The Effect of Tethering on the Glass Transition Temperature in Thin Polymer Films

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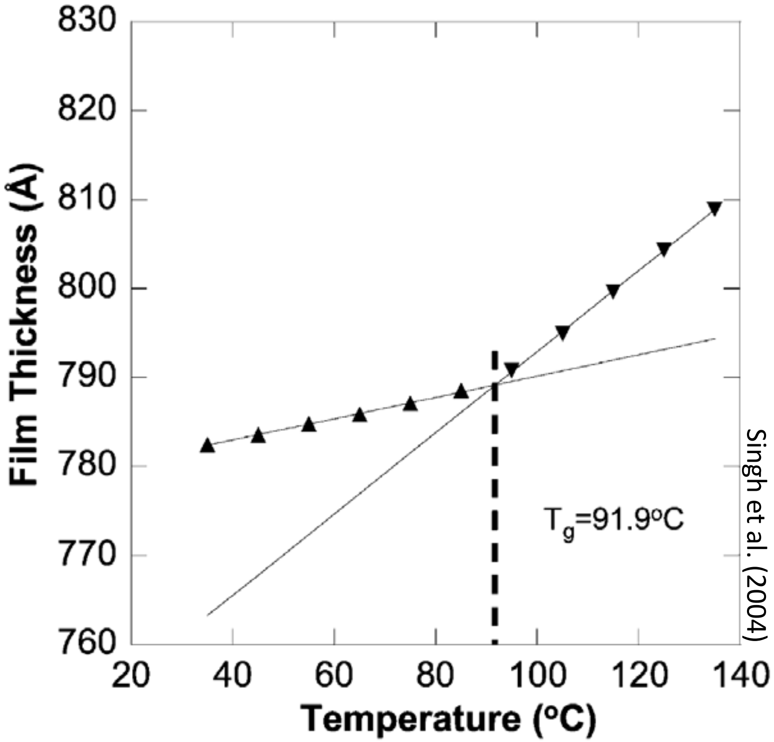
The Glass Transition Temperature (T_g)

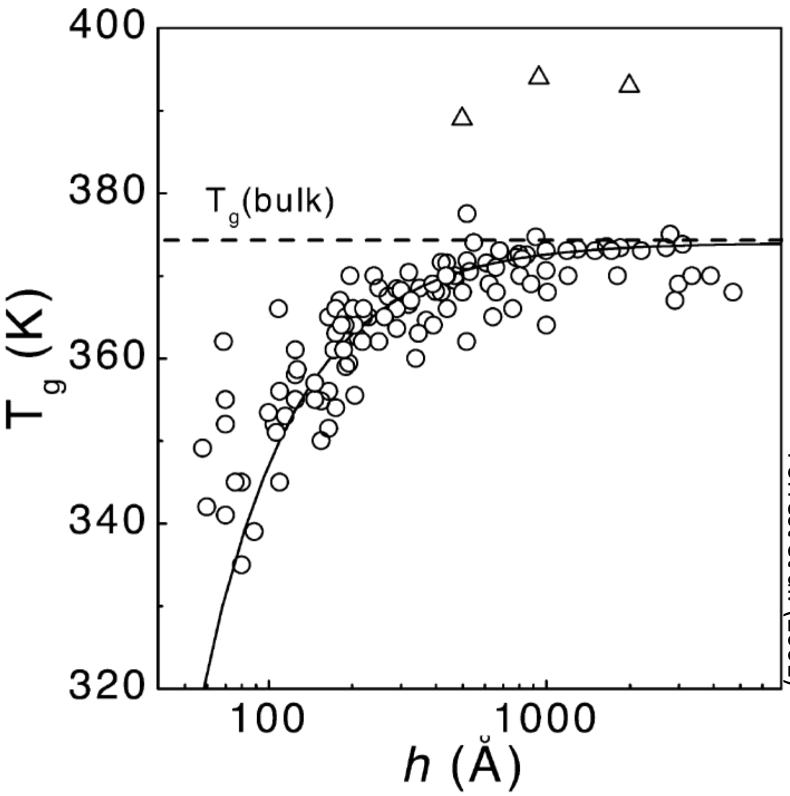
- Transition in amorphous materials from brittle, glass state to soft, rubber state.
- Sudden change in the coefficient of thermal expansion, α.



Singh et al. (2004)

Figure 1: Thickness vs. temperature data for polystyrene (PS) film 78 nm thick on silicon substrate.

