Supporting Information

Experimental methods, scanning electron microscopy (SEM) images of monoaxial PAN fibers and small-angle X-ray scattering (SAXS) analysis of the bulk composite.

Experimental methods

Solution preparation: The block copolymer poly(isoprene-*block*-dimethylaminoethyl methacrylate) (PI–*b*–PDMAEMA) was synthesized as described previously. [47, 33, 49] Gel permeation chromatography (GPC) was used to determine the molecular weight of the first block (polyisoprene, PI) and the polydispersity of the block copolymer. ^{1}H NMR was used to determine the overall molecular weight and composition. The resulting PI-*b*-PDMAEMA polymer had a molecular weight of 31 kg/mol and 33 wt% PDMAEMA with a polydispersity of 1.04. To prepare the core solution, 0.3 g PI-*b*-PDMAEMA block copolymer was dissolved in 0.6 g anhydrous hexane (95%, Sigma-Aldrich, used as received) and PUMVS (KiON Corp) was added in a 1/2 weight ratio to the block copolymer.[37] Dicumyl peroxide (DCP) (98%, Aldrich) was added to the solution to serve as the radical initiator to crosslink the PUMVS.
To prepare the shell solution, 8 wt% PAN (Aldrich), with a molecular weight of 150 kg/mol, was dissolved in DMF. Before electrospinning, a fresh shell solution was prepared by placing the DMF/PAN mixture at 100 °C for 2 hrs under vigorous stirring.

Electrospinning:

Monoaxial electrospinning of PAN fibers. 5, 8, 10 and 15 wt% PAN solutions in DMF were spun monoaxially to find the suitable viscosity for electrospinning. The voltage applied across the spinneret and collector was 20 kV, the distance between the spinneret and collector was 10 cm and the feeding rate was 0.015 ml/min. The 15 wt% PAN solution was too viscous to create non-woven mats. SEM images show that beads are present in the fiber samples made with 5 wt% PAN solution. Fibers made with 8 wt% and 10 wt% PAN solutions were continuous and uniform.

