

# Thin Film Self-assembly of Poly(trimethylsilylstyrene-*b*-D,L-lactide) with Sub-10 nm Domains

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## Supporting Information

### Polymer Synthesis Details

#### Synthesis of hydroxyl-terminated poly(trimethylsilyl styrene) (PTMSSOH)

PTMSSOH was synthesized by anionic polymerization via standard Schlenk techniques under Ar atmosphere as previously reported [1]. An appropriate amount of *sec*-butyllithium was added dropwise to purified cyclohexane under Ar atmosphere and stirred at 40°C for ten minutes. Several drops of TMSS were added to seed the polymerization and allowed to react for fifteen minutes to initiate all chains without significant propagation. After this time, the remaining TMSS was added dropwise. The solution reacted for 24 hours. The polymer was endcapped with a hydroxyl functionality by adding purified ethylene oxide and allowed to react for 24 hours. In the presence of lithium counter-cations, only one unit of ethylene oxide will add to the living chain ends [2]. Degassed methanol was added after this time to quench the living anions. The polymer was precipitated in methanol and dried *in vacuo*. The absolute molecular weight and PDI of the PTMSSOH polymer was determined by GPC using appropriate dn/dc.

#### Synthesis of poly(trimethylsilylstyrene-*b*-D,L-lactide) (PTMSS-*b*-PLA)

Lactide polymerizations were performed in a drybox using dry toluene. One mole of triethylaluminum (AlEt<sub>3</sub>) solution (1.1 M) was added dropwise to PTMSSOH in toluene per two

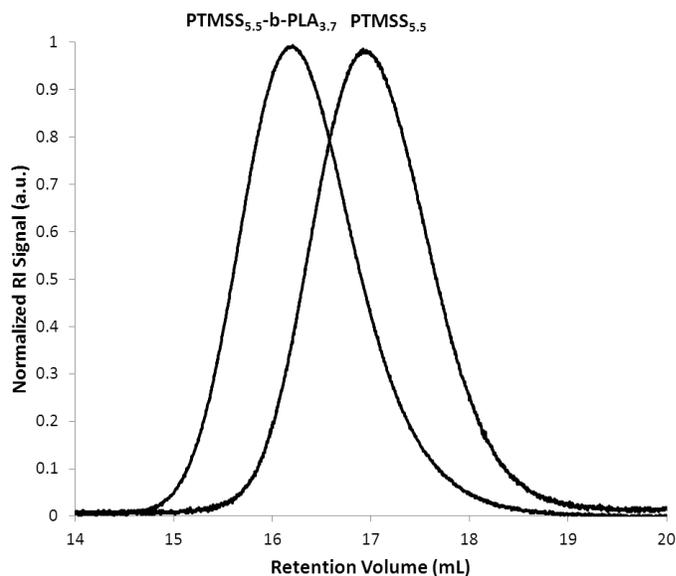
moles PTMSSOH to form an aluminum alkoxide macroinitiator. After stirring this solution for 2 hours, D,L-lactide was added, the flask was capped, brought out of the drybox, submerged in an oil bath at 90°C and stirred for 6 hours. After this time, the reaction was quenched with 1 mL 1N HCl and precipitated in a 50:50 methanol:water mixture. The polymer was filtered and dried under vacuum. The PDI of the block copolymer was determined by GPC and the molecular weight of the PLA block was determined by  $^1\text{H}$  NMR.

### Synthesis of polylactide (PLA) homopolymer

PLA homopolymer was synthesized using the same procedure as PTMSS-*b*-PLA, however dry isopropanol was used as the initiator instead of PTMSSOH.

