

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 ($M_w = 575 \times 10^3$, 767×10^3 , 1250×10^3 , 2240×10^3 , 6680×10^3 , 9100×10^3 , 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 °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 °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

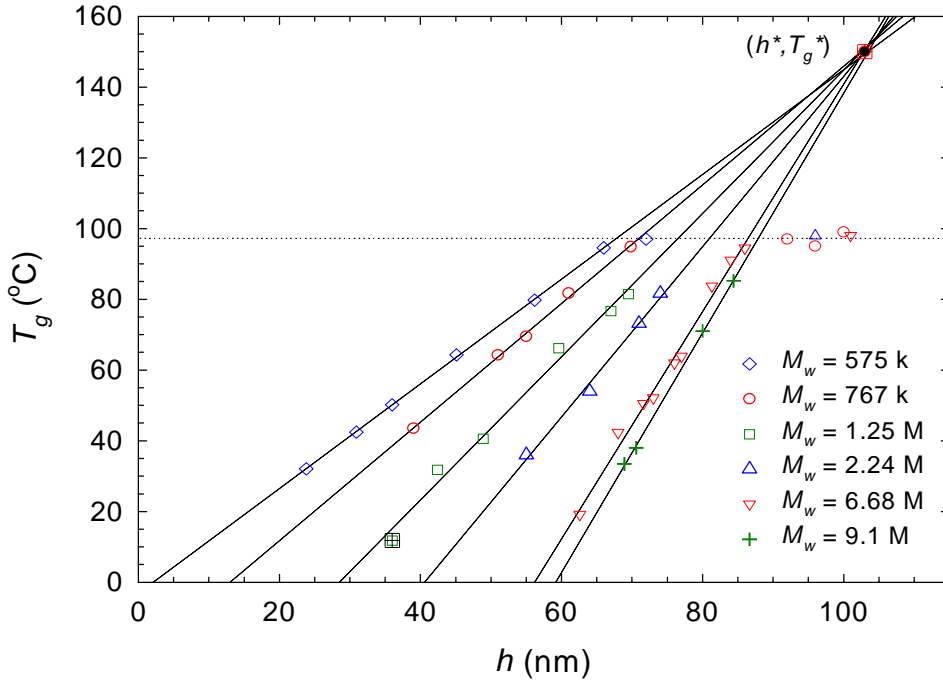


Figure 1. Plot of T_g versus the film thickness for all the molecular weights studied ($575 \times 10^3 < M_w < 9100 \times 10^3$) in reference [7]. The straight solid lines are best fits to the reduced T_g data and are extended to a common intersection point (h^*, T_g^*) . The dashed line corresponds 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 $T_g^* = (150 \pm 2)$ °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 α - and β -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 :

