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Using M_w dependence of surface dynamics of glassy polymers to probe the length scale of free surface mobility

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Abstract

We describe a series of surface levelling experiments in glassy polystyrenes (PS) of varying molecular weight. The resulting evolution through a mobile surface layer is described by the glassy thin film equation that was introduced and used in previous works. Previously defined correlation functions provide figures of merit that indicate if one waits long enough after the initial preparation of the stepped film, that the profiles

are well described by known evolution equations. The results are discussed in terms of the length scale for surface mobility in glassy PS.

Introduction

The structure and dynamics of polymers in the near surface region near the glass transition temperature (T_g) has attracted much attention over the past decade because they have significant implications for polymer thin film fabrication, coating, and the lubrication industry.¹ In addition, from a basic science perspective, understanding how and why polymers behave differently at the surface near T_g from those in the bulk is an important ongoing question.^{2,3} With more than 20 years of continuous research, accumulated evidence shows that the surface of glassy polymers is not glassy. In particular, polymer glass surfaces exhibit enhanced mobility compared to the same material in the bulk.⁴⁻⁸

This enhanced mobility in the near surface region of glassy polymers is often described qualitatively and even quantitatively^{5,9} as a liquid-like layer near the surface. It has been widely (though not universally) accepted that this liquid-like layer is the boundary condition that leads to the decreases in the measured T_g observed in ultra-thin polymer films.^{10,11} While theoretical and experimental^{6,12,13} efforts have been made to quantify this liquid-like layer, the nature of enhanced surface dynamics of glassy polymers is far from being fully understood. Direct measurements of depth dependent relaxation rates of local relaxations with nanometer precision have been measured using β -NMR, but it is not clear how much these studies can be used to shed light on the α -relaxation dynamics that are responsible for bulk flow. Quantification of polymer flow in the near surface region of polymer glasses has been used to provide a more quantitative picture, but none of those experiments have yet to be able to quantitatively provide a size of the liquid-like layer, h^* . In particular we note that surface levelling experiment provides a quantitative determination of $\frac{h^*}{3\eta}$ where η and h^* are the viscosity and the size of the liquid-like layer respectively.

One possibility to isolate the size of the liquid-like layer is to utilize the natural and tunable size of polymer molecules. This was done at a semi-quantitative level by Qi *et al.* where nanoparticle embedding onto glassy PS surfaces as a function of the M_w of the PS was studied.⁸ In that study there was a distinct difference in the behaviour between the large M_w values (87 kg/mol to 1200 kg/mol) where there was a near-surface nanoparticle embedding, and the lower M_w (3 kg/mol to 22 kg/mol) values where no near-surface embedding was observed. For the lowest value of $M_w = 3$ kg/mol (and the ones later used in Ref.⁹) a surface flow was observed similar to that for surface diffusion of organic glasses.¹⁴ This brings up the suggestion of performing quantitative surface flow experiments while varying the M_w , and hence the size, of the polymer molecules. As the size of the polymer crosses h^* , there may be quantitative changes in surface flow that allow determination of h^* . Comparisons to the previous study of Qi *et al.*, in particular there seems to be differences between the flow at the lowest value of $M_w = 3$ kg/mol, and that at the larger M_w values, suggesting that the range 3 kg/mol to 22 kg/mol should provide this transition regime in flow dynamics. In addition, we limited the M_w values less than the critical molecular (32 kg/mol for PS) as the entanglement of polymer chains can potentially affect the surface property.

Results and discussion

In this paper we describe a quantitative study of the levelling of PS stepped films (of varying M_w) at temperatures above and below the measured T_g value. By measuring the levelling process and fitting to numerical solutions of the fluid dynamic functions, we are able to distinguish without ambiguity the bulk and surface flow.

