Supplementary Information

Thin Film Confinement of a Spherical Block Copolymer *via* Forced Assembly Co-extrusion

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Experimental

Materials

Poly (methyl methacrylate) (PMMA) was obtained from Arkema Inc. and is commercially available as Plexiglas VM-100M (number average molecular weight, M_n= 70 kg/mol, polydispersity (*DP)*=1.53). Polystyrene (PS) was donated by the Dow Chemical Company, Styron 666D (M_n = 128 kg/mol and DP=1.60). Styroflex 2G 66 (STF), a styrene butadiene triblock copolymer containing 70 wt% of styrene, was donated by BASF Corporation and has a weight average molecular weight, Mw, of 120 kg/mol.[32] Styroflex is a symmetric, triblock copolymer consisting of polystyrene glassy, end blocks and a statistical soft block comprised of polystyrene/polybutadiene (PS/PBD). The block length ratio is 15:70:15 with an overall PS content of ~70% with an order-disorder temperature (ODT) of approximately 145 ˚C.[32, 33]

Co-extruded Samples

Processing temperatures of the PS, PMMA, and STF were determined as a function of viscosity using a melt flow indexer (Galaxy I Model D7054, Kayeness Inc.) at a low shear rate (10 sec^{-1}) to simulate flow conditions during the co-extrusion process. The polymer controls were dried under vacuum for 24 hours prior to co-extruding to eliminate moisture from the pellets. The melt pumps were set to the following temperatures for the microlayering process: 210 ˚C for PMMA and STF and 220 ˚C for PS.

Multilayer films of alternating homopolymer and block copolymer were produced with 257 layers. The glassy polymer was extruded on both sides of the film to ensure that the STF did not adhere to the chill roll. The total film thicknesses were varied from 25 µm to 250 µm at a constant volume composition to provide equal layer thicknesses of the constituents.

Annealed Samples

The multilayer films and polymer controls were annealed for 4 days under vacuum to prevent degradation and allow sufficient chain mobility while under confinement. The annealing temperature for both systems was 90 ˚C to ensure that the confining layer remains above their glass transition temperature (T_g).

Small-angle X-ray Scattering

Small-angle X-ray scattering (SAXS) measurements were conducted using a Rigaku S-MAX 3000 SAXS system. Cu Kα X-rays from a MicroMax-002+ sealed tube source (λ = 0.154 nm) were collimated through three pinhole slits to yield a final spot size of 0.7 mm at the sample position. Multilayer films were mounted in a vacuum chamber and aligned in the normal direction (ND) with respect to the X-ray beam. Two-dimensional (2D) SAXS data were collected using a Rigaku multiwire area detector with a circular active area of 133 mm^2 and a spatial resolution of 1024 x 1024 pixels. The sample-to-detector distance and the scattering vector, q, were calibrated using a silver behenate (AgBe) standard with a characteristic (*001*) peak position at q=1.076 nm^{-1}. The calculated sample-to-detector distance was 1.5 m. Typical exposure times for ND SAXS patterns were 3 hours due to low scattering intensity from the SEPS. All X-ray images were processed using software named "POLAR" (Stonybrook Technology and Applied Research, Inc).

DMA

The thermal properties of the bulk PS and STF-PS 100nm layer multilayer films were analyzed by dynamic mechanical analysis (DMA) to determine an annealing temperature for the block copolymer, while maintaining the multilayer architecture. The glass transition temperatures (T_gs) of the PS layer were determined by the maxima in the tan delta (δ) curves and were found to be 107.8 ˚C and 106.4 ˚C for PS control and PS-STF multilayer films, respectively (Figure S1). The experiment was conducted at 3 ˚C/min from -100 ˚C to 130 ˚C.

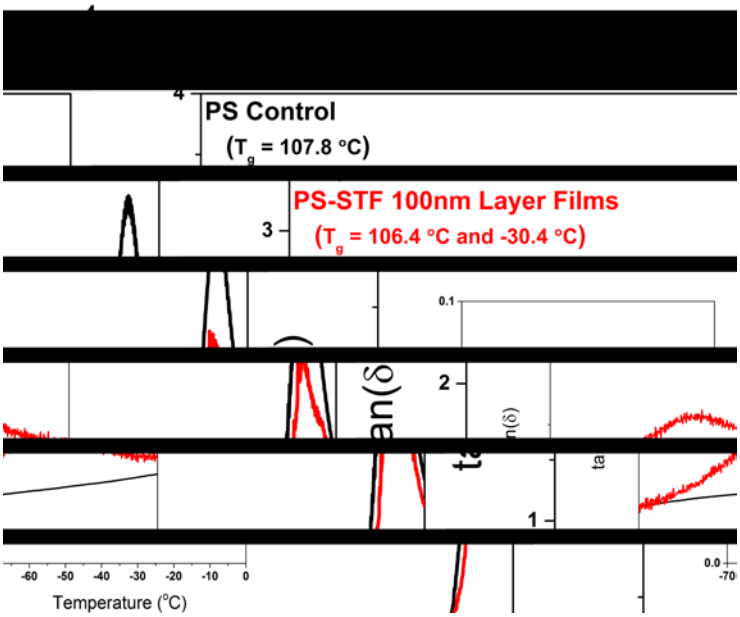

Figure S1. DMA tan delta (δ) curves of PS Control and PS-STF 100 nm multilayer films.