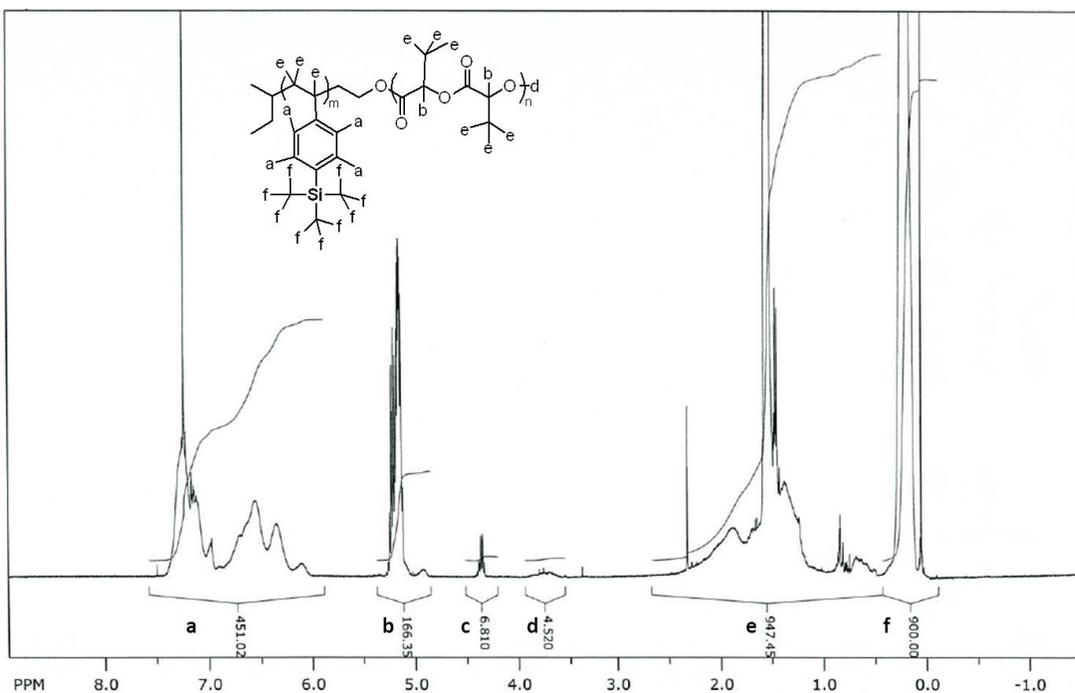
### PTMSS-*b*-PLA polymer characterization

The molecular weight of the PTMSS block and the PDI of the PTMSS block and PTMSS-*b*-PLA block copolymers were determined by GPC. Figure S1 shows representative GPC traces for PTMSS<sub>5.5</sub> and PTMSS<sub>5.5</sub>-*b*-PLA<sub>3.7</sub>.



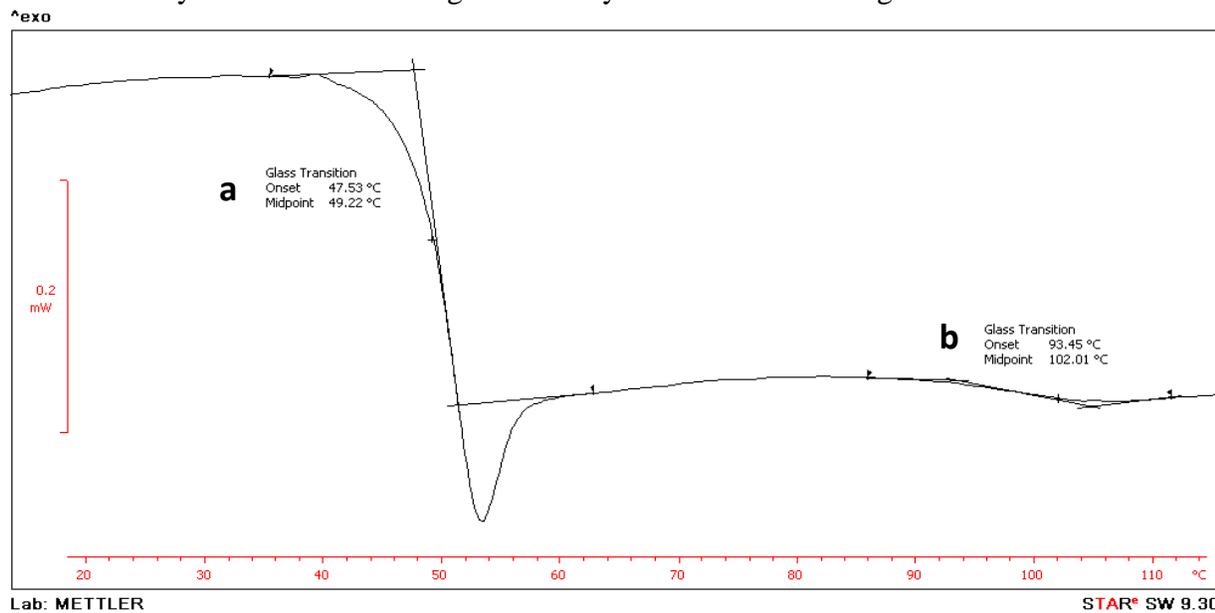
**Figure S1.** Normalized GPC traces for PTMSS<sub>5.5</sub> and PTMSS<sub>5.5</sub>-*b*-PLA<sub>3.7</sub>

