

Supporting Information

Supracolloidal Polymer Chains of Diblock Copolymer Micelles

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Experimental Section

Cross-linked PS-P4VP micelles

Diblock copolymers of polystyrene-poly(4-vinylpyridine), PS(51)-P4VP(18) and PS(25)-P4VP(7), were purchased from Polymer Source, Inc. The number in the parenthesis is a number average molecular weight in kg/mol. The polydispersity index (PDI) is 1.15 for PS(51)-P4VP(18) and 1.10 for PS(25)-P4VP(7). We first dissolved PS-P4VP copolymers in chloroform, which is a co-solvent for both PS and P4VP blocks, to yield a 0.2 wt% solution. Then, we added toluene, which is a selective solvent for the PS block, to the solution with stirring until the weight ratio of toluene to chloroform reached to 0.2. After mixing, chloroform was completely evaporated at 80 °C to obtain a 1.0 wt% toluene solution of PS-P4VP micelles. For cross-linking the P4VP core, 1,4-dibromobutane (DBB) was added to the micellar solution with a molar ratio of DBB to 4VP equal to 0.5 which can fully quaternize the 4VP units in the copolymer, followed by stirring at 45 °C for 48 hr. The same procedure was applied to both PS(51)-P4VP(18) and PS(25)-P4VP(7).

Colloidal monomers of PS-P4VP micelles

To produce colloidal monomers, we changed the polarity of the solvent by adding DMF to a 1.0 wt% toluene solution of cross-linked PS-P4VP micelles with 100 times of DMF to toluene in weight, resulting in a 0.01 wt% solution of colloidal monomers of PS-P4VP micelles with the reorganized corona of two PS patches. The same condition was used for PS(51)-P4VP(18) and PS(25)-P4VP(7).

Supracolloidal polymers of colloidal monomers of PS-P4VP micelles

We further increased the polarity of the solvent to synthesize supracolloidal polymer chains from colloidal monomers of PS(51)-P4VP(18) micelles by dropping a mixture of DI water and DMF (20 wt% water) to yield 10 wt% water in the final solution. The solution was kept without stirring at room temperature for 48 hr. For PS(25)-P4VP(7), a mixture of water and DMF containing 30 wt% water was dropped to yield 15 wt% water in the final solution.

Supracolloidal random and block copolymers

For supracolloidal random copolymerization, two colloidal monomer solutions of PS(51)-P4VP(18) and PS(25)-P4VP(7) were mixed in the same weight. Then, a mixture of water and DMF (30 wt% water) was dropped into the solution to obtain 15 wt% water in the final solution. The solution was kept without stirring at room temperature for 24 hr. To synthesize supracolloidal block copolymers, we first prepared two homopolymer chains of colloidal monomers of PS(51)-P4VP(18) and PS(25)-P4VP(7) for 24 hr polymerization as described above. But both solutions had 15 wt% water. Then, we mixed two solutions of supracolloidal homopolymers of PS(51)-P4VP(18) and PS(25)-P4VP(7) in the same weight. The mixed solution was kept without stirring at room temperature for additional 24 hr.

Characterization

Transmission electron microscopy (TEM) was performed on a Hitachi H-7600 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 I₂ vapor for staining the P4VP block. Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet iS10 FT-IR Spectrometer (Thermo Scientific). Dynamic light scattering (DLS) was carried out with a Zetasizer Nano-S Instrument (Malvern Instruments) at the fixed scattering angle of 173°.

