# Glass Transition Reductions in Thin Freely-standing Polymer Films: a Scaling Analysis of Chain Confinement Effects

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**Abstract.** In this paper we present a new analysis of data on the reduced glass transitions observed in thin freely-standing films. The empirical analysis presented is highly suggestive of the existence of a mechanism of mobility in thin freely-standing films that is inhibited in the bulk and distinct from the usual cooperative motion near the glass transition temperature $T_g$. A tentative mechanism for $T_g$ reductions in thin freely-standing films is discussed.

## 1. INTRODUCTION

A promising way to investigate the possibilities of characteristic length scales in glass forming materials is to study the dynamics in samples with a size approaching this characteristic length. Studies of samples confined to porous glass, intercalated into layered silicates, or naturally occurring between crystalline regions in semi-crystalline polymers have all been utilised. A sample geometry in which there has been much recent interest is thin polymer films [1]. Of particular interest is how the glass transition and related dynamics are affected for films of decreasing thickness. A detailed review of this literature has recently been presented [1]. For polymer - substrate combinations where there is not a specific attractive interaction, the measured glass transition temperature values, $T_g$, are observed to decrease monotonically below the bulk $T_g$ for films with thickness less than ~ 50 nm. This same conclusion has been found by different groups using various techniques [2-4]. In contrast, for systems where there is a strongly attractive interaction between the polymer and substrate [5] the measured $T_g$ values are increased above the bulk value $T_g^{bulk}$.

The sensitivity of the measured $T_g$ value to the interaction between the polymer and the substrate suggests that fundamental information may be gained by studying the more technically challenging sample geometry of freely-standing films. The lack of specific substrate interactions make such samples ideal for the study of finite size effects in glass forming systems. Measurements of the $T_g$ value for freely-standing films revealed $T_g$ reductions which occurred for larger values of the thickness and which were much larger in magnitude than those observed for similar supported films [6]. Extension of these studies to a polymer with a different value of the molecular weight, $M_w$, revealed a strong $M_w$ dependence [4]. This observation suggests that a mechanism related to the confinement of the polymer chains is necessary to describe these results, thereby introducing the end-to-end size of a polymer chain, $R$, as an important parameter.

The $M_w$ dependence of the $T_g$ value in freely-standing polystyrene (PS) films has recently been studied independently by two groups [7,8]. These studies have revealed that for $M_w < 350 \times 10^3$, the $T_g$ values exhibit *no $M_w$* dependence [9], while for larger values of $M_w$ the *strong $M_w$* dependence has now been extensively quantified [7]. This difference in $M_w$ dependence in the high and low $M_w$ regime and other qualitative changes in behaviour suggest that there are two mechanisms which can result in lower $T_g$ values for thin polymer films. A mechanism related to the length scale of cooperative motion has been introduced to describe the lower $M_w$ data [9], but as of yet no

mechanism has been published to explain the $M_w$ dependent $T_g$ reductions. We report in this manuscript a scaling analysis of the high $M_w$ data which shows that all of the $T_g$ values presented previously [4,6-8] (> 50) for freely-standing PS films can be described quantitatively by *only* 4 parameters. We also consider a simple model for the $T_g$ reductions based on the idea of a different mechanism for polymer mobility which is only effective in thin films and can be used to qualitatively account for the measured results.

## 2. EXPERIMENT

A detailed description of the experiments discussed in this paper are presented elsewhere [7]. For completeness we provide an abbreviated description below, and discuss here only the *results* of the findings.

### 2.1 Sample preparation

Monodisperse ($M_w/M_n \sim 1.05$), high molecular weight PS was dissolved in toluene ($M_w = 575\times10^3$, $767\times10^3$, $1250\times10^3$, $2240\times10^3$, $6680\times10^3$, $9100\times10^3$, with root-mean-squared end-to-end distance $R = 56$ nm, 64 nm, 82 nm, 110 nm, 190 nm, 222 nm). The solutions were spincoated onto clean glass slides, annealed at a temperature of 115 $^o$C for 12 hours in order to drive off any trapped solvent and relax the polymer chains after the spincoating procedure. After cooling the samples to room temperature at a rate of 1 $^o$C/min, the films were water transferred onto sample holders with a 4 mm hole. In this manner over 40 different freely-standing PS films were prepared and the glass transition temperature measured for each film. Film thicknesses, $h$, were obtained using ellipsometry.

