

Expanding Morphology Library of Block Copolymer Self-Assemblies with Clews of Tubules

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Experimental

Materials. Azobisisobutyronitrile (AIBN, Aladdin-reagent, 98%) was recrystallized in methanol. Styrene (St, Sinopharm, AR grade) was purified by passing it through a neutral alumina column, followed by distillation under reduced pressure. THF was distilled from Na/benzophenone prior to use. Small molecular and macromolecular chain transfer agents, S-1-dodecyl-S-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate (TC) and poly(4-vinylpyridine) (P4VP-TC) were reported previously ($M_{n,NMR} = 10\ 400\ \text{g mol}^{-1}$, $DP_{NMR} = 96$, $D_{GPC} = 1.08$).¹ Methanol (Aladdin-reagent, HPLC grade) and all other solvents were used without further purification.

Synthesis of P4VP-*b*-PS block copolymers via reversible addition-fragmentation transfer polymerization induced self-assembly (RAFT PISA). According to literature, typical RAFT PISA procedures are as follows.² P4VP-TC (20.8 mg, 2 μmol ; or 13.0 mg, 1.25 μmol), St (1.04 g, 10 mmol), AIBN (32.8 μg , 0.2 μmol ; or 20.5 μg , 0.125 μmol ; i.e., 3.3 μL or 2.1 μL of freshly prepared 10 mg/mL AIBN stock solution in methanol) and methanol (1.0 mL) were added into 5 mL glass polymerization tubes separately with a magnetic bar, followed by three freeze-pump-thaw cycles. After being sealed under vacuum, the polymerization tubes were placed in an oil bath at 80 °C for 24 hours. Then the polymerization was quenched in ice-water. Morphologies by RAFT PISA were frozen by pouring 10 μL polymerization solution into 1 mL methanol. Block copolymers were obtained by dissolving in THF firstly and then by pouring the polymer solution into excess petroleum ether while stirring. Polymer powders were collected by filtration, and then dried in a vacuum oven at room

temperature overnight.

Self-assembly of P4VP-*b*-PS block copolymers in methanol. According to literature, typical block copolymer self-assembly procedures are as follows.² Block copolymers were dissolved in co-solvent THF firstly to reach a concentration at 10 mg/mL overnight. Then, 9.0 mL selective solvent methanol was added dropwise to 1.0 mL polymer/THF solution by using syringe pump at a rate of 1.0 mL/hour. The morphologies of assemblies for TEM observation were frozen by pouring assemblies solution into excessive methanol (ten folds) under vigorous stirring, according to literatures.³ Then samples were deposited on copper grids immediately after sample preparation.

Dissipative particle dynamics (DPD) simulations. The DPD method which was firstly developed by Hoogerbrugge and Koelman,⁴ and successfully applied by Groot and Warren,⁵ is adopted in our present work. In DPD, a block or cluster of atoms are grouped into a single coarse-grained bead and the motion of all beads in the system obeys Newton's equations of motion.⁵ The time integration of motion equations is done by a modified velocity-Verlet algorithm with $\lambda = 0.65$ and time step $\Delta t = 0.04$.

In general, the force exerted on a bead i ; namely, f_i , consists of e three nonbonded forces acting between a pair of beads (conservative repulsive forces F_{ij}^C , dissipative forces F_{ij}^D and random forces F_{ij}^R) and two bonded interactions (the spring force F_{ij}^S and angle force F^A). f_i can be written as(25)

$$f_i = \sum_{j \neq i} (F_{ij}^C + F_{ij}^D + F_{ij}^R) + F_{ij}^S + F^A$$

The conservative repulsive force represents excluded volume, usually follows(24)

$$F_{ij}^C = a_{ij} \sqrt{\omega(r_{ij})} r_{ij}$$

Where $\alpha_{ij} = \alpha_{ji} > 0$, indicating that this force is always repulsive, r_{ij} is the distance between beads i and j , and \mathbf{e}_{ij} is the unit vector $(\mathbf{r}_i - \mathbf{r}_j)/r_{ij}$. The function $\omega(r_{ij})$ determines the radial dependence of the force; the function is continuous, positive for $r_{ij} < r_c$ and zero for $r_{ij} \geq r_c$, where r_c is cut-off radius. DPD uses a simple linear weight function for the conservative force: $\omega(r_{ij}) = 1 - (r_{ij} / r_c)$ for $r_{ij} < r_c$.(25)