When the surface of a liquid film is not flat, surface tension drives the surface to minimize its area. Such liquid films will evolve according to the equations of fluid dynamics. Recently a number of studies have applied these ideas to polymer stepped films, such as those shown in Fig. 1. If the polymer is at a temperature $T \gg T_g$ then the flow is simply that of a

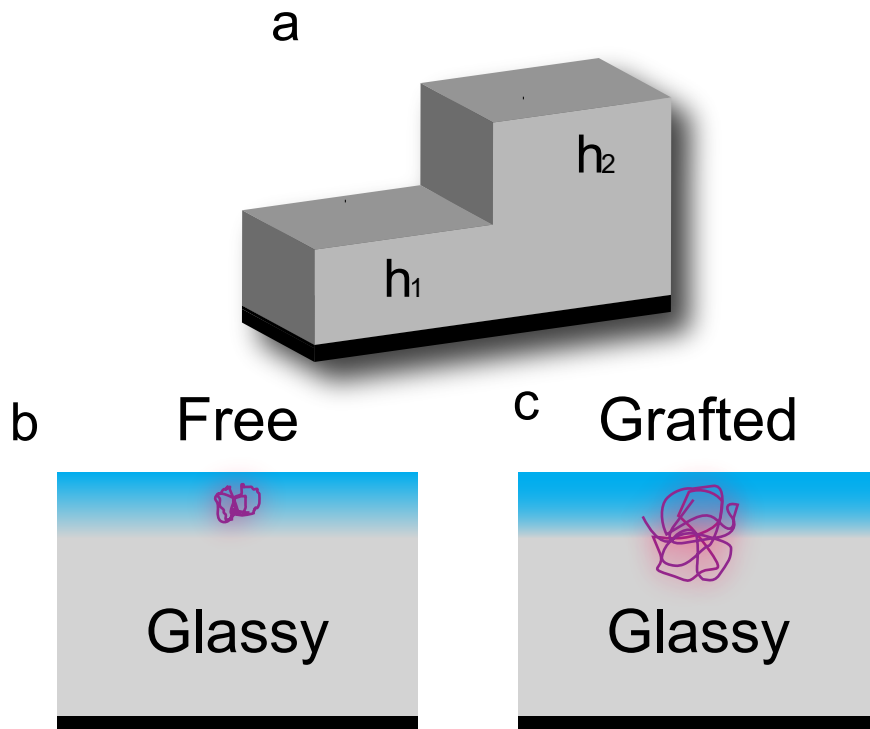


Figure 1: Fig. 1 (a) Schematic diagram of a stepped sample, where the thickness of the top layer is denoted as h_2 and that of the bottom layer is labeled as h_1 . Some representative polymer chains near the surface: In (b) $2R_g < h^*$ and in this case entire molecules are in the liquid-like layer and flow is uninhibited. In (c) $2R_g > h^*$ and while there are some polymer segments in the liquid-like layer, the fact that many parts of the chain are in the glassy immobile region means the flow should be inhibited.

thin liquid film. Such systems have been studied extensively and are well understood.^{15–17} In the case of glassy polymer films, bulk flow is not possible. However, experimentally, it has been shown that evolution still occurs in glassy films. In such cases, the evolution has been quantitatively described by a model consisting of a viscous fluid at the free surface of the glassy film.⁹

Mathematically flow in both cases is described by a 2D 4th order partial differential equation (PDE). For the case of $T > T_g$, the resulting equation is well studied, and we will refer to it as the Thin Film Equation (TFE)

$$\frac{\partial h}{\partial t} = \frac{\gamma}{3\eta} \frac{\partial}{\partial x} \left(h^3 \frac{\partial h}{\partial x} \right) \quad (1)$$

where h is the sample height, γ is surface tension, η is bulk viscosity, and x is the location variable. This equation is non-linear, and is solved numerically for comparisons with experiment. For $T < T_g$, flow occurs through a thin surface layer of size h^* . Because this layer is much thinner than the film ($h^* \ll h_1, h_2$), the equation can be linearized and solved exactly.⁹ This equation will be referred to as the Glassy Thin Film Equation (GTFE)

$$\frac{\partial h}{\partial t} = \frac{\gamma h^{*3}}{3\eta} \frac{\partial^4 h}{\partial x^4} \quad (2)$$

where now η refers to the viscosity of the liquid-like layer.