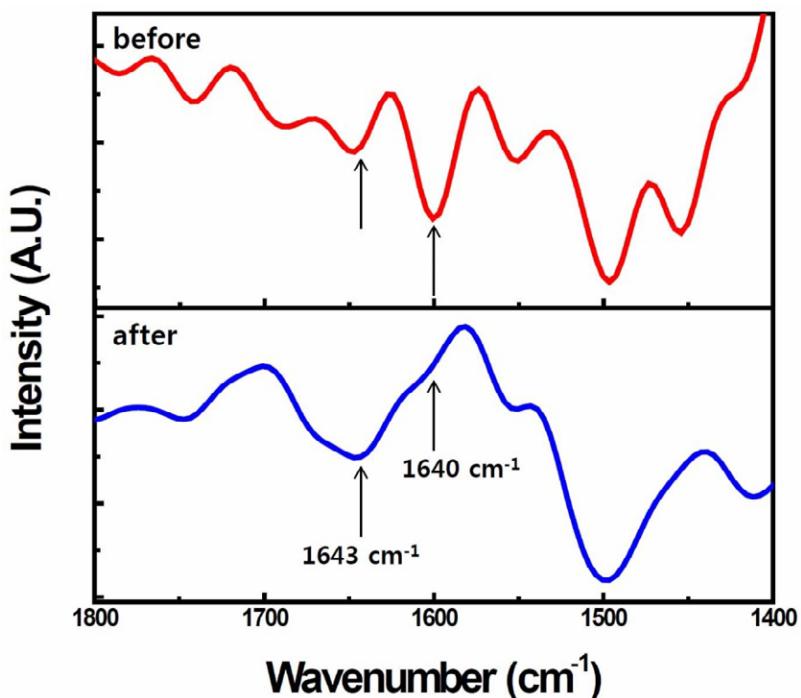


Figure S1. FT-IR spectra of PS(51)-P4VP(18) micelles before and after cross-linking by DBB with a molar ratios of DBB to 4VP equal to 0.5. The bands at 1600 cm^{-1} and 1643 cm^{-1} correspond to 4VP and quaternized 4VP, respectively.

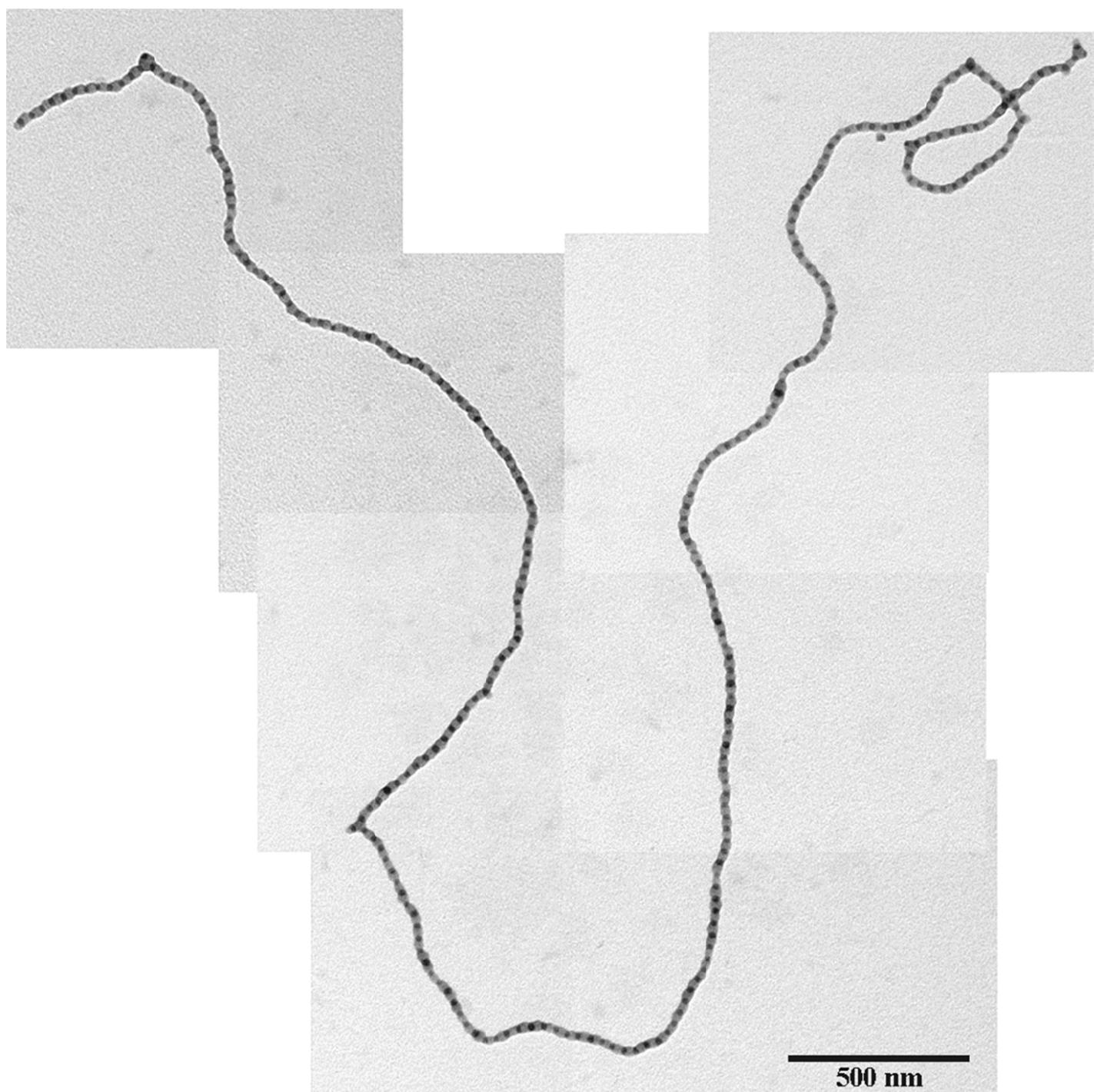


Figure S2. TEM image of a supracolloidal polymer chain of PS(51)-P4VP(18) colloidal monomers shown in the inset of Figure 1c.