TEM

The BCP morphology within the multilayer films was studied by transmission electron microscopy (TEM). The samples were embedded in a low viscosity Spurr's resin and placed under vacuum for 7 hours at 70 ˚C to cure the epoxy prior to cryosectioning on a Leica Ultramicrotome, UC6. In preparation for transmission electron microscopy (TEM), samples were cryomicrotomed at -100 ˚C with a Diatome cryodiamond knife and stained for 40 minutes with a 1% by weight solution of osmium tetroxide, OsO_4. A field-emission gun, energy-filtering TEM (Zeiss Libera 200FE) operating at 200 kV was utilized.

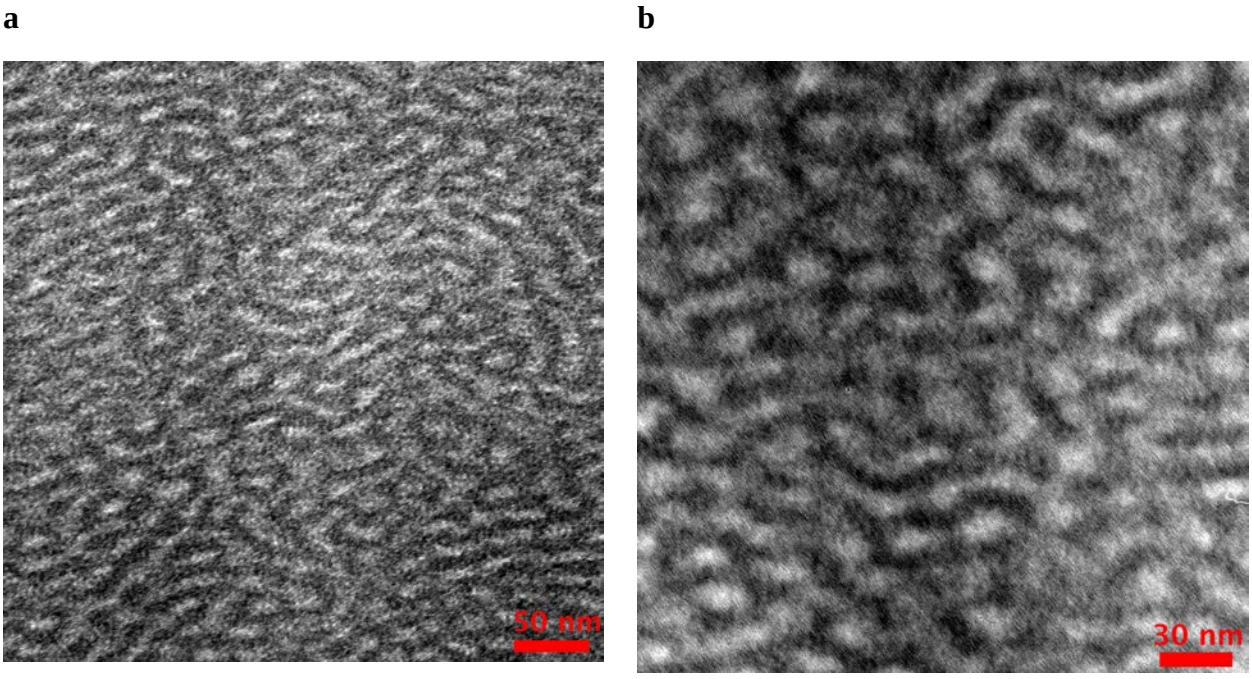

Figure S2. TEM images of Styroflex 2G 66 controls after a) 1 day and b) 4 days.