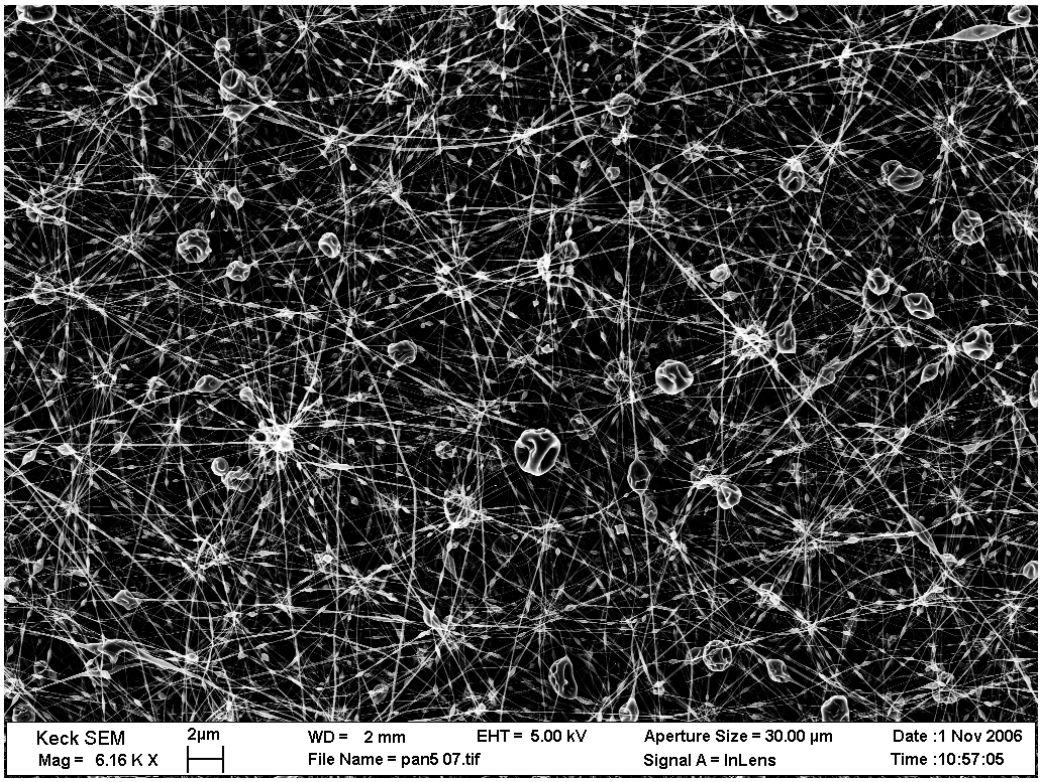

Figure S1: SEM image of electrospun fibers from a 5wt% PAN in DMF solution.

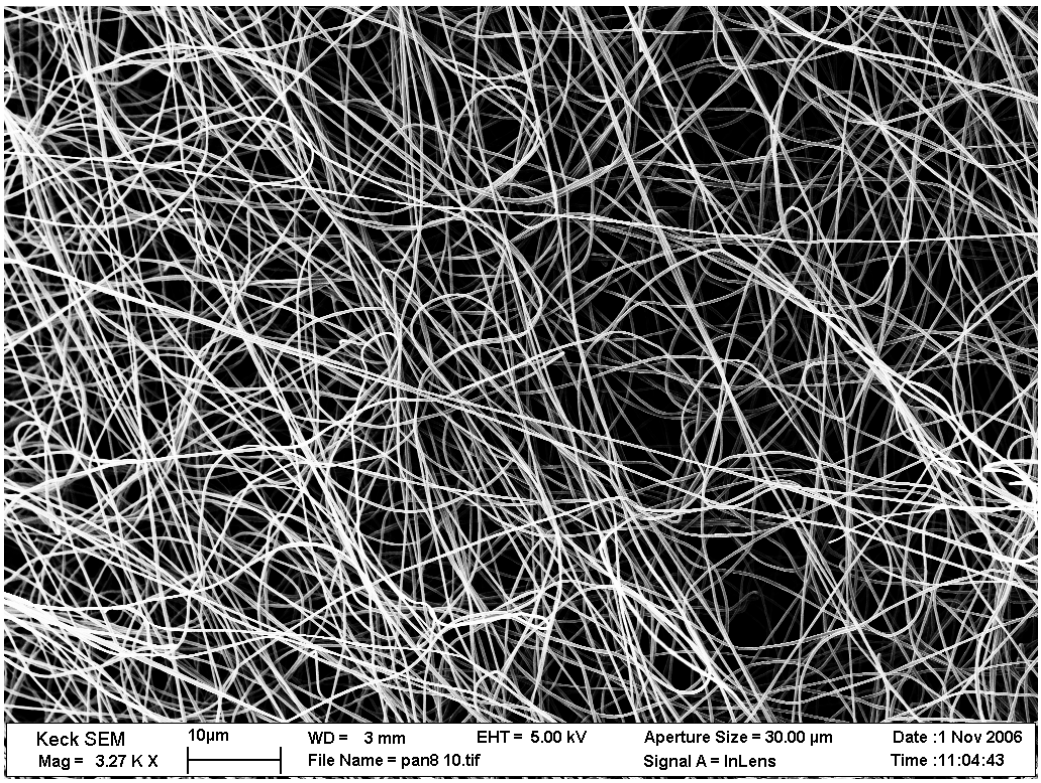

Figure S2: SEM image of electrospun fibers from a 8wt% PAN in DMF solution.

