Supporting Information

Blends of Poly (ε-caprolactone) and Intermediate Molar Mass Polystyrene as Langmuir Films at the Air/Water Interface

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1. Surface Elasticity ($\varepsilon_s$) Analysis for PCL/PS Blends

Esker et al. showed that the traditional approach for describing the scaling behavior of $\Pi$ with respect to surface concentration, $\Gamma = 1/A$, i.e., $\Pi \propto \Gamma^z$, in the semi-dilute regime, could be reduced to Eqs. 1 and 2 if one assumes that $\Pi = 0$ at the onset of semi-dilute monolayer regime.\(^{43}\)

$$\Pi = CA^{-z} \quad (1)$$

$$\varepsilon_s = z\Pi \quad (2)$$

where the static elasticity $\varepsilon_s$, the quasi-2D analog of the bulk modulus, is defined as

$$\varepsilon_s = \kappa^{-1} = -A \left( \frac{\partial \Pi}{\partial A} \right)_T \quad (3)$$

In Eq. 3, $\kappa$ is the 2D-analog of the bulk isothermal compressibility. In this treatment, $z$, the two-dimensional scaling exponent, has a value of $z = 2.86$ for a good solvent,\(^{44}\) and values ranging from 8 to 101 for theta conditions depending on the theoretical treatment used to obtain $z$.\(^{45,46}\) For comparison, mean field treatments yield $z = 3$ (good solvent) and $z \rightarrow \infty$ (theta solvent).\(^{47}\) Using the $\Pi$-$A$ isotherm data prior to the collapse transition, $\varepsilon_s$-$\Pi$ isotherms for all PCL/PS blend films were obtained as seen in the inset graph of Figure S1. The $\varepsilon_s$-$\Pi$ isotherm for the pure PS sample is located between the extreme conditions of the theta solvent and good solvent. Given the fact that PS is non-amphiphilic, this curve is really an apparent isotherm and reflects the fact that rigid PS forms large aggregates at the air/water (A/W) interface rather than a poor solvent condition. The interesting feature of $\varepsilon_s$-$\Pi$ plots for PCL/PS blend films is that the surface elasticity of each PCL/PS blend exhibits $\varepsilon_s$ behavior that is identical to pure PCL. This result is not surprising given Figure 3 of the main text, $\Pi$ vs. $A_{PCL}$, where all blend isotherms collapse down to identical behavior in the monolayer regime, indicating completely immiscible behavior for high molar mass (glassy) PS blends with PCL blends at the A/W interface.
Figure S1. Static elasticity, $\varepsilon_s$ vs. $<A>$ for PCL/PS mixed Langmuir films with various PS mole fractions. The inset is a plot of $\varepsilon_s$ as a function of $\Pi$ for all PCL/PS blends. The two solid lines in the inset are theoretical curves, $\varepsilon_s = z\Pi$, for good solvent conditions ($z = 2.86$)\textsuperscript{44} and the most extreme numerical value reported for theta solvent conditions ($z = 101$)\textsuperscript{46}. The symbols correspond to $X_{PS} = 1.00$ (▃), 0.81 (♬), 0.69 (♫), 0.65 (▼), 0.34 (▲), 0.13 (▽), and 0.00 (●).
Figure S2. AFM height (left) and phase (right) images of LS-films for a representative PCL/PS blend, $X_{PS} \sim 0.69$. Single layer LS-films were transferred onto PS coated silicon substrates at $\Pi \sim 2$ mN·m$^{-1}$ (A, A'), $\Pi \sim 8$ mN·m$^{-1}$ (B, B'), and $\Pi \sim 11$ mN·m$^{-1}$ (C, C'). 5×5 µm$^2$ images are provided as they are more easily compared to BAM images at similar $\Pi$. The z-scales in the height images are 0-60 nm and the z-scales in phase images are 0-60 deg.
3. AFM Phase Images of LS-Films for a Representative PCL/PS Blend, $X_{ps} \sim 0.13$.

