

Supporting Information:

The solution concentrations and operating parameters for different block copolymers in the two-fluid electrospinning are listed in Table S1.

solution concentrations		voltage (kV)	plate-to plate distance (cm)	flow rates (ml/min)	
P(MMA- <i>ran</i> -MAA)	BCP's			shell	core
21 wt%	SIS, 18 wt%	31.6	45	0.05	0.005
18 wt%	SI, 18 wt%	30	45	0.05	0.005

Table S1. Solution concentrations and operating parameters of two-fluid electrospinning

To view the internal structures, the fibers were either put on TEM grids or embedded in epoxy resin (LR White-Medium Grade, Ladd Research) and microtomed at room temperature or -100 °C into 50-100 nm thick sections. The samples were then stained with osmium tetroxide (OsO₄) vapor for 1-2 hours and examined using TEM (JEOL JEM200 CX or JOEL 2010F with a Gatan imaging filter).

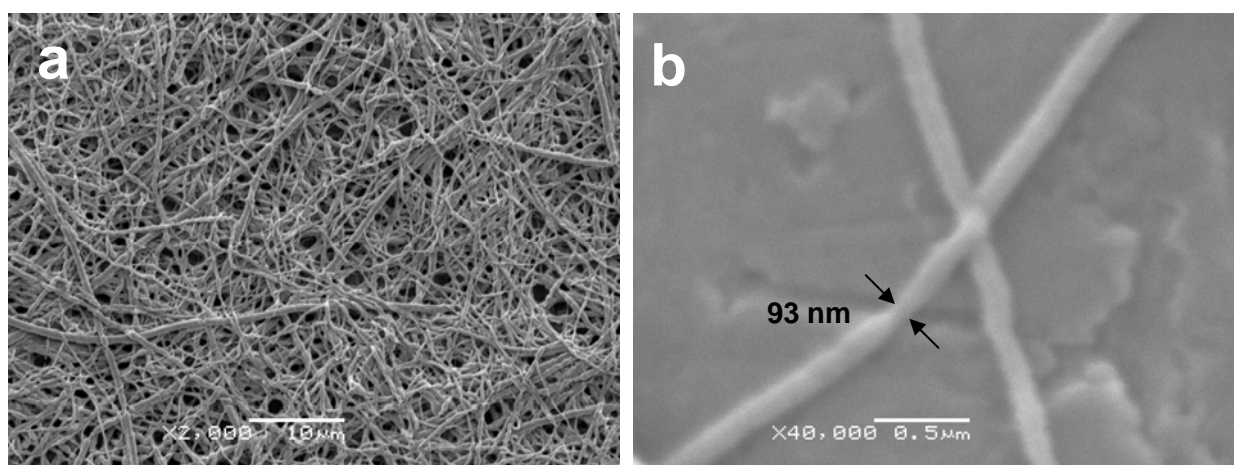


Figure S1. SEM images of the SIS core fibers after annealing and selective dissolution of the P(MMA-*ran*-MAA) shell using methanol. For comparison, see Figure 1 of manuscript, where the same fibers are shown to have a core diameter of approximately 100 nm, consistent with Figure S1(b), and a shell diameter of approximately 500 nm. (Scale bars in a and b are 10 μm and 500 nm,

respectively.)

