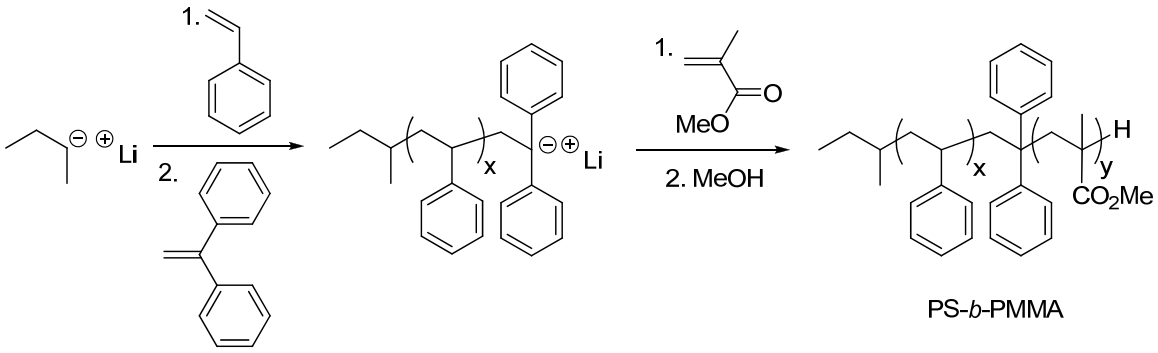
Supporting Information

Synthesis and characterization of cylinder-forming P(S-*b*-MMA) including ^{1}H-NMR and SAXS.

Cylinder-forming P(S-*b*-MMA)

P(S-*b*-MMA) was synthesized as previously reported by sequential anionic polymerization under Ar atmosphere via standard Schlenk line techniques.[37] *sec*-BuLi was added to a stirred solution of THF and LiCl at -78 °C and mixed for 5 minutes. A 10-fold excess of LiCl was present in the reaction to maximize control of the MMA block polymerization.[38] The appropriate amount of styrene was then added dropwise to the reactor, resulting in an immediate formation of an orange color. After 15 minutes, the remaining styrene was added dropwise to the reactor while maintaining the internal temperature at or below -65 °C. Four hours after the addition was complete an aliquot of the polystyrene was taken and a 5-fold excess of diphenylethylene was added quickly, which instantly turned the solution dark red. Diphenylethylene was used to bias the subsequent MMA polymerization towards 1,4 addition instead of chain-terminating 1,2 addition.[37b] After 3 hours, 10 drops of MMA were added to react all living diphenylethylene anions with approximately one MMA molecule, yielding a colorless solution. The remaining MMA monomer was added dropwise 15 minutes later. Degassed methanol was rapidly injected 3 hours after MMA addition to quench all living anions. The resulting polymer was precipitated in methanol, filtered, and dried *in vacuo*, yielding a white powder.



Scheme S1: Anionic Synthesis of P(S-*b*-MMA).

^{1}H-NMR showed the resulting polymer is 31 mol% PMMA, which corresponds to a volume fraction of 0.27 using density values reported by Fetters et. al.[39] This is within the range for the cylindrical morphology.[2] The weight average molecular weight of the PS aliquot was 45.8 kDa with a PDI of 1.18; the weight average molecular weight of the block was 65.6 kDa with a PDI of 1.18.

To confirm the bulk ordering of P(S-*b*-MMA), samples of this polymer were analyzed via small angle x-ray scattering (SAXS). Figure S1 shows the diffraction pattern of a sample of this polymer that was collected at 170 °C. Assigning the first peak as q* and relating all other peaks to this value as shown in Table S1, this polymer's bulk ordering is consistent with hexagonally packed cylinders.