The dissipative forces F_{ij}^D is a friction force, proportional to the velocity with which two beads approach each other, given by

$$F_{ij}^D = -\gamma\omega^D(r_{ij})(\mathbf{r}_{ij} \cdot \mathbf{v}_{ij})\mathbf{r}_{ij}$$

The random forces F_{ij}^R is defined by

$$F_{ij}^R = \sigma\omega^R(r_{ij})\theta_{ij}\mathbf{r}_{ij}$$

where \mathbf{v}_{ij} is defined as $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, γ is the friction factor, σ is the noise amplitude, $\omega^D(r_{ij})$ and $\omega^R(r_{ij})$ are r -dependent weight functions vanishing for $r > r_c$ that describe the range of the dissipative and random forces, and θ_{ij} is a randomly fluctuating variable with Gaussian statistics:

$$\langle \theta_{ij}(t) \rangle = 0; \langle \theta_{ij}(t)\theta_{kl}(t') \rangle = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t - t')$$

To obey the fluctuation–dissipation theorem, only one of $\omega^D(r_{ij})$ and $\omega^R(r_{ij})$ can be chosen arbitrarily and the other one is then fixed by the relation

$$\omega^R(r_{ij}) = [\omega^D(r_{ij})]^2 = \omega(r_{ij})$$

and the system temperature is determined from the relation between σ and γ , $\frac{\sigma^2}{\gamma} = 2k_B T$, where k_B is the Boltzmann constant. The values of γ and σ were set to be 4.5 and 3.0 in our simulations.

The bonded interactions are the spring force F_{ij}^S and angle force F^A . F_{ij}^S is given by

$$F_{ij}^S = C(1 - r_{ij}/r_{eq})\mathbf{r}_{ij}$$

and F^A is given by

$$F^A = -\nabla[k_\theta(\theta - \pi)^2]$$

In this work, the spring constants $C = 100$, angle constant $k_\theta = 50$, and the equilibrium bond distance r_{eq} is set as 0.7.

To investigate the effect of solvophobic block length of P4VP-*b*-PS copolymer system on self-assembled aggregations, three DPD models of BCPs with different block length were conducted (Figure S7). The red bead represents solvophilic P4VP

block, and the green beads represent the solvophobic PS block. Our simulations were carried out in a $30 \times 30 \times 30$ cubic box with periodic boundary conditions applied in three directions. The number of beads in box was fixed as 81000. In our simulation, the units of mass, distance, time and energy are scaled by the bead mass m , cut off r_c , time τ , and $k_B T$, respectively. The values of γ and σ were set to be 4.5 and 3.0. And τ is represented by $\tau = (mr_c^2/k_B T)^{1/2}$. The time step Δt , the bead mass m , the temperature $k_B T$ and the cut-off radius r_c were chosen as 1.0, 1.0, 0.04 and 1, respectively. Thus, the time unit was $\tau = \sqrt{mr_c^2/k_B T} = 1.0$. Real value of τ can be estimated by matching the simulated lateral diffusion coefficient to the experimental measured value. The repulsive parameters between solvophilic bead A, solvophobic bead B and solvent bead S are set as follows: $\alpha_{AA} = \alpha_{BB} = \alpha_{SS} = \alpha_{AS} = 25$, $\alpha_{AB} = \alpha_{BS} = 60$. Each simulation was carried out for at least 10^6 steps to achieve an equilibrium state.

Characterizations.

Nuclear Magnetic Resonance (NMR) Spectra. The ^1H NMR measurements were performed on Bruker DMX300 spectrometer in CDCl_3 using tetramethylsilane as an internal reference.