T_g of Confined Polymers



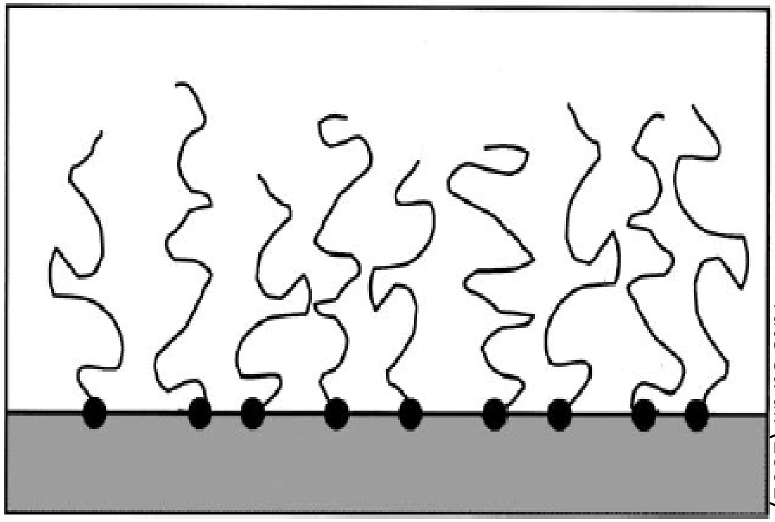
Forrest et al. (2001)

Figure 2: Summary of results from 7 different studies on the thickness-dependence of T_g of thin polystyrene (PS) films.

- For polymer thin films, thickness is the confining dimension.
- T_g of confined polymers may deviate from that of the polymer in bulk.

Polymer brushes

- Polymer chains are grafted at one end to a surface or interface.
- High grafting density leads to chains stretching normal to the surface: a highly confined system.
- Applications in microelectronics, biosurfaces, and drug delivery.

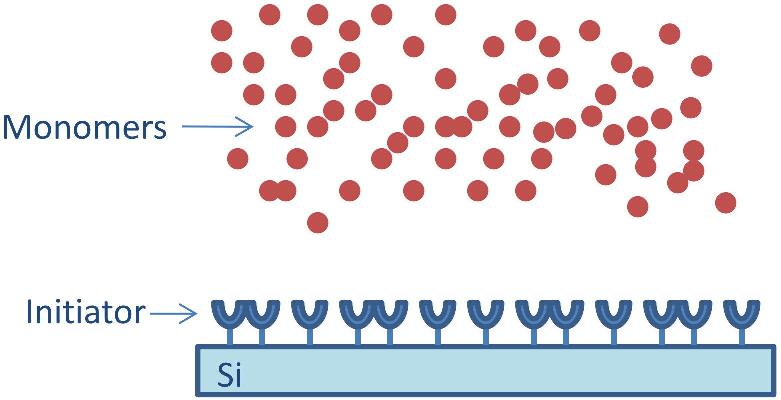


Tate et. al. (2001)

Figure 3: Diagram of an end-grafted polymer brush.

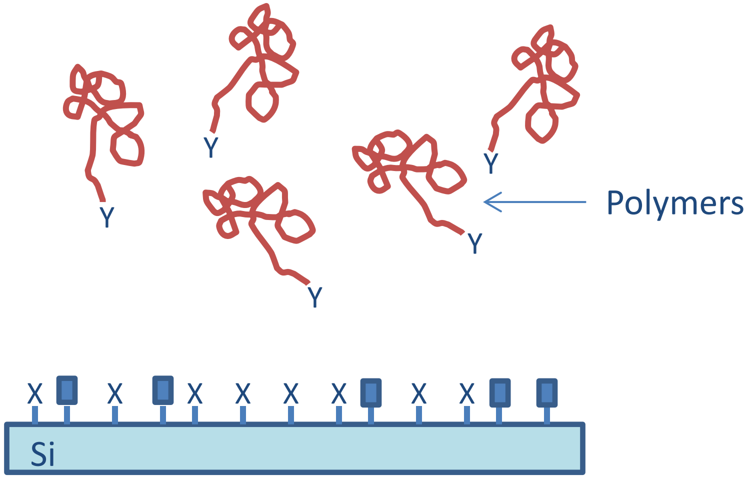
Polymer Brushes (cont.)

Grafting-*from*



- Forms higher-density brush.
- Chains stretch normal to the surface.
- Brushes can grow very thick.

Grafting-*to*

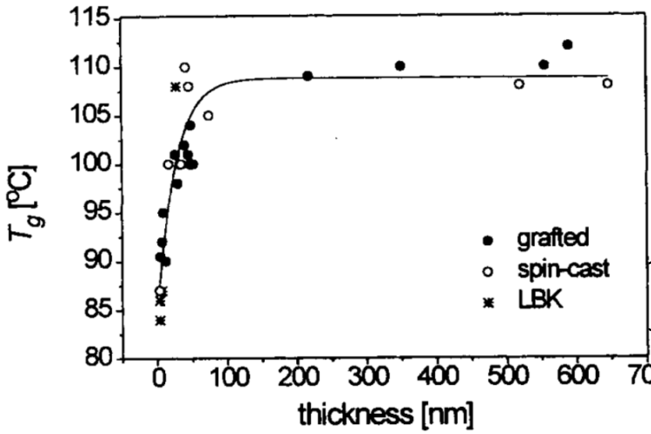


- Forms lower-density brushes.
- Chains are less stretched.
- Diffusion-limited process.

T_g of Polymer Brushes

Prucker et al. (1998)

- PMMA brushes made via grafting-*from* techniques.