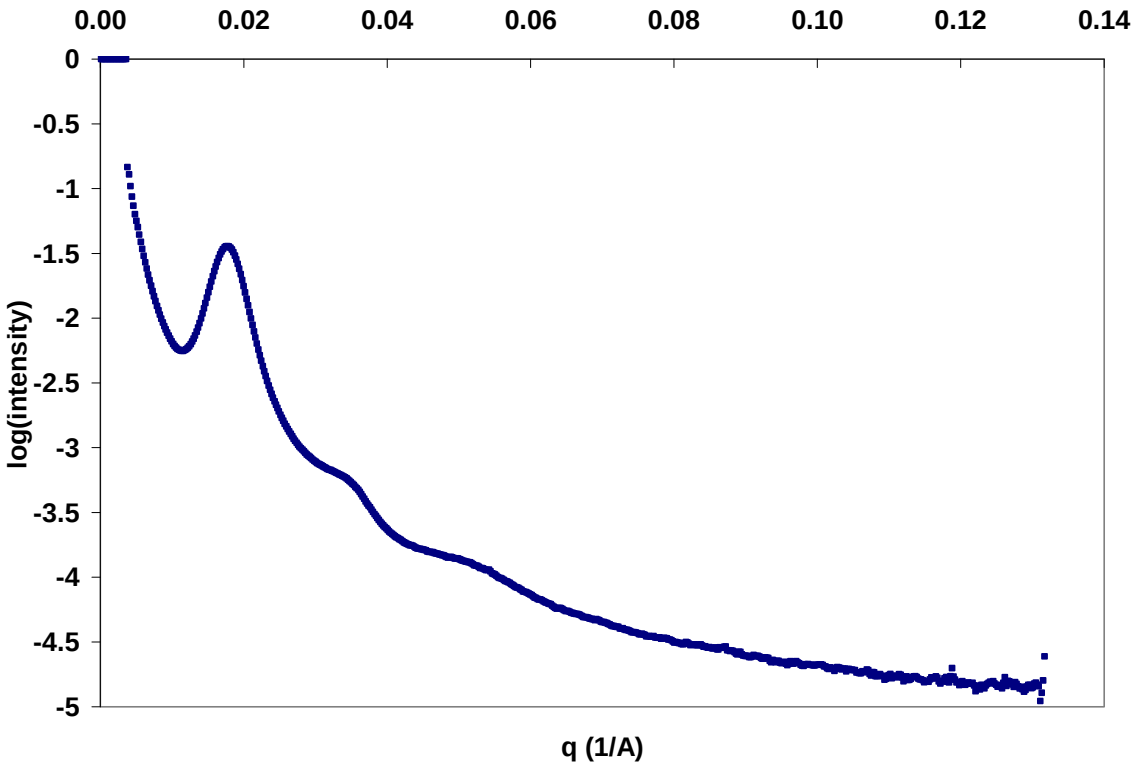


Figure S1: SAXS diffraction pattern of cylindrical P(S-*b*-MMA).

Table S1: SAXS peak assignment of cylindrical P(S-*b*-MMA).