Gel permeation chromatography (GPC). The molecular weight and molecular weight distribution were determined on a Waters 150C gel permeation chromatography (GPC) equipped with three ultrastyrigel columns (500, 10^3 , 10^4Å) in series and RI 2414 detector at $30 \text{ }^\circ\text{C}$, and THF was used as eluent at a flow rate of 1.0 mL/min. Monodispersed polystyrene standards were used in the calibration of molecular weight and molecular weight distribution.

Field emission scanning electron microscopy (FESEM). The FESEM images were measured on a JEOL JSM-6700F. The samples were prepared by placing a drop of the polymer solution in methanol on copper grids, and gilding a shell of Pt nano-particle. The pore sizes of clews of tubules were determined by measuring 50 pores from SEM images. Errors were calculated by using standard deviation function of these measured value.

Transmission Electron Microscopy. The transmission electron microscope (TEM) observations were performed on a Hitachi H-800 TEM at an accelerating voltage of 200 kV. The samples for TEM observations were prepared by depositing a drop of the polymer solution in methanol on copper grids. The wall thickness and diameter of tubular structures were determined by measuring 50 cross-sections from the TEM images. Errors were calculated by using standard deviation function of these measured value.

References.

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4. P. J. Hoogerbrugge and J. M. V. A. Koelman, *Europhys. Lett.*, 1992, **19**, 155-160.
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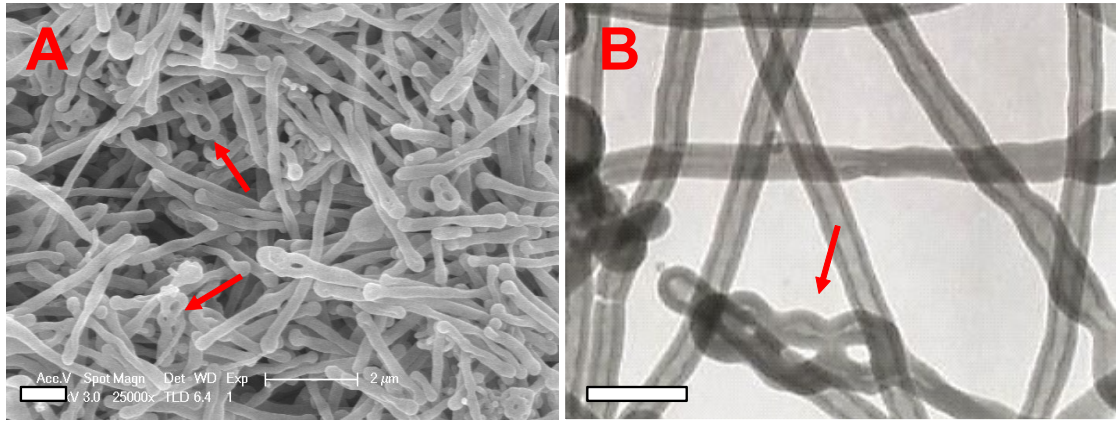


Figure S1 A) SEM and B) TEM results of P4VP₉₆-*b*-PS₁₈₃₄ self-assemblies formed by BCP self-assembly in methanol. Starting BCP concentration is 10 mg/mL. Scale bar is 1 μm for all.