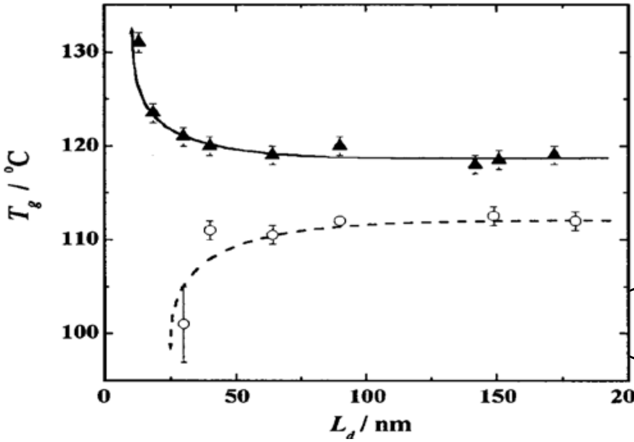
Prucker et. al. (1998)

Figure 4: Results from experiments of Prucker et al.

"There is no obvious influence of the internal configuration of the individual polymer chains on the film's glass transition temperature."

Yamamoto et al. (2002)

- PMMA brushes made via grafting-*from* techniques.



Yamamoto et. al. (2002)

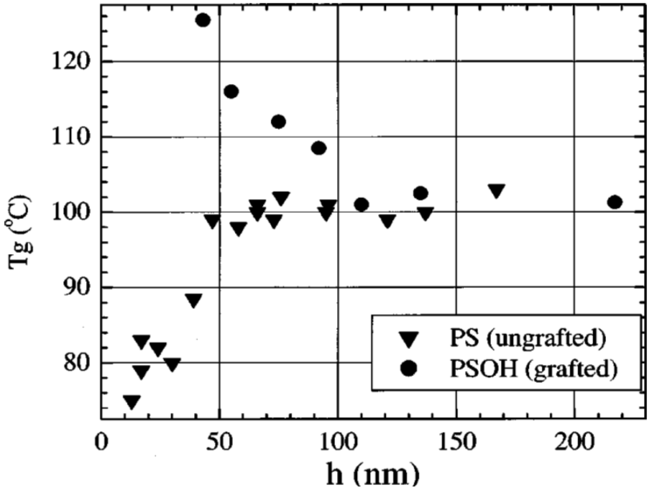
Figure 5: Results of Yamamoto et al. Triangles and circles represent brushes and cast films respectively.

"[The T_g difference] can be totally ascribed to grafting…one of the chain ends to the substrate."

T_g of Polymer Brushes (cont.)

Tate et al. (2001)

- PS brushes made via grafting-*to* techniques; PS chains mixed in.



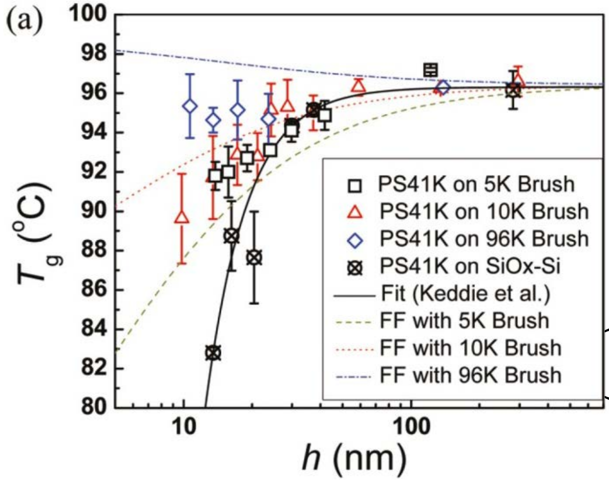
Tate et. al. (2001)

Figure 6: Results from experiments of Tate et al.

"Grafting polymer chains…leads to substantial increases…in the degree of elevation of T_g from the bulk value with decreasing film thickness"

Tsui et al. (2011)

- PS brushes made via grafting-*to* techniques; swollen with PS chains.



Tsui et. al. (2011)

Figure 7: Results from experiments of Tsui et al.

"…the T_g correlates well with the interfacial energy between the film and the substrate, with T_g decreasing with increasing interfacial energy…"

Objective

- What is the behavior of the T_g of high-density polystyrene brushes as thickness decreases?

- How does this behavior compare to that found in the literature for sparsely grafted chains and ungrafted chains?

Experimental

- High-density (~0.5 chains/ nm^2) PS brushes were synthesized at the University of Akron via grafting-*from* techniques.
- Each sample was annealed at 120°C for at least 2 hrs before measurement.

