SUPPORTING INFORMATION

FOR

# The Role of Architecture in the Melt-State Self-Assembly of (Polystyrene)$_{star}$-*b*-(Polyisoprene)$_{linear}$-*b*-(Polystyrene)$_{star}$ Pom-Pom Triblock Copolymers

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## S.1 Chemical Characterization of all 18 $S_nIS_n$ Pom-Pom Triblock Copolymers

**Table S1:** Chemical characterization data

| Sample | $M_{n,star}$[a] [g mol$^{-1}$] | $n_{arms}$[b] ($M_{n,arms}$)[a] [g mol$^{-1}$] | $PDI_{star}$[a] ($PDI_{arm}$)[a] | $w_{PI}$[c] ($w_{PI,feed}$) | $f_{PI}$[d] | dn/dc[e] [mL g$^{-1}$] | $M_{n,}$[a] ($M_n$)[f] [g mol$^{-1}$] | PDI[a] |
|---|---|---|---|---|---|---|---|---|
| TPE01 | 16,500 | 7.1 (2,160) | 1.20 (1.02) | 0.69 (0.70) | 0.72 | 0.141 | 73,600 (106,000) | 1.06 |
| TPE02 | 16,500 | 7.1 (2,160) | 1.20 (1.02) | 0.77 (0.75) | 0.80 | 0.133 | 89,800 (143,000) | 1.07 |
| TPE03 (B7) | 16,500 | 7.1 (2,160) | 1.20 (1.02) | 0.81 (0.80) | 0.83 | 0.131 | 105,000 (174,000) | 1.07 |
| TPE04 | 16,500 | 7.1 (2,160) | 1.20 (1.02) | 0.86 (0.85) | 0.88 | 0.128 | 138,000 (236,000) | 1.06 |
| TPE05 | 14,300 | 4.1 (3,300) | 1.08 (1.02) | 0.69 (0.70) | 0.72 | 0.141 | 73,500 (92,300) | 1.07 |
| TPE06 (C4) | 14,300 | 4.1 (3,300) | 1.08 (1.02) | 0.75 (0.75) | 0.78 | 0.136 | 92,000 (114,000) | 1.06 |
| TPE07 (B4) | 14,300 | 4.1 (3,300) | 1.08 (1.02) | 0.80 (0.80) | 0.82 | 0.132 | 107,000 (143,000) | 1.04 |
| TPE08 (A4) | 14,300 | 4.1 (3,300) | 1.08 (1.02) | 0.87 (0.85) | 0.89 | 0.127 | 158,000 (220,000) | 1.06 |
| TPE09 | 15,500 | 2.9 (5,400) | 1.30 (1.01) | 0.71 (0.70) | 0.74 | 0.139 | 102,000 (107,000) | 1.03 |
| TPE10 | 15,500 | 2.9 (5,400) | 1.30 (1.01) | 0.75 (0.75) | 0.78 | 0.136 | 113,000 (124,000) | 1.03 |
| TPE11 (B3) | 15,500 | 2.9 (5,400) | 1.30 (1.01) | 0.80 (0.80) | 0.82 | 0.132 | 132,000 (155,000) | 1.02 |
| TPE12 | 15,500 | 2.9 (5,400) | 1.30 (1.01) | 0.84 (0.85) | 0.86 | 0.129 | 160,000 (194,000) | 1.04 |
| TPE13 | 10,600 | 4.5 (2,200) | 1.20 (1.05) | 0.56 (0.60) | 0.60 | 0.150 | 34,600 (48,200) | 1.10 |
| TPE14 | 10,600 | 4.5 (2,200) | 1.20 (1.05) | 0.69 (0.70) | 0.72 | 0.141 | 50,000 (68,400) | 1.03 |
| TPE15 | 10,600 | 4.5 (2,200) | 1.20 (1.05) | 0.81 (0.80) | 0.83 | 0.131 | 74,200 (112,000) | 1.03 |
| TPE16 | 15,600 | 3.9 (3,890) | 1.23 (1.01) | 0.57 (0.60) | 0.61 | 0.150 | 59,500 (72,600) | 1.04 |
| TPE17 | 15,600 | 3.9 (3,890) | 1.23 (1.01) | 0.69 (0.70) | 0.72 | 0.141 | 76,700 (101,000) | 1.03 |
| TPE18 | 15,600 | 3.9 (3,890) | 1.23 (1.01) | 0.81 (0.80) | 0.83 | 0.131 | 115,000 (164,000) | 1.03 |