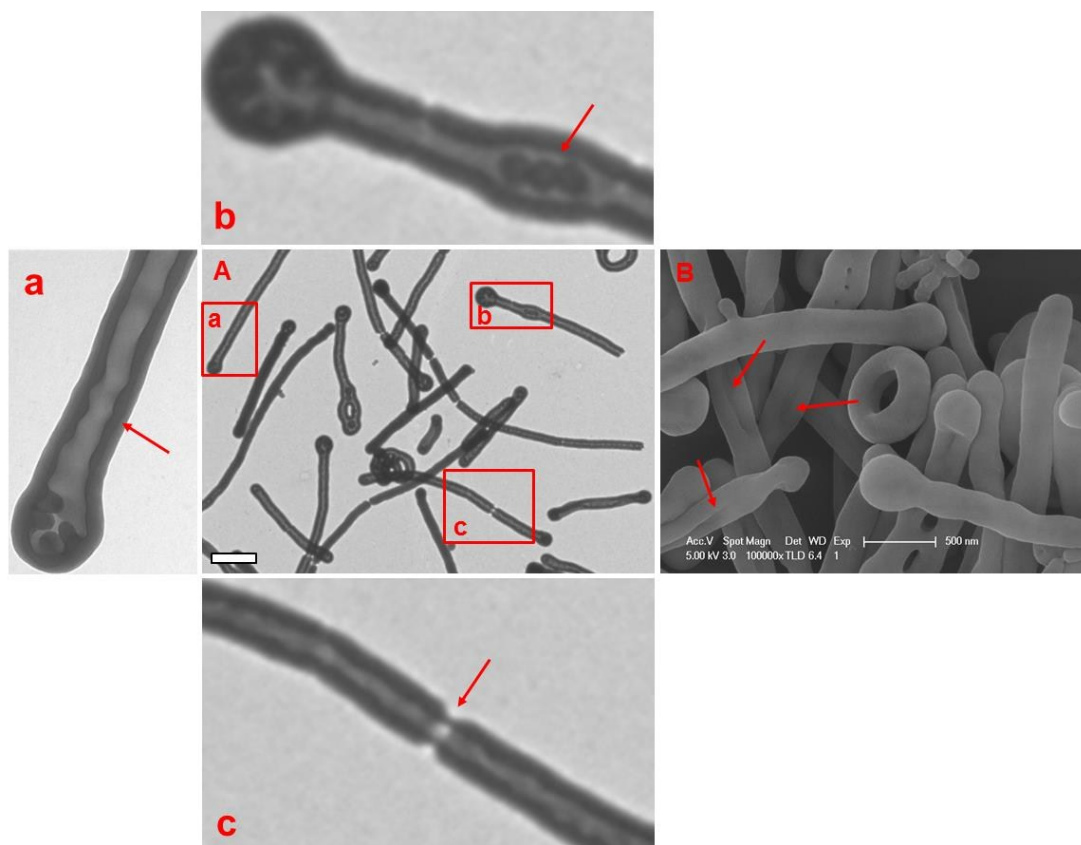


Figure S2. TEM (A) and SEM (B) results of P4VP₉₆-*b*-PS₁₈₃₄ self-assemblies formed by BCP self-assembly in methanol, where a), b) and c) are enlarged areas indicated by red boxes a, b and c respectively. Starting BCP concentration is 10 mg/mL. Scale bar is 1 μ m. Tubular structure formation was confirmed by red arrows.

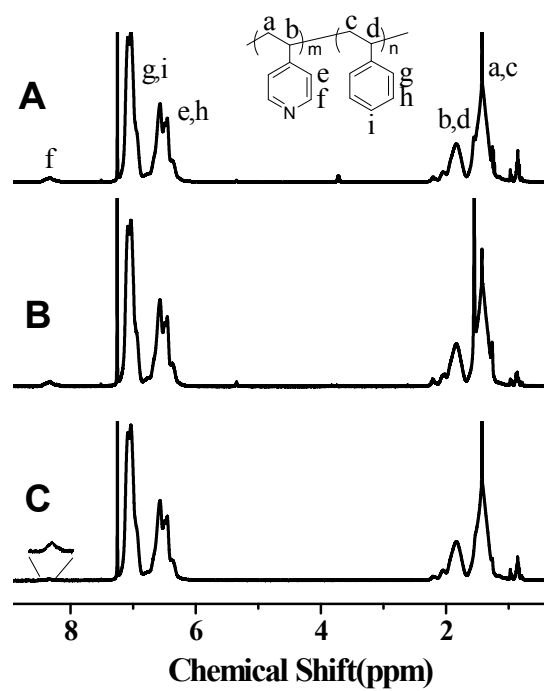


Figure S3. ^1H NMR spectra of A) $\text{P4VP}_{96}\text{-}b\text{-PS}_{1834}$, B) $\text{P4VP}_{96}\text{-}b\text{-PS}_{2681}$ and C) $\text{P4VP}_{96}\text{-}b\text{-PS}_{3469}$.