The molecular weight of the PLA block was determined using  $^1\text{H}$  NMR. Figure S2 shows the  $^1\text{H}$  NMR spectrum for PTMSS<sub>5.5</sub>-*b*-PLA<sub>3.7</sub>.

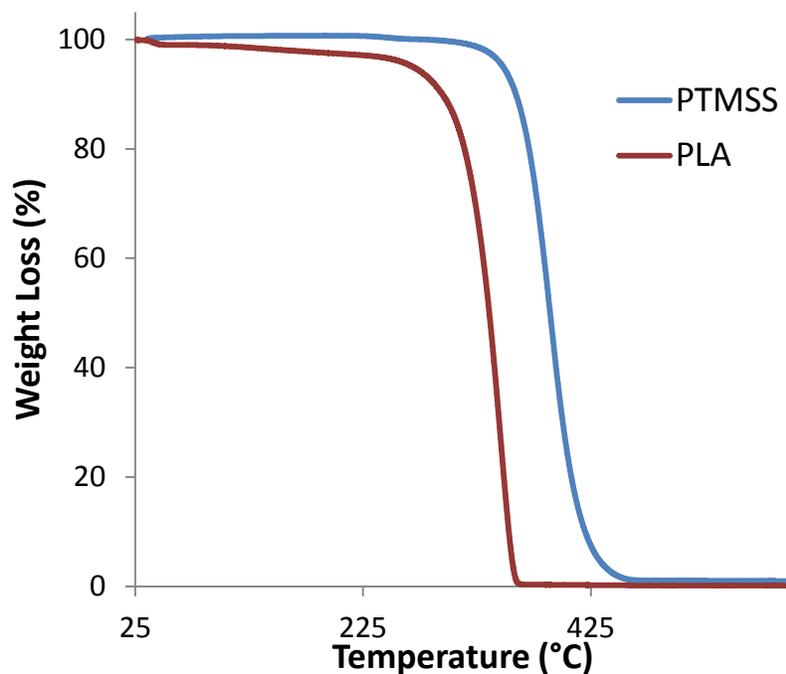


**Figure S2.**  $^1\text{H}$  NMR Spectra for PTMSS<sub>5.5</sub>-*b*-PLA<sub>3.7</sub>. Peaks b and f were used to determine the molecular weight of PLA. Peak c represents a small amount of residual D,L-lactide monomer in the sample.