**Figure S3.** AFM height (left) and phase (right) images of LS-films for a representative PCL/PS blend, $X_{ps} \sim 0.13$. Single layer LS-films were transferred onto PS coated silicon substrates at $\Pi \sim 2 \text{ mN}\cdot\text{m}^{-1}$ (A, A') and $\Pi \sim 11 \text{ mN}\cdot\text{m}^{-1}$ (B, B'). 5×5 µm² images are provided as they are more easily compared to BAM images at similar $\Pi$. Z-scales: (A, B) 0-60 nm, (A') 0-40 deg, and (B') 0-60 deg.

Another important feature of the hysteresis loops is their reversibility. Representative hysteresis loops are shown in Figure S4, where the compression isotherms are represented by dotted lines and solid lines highlight the expansion isotherms. In Figure S4A, the arrow inside the figure indicates the start and ending points of each individual hysteresis loop as well as its composition. All blend films were compressed to sufficiently small \(<A>\) values to ensure that all films have gone through the collapse transition within the limitation of the compression ratio for the Langmuir trough. The expansion isotherm for pure PCL is analogous to a "melting" process. The surface pressure corresponding to the plateau in the expansion isotherm is characteristic of the “melting pressure” of PCL crystals. As seen in Figure S4A, there is a definite change in the expansion isotherm with a change in blend composition. On the basis of the observation that the surface activity of the blends is controlled by the PCL component \(\Pi - APCL\) plots were constructed. Figure S4B clearly shows that the expansion isotherms for blends of \(X_{PS} \sim 0.13\) and \(\sim 0.34\) are consistent with pure PCL where the plateau corresponds to the melting of PCL crystals formed during compression. In contrast, the hysteresis loops for binary blends where PS is the major component are smaller without clearly observable plateaus. As expected, the surface tension and surface area of the blend films during expansion are only controlled by the surface-active PCL component, even though there are dramatic morphological changes when non-amphiphilic PS is blended with PCL.
Figure S4. (A) Π-<A> hysteresis loops (1\textsuperscript{st} cycle) for PCL/PS blends and pure PCL obtained at 22.5 °C and a compression rate of 20 cm\textsuperscript{2}\textperiodcentered min\textsuperscript{-1}. The numbers with arrows inside the figure indicate the $X_{PS}$ value of each blend as well as the starting and ending points of each hysteresis loop. (B) Π-$A_{PCL}$ hysteresis loops for different PCL/PS blends and pure PCL. This plot was obtained by converting the <A> values from Figure 12A to $A_{PCL}$ values using the same method used to prepare Figure 3 of the main paper. The numbers with arrows indicate the $X_{PS}$ value of each blend and the corresponding expansion isotherm. The compression isotherms are represented by dotted lines and solid lines highlight the expansion isotherms in both (A) and (B).
Figure S5. Multiple Π-<A> hysteresis loops for a $X_{PS} \sim 0.65$ PCL/PS blend obtained at 22.5 °C and a compression rate of 20 cm$^2$·min$^{-1}$. The 1st hysteresis loop is represented by solid line, a dotted line indicates the 2nd cycle, and the dashed line shows the 3rd cycle.
5. Brewster Angle Microscopy Studies for PCL (M<sub>w</sub> = 10 kg·mol<sup>-1</sup>)/PS (M<sub>w</sub> = 1.56 kg·mol<sup>-1</sup>) Blends.

![Diagram showing isotherm and BAM images](image)

**Figure S6.** BAM images for a X<sub>PS</sub> ~ 0.81 PCL (M<sub>w</sub> = 10 kg·mol<sup>-1</sup>)/PS (M<sub>w</sub> = 1.56 kg·mol<sup>-1</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.06, Polymer Source, Inc.) blend film obtained at 22.5 °C and an expansion rate of 20 cm<sup>2</sup>·min<sup>-1</sup>. The letters on the isotherm indicate where the BAM images were taken during the hysteresis experiments and correspond to the average surface area (<A> / Å<sup>2</sup>·monomer<sup>-1</sup>) for compression: A (28.8), B (8), C (5.8), and D (4.7); and expansion: E (4.8), F (7.9), G (17.7), and H (25). Solidlike domains appear bright in all of the 2.4×3.2 mm<sup>2</sup> BAM images.
**Figure S7.** BAM images for a $X_{PS} \sim 0.13$ PCL ($M_w = 10 \text{ kg} \cdot \text{mol}^{-1}$)/PS ($M_w = 1.56 \text{ kg} \cdot \text{mol}^{-1}$, $M_w/M_n = 1.06$, Polymer Source, Inc.) blend film obtained at 22.5 °C and an expansion rate of 20 cm²·min⁻¹. The letters on the isotherm indicate where the BAM images were taken during the hysteresis experiments and correspond to the average surface area ($<A>/Å^2\cdot\text{monomer}^{-1}$) for compression: A (~18.7), B (~12), C (~10.4), and D (~9.8); and expansion: E (~9.6), F (~16.3), G (~35), and H (~64). Solidlike domains appear bright in all of the 2.4×3.2 mm² BAM images.
6. Brewster Angle Microscopy Studies for PCL ($M_w = 10$ kg·mol$^{-1}$)/PS ($M_w = 64.4$ kg·mol$^{-1}$) Blends.