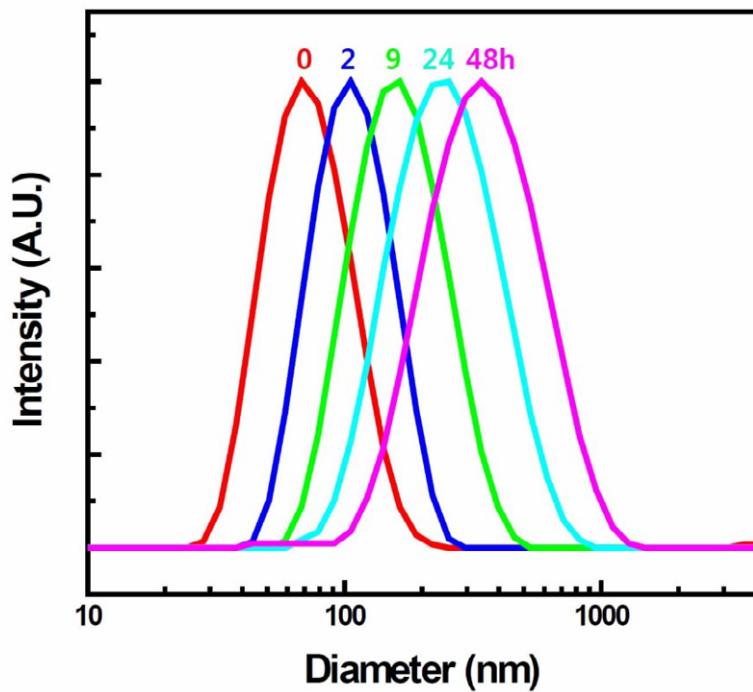


Figure S3. A change of colloidal diameters as polymerization of PS(51)-P4VP(18) colloidal monomers by DLS measurements. The maximum intensities after 0, 2, 9, 24, and 48 hr correspond to the diameters of 77, 112, 174, 269, and 387 nm, respectively.