The premise of using of polymer chains to probe h^* derives from the natural length scale of polymers. Polymer chains of sufficient number of monomers can be described as a random coil where each molecule takes on a configuration of a random walk. While random chains do not have definitive shapes, we can define statistical distribution of shapes for all polymer chains which leads to ensemble averages of variables such as end-to-end distance (R_{EE}) and radius of gyration (R_g). The relationship between h^* and R_g (or R_{EE}) can be expected to lead to different types of flow behaviour. For example in Fig. 1b $2R_g < h^*$, entire molecules are in the near surface mobility region and flow is uninhibited. In Fig. 1c $2R_g > h^*$ while

there are some polymer segments in the mobile region, the fact that many parts of the chain are in the glassy immobile region means the flow should be inhibited.

Polystyrene (from Polymer Source Inc.) with $M_w = 3.0$ kg/mol ($T_g = 343$ K), 11.9 kg/mol ($T_g = 366$ K), and 22.2 kg/mol ($T_g = 369$ K) were used in this study, where $2R_g$ are ~ 4 nm, 6 nm, and 8 nm respectively. Although there is no consistent answer to how thick the liquid-like layer is, it has been reported by several groups that h^* is only a few nanometers. Here we use the value reported by Paeng and co-workers¹⁸ as an estimation. In their study, a temperature dependent mobile layer of glassy PS was observed, in which h^* in our experimental temperature regime is 4 nm ($T = T_g - 6$ K) to 6 nm ($T = T_g - 3$ K). Given these values of h^* and $2R_g$ for PS, it suggests (as well as the study of Ref.⁸) that this range of M_w should enable us to probe the range from uninhibited to inhibited flow.

Stepped films were made in a two-step process. First, polymer solutions in toluene were spin-coated onto two substrates, Si wafers with a size of 1 cm \times 1 cm (University Wafer), and mica plates with a size of 2 cm \times 2 cm. These spin-coated films were then annealed in a home-made oven flushed with dry nitrogen above their bulk T_g s (as measured) for more than 12 hours to remove internal stresses and residual solvents. The films were then slowly cooled back to room temperature. The thickness of the supported films on Si was measured by nulling ellipsometry, and that of mica supported films was measured by atomic force microscopy (JPK NanoWizard 3). Second, mica supported films were then transferred onto the surface of a clean water bath (Milli-Q). Typically, low M_w PS samples on water break up into small pieces that remain on the water surface. These film pieces were picked up by Si supported films. For the $M_w = 22$ kg/mol films, an initial cut with a razor blade was done on the mica supported films for 22.2 kg/mol samples before floating as these films did not break by themselves during the transfer process. Final stepped samples ($h_1 = h_2 = 90$ nm) with many sharp steps were dried for later study.

All experiments were conducted on a JPK AFM with a heating stage, and the annealing temperature and time were controlled by a Python script. The required precision of the

film evolution meant it was necessary to keep track of the evolution of the same nanostep in one single measurement. Consequently, all measurements were conducted in series meaning only one sample was measured in one period of time *in-situ*. During the measurement, a sample was placed on the heating stage, and annealed at a predetermined temperature for a certain period of time. After each annealing cycle, the sample was cooled down to room temperature, and the height profile of the nanostep was measured by AFM in tapping mode. Time dependent height profiles of the nanostep were obtained at one temperature by repeating the annealing and imaging process until either (1) the experimental profile is saturated, or (2) at least 90 hours of accumulated annealing time is reached (except for the $M_w = 22$ kg/mol sample, where measurements were made to 670 hours).

