SUPPORTING INFORMATION

Materials

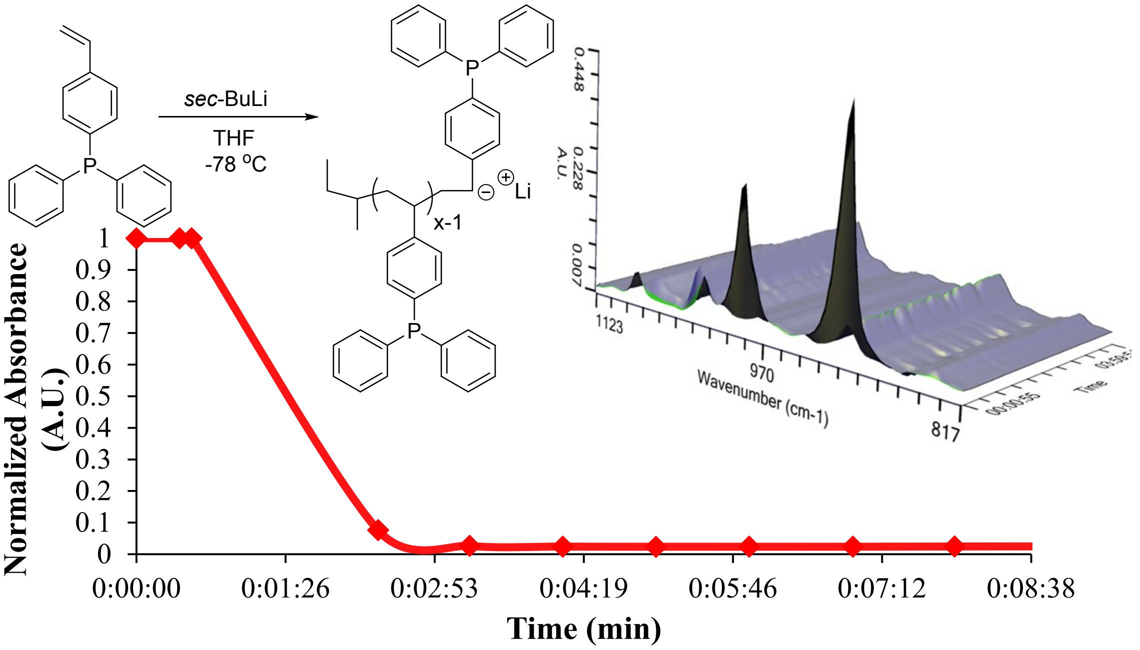
4-diphenylphosphino styrene (99%), styrene (99%), isoprene (99%), and 1.4 M *sec*-butyllithium solution in cyclohexane were purchased from Sigma Aldrich and used as received unless otherwise noted. Styrene and isoprene, containing 10-15 ppm of *t*-butyl catechol, were distilled from calcium hydride and dibutyl magnesium.

Instrumentation

In situ FTIR analysis employed a Mettler Toledo ReactIR 45M attenuated total reflectance reaction apparatus equipped with a light conduit and DiComp (diamond composite) insertion probe. Size-exclusion chromatography (SEC) was used to determine the molecular weights of phosphino-containing polymers at 40 ^{o}C in THF at 1 mL/min. THF SEC was performed on a Waters SEC equipped with two Waters Styragel HR5E (THF) columns, a Waters 717 plus autosampler, a Wyatt MiniDAWN, and a Waters 2414 differential refractive index detector. An Optilab T-rEX refractometer (λ = 658) was used to measure d*n*/d*c* values offline for determination of absolute weight-average molecular weights. SAXS experiments were performed using a Rigaku S-Max 3000 3 pinhole SAXS system, equipped with a rotating anode emitting X-ray with a wavelength of 0.154 nm (Cu Kα). The sample-to-detector distance was 1604 mm, and q-range was calibrated using a silver behenate standard. Two-dimensional SAXS patterns were obtained using a fully integrated 2D multiwire, proportional counting, gas-filled detector, with an exposure time of 2 hours. All the SAXS data were analyzed using the SAXSGUI software package to obtain radially integrated SAXS intensity versus scattering vector q, where $q = (4\pi/\lambda)\sin(\theta)$, θ is one half of the scattering angle and λ is the wavelength of X-ray. SAXS profiles were vertically shifted to facilitate a comparison of the peak positions.

