EFFECTS OF TETHERING ON GLASS TRANSITION TEMPERATURE (T_G) FOR CONFINED THIN FILMS

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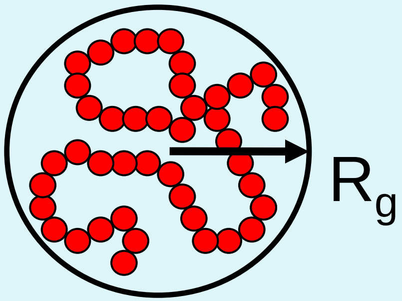
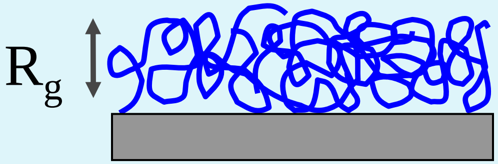
BACKGROUND - CONFINEMENT

BULK

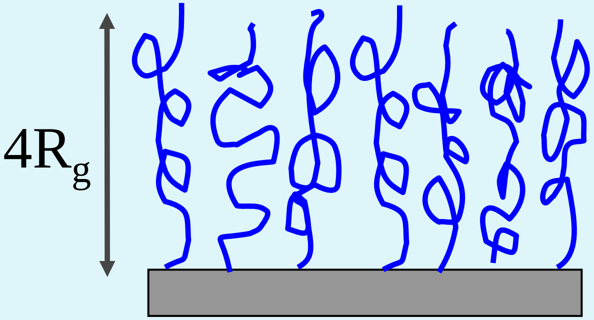


Polymer chains in bulk have random coil conformation with average size of radius of gyration (R_g).

POLYMER UNDER CONFINEMENT



Polymer thin film

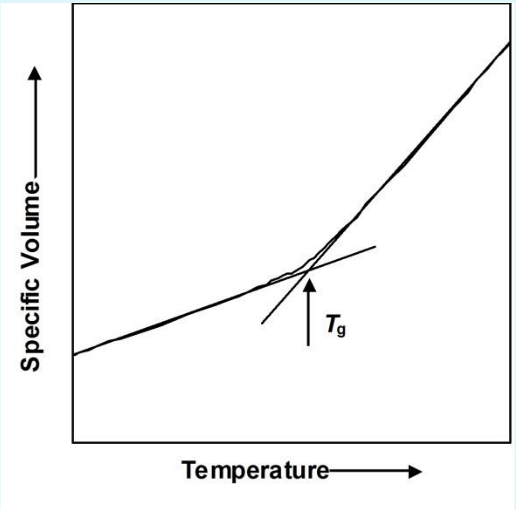


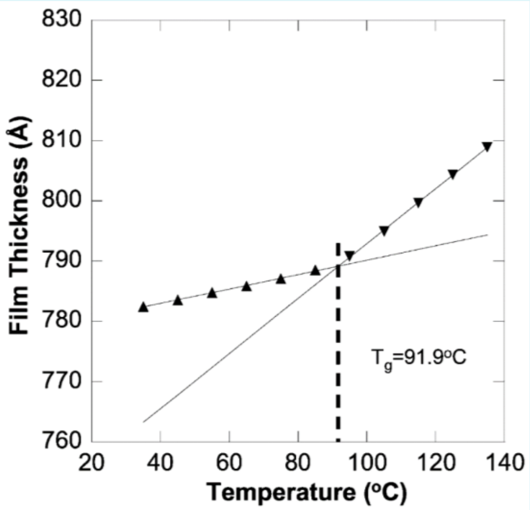
Polymer brush

- High grafting density (~0.5 chains/nm^2) leads to chains stretching normal to the surface, creating a highly confined system.

WHAT IS T_G?

- **Glass transition temperature** (T_g) – the point of transition at which amorphous materials change from brittle, glass state to soft, rubber state.