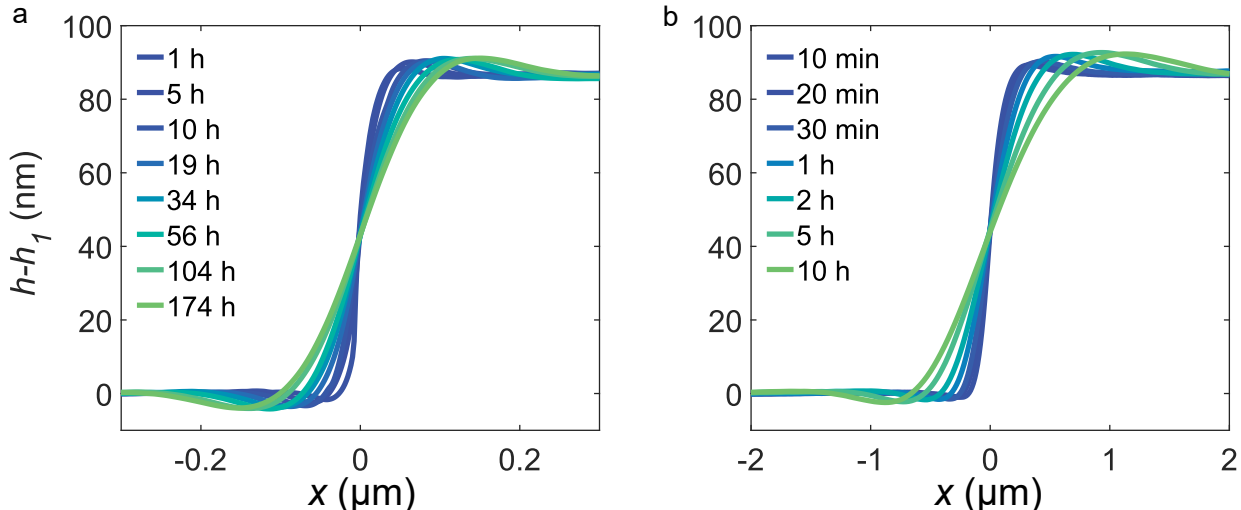


Figure 2: Time evolution of the height profiles for $M_w = 11.9$ kg/mol PS samples annealed at different temperatures, (a) $T = T_g - 3$ K, (b) $T = T_g + 12$ K.

Fig.2 shows typical evolution of PS bilayer samples of $M_w = 11.9$ kg/mol ($2R_g \sim h^*$) at temperatures both above and below the measured T_g . In particular Fig. 2a shows the evolution at $T = T_g - 3$ K, and Fig. 2(b) shows the evolution at $T = T_g + 12$ K. There are two things immediately evident from Fig. 2(b). First it is clear that 11.9 kg/mol PS at $T = T_g - 3$ K exhibits some type of flow below T_g . Second, it is clear by comparing the horizontal axis, and the annealing times that evolution is much slower at $T = T_g - 3$ K, than at $T = T_g$

+ 12 K. However, the difference in time scales is less than one might expect. The glassy film takes about 20 times longer to evolve about 5 times less distance. Roughly speaking this makes the glassy film about 100 times slower than the liquid film. A factor of 100 change in dynamics over 15K change in temperature near T_g is much less than one would expect in bulk materials. We can be more quantitative by comparing to our previous levelling study of 3.0 kg/mol PS. In that work we showed that above T_g the profile evolution proceeds by way of whole film flow, but below T_g profile evolution proceeds by way of surface layer flow.

In order to properly quantify the type of flow, we need to consider the detailed shape of the flow profile. While it may not be clear from a casual inspection of the profiles in Fig. 2, we have previously developed a direct method to distinguish these two different flow mechanisms. As long as the profiles have evolved sufficiently that the curvature based surface stress can be approximated as $P = -\gamma \frac{\partial^2 h}{\partial x^2}$, then we can write the curve as a function of the self-similar variable $xt^{\frac{1}{4}}$ and compare to profiles calculated using either the TFE or GTFE equation. This comparison is done most quantitatively through our previously defined correlation functions: χ_{GTFE} and χ_{TFE}

$$\chi_{\text{GTFE}} = \frac{\int dx (h_{\text{EXP}} - h_{\text{TFE}})}{\int dx (h_{\text{GTFE}} - h_{\text{TFE}})} \quad (3)$$

$$\chi_{\text{TFE}} = \frac{\int dx (h_{\text{EXP}} - h_{\text{GTFE}})}{\int dx (h_{\text{GTFE}} - h_{\text{TFE}})} \quad (4)$$

where h_{EXP} , h_{TFE} , h_{GTFE} are experimental, calculated TFE, and calculated GTFE profile respectively. Given an experimental nanostep profile, if χ_{TFE} is equal to 1, and χ_{GTFE} is equal to 0, the levelling process can be precisely described by TFE. In other words, the entire film flows. In contrast, if χ_{TFE} is equal to 0, and χ_{GTFE} is equal to 1, the levelling process can be precisely described by GTFE implying only the liquid-like layer flows.