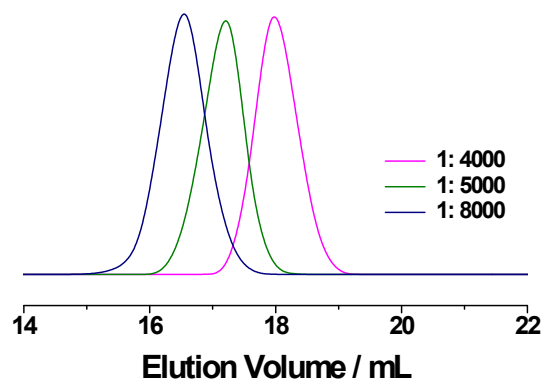


Figure S4. GPC curves of P4VP-*b*-PS block copolymers prepared by RAFT PISR of styrene (St) with P4VP-TC/St(1.04 g) = 1: X in methanol (1.0 mL) at 80°C for 24 h.

Table S1 Data for P4VP-*b*-PS via RAFT PISA and morphologies obtained via RAFT PISA and BCP self-assembly in methanol

N	Feed ratio	Conversion	DP _{P4}	DP _P	P4VP%	M _{n,NMR}	M _{n,GPC}	M _w /M _n	Morphology ^d	Morphology ^e
o.	^a	(%)	VP	S	^b	(kDa) ^b	(kDa) ^c	_n ^c		
1	1: 4000: 0.1	48	96	183 4	4.97%	201	175	1.25	vesicles	tubules
2	1: 5000: 0.1	56	96	268 1	3.46%	289	259	1.24	fused vesicles	loose clews of tubules
3	1: 8000: 0.1	45	96	346 9	2.69%	371	353	1.26	large compound vesicles	tight clews of tubules

^a Feed ratio of P4VP-TC: St: AIBN. ^b Calculated from the ¹H NMR spectra. ^c Measured by GPC. ^d Obtained via RAFT PISA. ^e Obtained via BCP self-assembly.

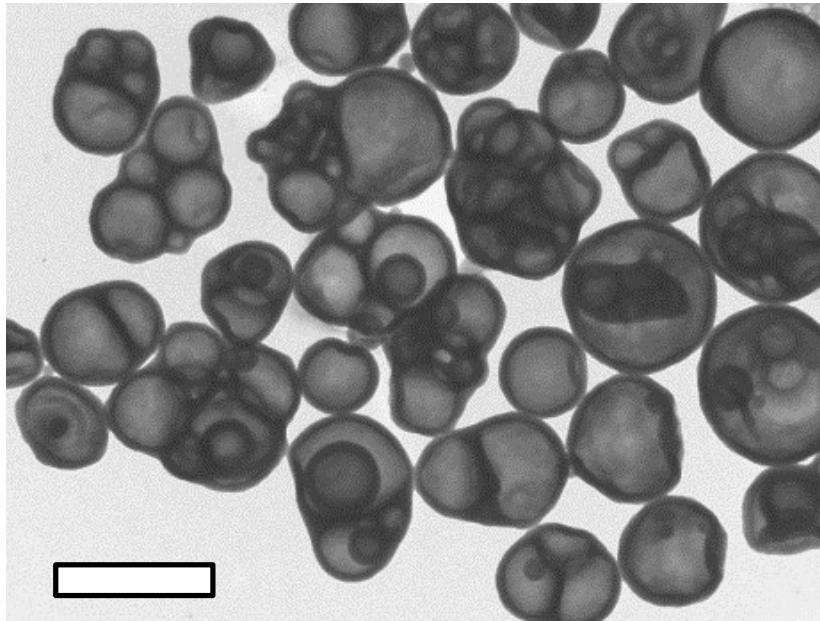


Figure S5. TEM result of morphologies formed by RAFT PISA technique with feed ratio of P4VP: St = 1: 5000. Scale bar is 1 μm .