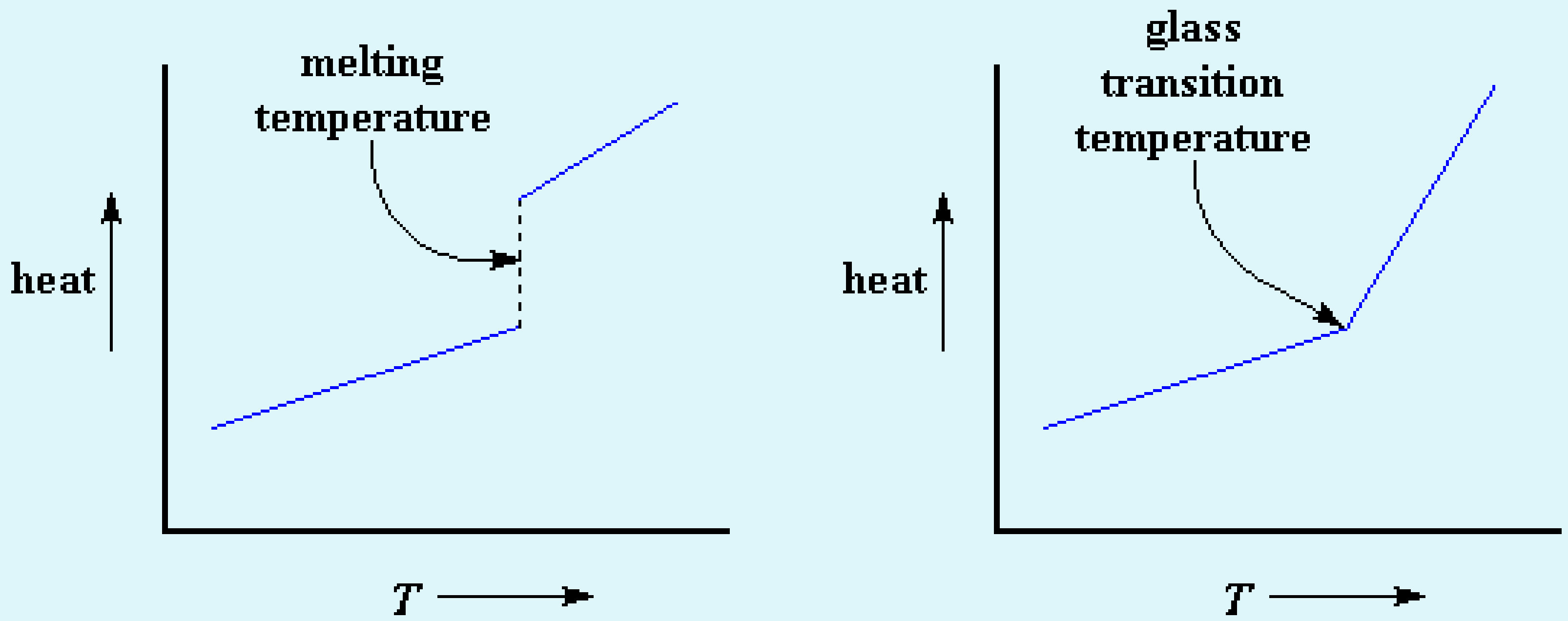




- Physical properties (specific volume, heat capacity, viscosity, thermal expansion coefficient) change.

- Thermal expansion coefficient change is directly proportional to the thickness change for the thin films.