Fig. 3 shows the time dependent correlation functions of PS with the three different molecular weights annealed above or below their T_g s, where the blue squares stand for χ_{GTFE} and the red triangles represent χ_{TFE} . For the case $M_w = 3$ kg/mol PS (Fig. 3a, it is evident

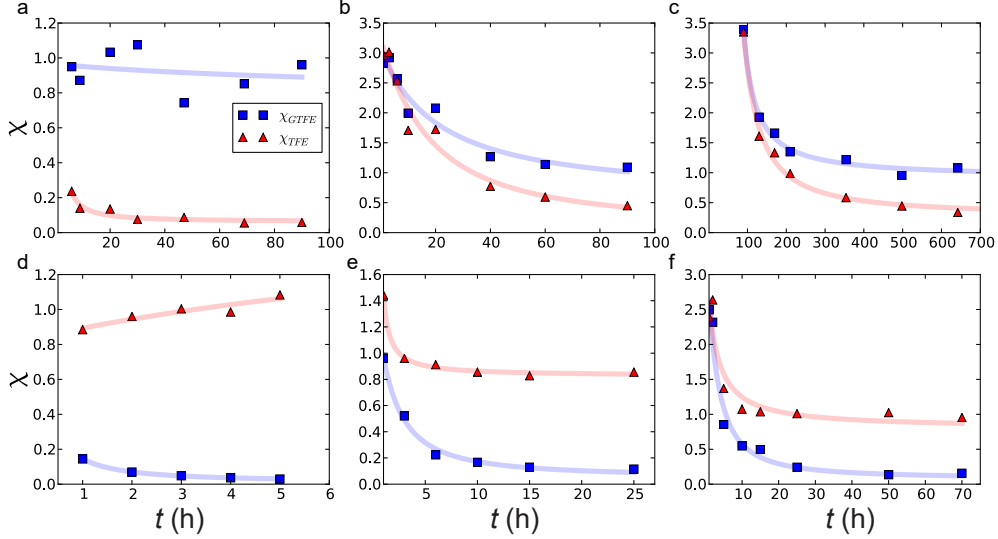


Figure 3: Time evolution of the correlation factors χ of three kinds polymers, $M_w = 3.0$ (a, d), 11.9 (b, e), 22.2 (c, f) kg/mol annealed at different temperatures, where the blue squares stand for χ_{GTFE} , and the red triangles stand for χ_{TFE} . The annealing temperatures are (a) $T_g - 10$ K, (b, c) $T_g - 6$ K, (d) $T_g + 10$ K, (e, f) $T_g + 9$ K.

that both the correlation functions (and whether the sample is annealed above or below T_g) reach their steady state values rapidly. Further, it is clear that for $T > T_g$, $\chi_{TFE} \simeq 1$ and $\chi_{GTFE} \simeq 0$. While, for $T < T_g$, $\chi_{TFE} \simeq 0$ and $\chi_{GTFE} \simeq 1$. The results clearly indicate (as described previously⁹) that for 3.0 kg/mol PS, the levelling process occurs by whole film flow for $T > T_g$ and through surface flow for $T < T_g$.

For 11.9 (Fig. 3b) and 22.2 kg/mol PS (Fig. 3c), the behaviour of the correlation functions is much less definitive but still convincing. Perhaps the first thing to notice is that the values of all correlation functions are initially greater than 1. This is an indication that the flow profiles are not fit well by either the calculated GTFE or TFE profile. The correlation functions χ are devised to be able to distinguish whole film flow from surface flow in cases where either of the two equations represents an excellent description of the data. The functions are not meant to provide quantitative measures in cases where *neither* of the two cases is likely to apply. In the data for Fig. 3b and Fig. 3c and $T < T_g$ the profiles are still close to their initial condition. In this case the expression used for surface pressure is most certainly incorrect and we can not expect χ to be a meaningful metric. For the case of

