*Supplementary Material*

Dynamics of Interacting Interphases in Polymer Bilayer Thin Films

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## **S1. Calculation of Interfacial Tension**

In order to calculate the non-bonded interaction parameters between PS and PMMA chains, we tune the strength of the cross-cohesive interactions to the experimental PS-PMMA interfacial tension. Because each polymer contains two bead types, APMMA, BPMMA, APS, and BPS, where A and B represent the backbone and sidechain bead, respectively, there are four cross interactions which must be defined.

We simplify the parameterization by defining a common scaling factor α as a prefactor for the arithmetic average between the two-bead type self-interactions. For instance, APMMA-APS = α/2(APMMA-APMMA+APS-APS) and so on. Next, for each value of α, the interfacial tension is calculated for 7.5 nm PS and PMMA thick slabs which interact across a 15 x 15 nm2 interface in the x-y plane. The interfacial tension is defined as the free energy required to increase the interface by a unit area and is estimated using the Kirkwood-Buff equation1-4:

  (S1)

where *Lz* is the length of the simulation box in the z direction and *Pii* are the lateral pressures on the *xx, yy,* and *zz* dimensions. (See Figure S1.) It was found that α = 1 provided the interfacial tension closest to experimental values, which is the arithmetic average of self-interactions for respective polymers. (Cross parameters can be found in Table S4.)



**Figure S1.** The interfacial tension γPS-PMMA is calculated for the PS-PMMA interface at 425 K using the Kirkwood-Buff equation as a function of the prefactor α that scales the intermolecular LJ interactions (see text for definition). A linear fitting is used to correlate γPS-PMMA and $α$ (dashed line).

## **S2. Supported Film Local Tg for PS**

The local $T\_{g}$ for supported PS films from 10 nm to 40 nm thickness is measured in 2 nm increments. (See Figure S2.) The PS film is supported by an implicit wall with interaction energy = 10 kcal/mol. The local $T\_{g}$ near the supported interface shows appreciation over 50 K above the bulk $T\_{g}$ and converges to the bulk-like interior for film thicknesses above 20 nm. The local $T\_{g}$ behavior can be described relatively well using an analytical $T\_{g}$ function (Eq. 6) with universal parameters found in Table 1. The supported 20 nm PS film shows some deviation for 20 nm in the interior region, which we presume is caused by high variation and insufficient sampling.



**Figure S2.**  The local $T\_{g}$ of PS supported films from 10 nm to 40 nm is shown for simulations (open symbols), which is found to be well approximated by the superposed analytical fitting model (dashed lines) for the supported and free surface interphases. The z axis is defined here to be zero at the substrate and points into the film interior.

## **S3.** **Predictive Models of Bilayer Local** $T\_{g}$ **Behavior**

The fitting model for the bilayer master curve can be derived from superposing the freestanding region, the polymer-polymer interphase, and the supported interphase region using universal fitting parameters found in Table 1. This equation is found to be:

|  |  |  |
| --- | --- | --- |
|  |  | (S2) |

which is used to generate the model shown in Figure 4A (dashed lines). More generally, for a bilayer of polymer 1 and polymer 2 the master curve follows the equation:

|  |  |  |
| --- | --- | --- |
|  |  | (S3) |

**SUPPORTING TABLES**

**Table SI.** Functional form of force field and optimized potential parameters for PS. A random distribution of meso and racemo B-A-A-B dihedral potentials are applied along the CG chain to reproduce atactic stereoisometry as described in our previous study.5

|  |  |  |
| --- | --- | --- |
| Interaction | Potential Form | Parameters |
| A-A Bond Length |  | *k* = 80.69 kcal/mol∙Å2*l0* = 2.568 Å |
| A-B Bond Length |  | *k* = 224.6 kcal/mol∙Å2*l0* = 2.871 Å |
| A-A-A Angle |  | *a1* = 2.277e-1 *b1* = 10.76°*θ1* = 177.1°  | *a2* = 5.588e-1 *b2* = 19.27°*θ2* = 148.8° | *a3* = -5.497e-1*b3* = 18.78°*θ3* = 148.5° |
| A-A-B Angle |  | *a1* = 1.451e-1 *b1* = 6.762°*θ1* = 141.5° | *a2* = 1.767e-2 *b2* = 9.745°*θ2* = 93.22° | *a3* = 3.199e-2*b3* = 11.01°*θ3* = 134.7° |
| A-A-A-A Dihedral Angle |  | *A* (atactic) = 0.5 (kcal/mol) |
| B-A-A-B Dihedral Angle |  | *meso**A1* = 4.236 (kcal/mol)*A2* = -1.274 (kcal/mol)*A3* = 0.5337 (kcal/mol)*A4* = -0.8179 (kcal/mol)*A5* = -0.4622 (kcal/mol) | *racemo**A1* = 3.762 (kcal/mol)*A2* = 0.3631 (kcal/mol)*A3* = 2.128 (kcal/mol)*A4* = -0.9691 (kcal/mol)*A5* = -1.880 (kcal/mol) |
| Non-bonded  |  | *(See Table S3)* |