[a]calculated from GPC-MALLS; [b]calculated from $M_{n,star} = nM_{n,arm} + (n-1)M_{DMSS}$; [c]calcluated from $^1$H NMR of fractionated product; [d] volume fraction of PI calculated using nominal densities at 140°C)[1]; [e]calculated based on the summation of the products of the *dn/dc* of each block times its weight fraction; [f]calculated from $M_{n,star}$ in combination with $^1$H NMR of final product.

## S.2 GPC-MALLS of Selected $S_nIS_n$ Pom-Pom Triblock Copolymers and Precursor Molecules

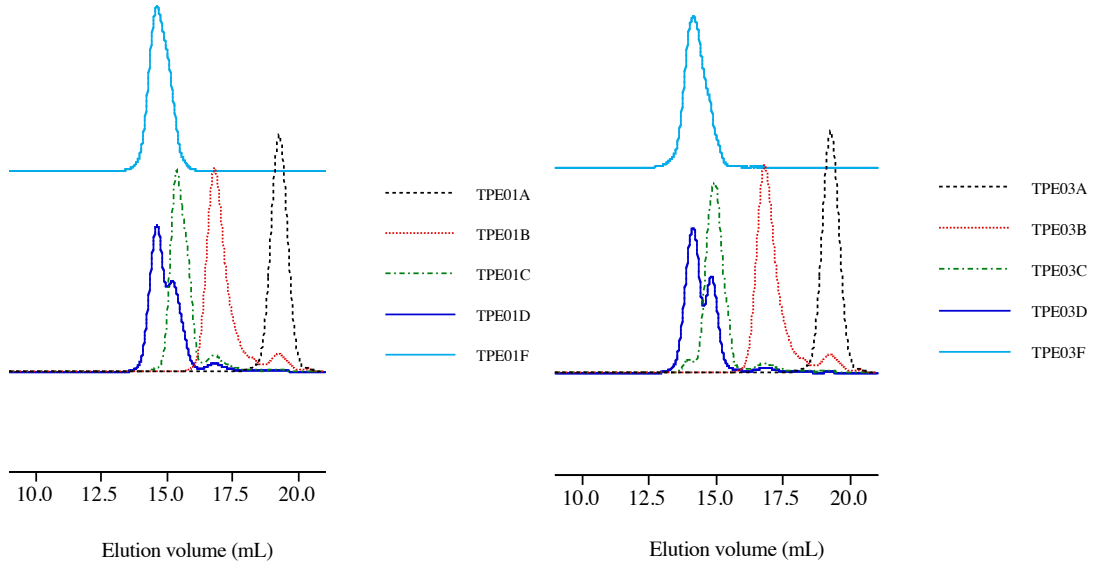