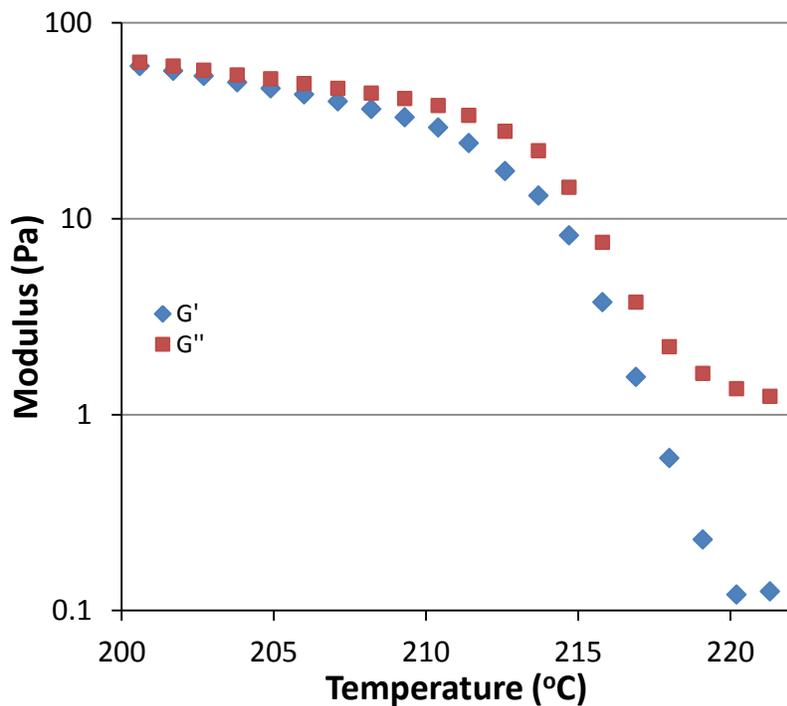
The glass transition temperatures of the PTMSS and PLA blocks for PTMSS<sub>5.5</sub>-*b*-PLA<sub>3.7</sub> were determined by differential scanning calorimetry and are shown in Figure S3.



**Figure S3.** DSC trace of PTMSS<sub>5.5</sub>-*b*-PLA<sub>3.7</sub> showing the glass transitions of a) the PLA block at around 49°C and b) the PTMSS block at around 102°C



**Figure S4.** TGA data for PTMSS and PLA homopolymers showing degradation of PLA around 250°C and degradation of PTMSS around 320 °C



**Figure S5.** Rheology data for PTMSS<sub>3.0</sub>-b-PLA<sub>5.0</sub> demonstrating an order of magnitude drop in the storage and loss modulus around 212 °C indicating the presence of an order-disorder transition. Data were collected on a TA Instruments AR-2000ex in strain controlled mode at 1 rad/s frequency in the linear viscoelastic regime.

### Calculating the $\chi$ -parameter of PTMSS-*b*-PLA by absolute intensity SAXS

Equations have been summarized previously in the literature and are shown below.

$$I(q) = K[S(q)/W(q)-2\chi]^{-1} \quad (S1)$$

$$S(q) = \langle S_{TMSS, TMSS} \rangle + 2\langle S_{TMSS, LA} \rangle + \langle S_{LA, LA} \rangle \quad (S2)$$

$$W(q) = \langle S_{TMSS, TMSS} \rangle * \langle S_{TMSS, LA} \rangle - \langle S_{LA, LA} \rangle^2 \quad (S3)$$

$$\langle S_{X, X}(q) \rangle = r_{c,n} f_{X,n}^2 g_{X,n}^{(2)}(q) \quad (S4)$$

$$\langle S_{TMSS, LA}(q) \rangle = r_{c,n} f_{TMSS} f_{LA} g_{TMSS,n}^{(1)}(q) g_{LA,n}^{(1)}(q) \quad (S5)$$

$$r_{c,n} = (v_{TMSS} N_{TMSS,n} + v_{LA} N_{LA,n}) / (v_{TMSS} * v_{LA})^{1/2} \quad (S6)$$

