Electronic Supporting Information for:

Enhancing Covalent Mechanochemistry in Bulk Polymers Using Electrospun ABA Triblock Copolymers

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Small Angle X-ray Scattering (SAXS)

SAXS patterns were acquired at ambient temperature at the Sector 12-ID-B beamline (Sector 12) at the Advanced Photon Source at Argonne National Lab (Argonne, IL), using a beam energy of 12 keV (λ = 1.034 Å) with a sample-to-detector distance of 2.028 m that was calibrated against a silver behenate standard sample (d = 58.37 Å). A Pilatus 2M detector (25.4 cm x 28.9 cm) with 1475 x 1697 pixel resolution was used to collect 2D-XRD patterns (typical exposure times ~1 s). 2D XRD patterns were azimuthally-integrated to produce $q^2I(q)$ *v.* q Kratky plots of the SAXS.

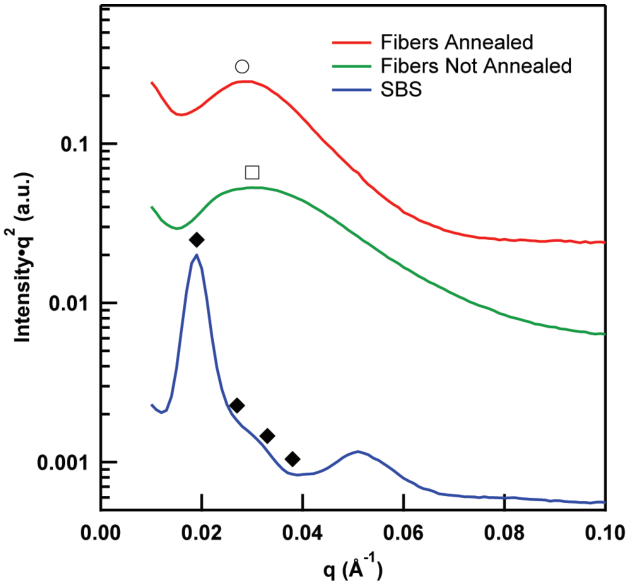

Figure S1. Small-angle X-ray scattering Kratky plot of of $q^2I(q)$ v. q of annealed fibers of modified SBS, non-annealed fibers of modified SBS, and a film of as-received SBS for comparison. The modified SBS fibers exhibit only a broad scattering peak typical of a disordered morphology. These scattering maxima occur at q = 0.028 Å^{-1} (d = 22.4 nm) and q = 0.030 Å^{-1} (d = 20.9 nm) (open symbols) for the annealed and non-annealed fibers respectively. The as-received SBS film is shown at the bottom for reference.

Table S2. Summary of morphological characterization by SAXS

Sample	***q**** **(Å^{-1})**	***d*** **(nm)**	**Morphology**
As-received SBS	0.019	33.1	Spheres
Film Annealed	0.029	21.7	Cylinders
Film Non Annealed	0.030	20.9	Cylinders
Fibers Annealed	0.020	31.4	Disordered
Fibers Non Annealed	0.018	34.9	Disordered

Synthetic Details:

In a 2 L round bottom flask, 8.0 g (0.126 moles of butadiene, 1 eq) SBS (Sigma Aldrich, MW = 140 kDa and 30 wt% as reported by supplier) was dissolved in 400 mL $CHCl_2$ before adding 66 mL (0.755 moles, 6 eq) $CHBr_3$ and 4.6 g (0.0126 moles, 0.1 eq) cetyltrimethylammonium bromide and deoxygenating for 30 minutes with bubbling N_2. In a separate flask, 40.2 g (1.01 moles, 8 eq) NaOH was dissolved in 80 mL of deionized H_2O and deoxygenated for 30 minutes with bubbling N_2. The NaOH solution was then added dropwise to the stirring polymer solution via syringe. The reaction was stirred at room temperature under a headspace of N_2 for 21 h and then washed three times with 250 mL DI H_2O and 250 mL brine, and the organic layer was collected via separatory funnel. The organic layer was then concentrated to minimal volume and the polymer was precipitated by pouring the solution into rapidly stirring CH_3OH. The polymer was redissolved in CH_2Cl_2, concentrated, and precipitated twice more in a similar fashion before drying overnight under vacuum. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.091 (b, 1.796 H), 6.558, 6.479 (b, 1.224 H), 5.509, 5.413 (b, 2.00 H). 5.073, 4.982 (b, 0.457 H), 2.165, 2.049 (b, 4.305 H), 1.779, 1.623, 1.460 (b, 9.538 H), 1.136 (b, 1.761 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 145.489, 131.322, 130.357, 129.791, 129.343, 128.148, 127.617, 125.826, 44.066, 40.599, 38.455, 36.715, 33.581, 32.831, 31.513, 27.443, 26.252. M_N = 220 kDa (GPC-MALS), *dn*/*dc* (THF) = 0.122 mL/g.

Mechanical Testing:

Uniaxial tensile tests were performed on a TA Instruments RSA III Dynamic Mechanical Analyzer (Force resolution: 0.0001 N, strain resolution: 1 nm) at Duke University's Shared Material Instrument Facility (SMIF). The applied normal force was divided by the initial cross-sectional area of the films to calculate the stress; no correction for material deformation was applied.