Peak	q (1/Å)	peak/q*
q*	0.0181	1
2	0.0339	1.8729
3	0.0358	1.9779
4	0.0548	3.0276

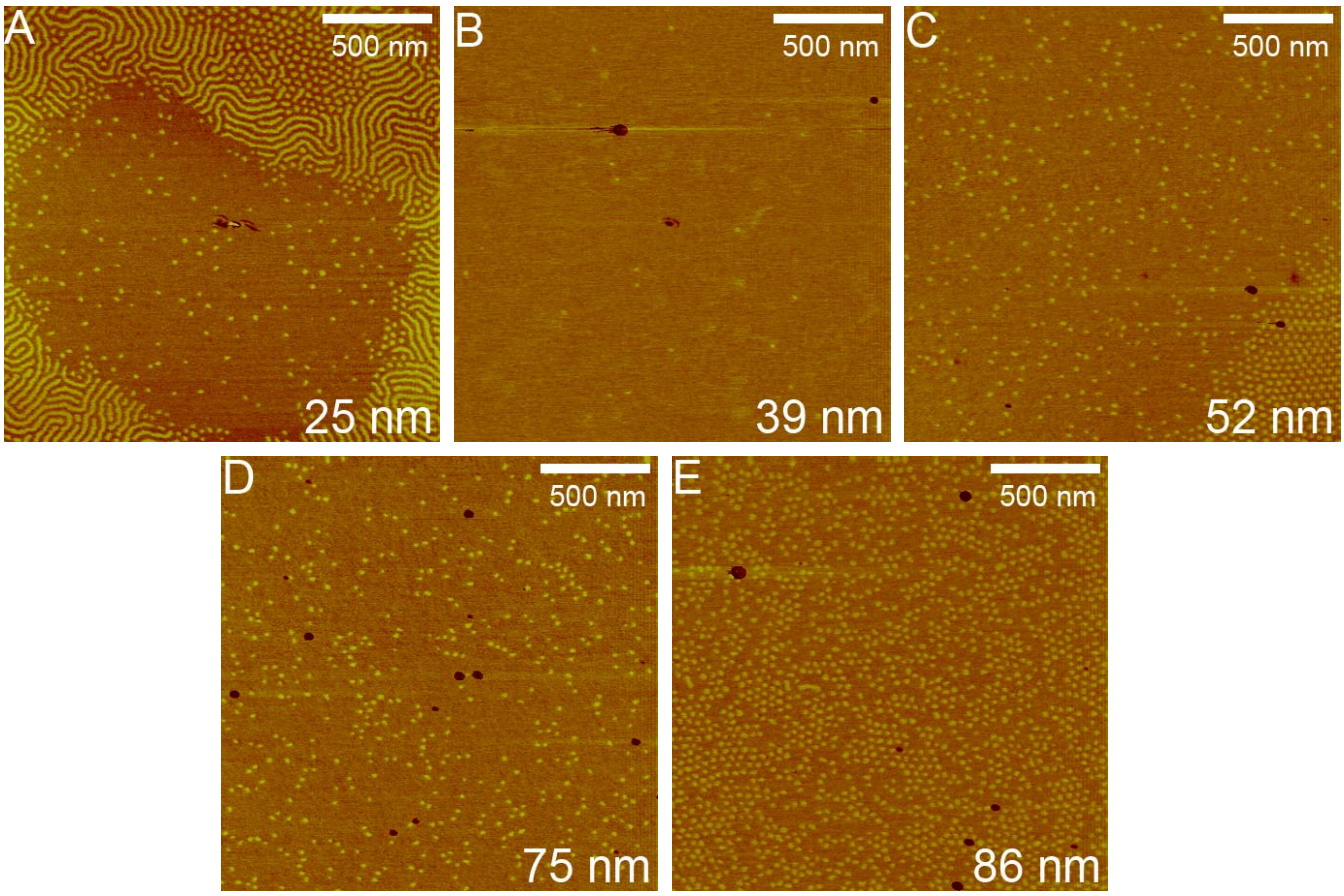


Figure S2: Full AFM images of P(S-*r*-VBzAz) with 5 mol% VBzAz.