### 2.2 Measurement of the glass transition

Ellipsometry was used to measure the $T_g$ values in the freely-standing films [10] in the following manner. The sample was placed in a furnace and the ellipsometric angles $P$ and $A$ were measured as a function of the sample temperature $T$ both upon heating *and* cooling. Using the equations of ellipsometry and assuming an isotropic film, it is straightforward to invert the data to obtain the temperature dependence of the film thickness $h(T)$ and the index of refraction $n(T)$ [7,10]. The near discontinuity of the thermal expansion for $T \sim T_g$ results in a 'kink' in both $h(T)$ and $n(T)$ at $T_g$ which was used to obtain the value of $T_g$ for any temperature ramp. Several measurements of $T_g$, measured on both heating and cooling, were averaged and resulted in a reliable value of $T_g$ for each film.

## 3. RESULTS AND DISCUSSIONS

We first present a detailed analysis of the data showing some surprising scaling behaviour of the $M_w$ dependent $T_g$ reductions, followed by a discussion of a new possible mechanism for chain mobility which may be important for films with thickness of the order of the root-mean-squared end-to-end distance, $R$, of the polymer molecules.

### 3.1 Scaling analysis

The data on thin free standing PS films for all of the molecular weights studied in ref. [7] are summarised in Fig. 1. There are two particularly surprising aspects of the data. Firstly, as noted previously [3,4,7,8], the *reduced $T_g$* data are well characterised by $T_g$ values which decrease linearly with decreasing film thickness $h$. The second surprising feature of the data is revealed by
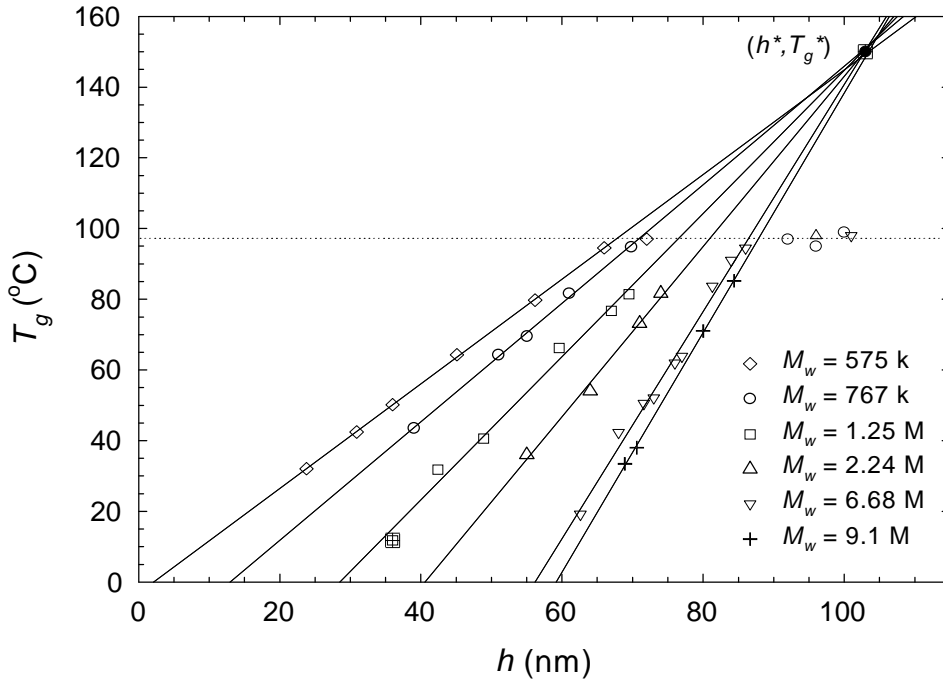
**Figure 1.** Plot of $T_g$ versus the film thickness for all the molecular weights studied ($575 \times 10^3 < M_w < 9100 \times 10^3$) in reference [7]. The straight solid lines are best fits to the reduced $T_g$ data and are extended to a common intersection point ($h^*$, $T_g^*$). The dashed line corresponds to the bulk value of the glass transition temperature.

extrapolating the best fit straight lines to larger values of $T_g$ and $h$. The extrapolation suggests a common intersection point ($h^*$, $T_g^*$) of *all* of the best fit lines to the data obtained in the reduced $T_g$ regime.