$$g_{X,n}^{(1)}(q) = 1/X_{X,n} \{ 1 - [X_{X,n}(\lambda_X - 1) + 1]^{-(\lambda_X - 1)^{-1}} \} \quad (S7)$$

$$g_{X,n}^{(2)}(q) = 2/X_{X,n}^2 \{ -1 + [X_{X,n}(\lambda_X - 1) + 1]^{-(\lambda_X - 1)^{-1}} \} \quad (S8)$$

$$X_{X,n} = (N_{X,n} b_X^2 / 6) q^2 \quad (S9)$$

$$\lambda_{PTMSS} = N_{X,w} / N_{X,n} \quad (S10)$$

$$\lambda_{PLA} = (-(\lambda_{BCP} - 1) - (\lambda_{PTMSS} - 1) * W_{TMSS}^2) / (1 - W_{TMSS})^2 + 1 \quad (S11)$$

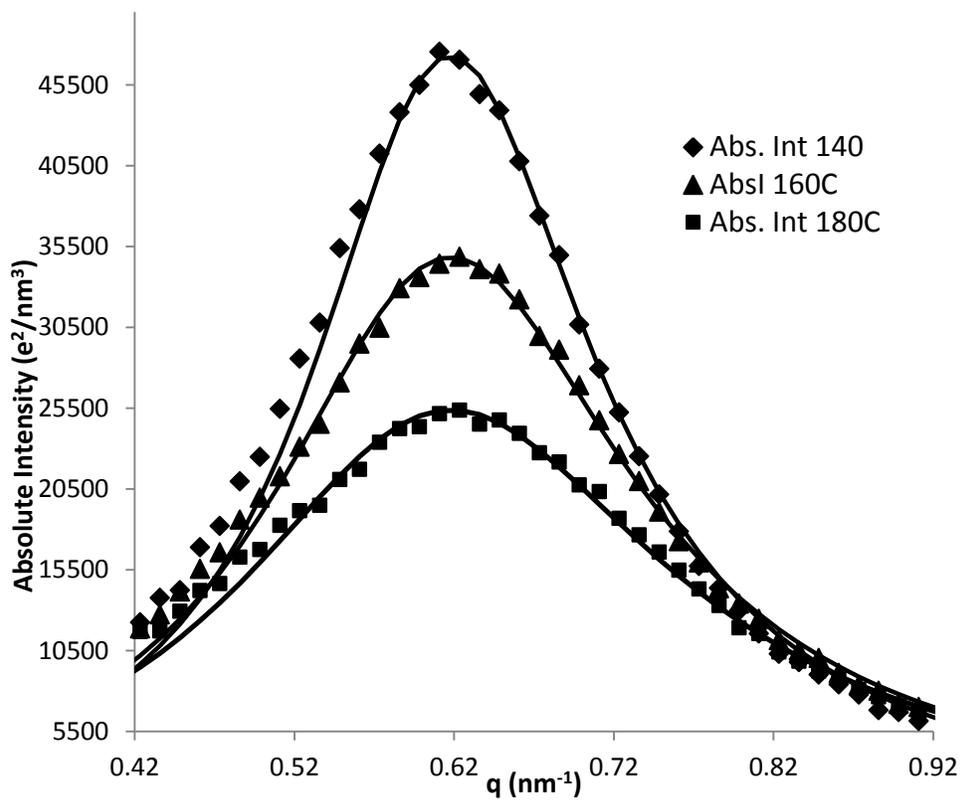
Where X = PTMSS or PLA.  $f_X$  is the volume fraction of X,  $v_X$  is the molar volume of the X monomer,  $N_{X,n}$  and  $N_{X,w}$  are the number- and weight-average degree of polymerization, respectively.  $b_X$  is the segment length of X, and  $\lambda_X$  is the PDI of the X block.  $\lambda_{PLA}$  is determined by equation S11 from the PDI of the block copolymer, determined by GPC. Table S1 reports the parameters used in this study to determine  $\chi$ .