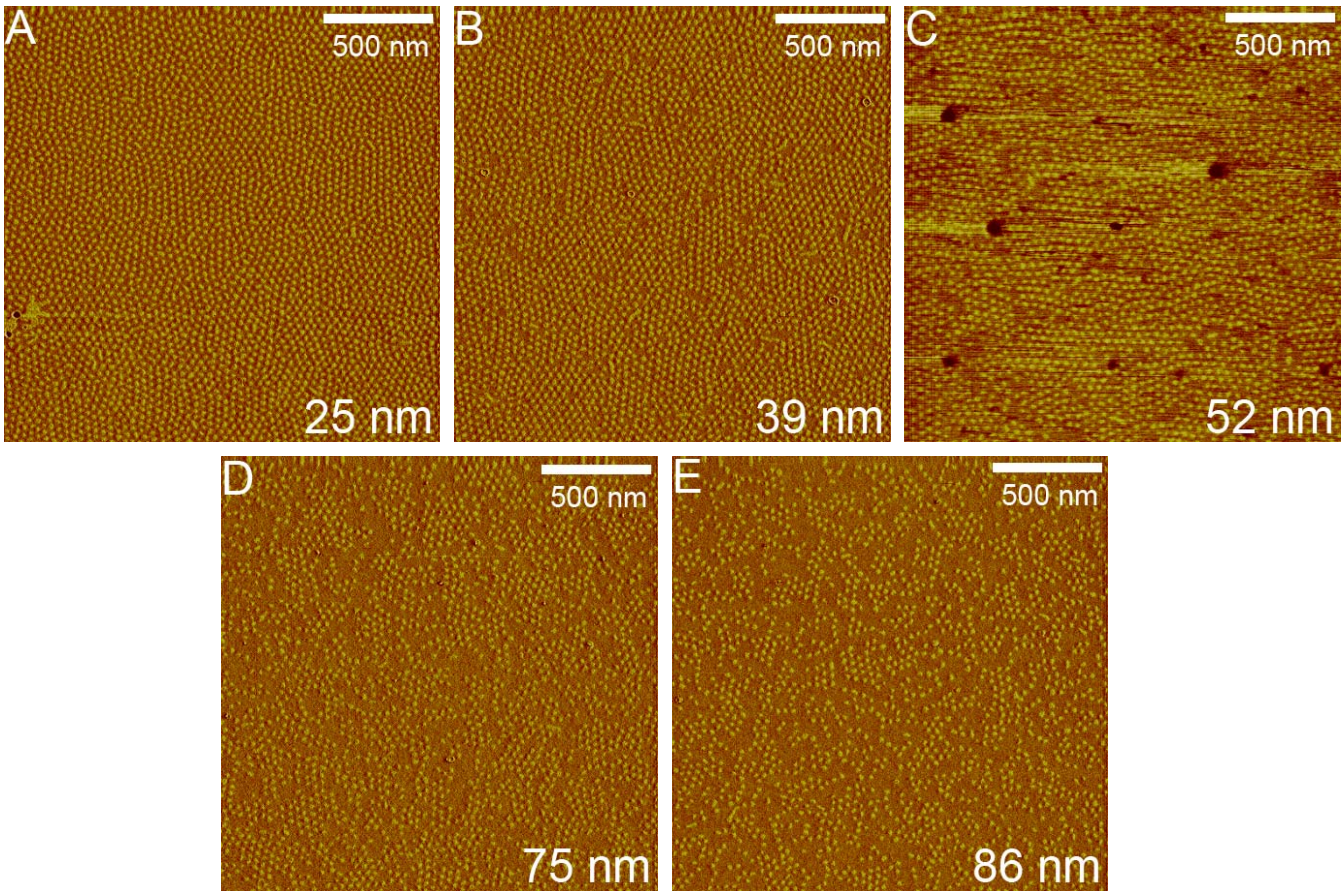


Figure S3: Full AFM images of P(S-*r*-VBzAz) with 28 mol% VBzAz.