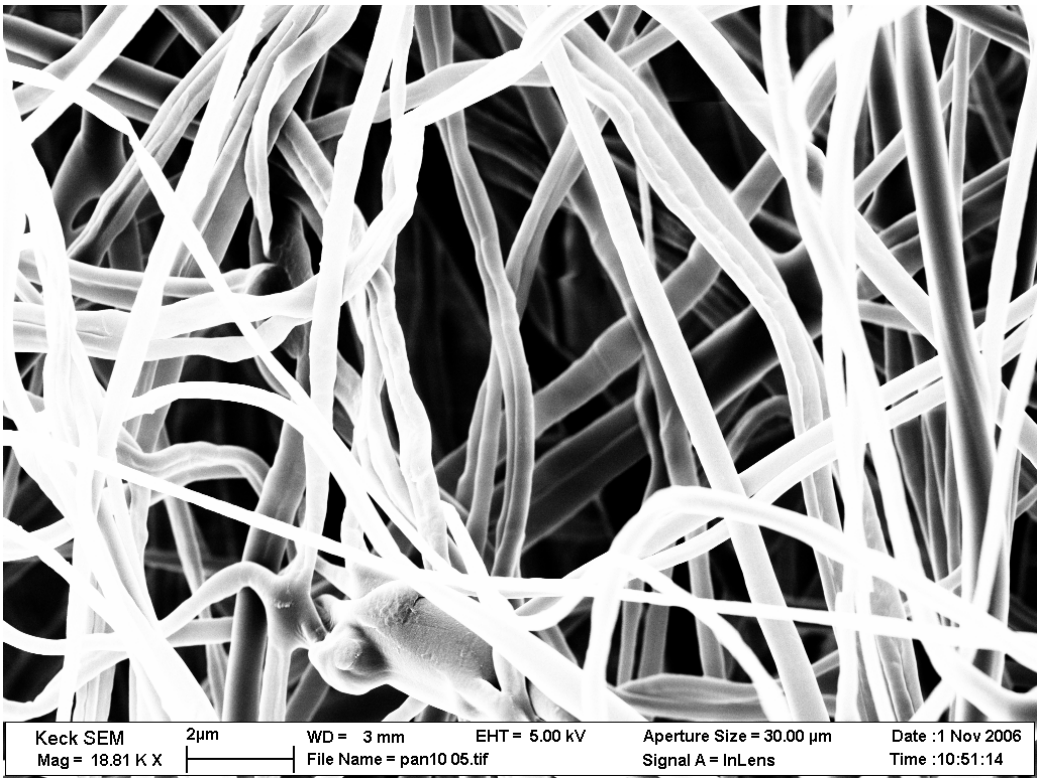

Figure S3: SEM image of electrospun fibers from a 10wt% PAN in DMF solution.

Coaxial electrospinning. Core-shell fibers were spun at room temperature at an electrical potential of 20kV with a distance of 10 cm between the spinneret and collector. A more detailed description of the experimental set-up can be found in ref 43. Flow rates were varied between 0.002 - 0.05 ml/min^{-1} for the core solution and between 0.006 – 0.08 ml/min^{-1} for the shell solution. It was found that all rates up to 0.045 ml/min^{-1} (core) and 0.075 ml/min^{-1} (shell) resulted in homogeneous fibers. The fibers shown here were spun using a flow rate of 0.016 ml/min^{-1} for the core solution and 0.048 ml/min^{-1} for the shell solution. The as-spun fibers were annealed in a vacuum oven at 50 °C for 24 hrs followed by crosslinking the PUMVS at 130 °C for 3 hrs.

Characterization: TEM was performed on a Tecnai T12 operating at 120 kV. Bulk composite samples were cut in 50-100 nm sections using a Leica Ultracut UCT microtome at -60 °C and fibers were embedded in epoxy and microtomed at room temperature. Sample

slices were subsequently transferred to copper grids for analysis. SEM images were obtained with a LEO 1550 field-emission scanning electron microscope after sputtering the films with gold. Small Angle X-Ray Scattering (SAXS) experiments were performed at the Cornell High Energy Synchrotron Source (CHESS). Data were collected with a CCD 2D detector operating at an X-ray energy corresponding to 1.223 Å, sample-to-detector distance of 165.0 cm and exposure times of 1-5 seconds.

