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# Glass Transition of Amorphous Polymer Surfaces

**Anne M. Mayes**

*Department of Materials Science and Engineering,*
*Massachusetts Institute of Technology,*
*Cambridge, Massachusetts 02139*

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For numerous commercial applications of polymers the near-surface properties are critical to performance. Properties such as chemical and abrasion resistance and wettability are determined predominantly by the structure within a few nanometers of the surface. Yet surprisingly little is known about the free surface structure of most polymer systems.

In general, surfaces modify the interplay of entropic and enthalpic forces that govern bulk polymer structure. Thus segmental distributions near a surface need not mirror bulk profiles. With the advent of new surface-sensitive probes and refined numerical models for macromolecular systems, a clearer picture is evolving of the near-surface regions of semicrystalline and amorphous polymers. Recent neutron reflectivity studies by Wu and co-workers[1] suggest that crystallinity is enhanced at the surface of poly(chlorotrifluoroethylene). Factor et al.[2] similarly observed higher surface crystallinity in aromatic polyimide films investigated by grazing-incidence X-ray diffraction. These results are significant in light of the dramatic difference in properties between the crystalline and amorphous phases of semicrystalline polymers.

Purely amorphous polymer systems are likewise expected to exhibit deviations in the segment density distribution near a surface. Molecular dynamic and Monte Carlo simulations by several groups[3-6] predict an excess in chain ends close to free or solid surfaces, even in the absence of strong preferential end-segment interactions. In this paper a simple scaling analysis is used to demonstrate that such end localization could have a marked influence on the properties of amorphous polymer surfaces. Herein it is argued that the near-surface region of glassy polymers will exhibit a significant depression in the glass transition due to chain end enrichment.

Chain end localization to a surface can arise solely from conformational entropy considerations at the material boundary.[3-7] In the language of confined random walks, the placement of chain ends at the surface obviates unfavorable "reflections" required of segments in the central portion of the chain (Figure 1). To simplify the present scaling analysis, we shall consider a monodisperse system of polymer chains, each having $N$ statistical segments of length $a$. If the polymer is amorphous, the spatial distribution of a single chain is known to be accurately represented by random-walk statistics. The characteristic diameter of the molecule is roughly equivalent to the root-mean-square end-to-end distance, $R_0 = N^{1/2}a$.

de Gennes[7] has argued that the extent of end segregation to a surface is controlled by the difference between the surface tension of an infinite polymer chain and that of the end groups, $\delta = \gamma_\infty - \gamma_e$. For values of $\delta a^2$ much smaller than the thermal energy ($kT$), the surface end concentration should equal that of the bulk, $\phi_\beta = 2/N$. When $\delta a^2/kT$ is of order unity, however, all chain ends within a distance $R_0$ from the surface will be localized to the surface.

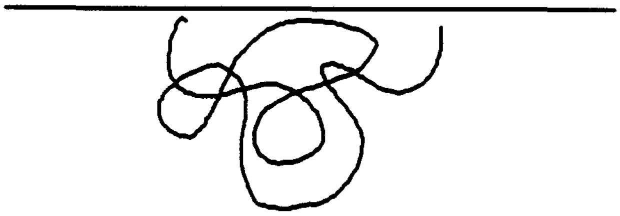

**Figure 1.** Chain end segregation which relaxes the reflection condition imposed on central portions of a polymer chain at a surface or interface.

In this case, the concentration of chain ends in a near-surface layer of thickness $d$ is[7]

$$\phi_\sigma = \phi_\beta(R_0/d) = 2N^{-1/2}(a/d) \qquad (1)$$

where the subscripts $\sigma$ and $\beta$ refer to the surface and bulk, respectively. For higher values of $\delta$, chains in the vicinity of the surface must stretch to accommodate more chain ends per unit surface area. Here we will be concerned with the regime where attraction to the surface is moderate, whereby eq 1 is assumed.