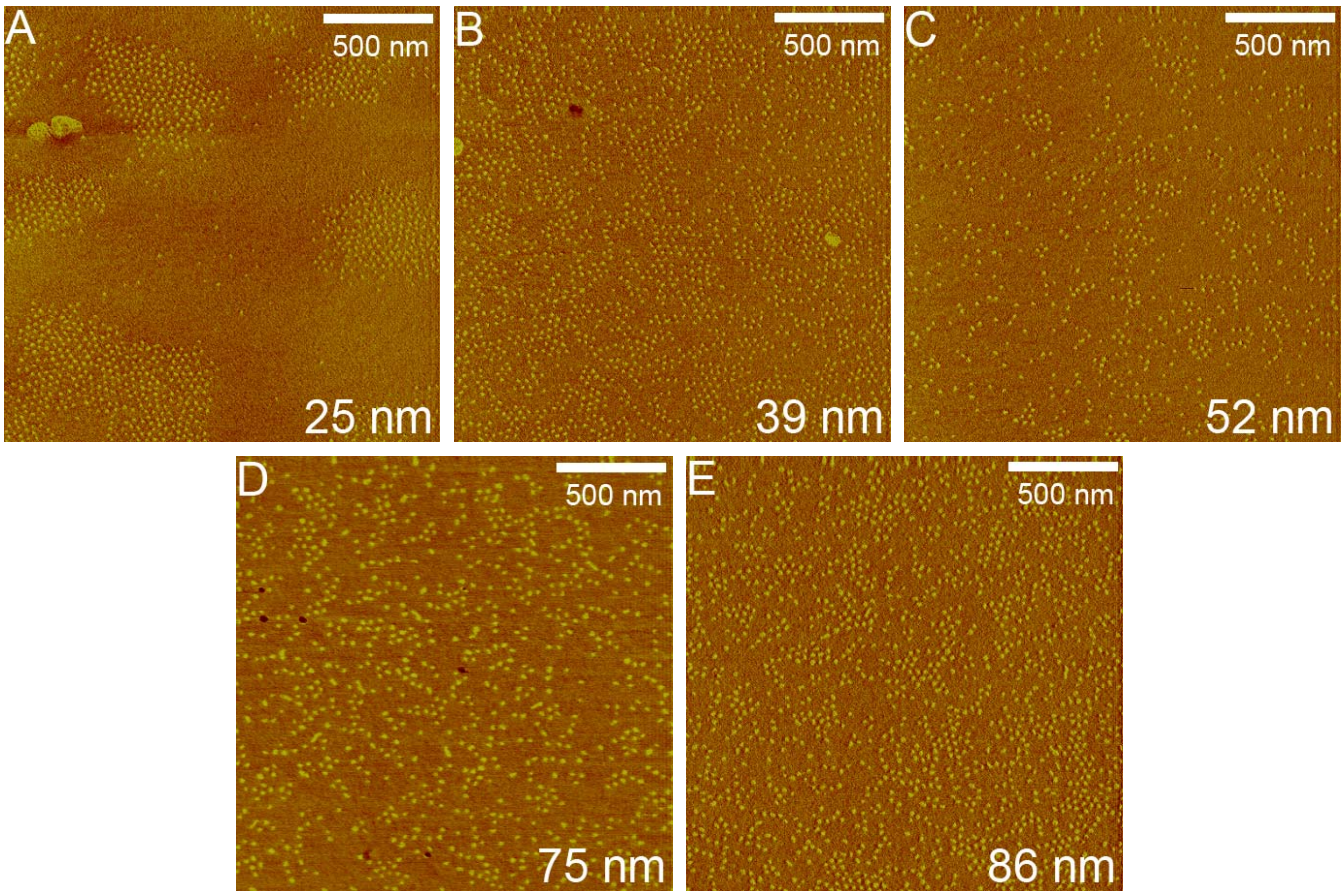


Figure S4: Full AFM images of P(S-*r*-VBzAz) with 49 mol% VBzAz.

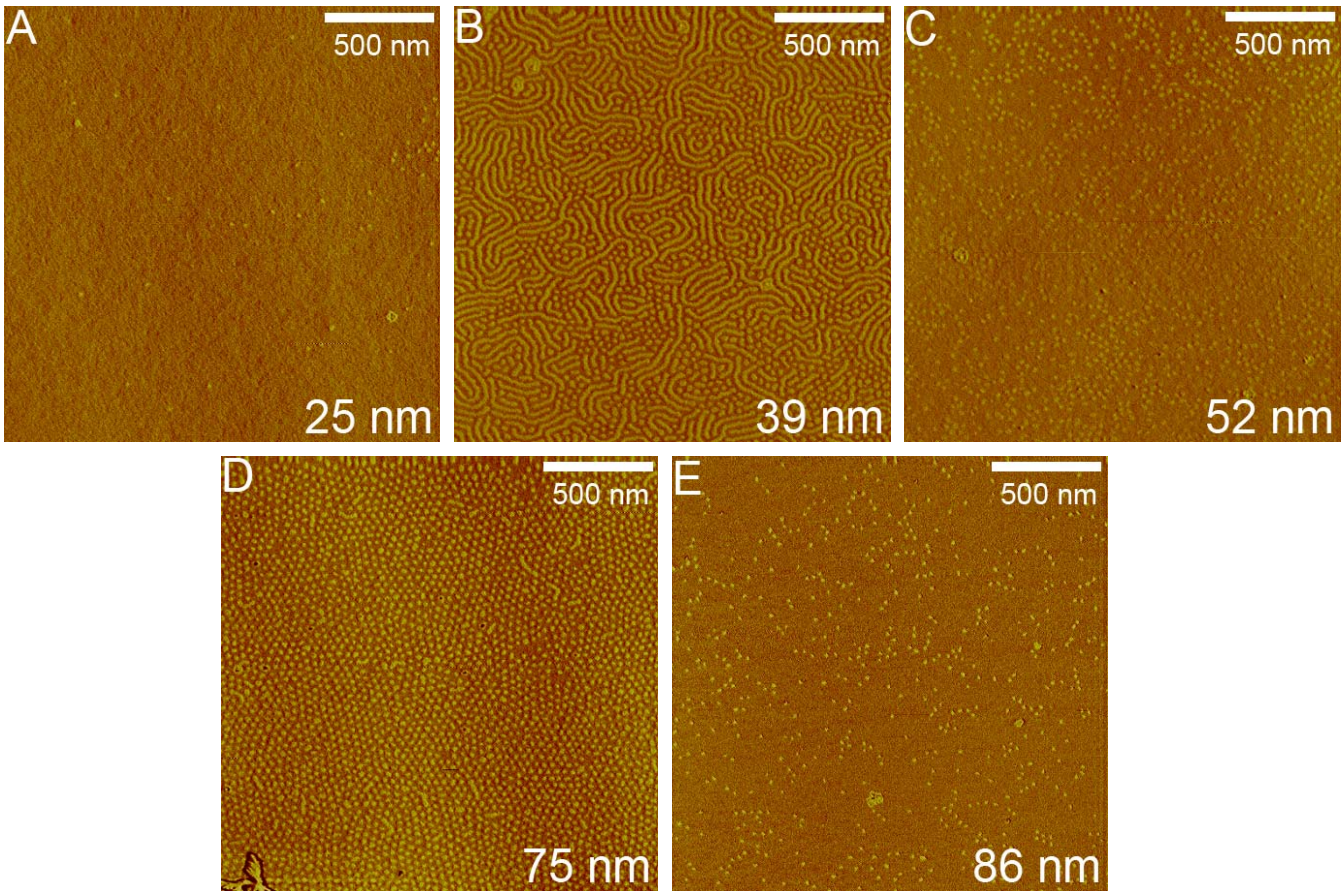


Figure S5: Full AFM images of P(S-*r*-VBzAz) with 56 mol% VBzAz.