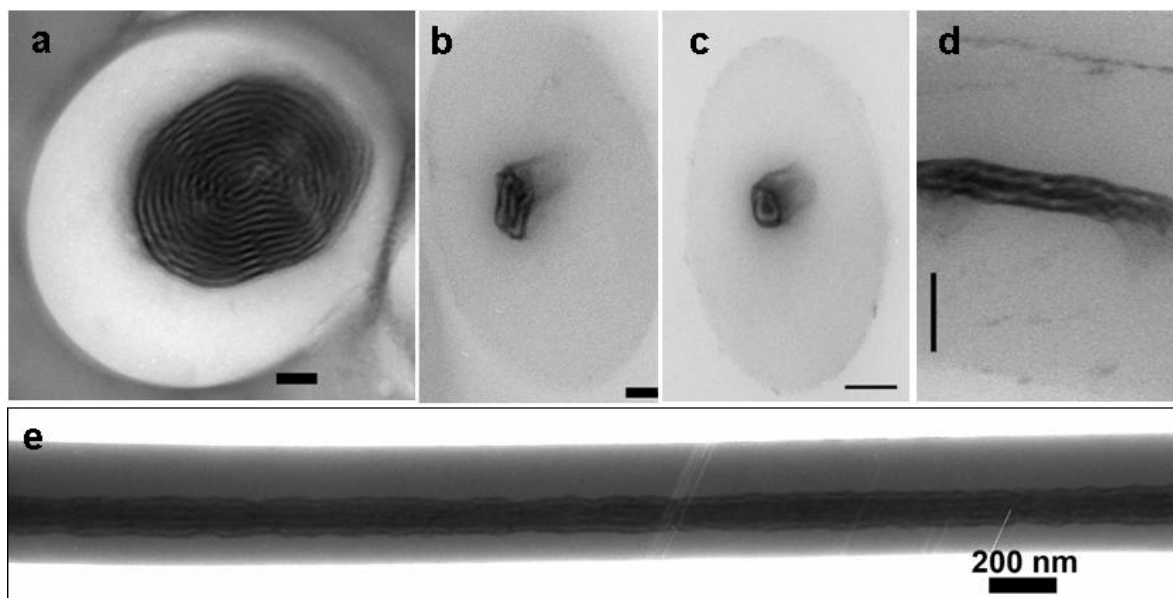


Figure S2. TEM images of annealed P(MMA-*ran*-MAA)/SIS fibers showing both core-shell structures and internal structures in the SIS BCP cores. (Scale bars in a-d are 100 nm.)

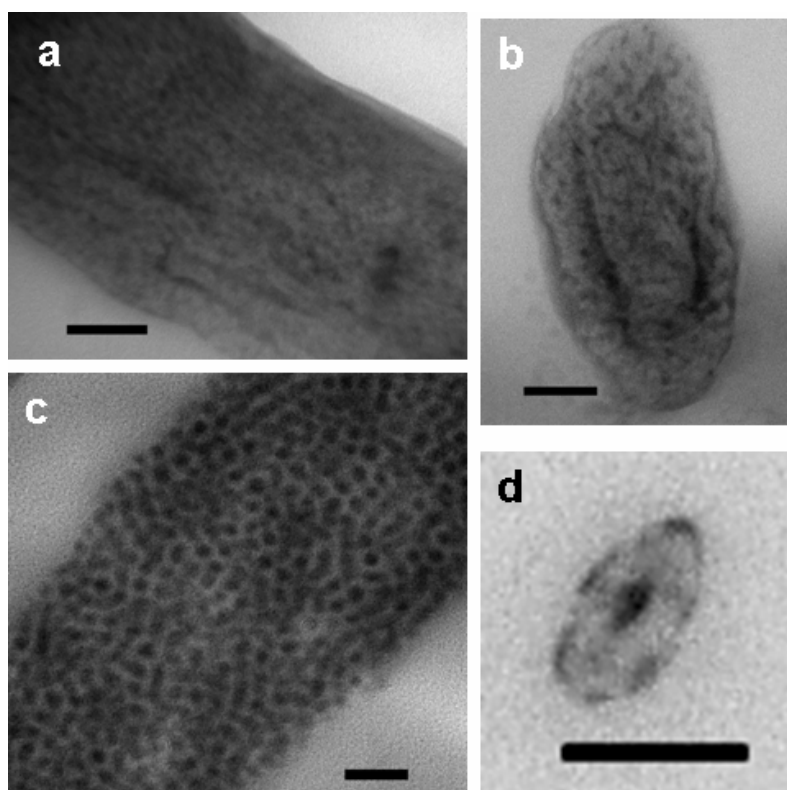


Figure S3. TEM images of the sphere-forming SI BCP in as-spun fibers (a and b) and in annealed fibers (c and d); a and c are longitudinal views; b and d are axial view. (Scale bars: 100 nm)