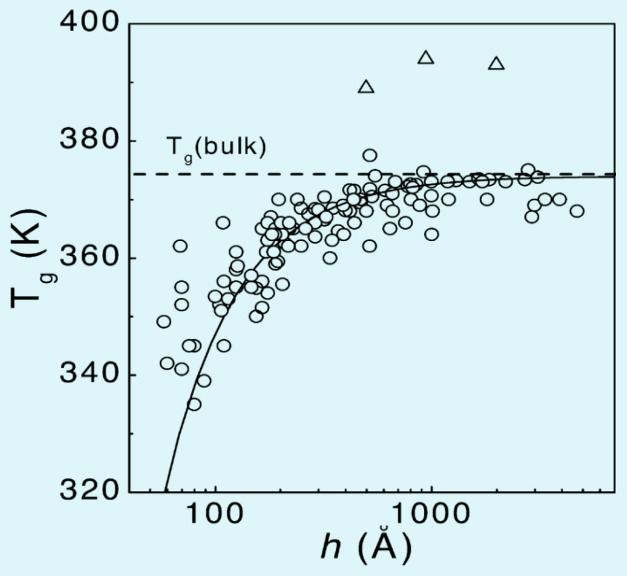
T_G VS. MELTING POINT



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?



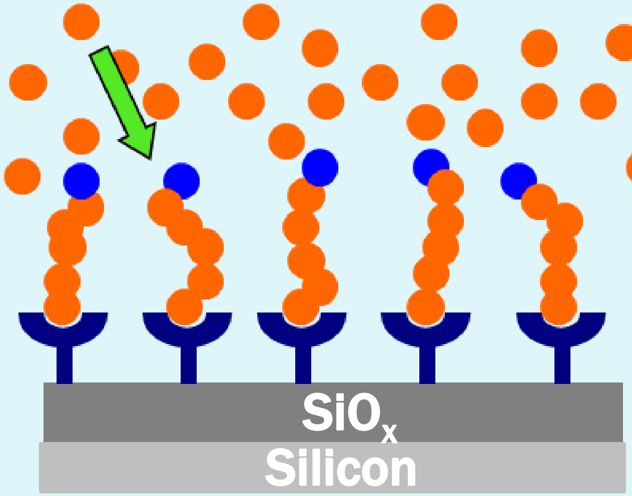
J.A. Forrest et al., The Glass Transition in Thin Polymer Films, *Advances in Colloid and Interface Science*, 2001, 94, 167.

- Fundamental Science
- Industry

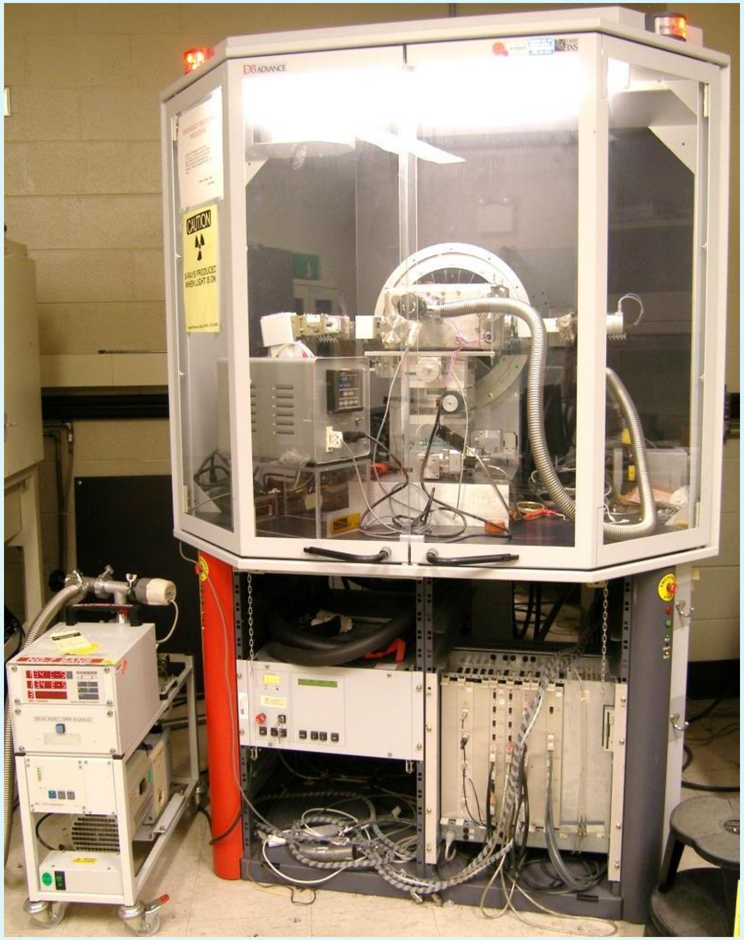
[1]Akgün B., et al. *Macromolecules* 2009, 42, 737.