In situ FTIR monitoring of the anionic polymerization of 4-diphenylphosphino styrene

2.0 g 4-diphenylphosphino styrene and 8 mL of dry THF were added to a two-necked, 25-mL, flame-dried, round-bottomed flask with a magnetic stir bar. One neck was sealed with a rubber septum, and the DiComp probe was inserted into the second neck and sealed. The probe tip was submerged below the monomer surface, and the ReactIR spectrometer was programmed to collect a spectrum every 1 min for 5 h (SI Figure 1). The flask was purged with nitrogen for 15 min and placed in an isopropanol/dry ice bath at -78 °C. *Sec*-butyllithium (0.02 mL) initiated growth of a 10,000 g/mol polymer. After 1 h with FTIR analysis, the product was diluted with THF or chloroform and precipitated into methanol.



SI Figure 1 *In situ* FTIR monitoring of DPPS vinyl concentration disappearance at 918 cm^{1} over time in a 3D waterfall plot and 2D normalized plot.

Anionic polymerization of poly(4-diphenylphosphino styrene-*b*-styrene)

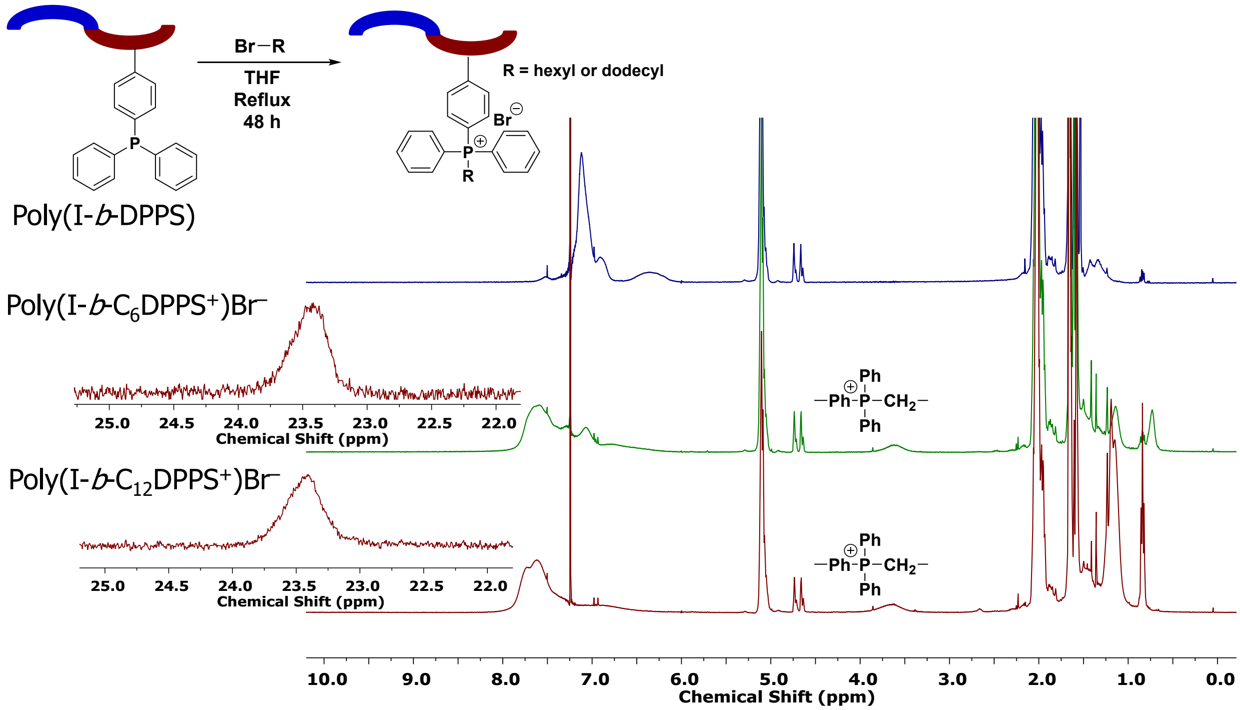
To a 100-mL flame dried, nitrogen purged, and sealed round bottom flask with stir bar, (3.00 g) DPPS and 50 mL of THF were added. The reaction flask was cooled to -78 °C for 10 min and *sec*-butyl lithium (0.07 mL, 0.1 mmol) was then added to the solution to initiate growth of a 30,000 g/mol polymer. The first reaction was allowed to proceed for 5 min and the second monomer, 2.97 mL styrene (3.00 g) was sequentially added to the reaction mixture. The polymerization was terminated after 5 min with degassed methanol (0.2 mL), and the resulting poly(DPPS-*b*-S) diblock copolymer solution was precipitated into methanol and dried at 23 °C under reduced pressure (0.5 mmHg) for 24 h to obtain a white powder (90-95% isolated yield).