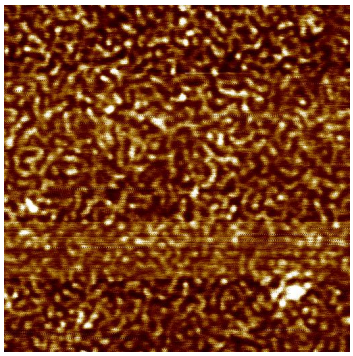
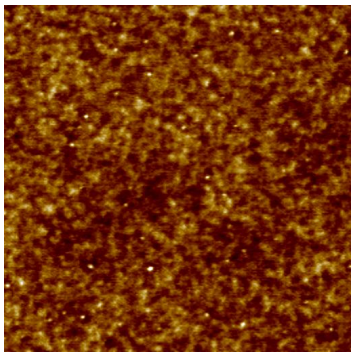
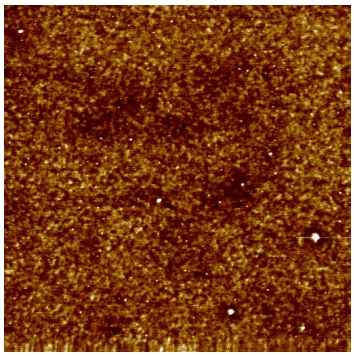
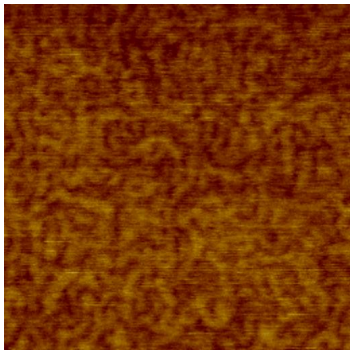
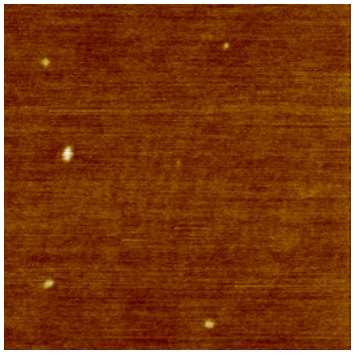
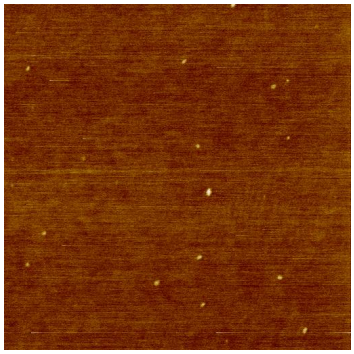
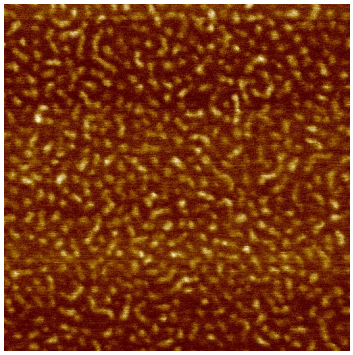
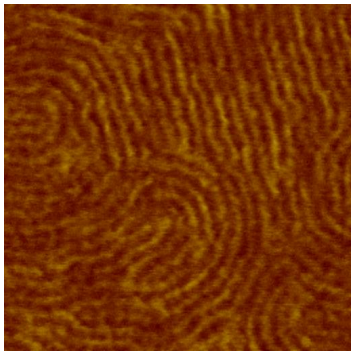
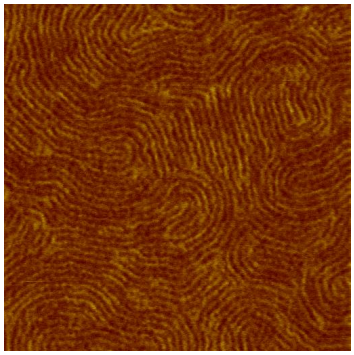
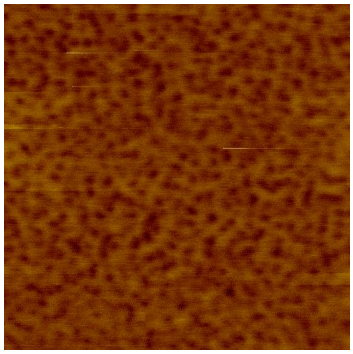
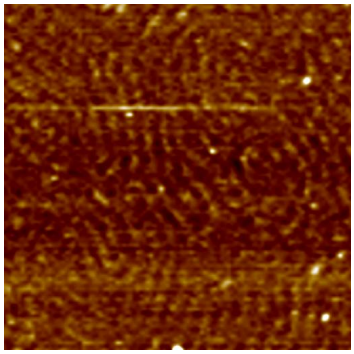
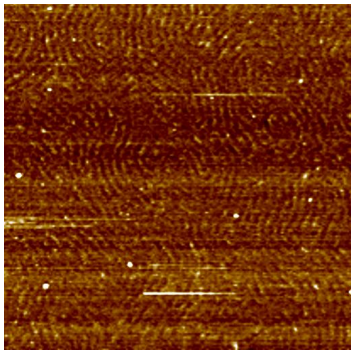