**Table S1.** Table of parameters used in the characterization of the  $\chi$ -parameter for PTMSS<sub>2.3</sub>-*b*-PLA<sub>1.7</sub>

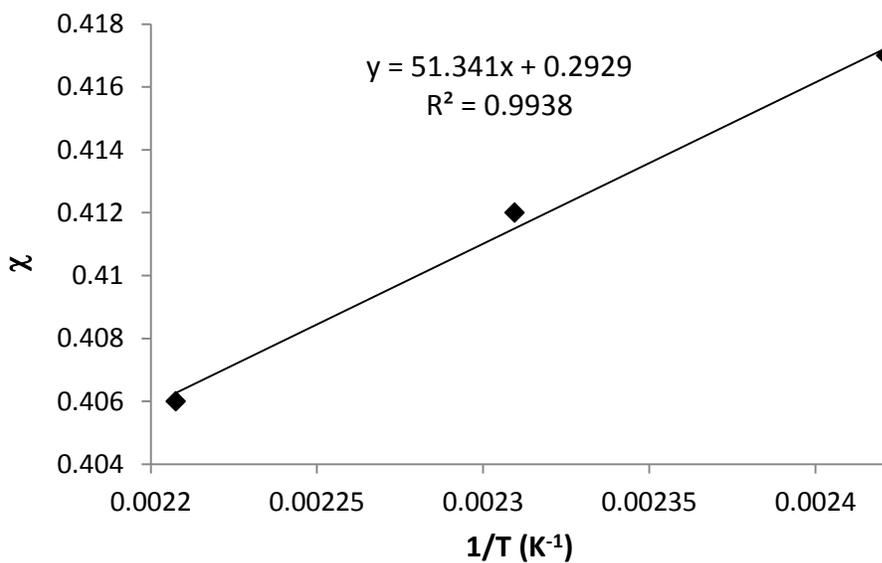
Block	w	f	N	b	v	$\lambda$
TMSS	0.589	0.615	13.04	0.47	194	1.11
LA	0.411	0.385	12.07	1.35	121.5	1.37