Anionic polymerization of poly(isoprene-*b*-4-diphenylphosphino styrene)

To a 100-mL flame dried, nitrogen purged, and sealed round bottom flask with stir bar, (15 mL, 10.2 g) isoprene and 50 mL of cyclohexane were added. The reaction flask was heated to 50 °C for 10 min and *sec*-butyl lithium (0.24 mL, 0.2 mmol) was then added to the solution to initiate growth of a 30,000 g/mol polymer. The first reaction was allowed to proceed for 2 h and 4-diphenylphosphino styrene (5.1 g) was sequentially added to the reaction mixture. The polymerization was terminated after 30 min with degassed methanol (1.0 mL), and the resulting AB diblock copolymer was precipitated into methanol and dried at 23 °C under reduced pressure (0.5 mmHg) for 24 h to obtain a white powder (95% isolated yield).

Alkylation of poly(I-*b*-DPPS) diblock copolymers

The following protocol describes a typical alkylation on DPPS-containing polymers. 2.00 g poly(I-*b*-DPPS) and 2.00 molar ratio of 1-bromohexane was dissolved in 25 mL tetrahydrofuran and the reaction refluxed at 70 °C for 48 h. The resulting phosphonium-containing diblock copolymer precipitated from the reaction solution. The final product was isolated and re-precipitated into diethyl ether. ^{1}H-NMR and ^{31}P-NMR tracked the appearance of alkyl substituents to confirm functionalization and production of a phosphonium cation. The final polymer was allowed to dry at 30 ^{o}C under reduced pressure (0.5 mmHg) for 48 h to obtain a white powder (98% isolated yield).

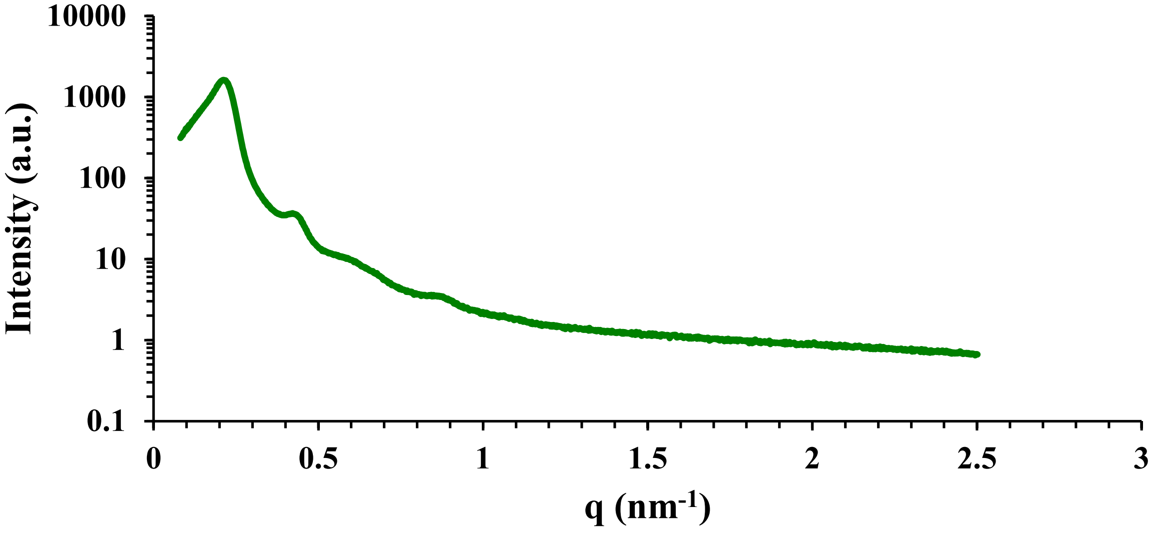


SI Figure 2 ^{1}H-NMR reveals P^+Ph_3-CH_2- protons and ^{31}P-NMR reveals production of the phosphonium cation, post-alkylation.