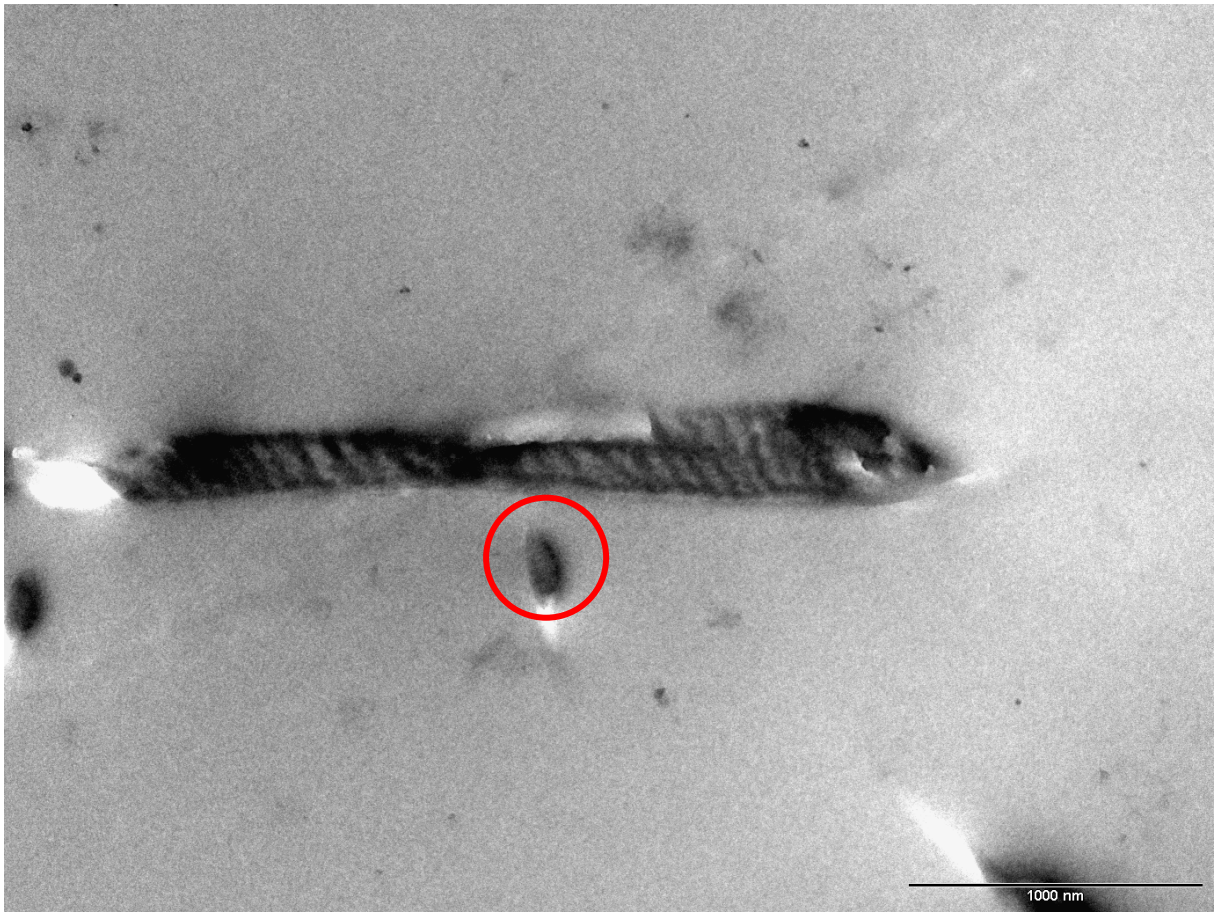

Figure S4: TEM image of electrospun PI-*b*-PDMAEMA/PUMVS nanocomposite fibers including perpendicular fiber axis cut.