**Table S2.** Calculated  $\chi$ -parameter at three different temperatures

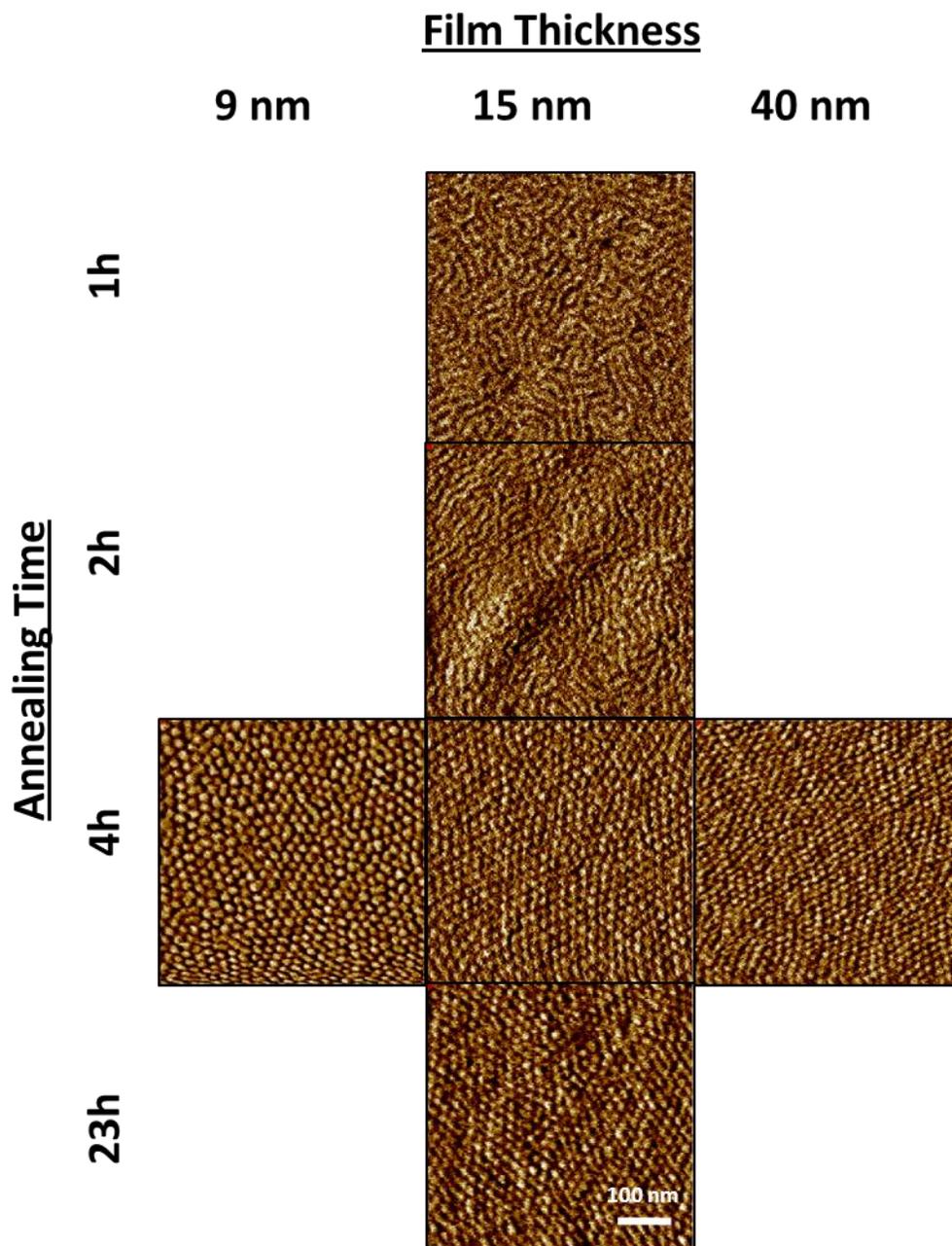
T (K)	$\chi$
413	0.417
433	0.412
453	0.406