**Table SII.** Functional form of force field and optimized potential parameters for PMMA as described in our previous study.6

|  |  |  |
| --- | --- | --- |
| Interaction | Potential Form | Parameters |
| A-A Bond Length |  | *k* = 105.0 kcal/mol∙Å2, *l0* = 2.735 Å |
| A-B Bond Length |  | *k* = 39.86 kcal/mol∙Å2, *l0* = 3.658 Å |
| A-A-A Angle |  | *a1* = 2.294e-2, *b1* = 9.493°,*θ1* = 121.0°  | *a2* = 4.367e-3, *b2* = 6.210°,*θ2* = 158.5° |
| A-A-B Angle |  | *k2* = 9.881 kcal/mol∙rad2, *k3* = -15.12 kcal/mol∙rad3, *k4* = 6.589 kcal/mol∙rad4, *θ0* = 1.690 rads |
| A-A-A-A Dihedral Angle |  | *A1* = 4.380 (kcal/mol), *A2* = 0.8739 (kcal/mol), *A3* = -0.3571 (kcal/mol), *A4* = -0.2774 (kcal/mol), *A5* = 0.09312 (kcal/mol) |
| B-A-A-B Dihedral Angle |  | *A1* = 4.519 (kcal/mol), *A2* = -0.8859 (kcal/mol), *A3* = -1.692 (kcal/mol), *A4* = 0.5625 (kcal/mol), *A5* = 0.9562 (kcal/mol) |
| Non-bonded  |  | *(See Table S3)* |

**Table SIII.** Bead masses and non-bonded 12-6 LJ potential parameters for PS and PMMA, as described in our previous CG studies.5, 6

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Polymer System | *mA*(g/mol) | *mB*(g/mol) | *εAA*(kcal/mol) | *σAA*(Angs) | *εBB*(kcal/mol) | *σBB*(Angs) | *εAB*(kcal/mol) | *σAB*(Angs) |
| *Polystyrene* | 27.0 | 77.1 | 0.285 | 4.421 | 0.812 | 5.421 | 0.481 | 4.921 |
| *Poly(methyl methacrylate)* | 85.1 | 15.0 | 0.500 | 5.500 | 1.500 | 4.420 | 1.000 | 4.960 |

**Table SIV.** Cross interaction non-bonded 12-6 LJ potential parameters for PS and PMMA.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Polymer System | $$ε\_{A\_{PS}A\_{PMMA}}$$(kcal/mol) | $σ\_{A\_{PS}A\_{PMMA}}$ (Angs) | $ε\_{A\_{PS}B\_{PMMA}}$ (kcal/mol) | $σ\_{A\_{PS}B\_{PMMA}}$ (Angs) | $ε\_{B\_{PS}A\_{PMMA}}$ (kcal/mol) | $σ\_{B\_{PS}A\_{PMMA}}$ (Angs) | $ε\_{B\_{PS}B\_{PMMA}}$ (kcal/mol) | $σ\_{B\_{PS}B\_{PMMA}}$ (Angs) |
| *Polystyrene-Poly(methyl methacrylate)* | 0.393 | 4.961 | 0.893 | 4.421 | 0.656 | 5.461 | 1.156 | 4.921 |

**References**

1. A.E. Ismail and G.S. Grest: Application of Ewald summations to long-range dispersion forces. *J. Chem. Phys.* **127**, 144711 (2007).

2. Y.J. Kim, K.-H. Lin and A. Strachan: Molecular dynamics simulations of PMMA slabs: role of annealing conditions. *Modell. Simul. Mater. Sci. Eng.* **21**, 065010 (2013).

3. R.J. Lang, W.L. Merling and D.S. Simmons: Combined Dependence of Nanoconfined T g on Interfacial Energy and Softness of Confinement. *ACS Macro Letters* **3**, 758 (2014).

4. K.C. Jha, A. Dhinojwala and M. Tsige: Local Structure Contributions to Surface Tension of a Stereoregular Polymer. *ACS Macro Lett.* **4**, 1234 (2015).

5. D.D. Hsu, W. Xia, S.G. Arturo and S. Keten: Thermomechanically Consistent and Temperature Transferable Coarse-Graining of Atactic Polystyrene. *Macromolecules.* **48**, 3057 (2015).

6. D.D. Hsu, W. Xia, S. Arturo and S. Keten: A Systematic Method for Thermomechanically Consistent Coarse-graining: A Universal Model for Methacrylate-based Polymers. *J. Chem. Theory Comput.* **10**, 2514 (2014).