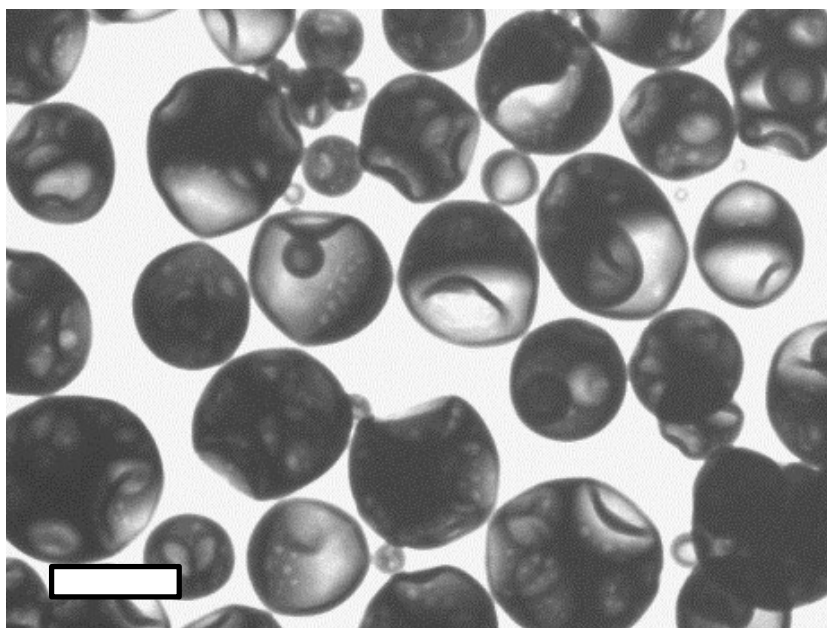


Figure S6. TEM result of morphologies formed by RAFT PISA technique with feed ratio of P4VP: St = 1: 8000. Scale bar is 1 μm .

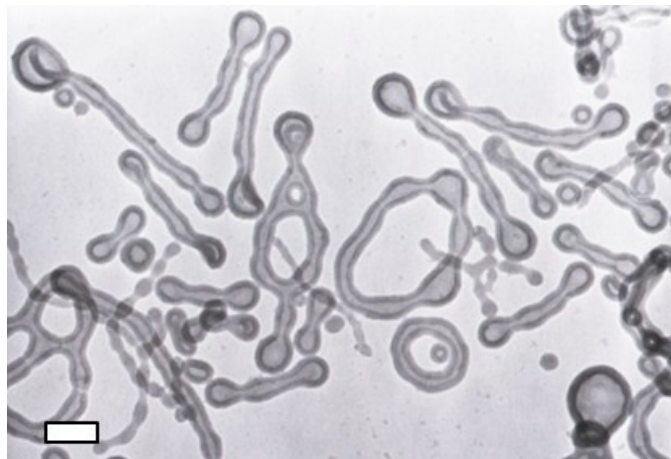
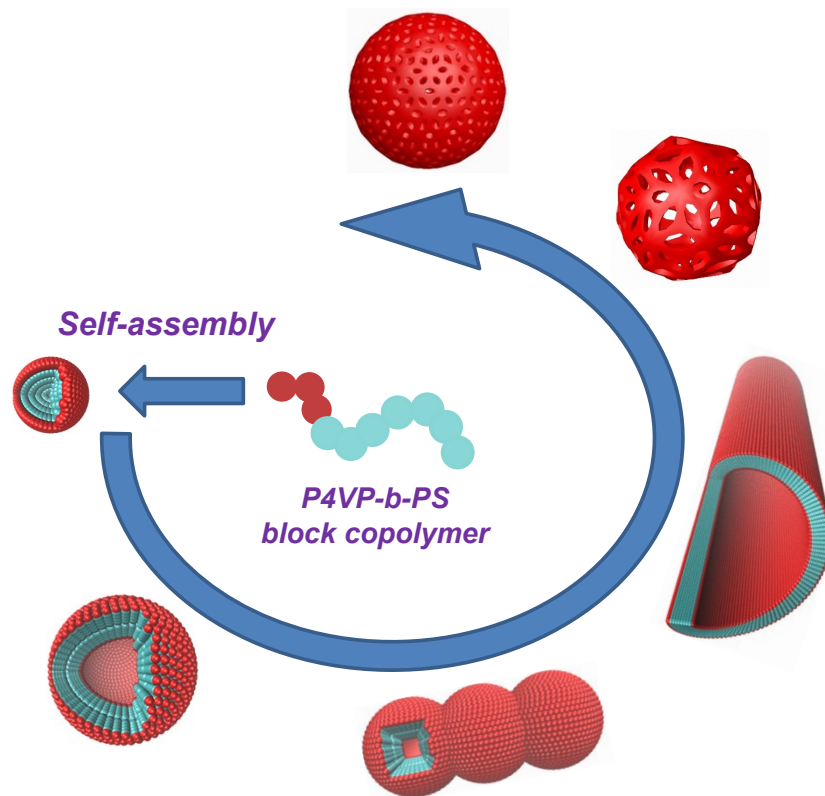