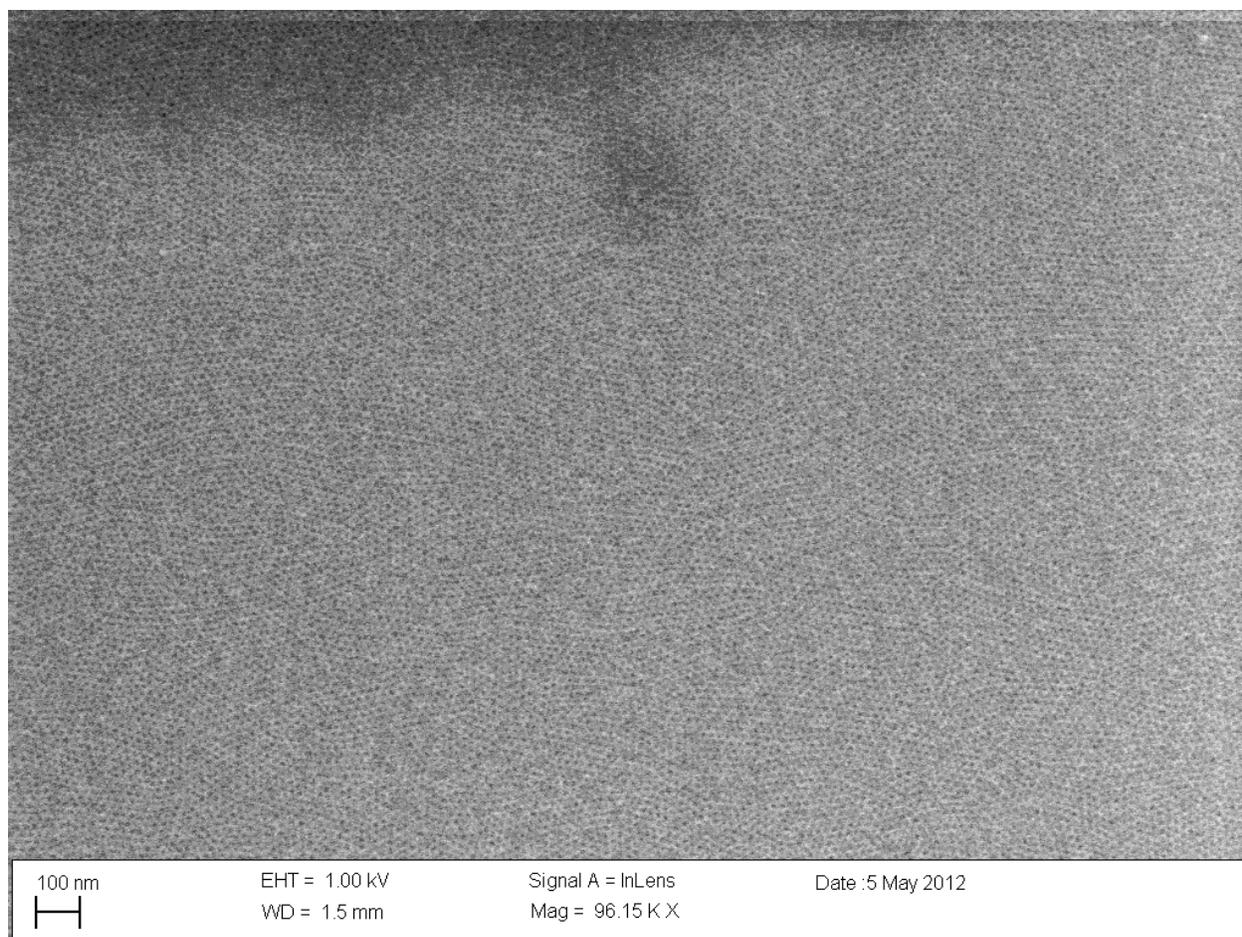
**Figure S6.** Absolute intensity SAXS profiles of PTMSS<sub>2.3</sub>-b-PLA<sub>1.7</sub> at 140 °C, 160 °C, and 180 °C (markers) and corresponding theoretical fits for chi using equations S1-S11 (lines).



**Figure S7.** Plot of  $\chi$  vs. inverse temperature and corresponding best fit line



**Figure S8.** AFM phase images of thin films of cylinder-forming PTMSS<sub>5.5</sub>-*b*-PLA<sub>3.7</sub> after solvent annealing under cyclohexane vapor for a variety of film thicknesses and annealing times



**Figure S9.** Large area SEM image of a cylinder-forming PTMSS<sub>5.5</sub>-*b*-PLA<sub>3.7</sub> film after solvent annealing under cyclohexane vapor for 4h showing the existence of features over a large area.

**Table S3.** Homopolymer etch rate data for PTMSS and PLA.

<u>Homopolymer</u>	<u>Initial Thickness (nm)</u>	<u>Final Thickness (nm)</u>	<u>Etch Rate (nm/sec)</u>
PTMSS	135.6 ± 0.3	122.8 ± 0.5	0.43 ± 0.02
PLA	596 ± 4	240 ± 10	12.0 ± 0.4

### Supporting Information References

- [1] Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M., Anionic polymerization: High vacuum techniques. *J. Polym. Sci. Pol. Chem.* 2000, 38 (18), 3211-3234.
- [2] Bailey, T. S.; Pham, H. D.; Bates, F. S., Morphological Behavior Bridging the Symmetric AB and ABC States in the Poly(styrene-*b*-isoprene-*b*-ethylene oxide) Triblock Copolymer System. *Macromolecules* 2001, 34 (20), 6994-7008.