Melt flow index (MFI)

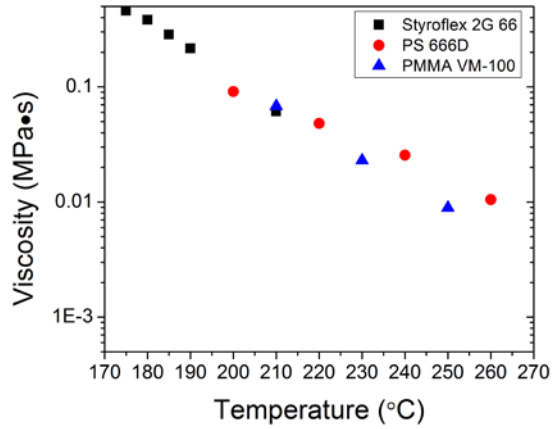

Figure S3. Melt flow index for Styroflex 2G 66 and confining layer PS and PMMA. Processing temperatures: ~ 210 ˚C for STF and PMMA and 220 ˚C for PS.

Interphase calculations of PS/STF and PMMA/STF multilayer films

Species	Molar Segmental Volume, V_i (cm^3/mol)	Solubility Parameter, δ_i ($MPa^{½}$)
Polybutadiene *PBD*	58.9	17.1
Poly (methyl methacrylate) *PMMA*	89.3	18.3
Polystyrene *PS*	114.6	17.5

- 70% polystyrene and 30% polybutadiene
- The solubility parameter and molar segmental volume contributions from the ethylene/propylene block can be taken as an arithmetic mean of the two polymer properties

STF consists of 70% by volume polystyrene (Φ_{PS} = 0.70)

$$\delta_{STF} = \phi_{PS}\delta_{PS} + (1-\phi_{PS})\delta_{PBD} = 17.4\ \mathrm{MPa}^{\frac{1}{2}}$$

$$V_{STF} = \phi_{PS}V_{PS} + (1-\phi_{PS})(V_{PBD}) = 97.9\ \frac{\mathrm{cm}^3}{\mathrm{mol}}$$

Flory-Huggins Interaction Parameter (χ)

$$\chi = \frac{\phi_1 V_1 + \phi_2 V_2}{RT}(\delta_1 - \delta_1)^2$$

- All films contain 50% by volume STF and either 50% by volume PMMA or PS, the average molar segmental volume of each set of films can again be taken as a simple arithmetic mean of the two components

$$\chi = \frac{\left(\frac{V_1 + V_2}{2}\right)}{RT}(\delta_1 - \delta_1)^2 = \frac{V_1 + V_2}{2RT}(\delta_1 - \delta_2)^2$$

- Since the interface forms during the co-extrusion process, the processing temperatures are used for the χ-parameter calculations

T= 482.15 K for PMMA/STF Films

$$\chi = \frac{89.3\ \frac{\text{cm}^3}{\text{mol}} + 97.9\ \frac{\text{cm}^3}{\text{mol}}}{2\left(8.3\ \frac{\text{cm}^3 \times \text{MPa}}{\text{mol} \times \text{K}}\right)482.15\ \text{K}}\left(18.3\ \text{MPa}^{\frac{1}{2}} - 17.4\ \text{MPa}^{\frac{1}{2}}\right)^2$$

$$\chi = 0.0207$$

T = 492.15 K for PS/STF Films

$$\chi = \frac{114.6\ \frac{\text{cm}^3}{\text{mol}} + 97.9\ \frac{\text{cm}^3}{\text{mol}}}{2\left(8.3\ \frac{\text{cm}^3 \times \text{MPa}}{\text{mol} \times \text{K}}\right)518.15\ \text{K}}\left(17.5\ \text{MPa}^{\frac{1}{2}} - 17.4\ \text{MPa}^{\frac{1}{2}}\right)^2$$

$$\chi = 0.0036$$

Interfacial Width Calculation (d_I)

- Statistical segment step length (b)
  - PMMA = 0.60 nm
  - PS = 0.67 nm
  - PBD = 0.44 nm

$$b_{STF} = \phi_{PS} b_{PS} + (1 - \phi_{PS}) b_{PB} = 0.601$$

$$b' = \sqrt{b_1 \times b_2}$$

$$d_I = \frac{2b'}{\sqrt{6\chi}} = \frac{2\sqrt{b_1 \times b_2}}{\sqrt{6\chi}}$$

PS Interface Thickness

$$d_I = \frac{2\sqrt{0.67\ \text{nm} \times 0.601\ \text{nm}}}{\sqrt{6(0.0036)}} = 8.6\ \text{nm}$$

PMMA Interface Thickness

$$d_I = \frac{2\sqrt{0.60\ \text{nm} \times 0.601\ \text{nm}}}{\sqrt{6(0.0207)}} = 3.4\ \text{nm}$$

"Due to the sensitive nature of the calculations and the strong dependence which results from the solubility parameter chosen, all values for the solubility parameter were taken from the polymer handbook as calculated by Ahmed and Yaseen based on the presence of functional groups in each polymer. By following the calculations above it is seen that the interfacial width of PMMA/STF films is approximately 3.4 nm, while the interfacial width of PS/STF films is approximately 8.6 nm."