**Figure S8.** BAM images for a $X_{PS} \sim 0.81$ PCL ($M_w = 10$ kg·mol$^{-1}$)/PS ($M_w = 64.4$ kg·mol$^{-1}$, $M_w/M_n = 1.03$, Polymer Source, Inc.) blend film obtained at 22.5 °C and an expansion rate of 20 cm$^2$·min$^{-1}$. The letters on the isotherm indicate where the BAM images were taken during the hysteresis experiments and correspond to the average surface area ($<A>/Å^2$·monomer$^{-1}$) for compression: A (34.4), B (10.8), C (7), and D (5.1); and expansion: E (6.2), F (14.6), G (19.4), and H (25). Solidlike domains appear bright in all of the 2.4×3.2 mm$^2$ BAM images.
Figure S9. BAM images for a X_{PS} \sim 0.13 \text{ PCL (M}_w = 10 \text{ kg} \cdot \text{mol}^{-1})/\text{PS (M}_w = 64.4 \text{ kg} \cdot \text{mol}^{-1}, \text{M}_w/\text{M}_n = 1.03, \text{Polymer Source, Inc.) blend film obtained at 22.5 °C and an expansion rate of 20 cm}^2\text{-min}^{-1}. \text{The letters on the isotherm indicate where the BAM images were taken during the hysteresis experiments and correspond to the average surface area (}<A> /\text{Å}^2\cdot\text{monomer}^{-1}) \text{ for compression: A (~22.2), B (~15.1), C (~11), and D (~9); and expansion: E (~12.2), F (~22.3), G (~30.9), and H (~57.6). Solidlike domains appear bright in all of the 2.4\times3.2 \text{ mm}^2 \text{ BAM images.}
7. Brewster Angle Microscopy Studies for PCL (M_w = 10 kg·mol^{-1})/PS (M_w = 217 kg·mol^{-1}) Blends.

Figure S10. BAM images for a X_{PS} ~ 0.81 PCL (M_w = 10 kg·mol^{-1})/PS (M_w = 217 kg·mol^{-1}, M_w/M_n = 1.05, Polymer Source, Inc.) blend film obtained at 22.5 °C and an expansion rate of 20 cm^2·min^{-1}. The letters on the isotherm indicate where the BAM images were taken during the hysteresis experiments and correspond to the average surface area (<A> /Å^2·monomer^{-1}) for compression: A (21.3), B (9.7), C (7.2), and D (6.2); and expansion: E (6.4), F (10.7), G (18.6), and H (25.5). Solidlike domains appear bright in all of the 2.4×3.2 mm^2 BAM images.
Figure S11. BAM images for a X_{PS} ~ 0.13 PCL (M_w = 10 kg·mol^{-1})/PS (M_w = 217 kg·mol^{-1}, M_w/M_n = 1.05, Polymer Source, Inc.) blend film obtained at 22.5 °C and an expansion rate of 20 cm^2·min^{-1}. The letters on the isotherm indicate where the BAM images were taken during the hysteresis experiments and correspond to the average surface area (\langle A \rangle / Å^2·monomer^{-1}) for compression: A (~16.3), B (~12.5), C (~8.6), and D (~7.9); and expansion: E (~10.4), F (~16.5), G (~38), and H (~49). Solidlike domains appear bright in all of the 2.4×3.2 mm^2 BAM images.

References

All numbered references correspond to the references in the main paper.