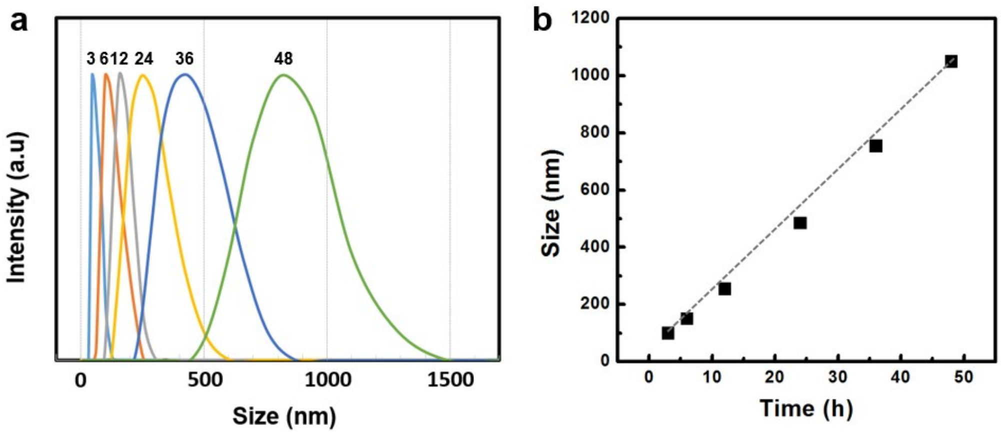


Figure S9. (a) Size distributions of supracolloidal chains of bifunctional micelles of PS(51k)-*b*-P4VP(18k) after various polymerization hours; (b) Linear dependence of the size on the polymerization time.