the $M_w = 11.9$ kg/mol and $T > T_g$ we see that after about 5-10 hours of annealing, we have $\chi_{\text{TFE}} \simeq 1$ and $\chi_{\text{GTFE}} \simeq 0$ as expected for whole film flow. For $T < T_g$ after 90 hours, we have $\chi_{\text{GTFE}} \simeq 1$, but the $\chi_{\text{TFE}} \simeq 0.5$. While this is a fairly strong indication of surface flow via the GTFE, it does indicate that the 90 hour experimental time window was probably too low. For this reason, the time window for the 22.2 kg/mol PS at $T < T_g$ was increased to 650 hours (27 days!). After this time we can see again that $\chi_{\text{GTFE}} \simeq 1$, but $\chi_{\text{TFE}} \simeq 0.5$. While χ_{TFE} does not saturate in the experimental time window for $M_w = 11.9$ kg/mol and $M_w = 22.2$ kg/mol PS, it is safe to conclude from Fig. 3 that two higher molecular weight PS samples show a bulk flow above T_g and a tendency of the surface flow below T_g in the experimental time window.

Unlike the conclusions suggested by Ref.,⁸ all of the M_w PS samples exhibit flow at $T = T_g - 5K$. As noted previously⁹ as long as the system has evolved to the point where it is self similar, and only a function of the variable $xt^{\frac{1}{4}}$, then the only variable in the shape of the profile is the mobility $\frac{h^*3}{3\eta}$ and fitting the calculated profile to the experimental profile provides this mobility. These mobility values are shown in Fig. 4 for the M_w and T values used in this study. From Fig. 4, we notice that the mobility parameter scales like $M_w^{-2.0}$. It is worth noting that this agrees well the molecular dependent viscosity of bulk PS above T_g near the entanglement molecular weight, i.e. the transition regime from a scaling of M_w to $M_w^{3.4}$.

While we have data only over a limited range of M_w , it is clear that the mobility parameter below T_g does not follow the same M_w scaling as it does above T_g . In addition, the time required for continuous AFM measurement (650 hours) suggests that further measurements would be exceedingly impractical. Even increasing the M_w by a factor of 2 (and ignoring possible entanglement effects) would require almost 4 months of continuous use of the AFM. Before attributing this change in mobility to relation between h^* and $2R_g$ it is worthwhile to examine the distribution of polymer shapes nears the interface.

We use a simple random-walk based simulation to explore the distribution of polymers