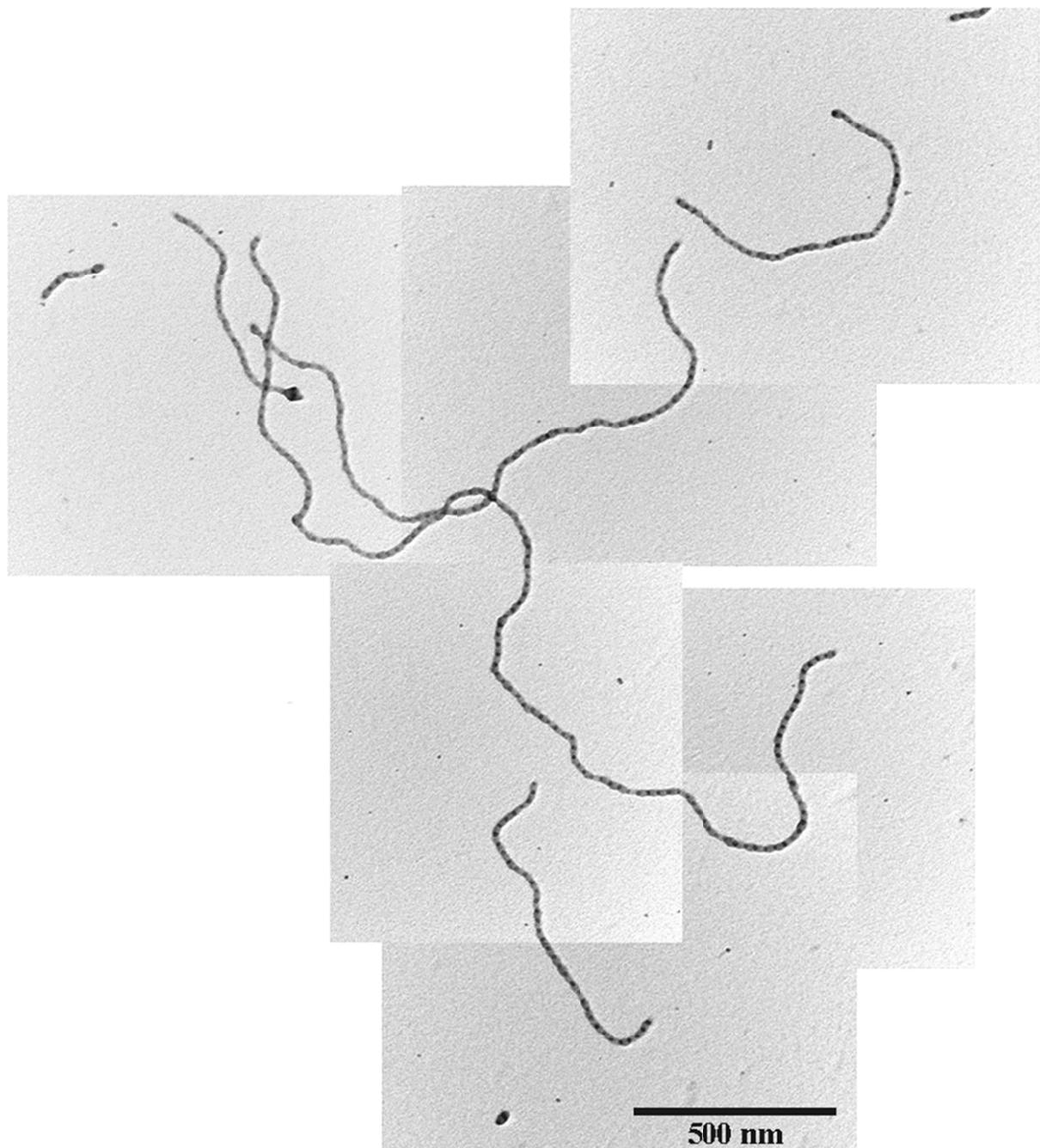


Figure S4. TEM image of supracolloidal polymer chains of PS(25)-P4VP(7) colloidal monomers shown in the inset of Figure 2c.