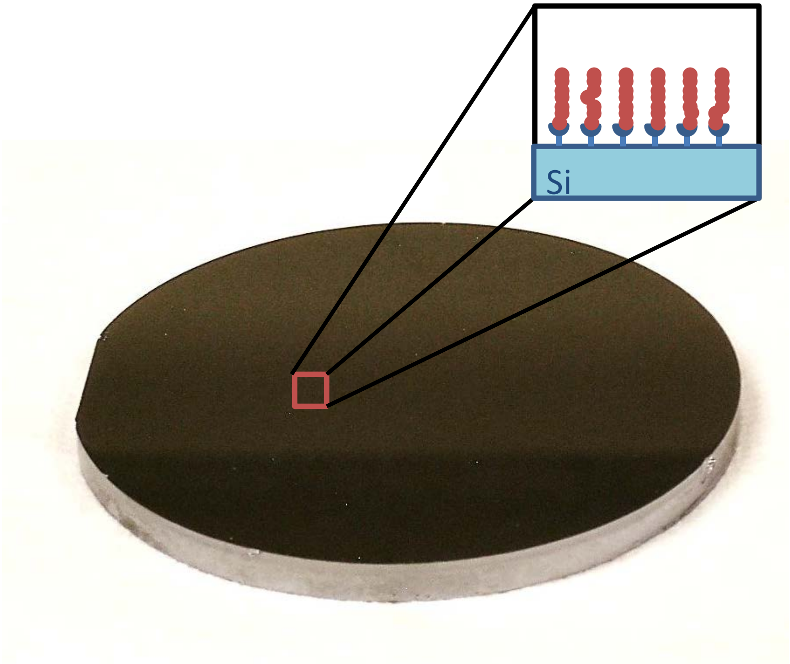
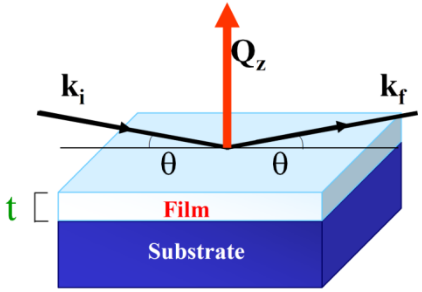


Figure 8: Example of a PS brush sample

X-ray Reflectometry



http://www.ncnr.nist.gov/

Figure 9: Theory of x-ray reflectometry

- Specular reflectivity