EXPERIMENTAL SETUP

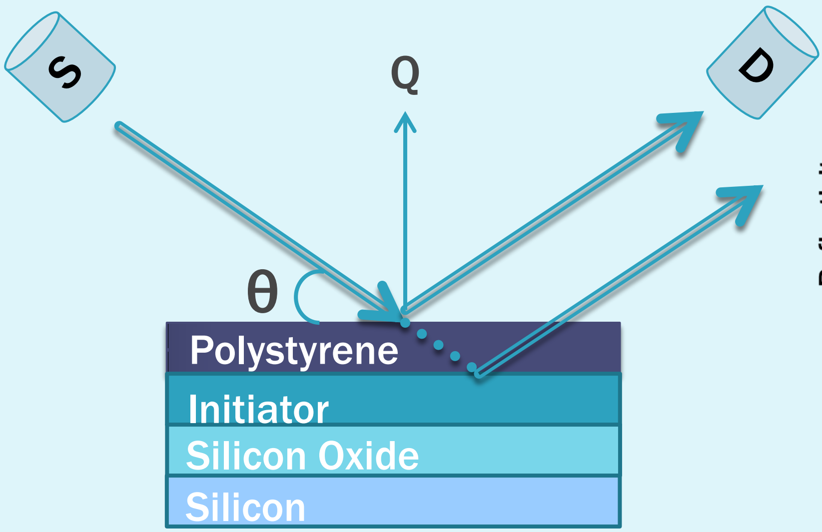
- Reflectivity scans on high-density PS brushes
- Annealed for two hours at 120°C

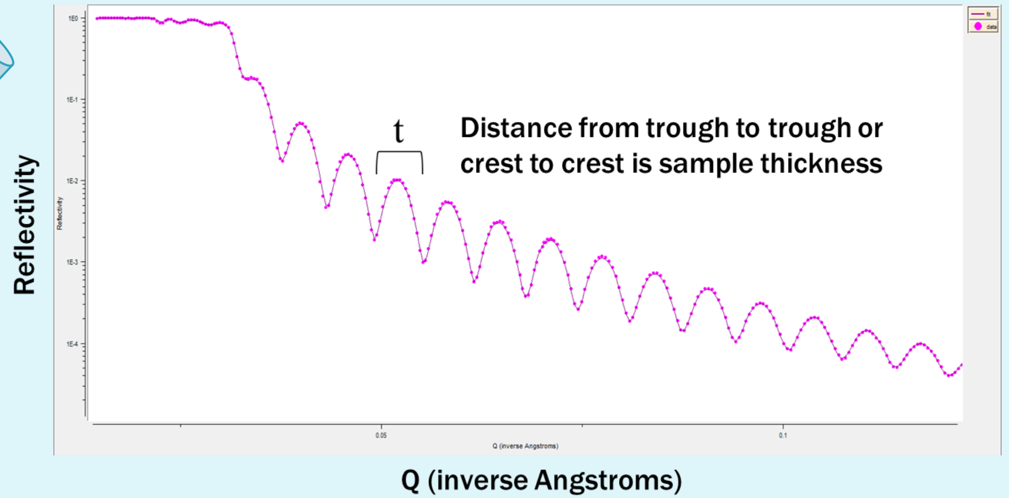


- Bromine
- Polystyrene
- 11-(2-bromo-2-ethyl)propionyloxy undecyltrichlorosilane (initiator layer)