From the data shown in Fig. 1, the intersection point is specified by $h^* = (103 \pm 1)$ nm and $T_g^* = (150 \pm 2)$ $^\circ$C. Though we do not imply any significance to *measured* $T_g$ data in the extrapolated regime of the fits, this surprising result does strongly suggest a second mechanism that becomes important for thin films ($h \sim R$). In a system in which there are two competing mechanisms for mobility, the faster mode will dominate the behaviour. The presence of a mode of mobility which dominates in very thin films (and distinct from the cooperative motion near $T_g$ in bulk samples) also explains the sharp transition between the bulk $T_g$ values measured for the thickest films and the reduced $T_g$ values measured for the thinnest films. The existence of a common intersection point for all of the extrapolated best fit curves in Fig. 1 implies that $(T_g - T_g^*) \propto (h - h^*)$. It is interesting to note that the value obtained for $T_g^*$ is approximately equal to the temperature at which the $\alpha$- and $\beta$-relaxations split into two distinguishable modes, perhaps indicating that the side chain motions might be important. Clearly the data can be parameterised if we define a $M_w$ dependent parameter $\alpha(M_w)$, which represents the slope of the linear reduction in $T_g$ with decreasing $h$ for a given $M_w$:

$$(T_g - T_g^*) = \alpha(M_w) (h - h^*). \tag{1}$$

Given expression (1), an understanding of $\alpha(M_w)$ becomes crucial to the understanding of the anomalous $T_g$ results for thin films. To gain some insight into the possible dependencies of $\alpha(M_w)$ on $T_g$, we plot $\alpha(M_w)$ in Fig. 2. The data fit remarkably well to a straight line on the semi-logarithmic plot, but *any* functional form that parameterises the slope of the $T_g$ reduction with decreasing $h$ to molecular weight can be used equally well in the subsequent analysis (for instance $\alpha(M_w) \propto (M_w/M_w')^c$ also provides an excellent parameterisation). Following the suggestion from the data in Fig. 2, we obtain the expression
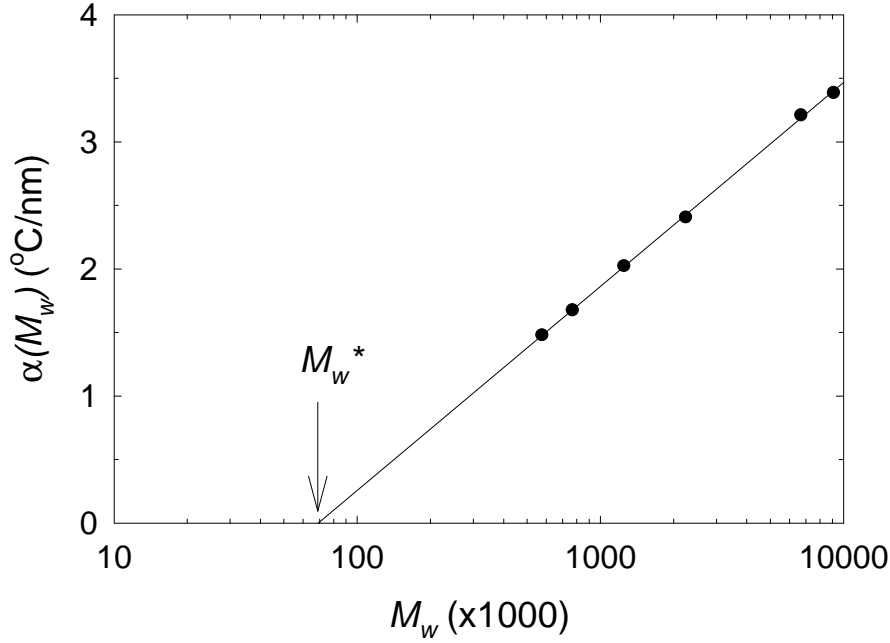
$$\alpha(M_w) = b \ln (M_w/M_w^*); \tag{2}$$

**Figure 2.** Plot of the slope of the linear reduction in $T_g$ with decreasing film thickness $h$.

where $b = (0.70 \pm 0.02)$ °C/nm and $M_w^* = (69000 \pm 4000)$. While the parameterisation given by equation (2) is only strictly valid for $M_w$ within the range studied, we note that extrapolating to $M_w^*$ leads to $\alpha(M_w) = 0$. The implication is that for polymers with $M_w < M_w^*$ no *chain confinement effects* due to this second mode can possibly be observed. Perhaps more importantly for comparison to the data, we can use Fig. 1 to show that for $\alpha(M_w) = (T_g^* - T_g^{bulk}) / h^* \sim 0.5$ °C/nm no $T_g$ reductions will be observed for any film with nonzero thickness. From Fig. 2 it is evident that this value of $\alpha(M_w)$ corresponds to a $M_w$ of $150 \times 10^3$, and thus no $T_g$ reductions will be observed for $M_w < 150 \times 10^3$ as a result of this second mode of mobility.