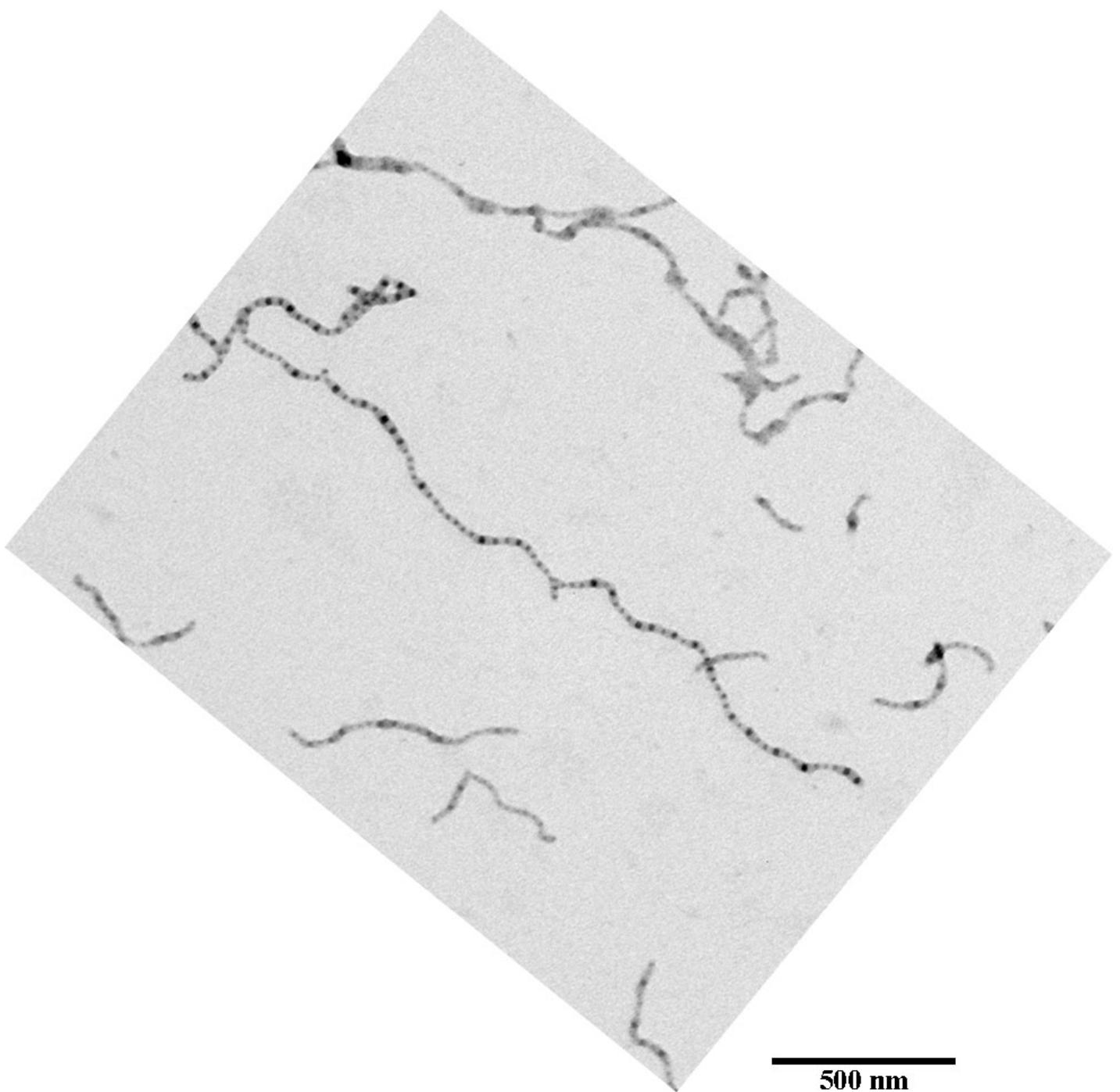


Figure S5. TEM image of supracolloidal random copolymer chains shown in the inset of Figure 3a.

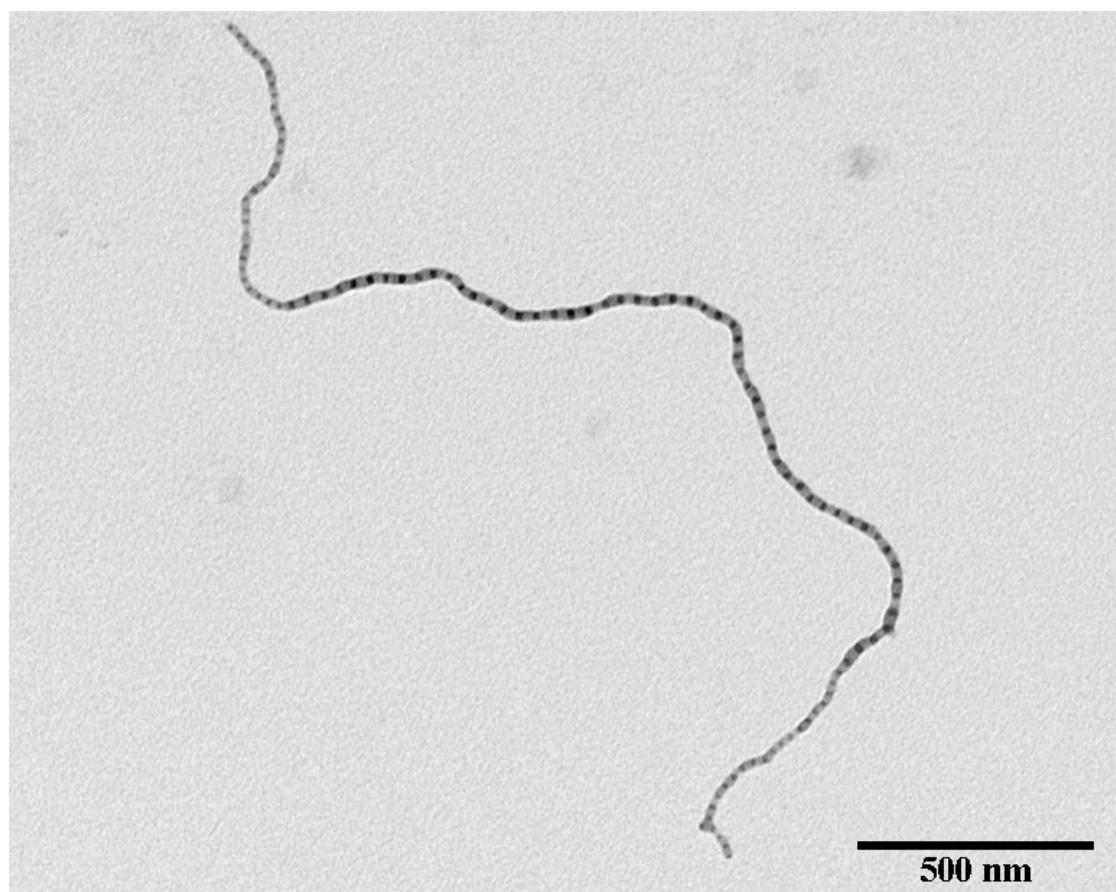


Figure S6. TEM image of a supracolloidal block copolymer chain shown in the inset of Figure 3b.