- Angle of incidence = exit angle

- Thickness of film is inversely proportional to the width of the fringes:

$$Q_z = (4\pi/\lambda)\sin\theta$$

$$\Delta Q_z = 2\pi/d$$

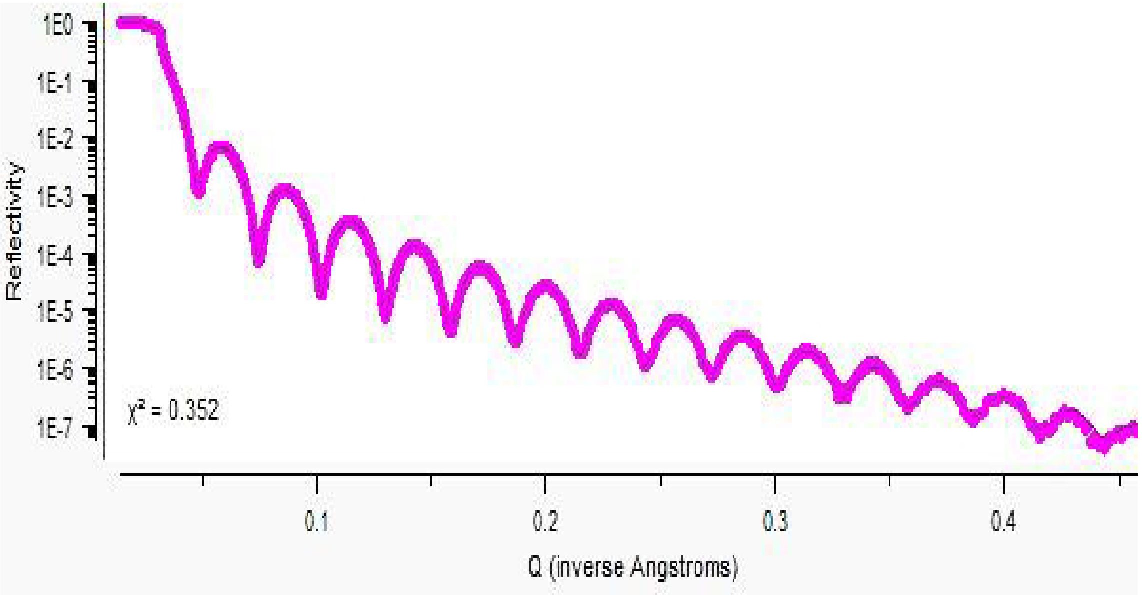
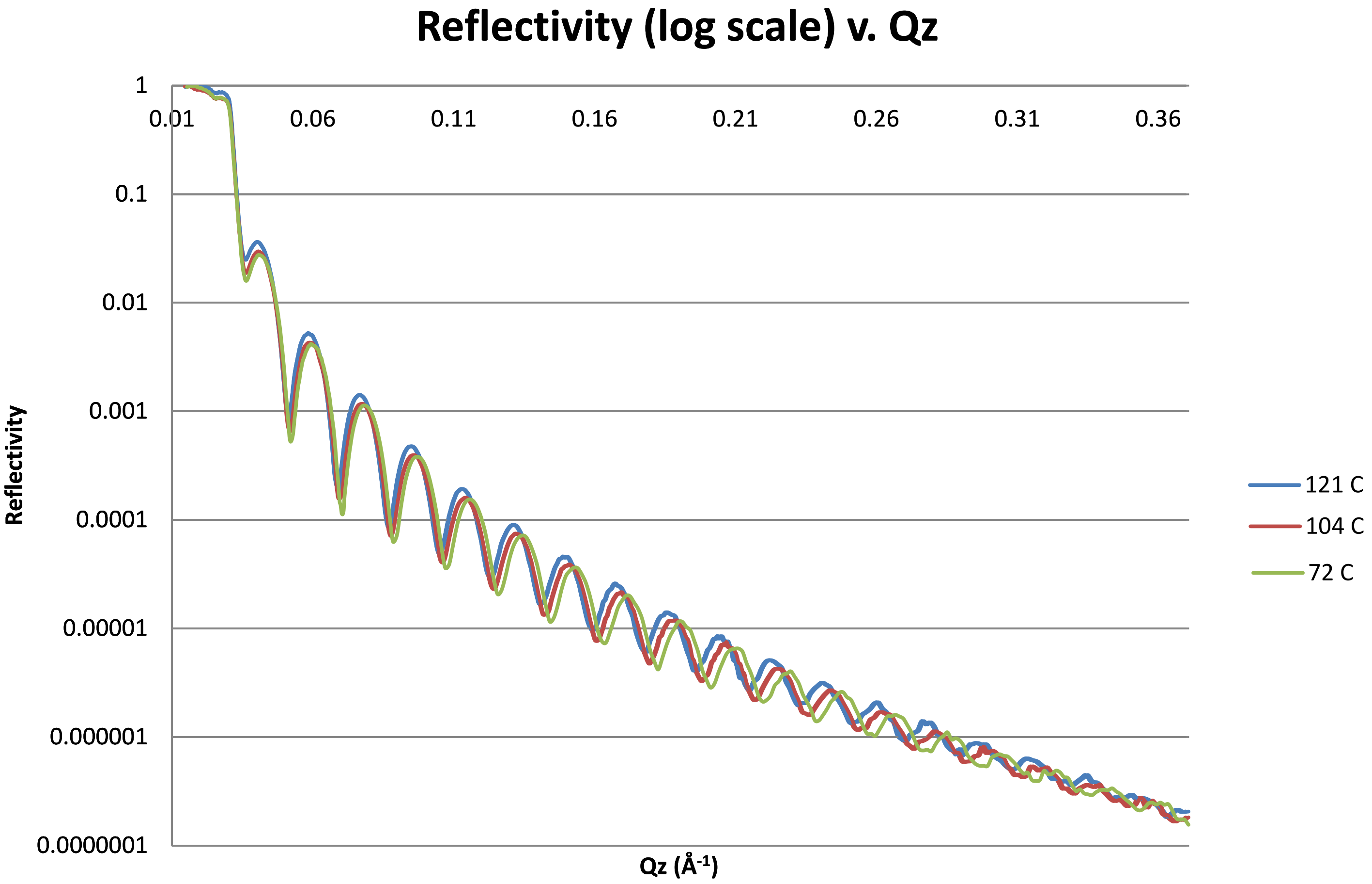