Studies on low $M_w$ freely-standing PS films show reduced $T_g$ values for film thicknesses less than about 50 nm [8,9]. In contrast to the mechanism proposed in reference [11] and discussed in section 3.2 of this manuscript, the reduced $T_g$ values for low $M_w$ values have been attributed to a *finite size effect* due to an intrinsic length scale for cooperative dynamics [9]. Clearly for some range of values of $M_w$ these finite size effects must compete directly with the chain confinement effects. To examine the regime corresponding to the crossover between the domination of each effect, we consider the following. Since $T_g$ reductions due to the intrinsic length scale of glass transition dynamics are observed to occur for $h \sim 50$ nm, we consider the straight line between ($h^*$, $Tg^*$) and the point ($h = 50$ nm, $T_g^{bulk}$) in Fig. 1. From the slope of this line, $\alpha \sim 1$ °C/nm, and Fig. 2, we can see that only modest $T_g$ reductions due to chain confinement effects in thin films should be observed for $M_w \sim 300 \times 10^3$. Since the $T_g$ reductions due to the finite size effects discussed in [9] are larger than the mechanism important for chain confinement effects, this value of $M_w$ is a lower limit for a crossover between the two mechanisms. It is very gratifying that this value for the crossover $M_w$ is in excellent agreement with that measured experimentally [9].

To summarise, from the experimental data, we obtain equations (1) and (2). Eq. (1) suggests a mode of mobility different from that observed in the bulk and hence has important theoretical implications. Eq. (2) is merely a satisfactory empirical parameterisation convenient for quantifying the relationship between $T_g$ and $h$. A detailed understanding of the data requires a theoretical argument for an acceptable form of $\alpha(M_w)$. Combining Eqs. (1) and (2), we obtain a single
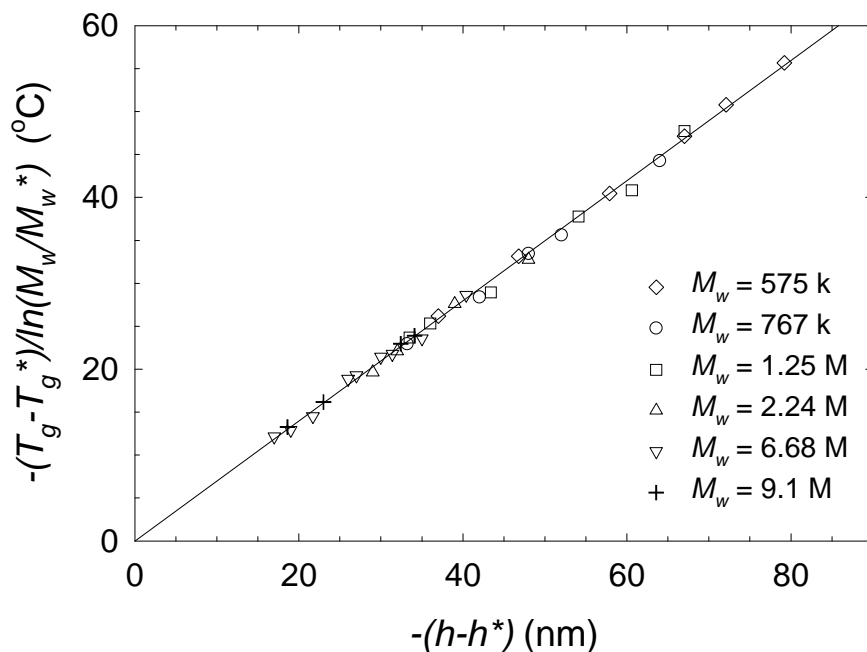
**Figure 3.** Scaling behaviour of the freely-standing PS film data for all of the molecular weights studied, as described by Equation (3).

relationship expressing the glass transition temperature in terms of film thickness and molecular weight dependence:

$$(T_g - T_g^*) = b \ln(M_w/M_w^*) (h - h^*).\qquad(3)$$

In Fig. 3 we test the scaling expression of Eq. 3 explicitly. Fig. 3 contains *all* of the reduced $T_g$ data for *all* of the molecular weights in the high $M_w$ regime ($> 350 \times 10^3$), and we find that the data is quantitatively described by only four parameters: $T_g^*$, $h^*$, $M_w^*$ and $b$. We expect that these four parameters will describe the $T_g$ reductions observed for all PS with $575 \times 10^3 < M_w < 9100 \times 10^3$.