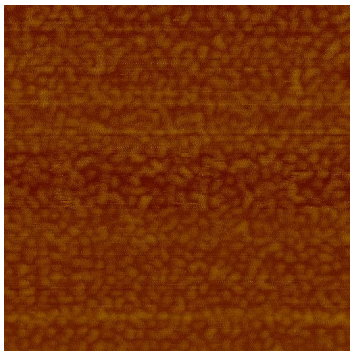
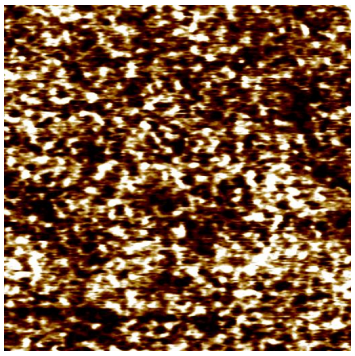
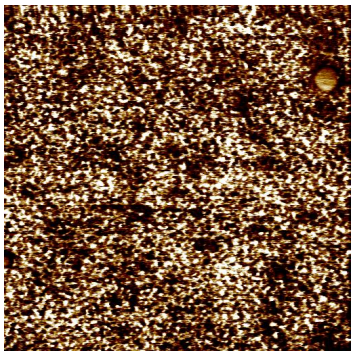
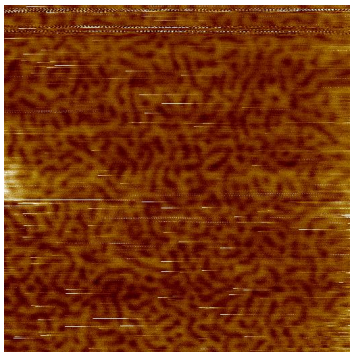
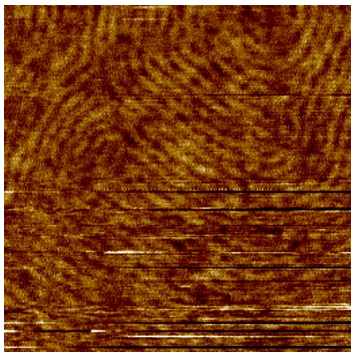
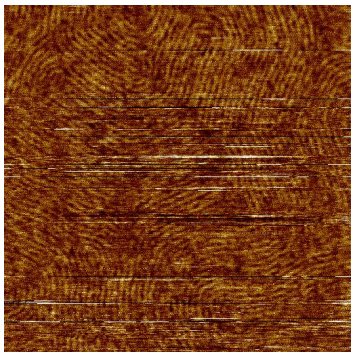
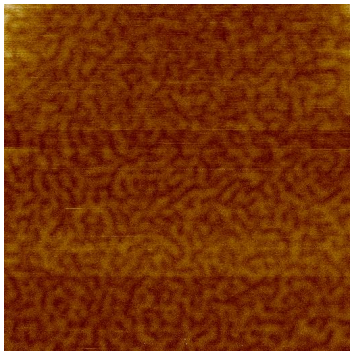
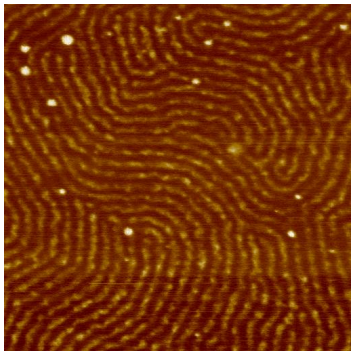
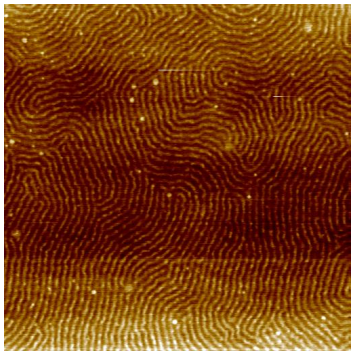
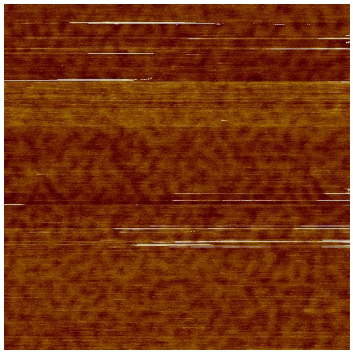
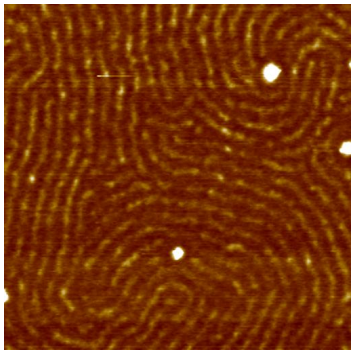
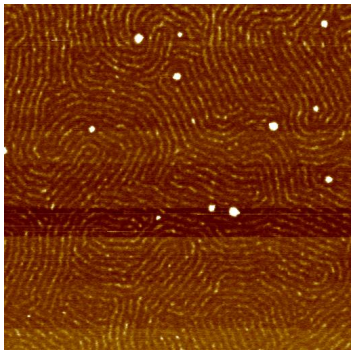