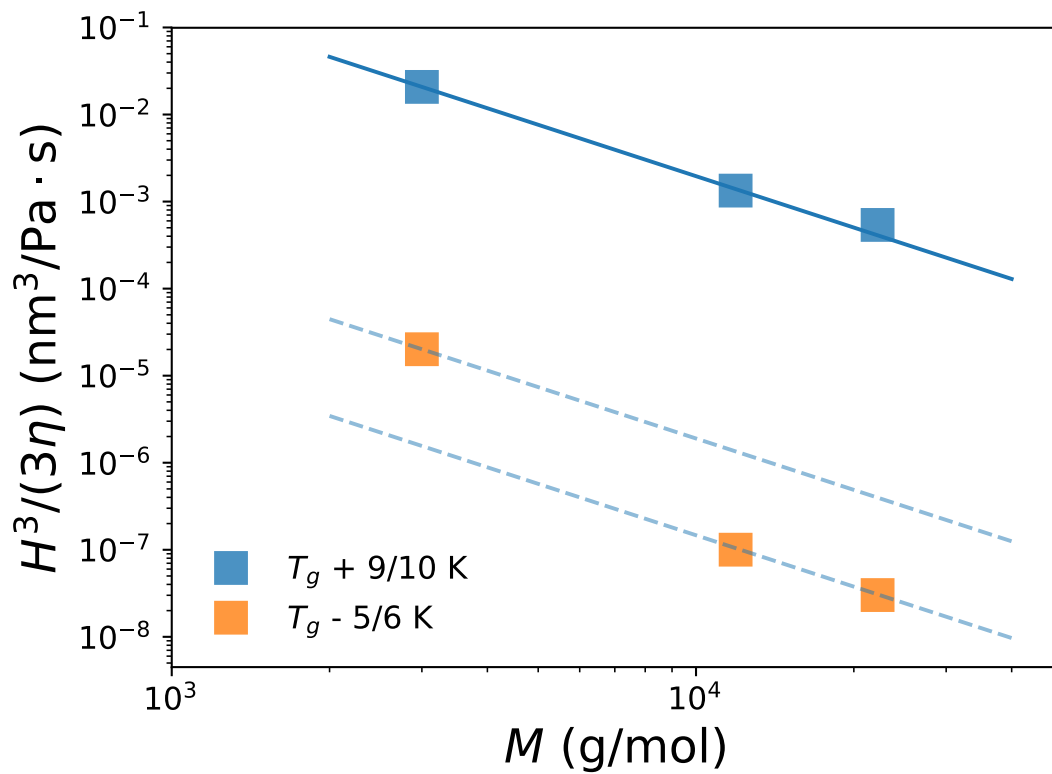


Figure 4: Mobility of different M_w PS samples at different temperatures, where the solid line represents the fitting to M_w dependent mobility at $T_g + 9/10 \text{ K}$ and the dashed lines represent the same scaling but vertically shifted to guide the eyes.

near the free surface. In order to make a transition between random walks and real molecular sizes, we consider that for PS, one Kuhn monomer (M_0) is 720 g/mol and one Kuhn length (b) is 1.8 nm.¹⁹ We use one Kuhn length as the smallest random step to ensure no correlation between two adjacent steps. h^* is thus set to be three Kuhn length ($3b = 5.4$ nm). For each value of M_w , we simulate random walks that can possibly have a segment in the mobile region. In order to accomplish this, each series of 10,000 random walks is started with one end at $z = z_0$. The value z_0 is then varied from the free surface to the value corresponding to the size of the fully extended chain plus h^* (i.e. no chains started at any z_0 greater than this value can *possibly* have a segment in the liquid-like layer. While this ignores effects such as chain end enrichment, and any non-random effects on chain configuration, it is a good starting point for our discussion.

During the simulation, two variables are defined. These variables are n_f , the number of free chains, and n_s the number of grafted chains. The question we want to answer is "What fraction of polymers that have at least one segment in the mobile region have *all* segments in the mobile region?". This is equivalent to asking what is the fraction of material in the region h^* that can be considered as freely flowing. We illustrate this by example in the inset of Fig. 4. In the case (a), the entire polymer chain is in the liquid-like layer, i.e., a free polymer chain. For this chain, n_f is increased by 1. For the chain in (b), only 50% of the polymer chain is in the liquid-like layer, thus, n_s is increased by 0.5. In the case (c), the entire polymer chain is embedded in the glassy film, i.e., an immobile polymer chain. In this case, both n_f and n_s remain unchanged.

After generating $10,000 \times n(z_0)$ random polymer chains, the fraction of free polymer chains in the liquid-like layer (φ) is calculated

$$\varphi = \frac{n_f}{n_f + n_s} \quad (5)$$

Fig. 4 shows the molecular weight dependent φ . Taking $M_w = 3.0$ kg/mol PS as an example,