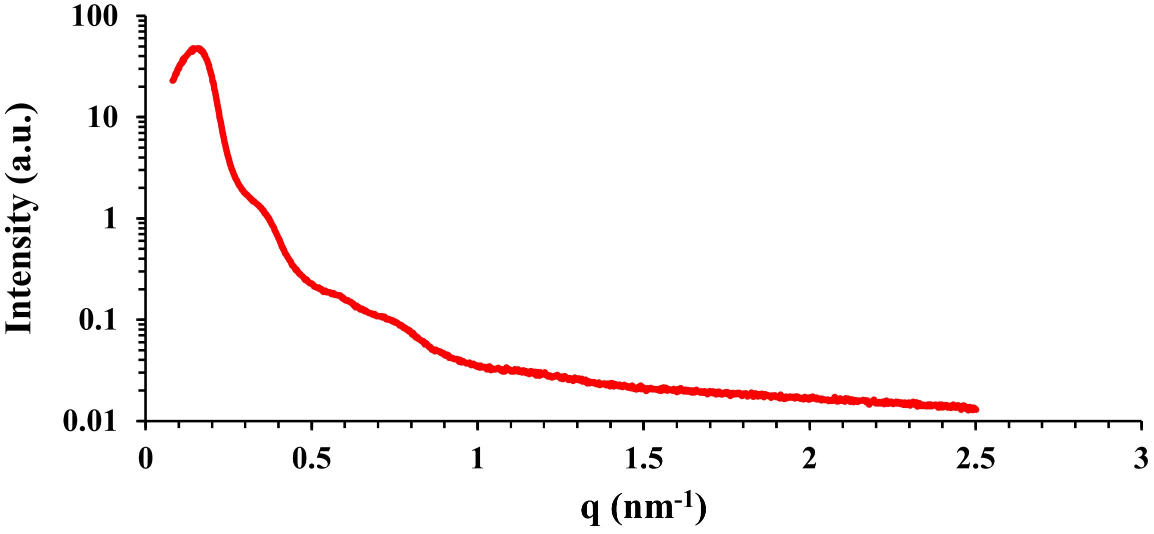
Small angle x-ray scattering peak positions

Peak Number	poly(I-*b*-DPPS)	poly(I-*b*-C_{12}DPPS)$^+$Br$^-$	poly(I-*b*-C_{12}DPPS)$^+$Br$^-$
q_1	0.223 nm^{-1}	0.171 nm^{-1}	0.157 nm^{-1}
q_2	0.443 nm^{-1}	0.346 nm^{-1}	0.339 nm^{-1}
q_3	0.654 nm^{-1}	0.536 nm^{-1}	_
q_4	0.874 nm^{-1}	0.734 nm^{-1}	_

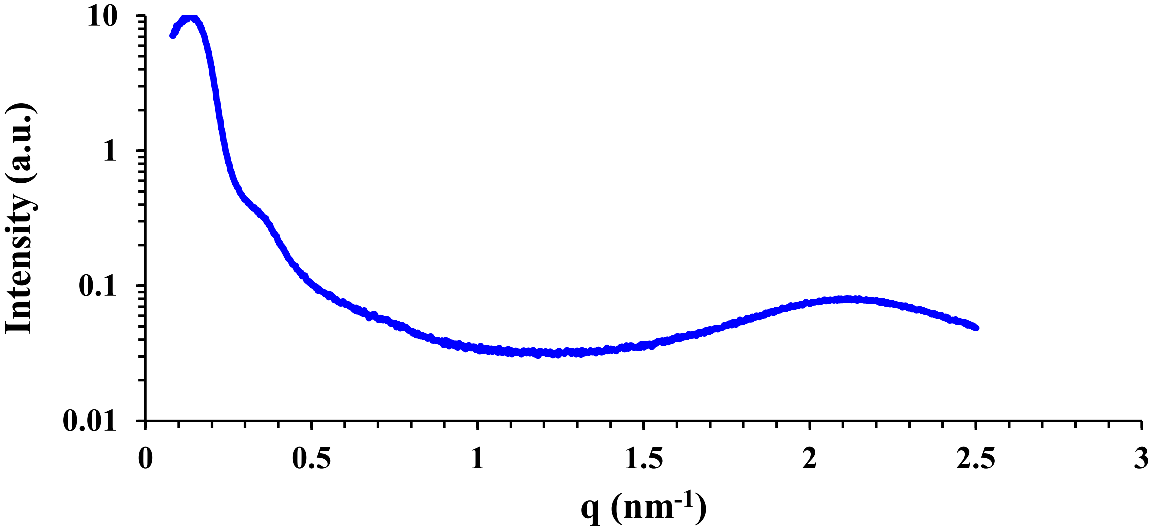
SI Table 1 Small angle x-ray scattering tabulated peak positions.



SI Figure 3 Small Angle X-Ray Scattering profiles reveal bulk morphologies for poly(I-*b*-DPPS). Scattering maxima are observed at q*, 2q*, 3q*, 4q*, indicating a lamellar morphology.



SI Figure 4 Small Angle X-Ray Scattering profiles reveal bulk morphologies for poly(I-*b*-C_6DPPS)$^+$Br$^-$. Scattering maxima are observed at q*, 2q*, 3q*, 4q*, indicating a lamellar morphology.



SI Figure 5 Small Angle X-Ray Scattering profiles reveal bulk morphologies for poly(I-*b*-C_{12}DPPS)$^+$Br$^-$. Scattering maxima are observed at q*, 2q*, suggesting a less ordered lamellar morphology. A broad scattering peak at approximately q = 2.1 nm^{-1} corresponds to the interdigitated packing of dodecyl chains on the phosphonium cation.