Figure 9: Reflectivity data for 20 nm PS brush at room temperature.

X-ray Reflectometry Data



Reflectivity data for 31 nm film. As the film contracts, the width of the fringes on the reflectivity curve increases.

Experimental (cont.)

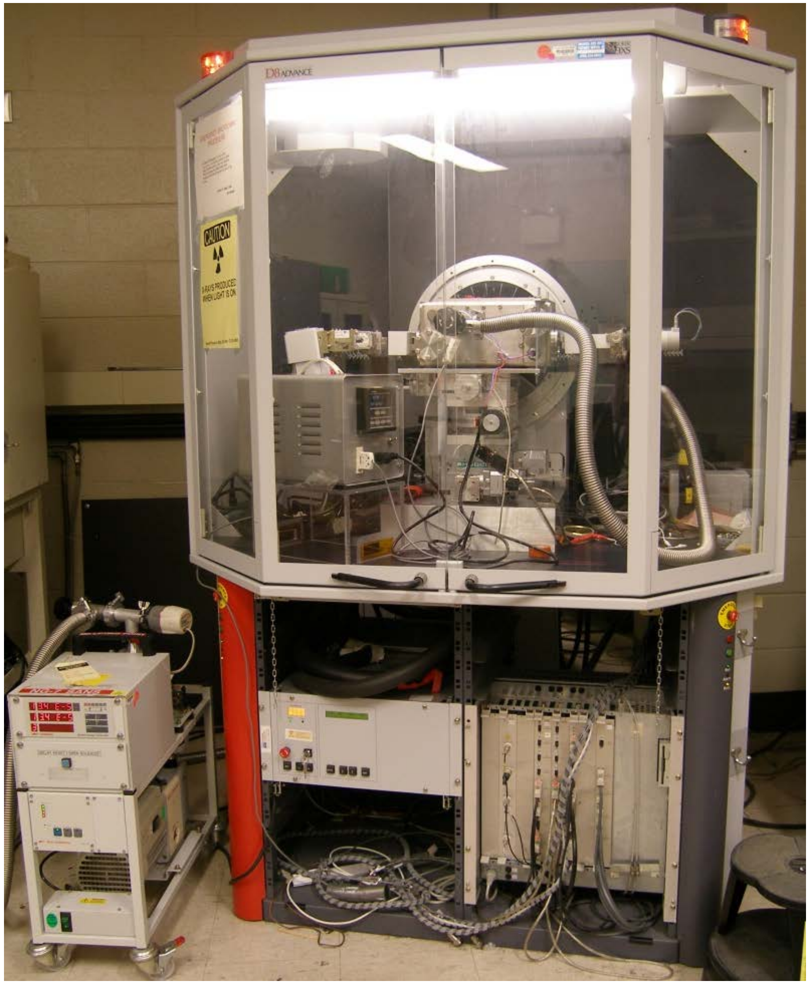


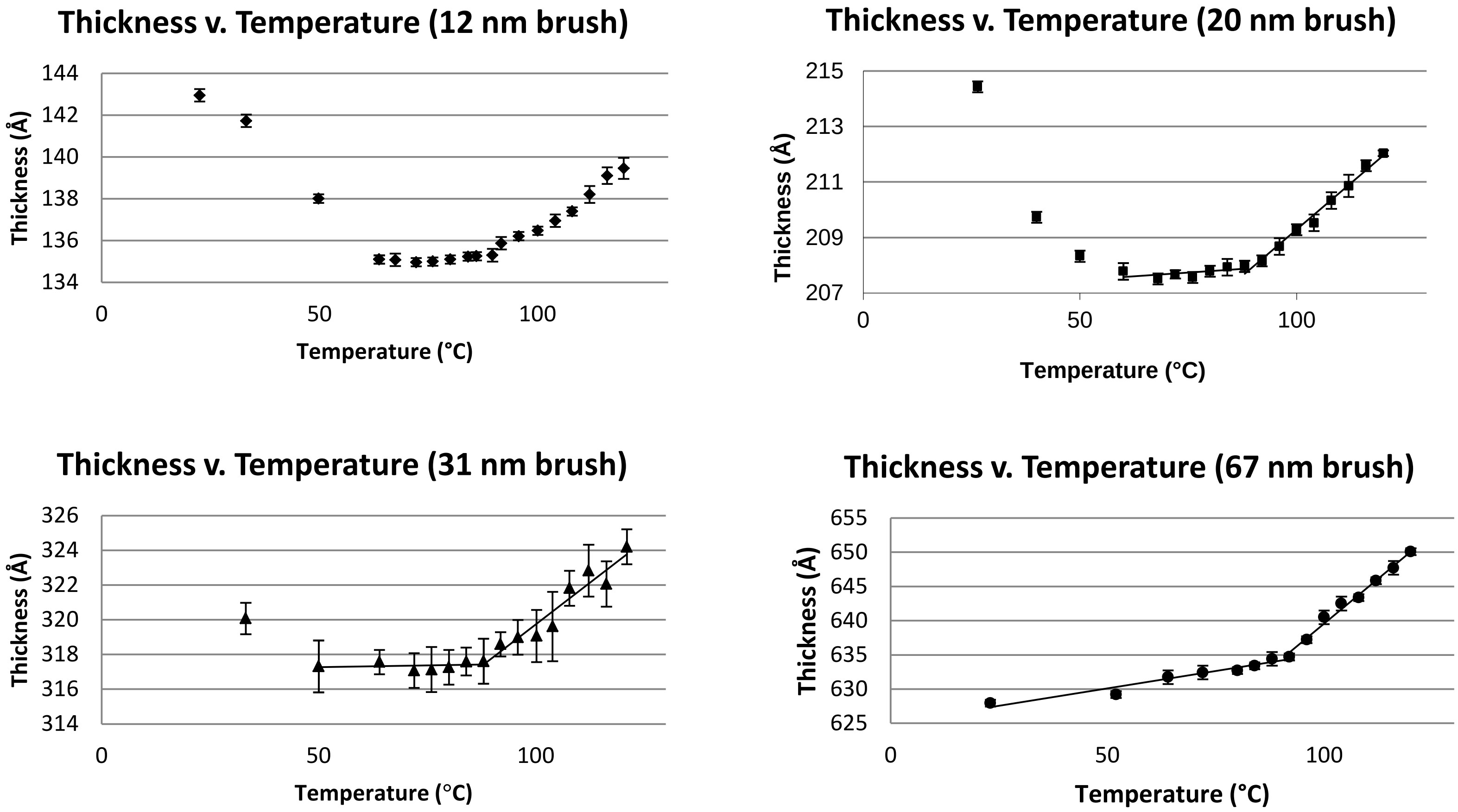
Figure 10: Photo of x-ray reflectometer with temperature-controlled vacuum chamber.

- Sample thickness was measured in temperature-controlled vacuum chamber using x-ray reflectometry.

- Samples were cooled from 120°C to room temperature.

- Thickness measurements were taken at increments of 4°C.

Results



Thickness v. Temperature (12 nm brush)

Thickness v. Temperature (20 nm brush)

Thickness v. Temperature (31 nm brush)

Thickness v. Temperature (67 nm brush)

Figure 11: Thickness vs. temperature plots obtained for 12 nm, 20 nm, 31 nm, and 67 nm PS brushes.