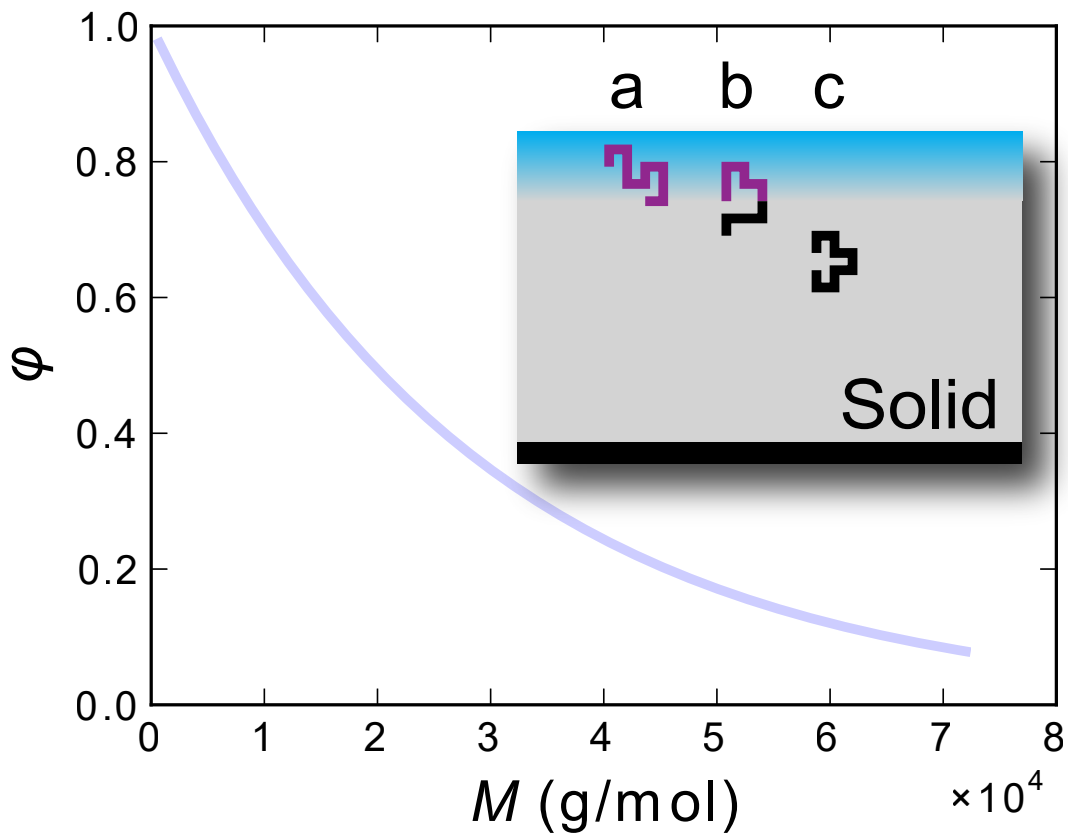


Figure 5: Fraction of the free polymers in the liquid-like layer as a function of the molecular weight of polystyrene. The inset shows three typical cases in the random-walk simulation with the thickness of liquid-like layer ξ : (a) free polymer chains, (b) partially grafted polymer chains, (c) embedded polymer chains.

it gives φ equal to 0.90 meaning there are 90% of the polymer chains in the liquid-like layer can flow. The same explanation applies to $M_w = 11.9$ and 22.2 kg/mol PS. They have φ values of 66% and 46% respectively. Based on the fractions listed above, it is evident that there are many polymer chains are mobile, even when $2R_g \geq h^*$. In other words, there are many polymer chains that naturally fit in a layer that is smaller than $2R_g$. It is not clear how this picture of some fraction of completely free chains, and some fractions that are effectively grafted by their monomers in the glassy layer can be transformed into an effective viscosity of the flowing layer. But the studies that do exist for comparison²⁰ do not suggest any reason for such a large change in effective viscosity over a relatively small change in the fraction of free/grafted chains. Thus it seems reasonable, that the order of magnitude shift in mobility between $M_w = 3$ kg/mol and $M_w = 11.9$ kg/mol is a reflection of the value of h^* . From this we would suggest that $4 \text{ nm} < h^* < 7 \text{ nm}$ or $h^* = 5.5 \pm 1.5 \text{ nm}$. We notice in comparing with Fig. 3 of Ref.⁸ that near surface embedding below T_g caused a change in the apparent nanoparticle size of 5 nm. The quantitative agreement of these values over polymer with M_w ranging from 3 kg/mol to 1211 kg/mol is encouraging. Using the result of $h^* = 5.5 \text{ nm}$, it suggests a viscosity of the liquid-like layer for $M_w = 3$ kg/mol at $T_g - 5 \text{ K}$ of $2.7 \times 10^6 \text{ Pa}\cdot\text{s}$, which is equivalent to that of bulk PS at 353 K ($T_g + 15 \text{ K}$).

Conclusion

In conclusion, we have measured the leveling process of PS stepped films with different molecular weights, found a tendency of surface flow with all different molecular weights below T_g even when $2R_g > h^*$. The difference between M_w scaling above and below T_g can be used to predict a thickness of the liquid-like layer below T_g as $h^* = 5.5 \pm 1.5 \text{ nm}$.

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