Figure S7. Two-dimensional growth of tubular structure of P4VP₉₆-*b*-PS₃₄₆₉ aggregates formed by BCP self-assembly in methanol. Starting BCP concentration is 10 mg/mL. Scale bar is 1 μ m.



Scheme S1 Illustration of tubular clew morphology evolution upon increasing of methanol content.

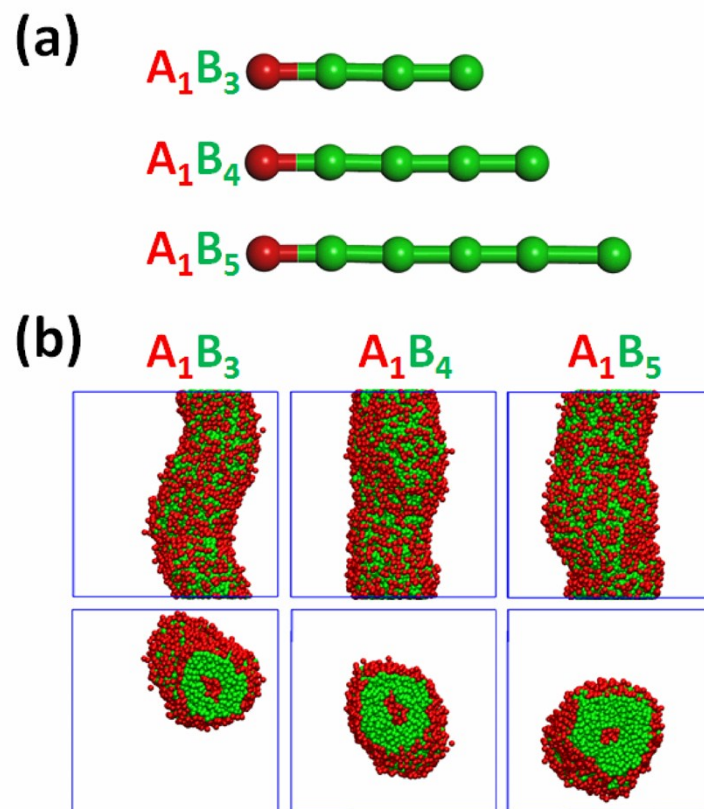


Figure S8. (a) Model of A_mB_n BCPs, the red beads and green beads represent the solvophilic head (A) and solvophobic tail (B), respectively. (b) Snapshots showing the aggregates of A_1B_3 , A_1B_4 and A_1B_5 , the top row and bottom row represent the side view and cross section view of the tube micelle, respectively. A, B, m and n represent P4VP, PS and the number of repeating units of corresponding block, respectively.