Results

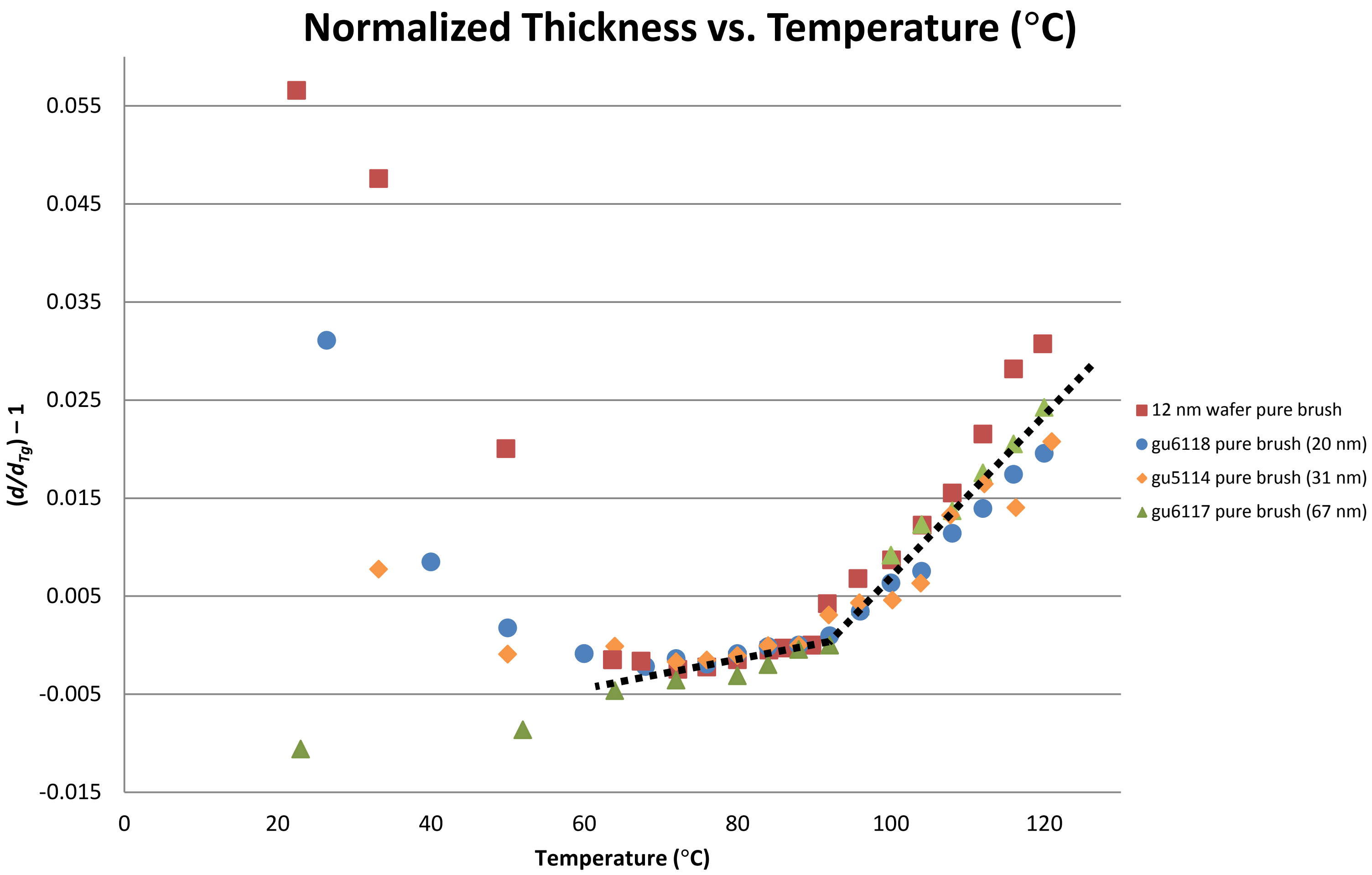


Figure 12: Graph of Normalized Thickness vs. Temperature for all pure brush samples.

Results

Table 1: Summary of experimental T_g, α_{glass}, and α_{melt} values for PS brushes

	T_g (°C)	α_{glass} (K^{-1})	α_{melt} (K^{-1})
12 nm PS	90	7.3×10^{-5}	9.87×10^{-4}
20 nm PS	88	5.0×10^{-5}	6.41×10^{-4}
31 nm PS	88	1.4×10^{-5}	6.07×10^{-4}
67 nm PS	92	1.60×10^{-4}	8.30×10^{-4}
PS in bulk[a]	100	1.1×10^{-4}	5.3×10^{-4}

[a] Kanaya et al. (2005)