$$(T_g - T_g^*) = \alpha(M_w) (h - h^*). \quad (1)$$

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

$$\alpha(M_w) = b \ln (M_w/M_w^*); \quad (2)$$

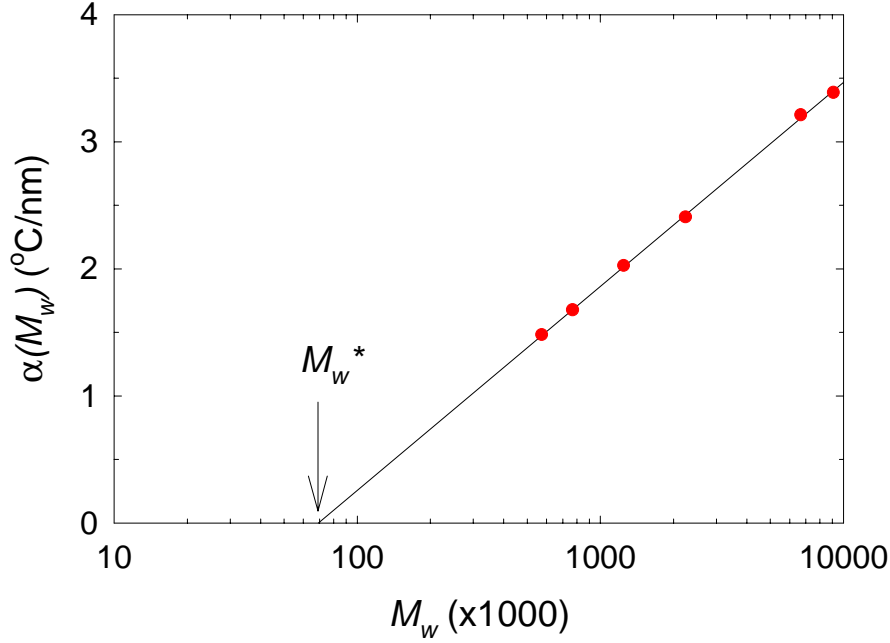


Figure 2. Plot of the slope of the linear reduction in T_g with decreasing film thickness h .

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 150×10^3 , 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^*, T_g^*) and the point $(h = 50 \text{ nm}, T_g^{bulk})$ 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

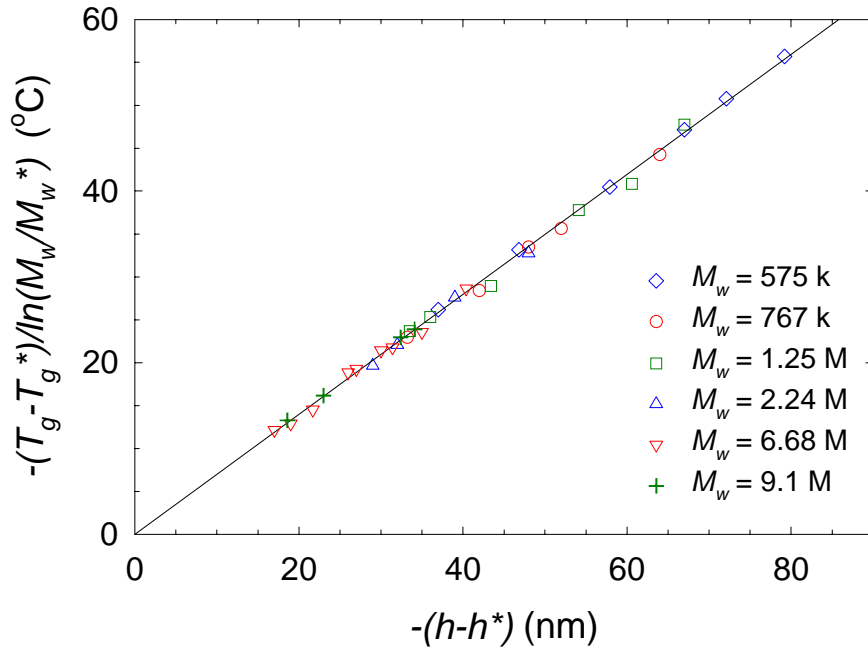


Figure 3. Scaling behaviour of the freely-standing PS film data for all of the molecular weights studied, as described by Equation (3).

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

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

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

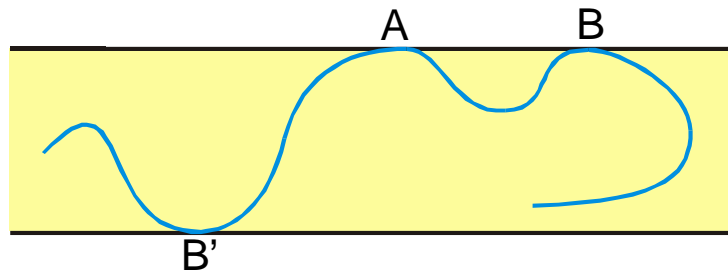


Figure 4. Schematic diagram of a polymer chain confined to a thin film. The segment **AB** forms a loop while **AB'** is a bridge across the film.

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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