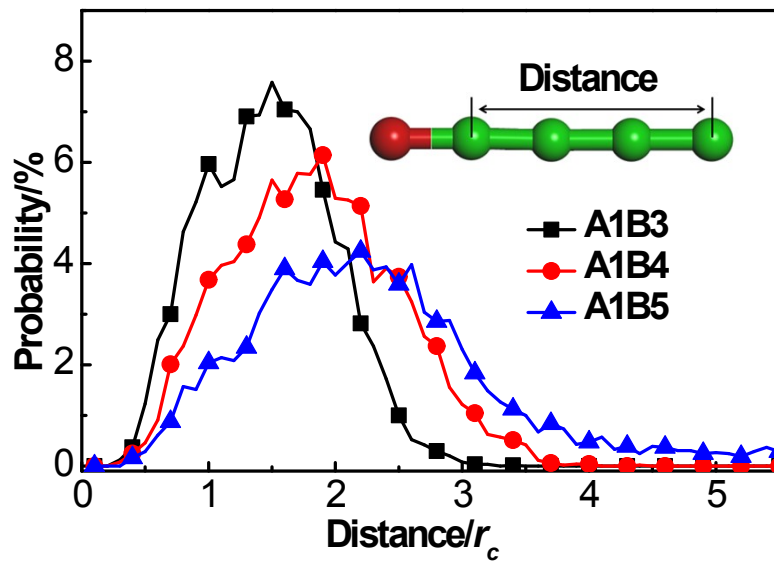


Figure S9. The distributions of end-to-end distance of block B in tubes.

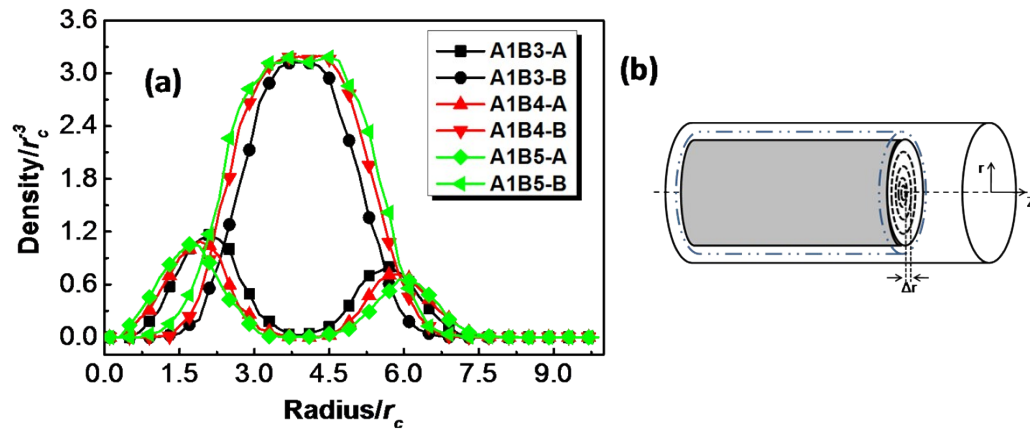


Figure S10. Density profile (a) of solvophilic head (A) and solvophobic tail (B) for A₁B₃, A₁B₄ and A₁B₅ as the function of the radius (r) from the center axis (Z) of tubule as shown in (b).

Table S2 Summary of distributions results of A and B in tubules

Sample	Density of A on outer surface ^a / r_c^{-3}	Density of A on inner surface ^b / r_c^{-3}	Half-high width of B peak ^c / r_c
A ₁ B ₃	0.80	1.08	2.60
A ₁ B ₄	0.72	1.03	3.08
A ₁ B ₅	0.65	0.95	3.28

- a. Calculated by second intersection point of A curve and B curve in Figure S10.
- b. Calculated by first intersection point of A curve and B curve in Figure S10.
- c. Obtained from peak of B in Figure S10.