Results

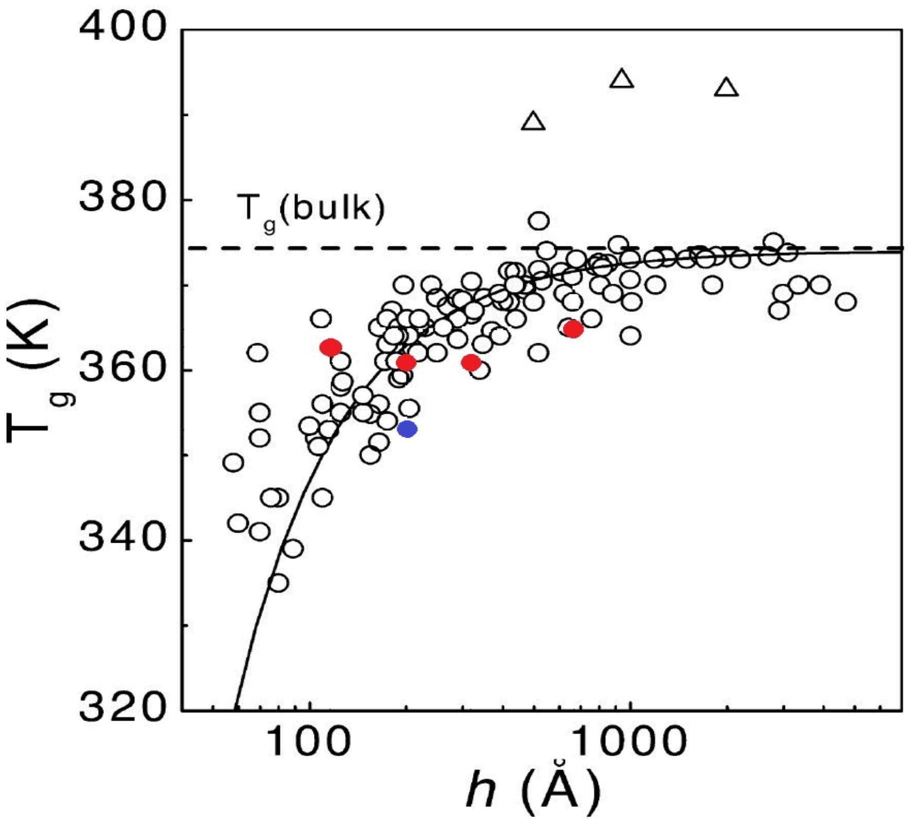


Figure 14: Experimental values for T_g of high-density PS brushes (red circles) plotted with data for spin-coated PS films (Forrest et al 2001). Blue circle represents experimental data for 20 nm spun-cast film.

Results

Table 2: Thermal expansion coefficient for pure brushes from room temperature to 68°C

Sample	α (K^{-1})
12 nm PS	-1.40×10^{-3}
20 nm PS	-7.67×10^{-4}
31 nm PS	-2.65×10^{-4}
67 nm PS	1.60×10^{-4}

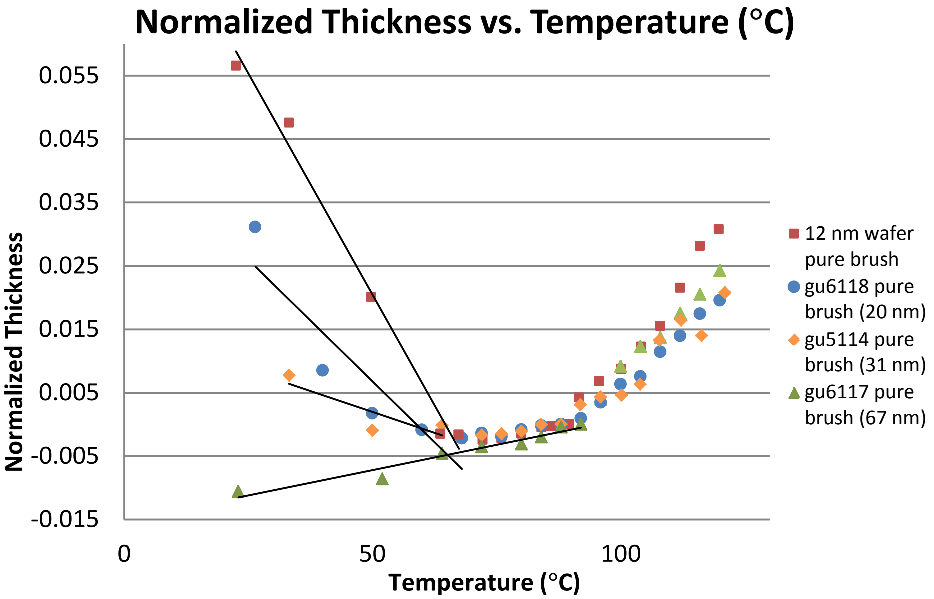


Figure 15: Graph of Normalized Thickness vs. Temperature for all pure brush samples with trend lines for glassy-state contraction.

Conclusions and Future Work

In conclusion…

- There is no apparent trend of T_g with decreasing thickness of high-density PS brushes.

- The magnitude of contraction from room temperature to 68°C of the PS brushes increases with decreasing thickness.

In the future…

- Measure T_g of thicker and thinner high-density PS brushes.

- Measure the T_g of brushes swollen with layers of low molecular weight polymer chains.

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