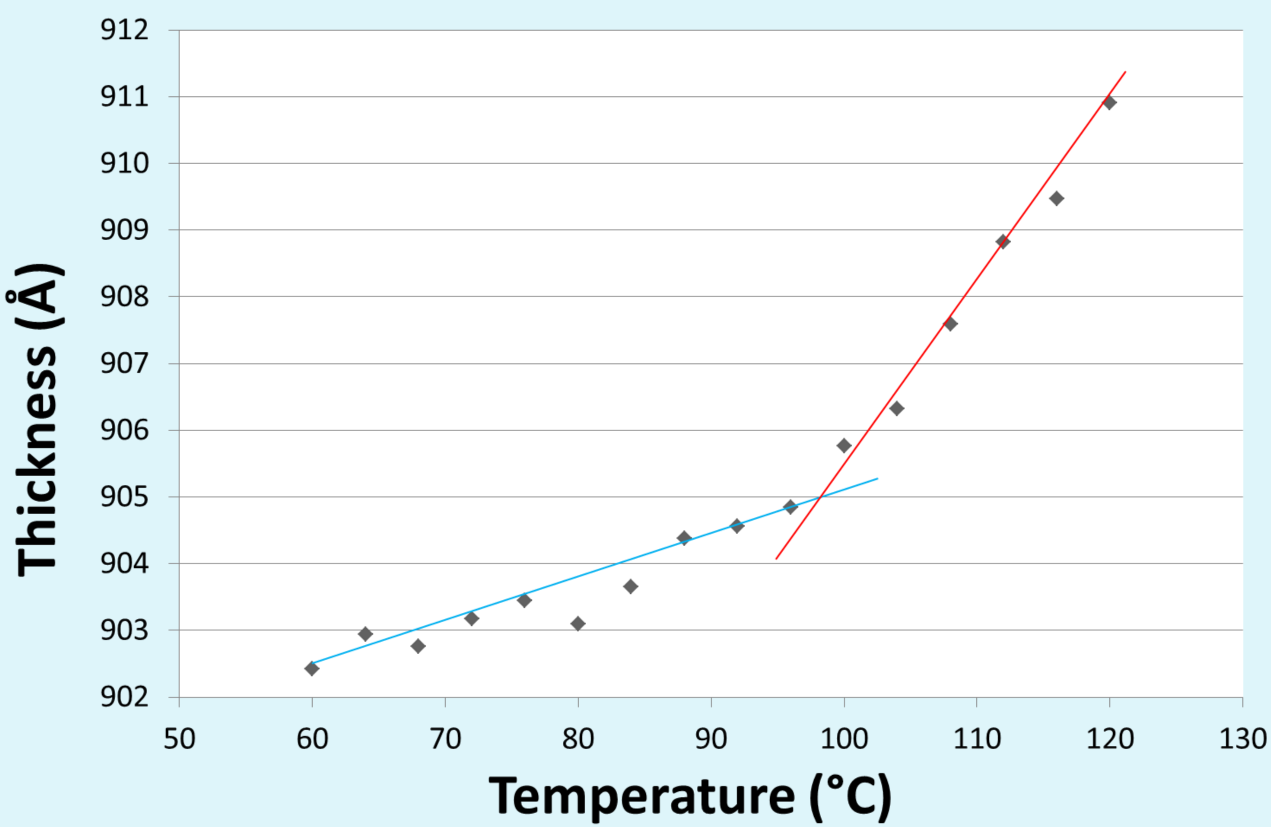
X-RAY REFLECTIVITY





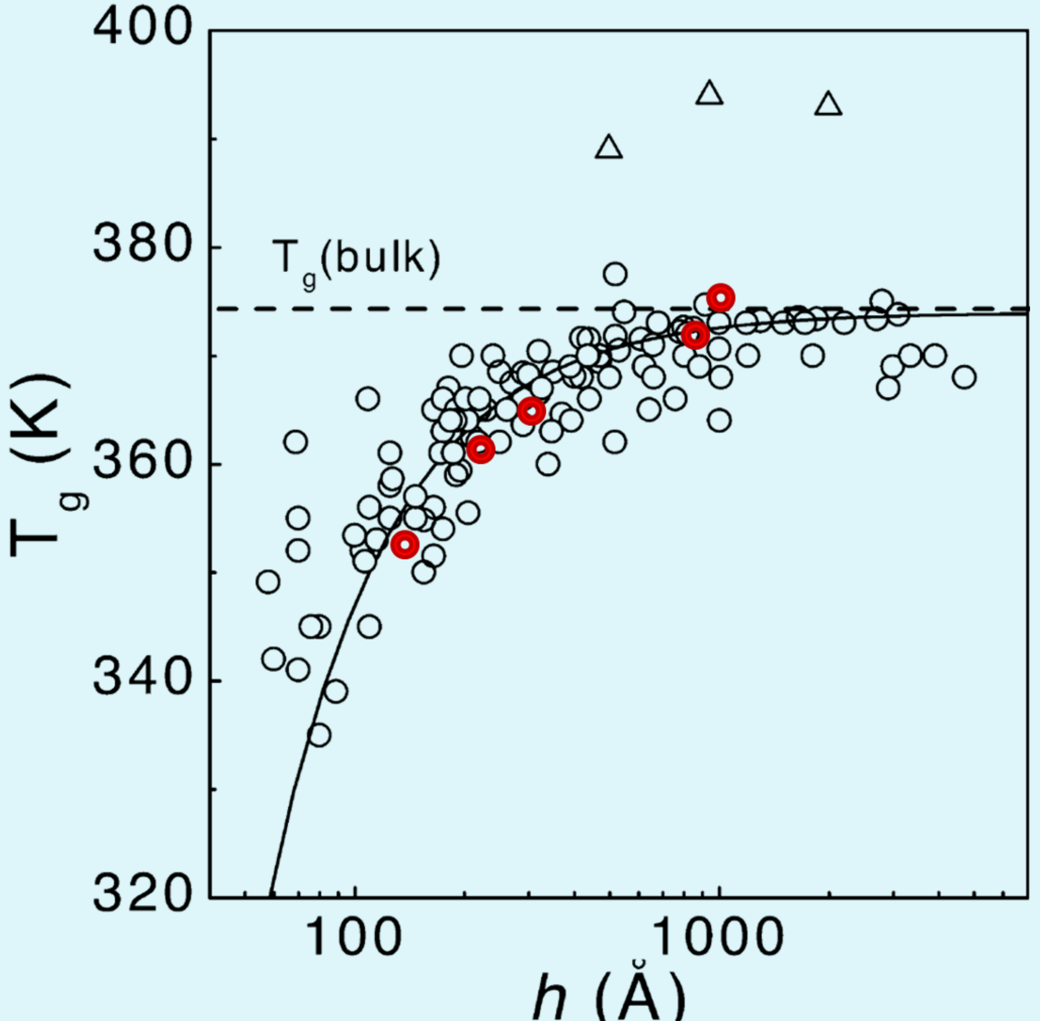
- Interference of these partially reflected x-ray beams creates a reflectometry pattern
- Kiessig fringes (maxima) occur because interference of waves can be constructive or destructive, $t=2\pi/\Delta q$

T_G, GLASS TRANSITION TEMPERATURE



Temperature	Thickness
25	906.17
40	903.581
60	902.427
64	902.941
68	902.76
72	903.169
76	903.447
80	903.089
84	903.652
88	904.378
92	904.558
96	904.846
100	905.763
104	906.321
108	907.587
112	908.825
116	909.466
120	910.913

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

J.A. Forrest et al., The Glass Transition in Thin Polymer Films, *Advances in Colloid and Interface Science*, 2001, 94, 167.

SUMMARY

- 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.

ACKNOWLEDGMENTS

Special thanks to:

- Bülent Akgün
- Julie Borchers
- Yamali Hernandez