### 3.2 Possible mechanism for $T_g$ reductions in thin films

Two striking facts emerge from the data: a) A depression of $T_g$ can occur for large film thicknesses $h$ comparable to the coil size $R$. b) The plots of $T_g(h)$ shown in Fig. 1 suggest a competition between *two types of motion*. One type is based on short range rearrangements and is associated with the usual dynamics responsible for the bulk $T_g$. The other type of motion could be a *sliding motion*, where a chain advances along its own path (probably via a few mobile 'kinks'). The free volume required for the sliding motion involves only the side chains (as eluded to above) and is much less than bulk cooperative motion. Sliding is blocked in the bulk, because chain ends would have to invade new territory, and this requires a large free volume. Near a free surface, the situation could be different: the monomers in direct contact with the air are nearly fluid. A loop **AB** touching the surface at points **A** and **B** should slide without impediment at **A** or **B** (see Fig. 4). One of us has
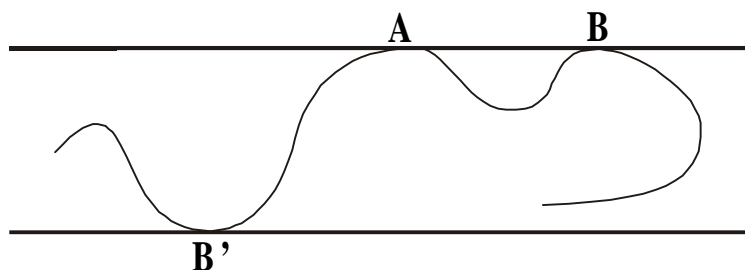


**Figure 4.** Schematic diagram of a polymer chain confined to a thin film. The segment **AB** forms a loop while **AB'** is a bridge across the film.

set up a crude model incorporating both of these motions [11]. The model leads to a glass transition $T_g(z)$ which is a function of the distance $z$ from a free surface (both in the bulk or in a film). In the model $T_g$ is reduced in regions comparable to the coil size as a result of the sliding motion. The model predicts a high molecular weight limit or a related depth beyond which sliding is quenched. Thus some qualitative features of the data are reproduced, while the detailed plots and the reduced form of equation (3) are yet far from being explained.

Measurements of the glass transition temperature of films on substrates are significantly different from those of freely-standing films with the dependence of $T_g$ on film thickness being much less pronounced without a clear $M_w$ dependence. This can also be understood from the model. Just as sliding is blocked in the bulk (as a result of a small amount of free volume being available), sliding motion is similarly inhibited at a substrate. The polymer segments can be divided into two classes, 'bridges' with **A** on the opposite side of the film to **B**, and 'loops' with **A** and **B** on the same surface (see Fig. 4). The difference between these two types of samples provides one additional piece of important evidence. Realising that the enhanced sliding motion is the result of segments with **A** *and* **B** ending at a free surface it becomes clear that the bridges must be responsible for the large $T_g$ reductions seen in freely-standing films. This is because loops with **A** *and* **B** at a free surface are present in both types of samples (although half as many for a supported film compared to a freely-standing film) but bridges with **A** *and* **B** at a free surface exist only for freely-standing films.

## 4. CONCLUSIONS

The glass transition temperature values measured for freely-standing PS films of high $M_w$ ($M_w \geq 575 \times 10^3$) display a fascinating dependence on both the film thickness $h$ and $M_w$ value. The linear dependence of $T_g$ on $h$ for reduced $T_g$ values and the abrupt transition from the bulk $T_g$ value to reduced $T_g$ values with decreasing $h$ are suggestive of two competing modes of motion. The $M_w$ dependence of the $T_g$ values suggests that one of the modes is related to confinement of the polymer chain. We have shown how a simple scaling analysis describes all $T_g$ values measured for freely-standing PS films with $575 \times 10^3 < M_w < 9100 \times 10^3$. We have also discussed a possible mode of 'sliding' motion which is only effective for thin freely-standing films. The sliding mode is able to account for many of the qualitative aspects of the data and will hopefully serve as a first step towards developing a model in full quantitative agreement with the data.

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