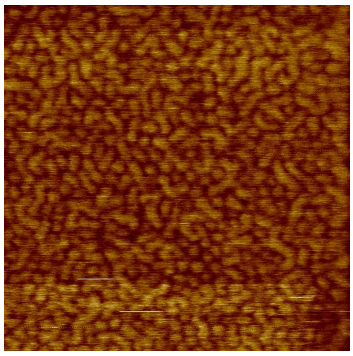
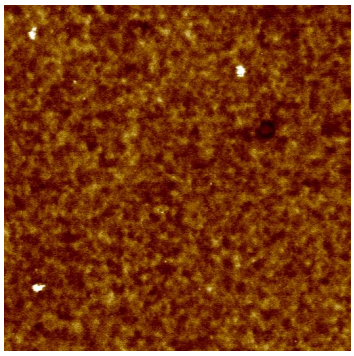
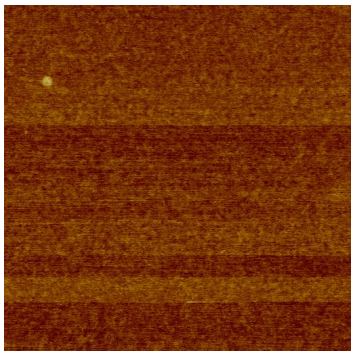
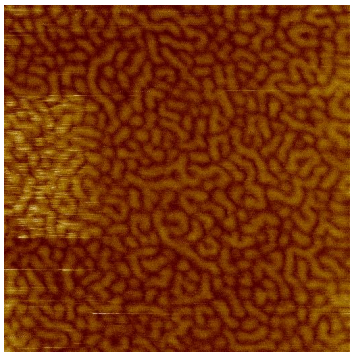
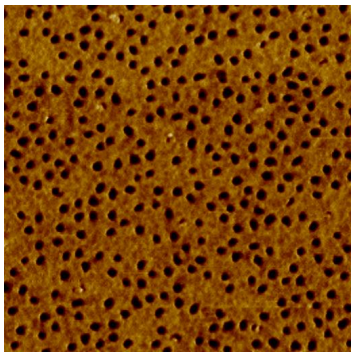
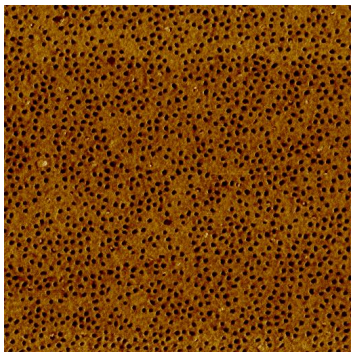
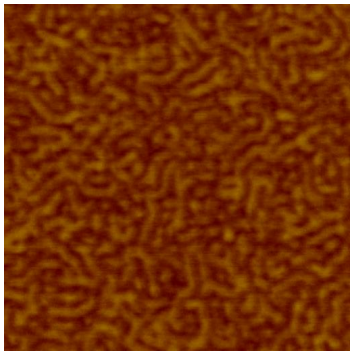
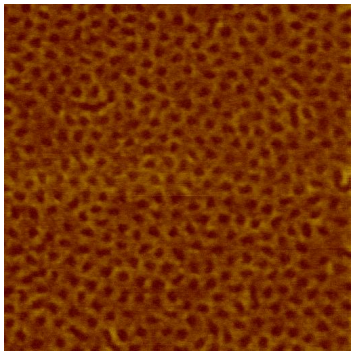
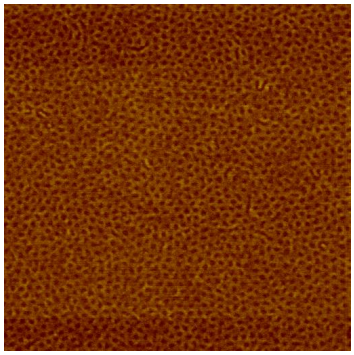
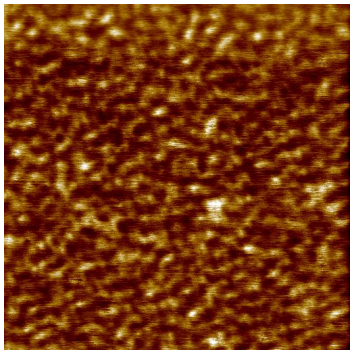
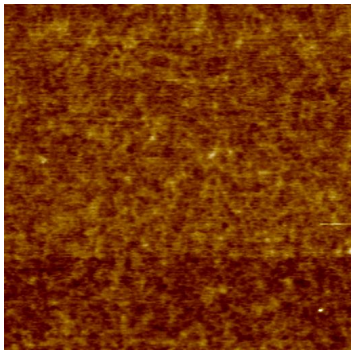
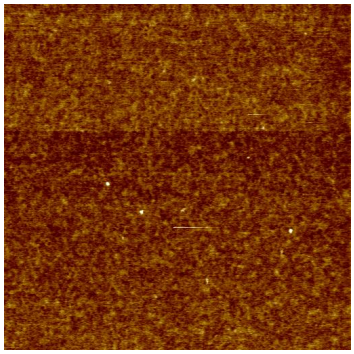

