EFFECTS OF TETHERING ON GLASS TRANSITION TEMPERATURE ($T_G$) FOR CONFINED THIN FILMS
Polymer chains in bulk have random coil conformation with average size of radius of gyration ($R_g$).

- High grafting density (~0.5 chains/nm$^2$) leads to chains stretching normal to the surface, creating a highly confined system.
Glass transition temperature ($T_g$) – the point of transition at which amorphous materials change from brittle, glass state to soft, rubber state.

- Physical properties (specific volume, heat capacity, viscosity, thermal expansion coefficient) change.

- Thermal expansion coefficient change is directly proportional to the thickness change for the thin films.
$T_G$ VS. MELTING POINT

A heat vs. temperature plot for an crystalline polymer, on the left; and a amorphous polymer on the right.
**MOTIVATION**

- For Polystyrene (PS) thin films the $T_g$ decreases as films get thinner.
- Proven recently that tethering alters the surface dynamics of the chains due to extreme lateral and vertical confinement.\(^1\)
- How does dense tethering alter the $T_g$ of the thin films?

**Fundamental Science**

**Industry**

EXPERIMENTAL SETUP

- Reflectivity scans on high-density PS brushes
- Annealed for two hours at 120 °C

- Bromine
- Polystyrene
- 11-((2-bromo-2-ethyl)propionyloxy undecyl)trichlorosilane (initiator layer)
Interference of these partially reflected x-ray beams creates a reflectometry pattern

Kiessig fringes (maxima) occur because interference of waves can be constructive or destructive, $t = \frac{2\pi}{\Delta q}$
$T_G$, GLASS TRANSITION TEMPERATURE

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$T_g$ DECREASES AS FILM THICKNESS DECREASES

- 14 nm (140 Å) – 351 K
- 22 nm (220 Å) – 359 K
- 31 nm (310 Å) – 363 K
- 90 nm (900 Å) – 370 K
- 100 nm (1000 Å) – 373 K

There is indeed a trend for thinner films to have lower $T_g$ values. The reduction in $T_g$ for thinner films implies that these films can be processed at lower temperatures and large amount of energy can be saved.

We need thinner (< 10 nm) PS brush samples to verify if tethering alters the $T_g$. So far our data suggests there is no difference between tethered and untethered chains.
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