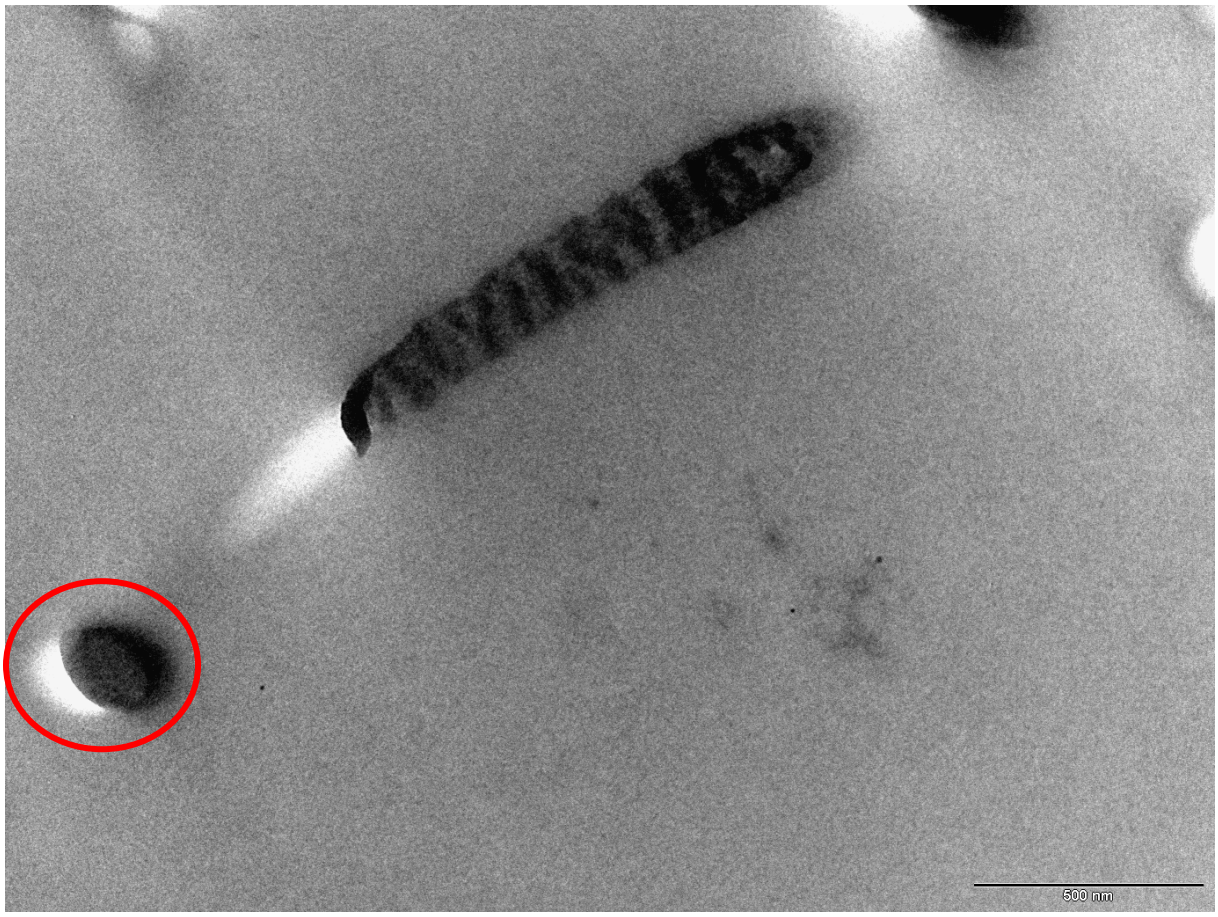

Figure S5: TEM image of electrospun PI-*b*-PDMAEMA/PUMVS nanocomposite fibers including perpendicular fiber axis cut.