**Figure S1.** GPC Chromatograms showing the molecular weight distribution for samples TPE01 and TPE03 (**B7**) throughout the multi-step continuous polymerization process, including the final fractionated product. **A**: PS arm; **B**: PS star; **C**: $S_nI$ diblock copolymer; **D**: Crude $S_nIS_n$ triblock copolymer; **F**: Fractionated $S_nIS_n$ triblock copolymer.

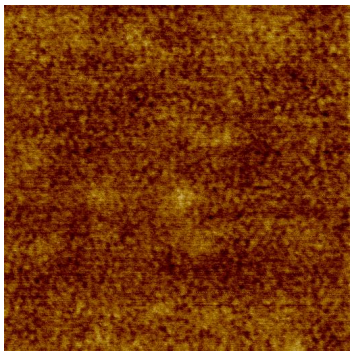
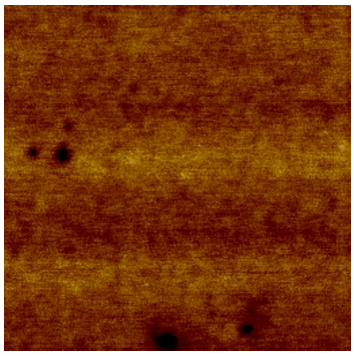
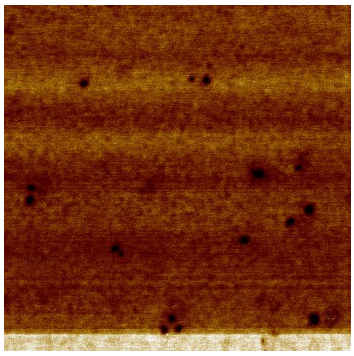
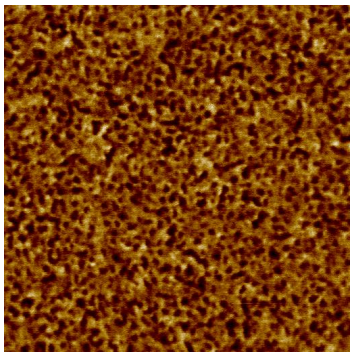
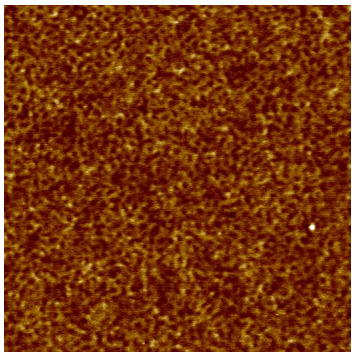
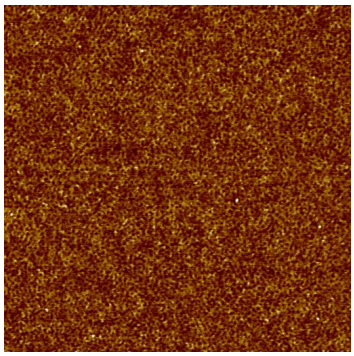
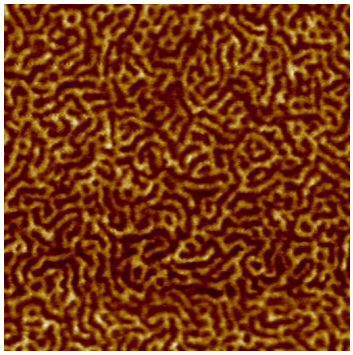
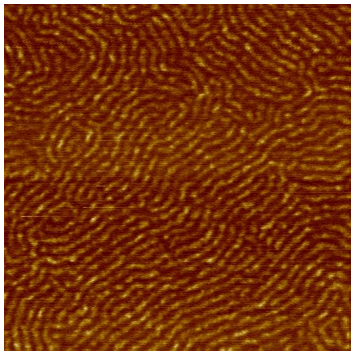
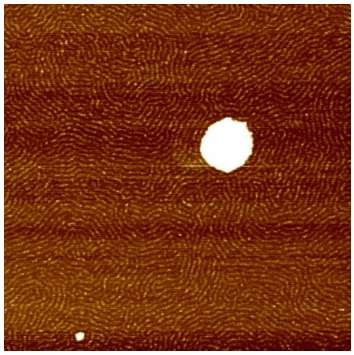
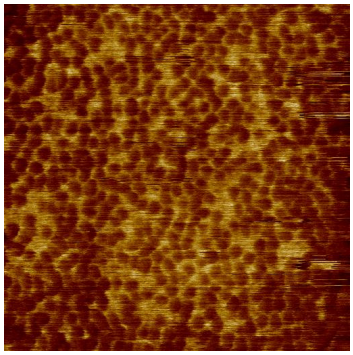
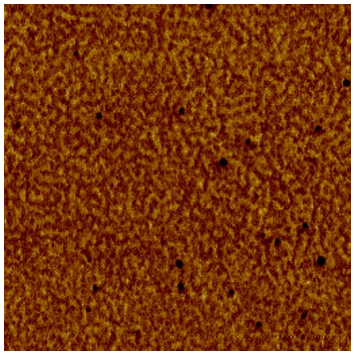
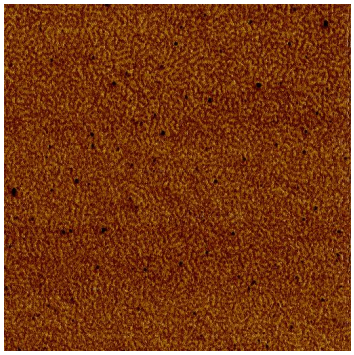
## S.3. AFM Images of Selected $S_nIS_n$ Pom-Pom Triblock Copolymers