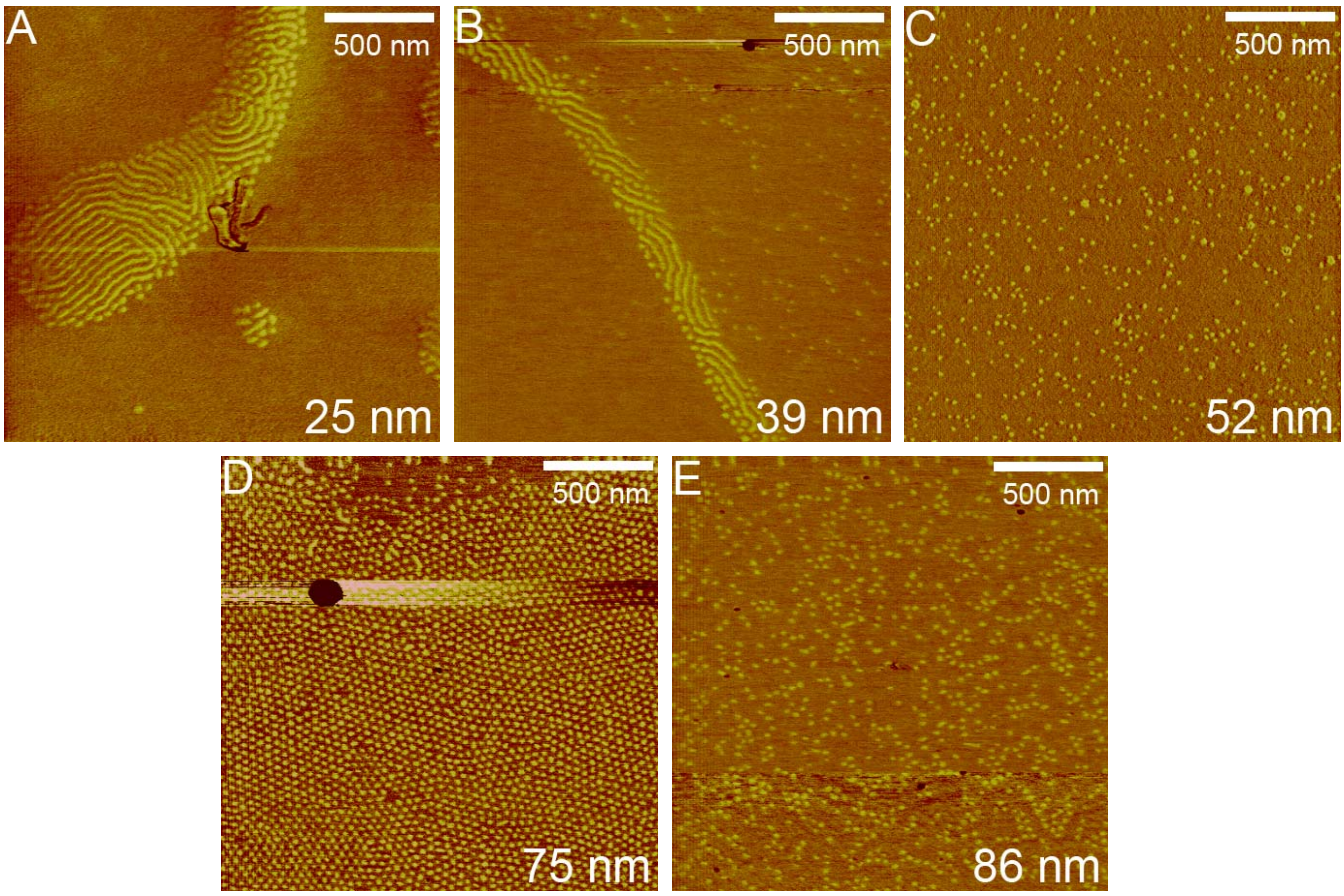


Figure S6: Full AFM images of P(S-*r*-VBzAz) with 100 mol% VBzAz.