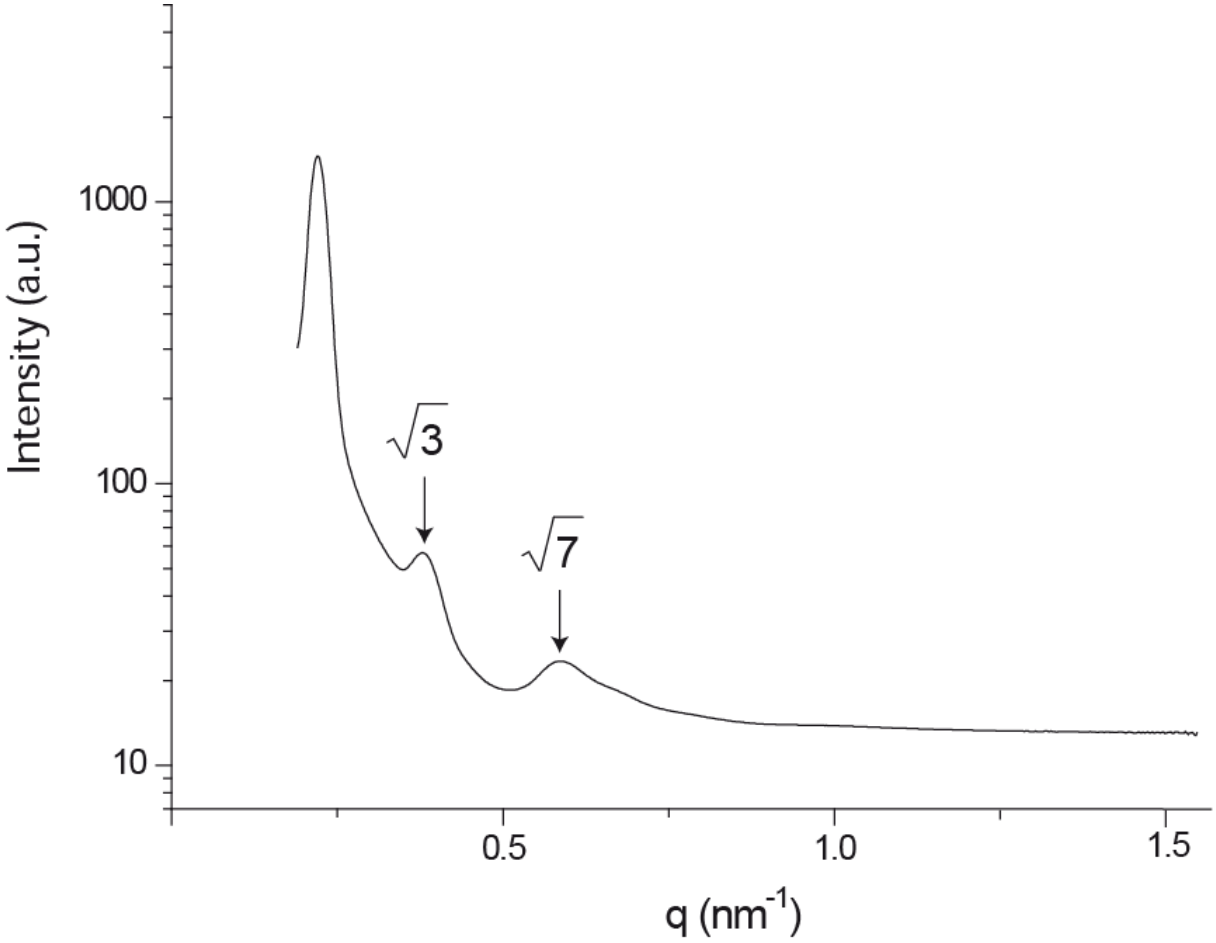

Figure S6: SAXS trace of bulk PI-*b*-PDMAEMA/PUMVS nanocomposite.

References

47. S. Creutz, P. Teyssie and R. Jerome, *Macromolecules*, 1997, **30**, 6-9.