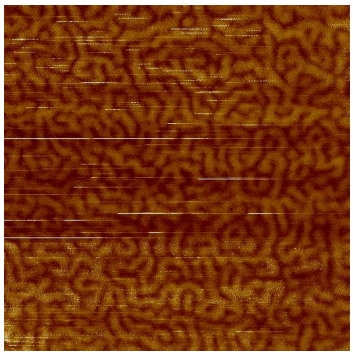
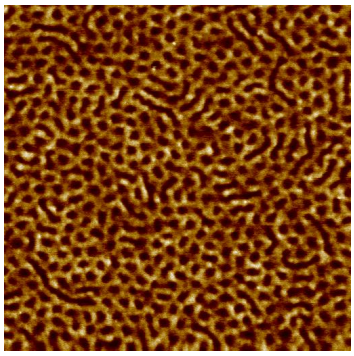
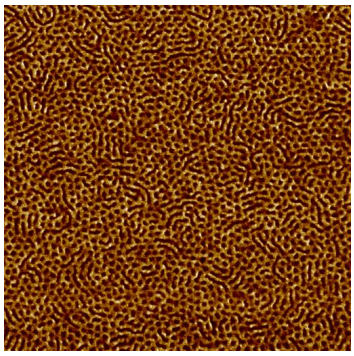
**Table S2:** Chemical characterization data

| $S_nIS_n$ | As Cast | Annealed | Annealed |
|---|---|---|---|
| TPE01 |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |
| TPE02 |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |
| TPE03 (**B7**) |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |
| TPE04 |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |

| $S_nIS_n$ | As Cast | Annealed | Annealed |
|---|---|---|---|
| TPE05 |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |
| TPE06 (**C4**) |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |
| TPE07 (**B4**) |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |
| TPE08 (**A4**) |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |

| $S_nIS_n$ | As Cast | Annealed | Annealed |
|---|---|---|---|
| TPE09 |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |
| TPE10 |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |
| TPE11 (**B3**) |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |
| TPE12 |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |

| $S_nIS_n$ | As Cast | Annealed | Annealed |
|---|---|---|---|
| TPE13 |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |
| TPE14 |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |
| TPE15 |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |
| TPE16 | No image | No image | No image |
| TPE17 |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |

| $S_nIS_n$ | As Cast | Annealed | Annealed |
|---|---|---|---|
| TPE18 |  1 μm × 1 μm |  1 μm × 1 μm |  2 μm × 2 μm |

## S.4 References


1. Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994,** 27, (17), 4639-4647.