In now considering only a near-surface zone of thickness $d$, we can define for this region a new *effective* degree of polymerization, $N_\sigma$, which gives the molecular weight equivalent for the same fraction of chain ends in bulk. This value is related to the end concentration at the surface by $\phi_\sigma = 2/N_\sigma$, or

$$N_\sigma = N^{1/2}(d/a) \qquad (2)$$

This expression has interesting implications regarding the glass transition of a polymer surface. For amorphous polymers in bulk, the variation in $T_g$ with molecular weight is well described by the empirical relation[8]

$$T_g = T_{g,\infty} - C/N \qquad (3)$$

where $T_{g,\infty}$ is the glass transition temperature for a system of infinitely long chains and $C$ is a material constant.[9] According to free volume models, the $1/N$ dependence in eq 3 arises from the enhanced contribution of chain ends to the total free volume of the system, as evidenced by an increase in the specific volume of bulk polymer systems with decreasing molecular weight. If we assume that eq 3 applies similarly to the material boundaries, then the effect of chain end segregation should be to reduce the glass transition of the near-surface zone. The predicted depression in the surface $T_g$ is obtained by replacing $N_\sigma$ for $N$ in eq 3.

$$\Delta T_{g,\sigma} = T_{g,\infty} - T_{g,\sigma} = CN^{-1/2}(a/d) \qquad (4)$$

To appreciate the magnitude of the predicted $T_g$ depression, consider as an example a system of polystyrene chains of $1 \times 10^5$ mol wt, or $N = 960$. For a segregated layer thickness $d \sim a$, the surface-equivalent molecular weight for this system from eq 2 would be $\sim$6500, or $N_\sigma = 31$. Using the known values of $T_{g,\infty} = 373$ K and $C = 1.1 \times 10^3$ for polystyrene,[10] one finds $T_{g,\sigma} = 337$ K, or a depression of 36 K relative to the bulk $T_g$ calculated from eq 3. With lower molecular weight materials the effect is even more pronounced. For a $2 \times 10^4$ mol wt polystyrene, $T_{g,\sigma} = 294$ K, about 79 K below the bulk $T_g$. The surface glass transition as a function of $N$ is calculated from eq 4 for several common commercial polymers in Figure 2.

The practical importance of a surface-reduced $T_g$ could extend to numerous commercial applications of glassy

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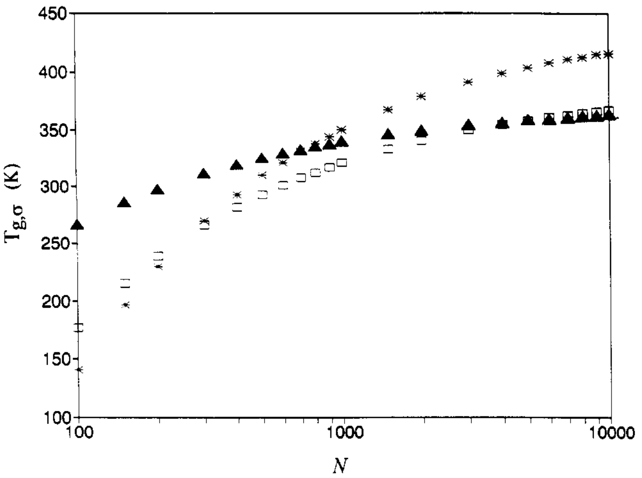

**Figure 2.** Surface glass transition values for poly(methyl methacrylate) (□), polystyrene (▲) and poly($\alpha$-methylstyrene) (*) as a function of $N$. (Values for $T_{g,\infty}$ and $C$ taken from ref 8.)

polymers. For amorphous polymer coatings, a significant reduction in $T_g$ at the surface could create buckling stresses on heating, due to differences in thermal expansion between the surface and interior.[11] Because mechanical and rheological response change dramatically above $T_g$, a surface-reduced glass transition would also be expected to influence such properties as adhesion and wear.

There is still only limited evidence for the segregation of chain ends to the surface of amorphous polymer systems. Chain end segregation has been suggested to account for the observed molecular weight dependence of polymer surface tensions.[7,12] However, Sauer and Dee[13] have alternately explained such data using the Cahn–Hilliard equation[14] to model the interfacial tension between a polymer-rich (liquid) phase and a hole-rich (gas) phase at the material surface. Their analysis employs Flory's equation of state model[15] to obtain the equilibrium densities of the liquid and gas phases, $\rho_l(N)$ and $\rho_g(N)$, respectively. The density gradient across the interface between these two states could also yield a locally reduced $T_g$, with a different molecular weight dependence than that derived in eq 4. For appreciable molecular weights, however, the predicted gas–liquid interface grows extremely sharp, while $\rho_g(N)$ becomes negligible. This would suggest a much weaker $T_g$ reduction than that predicted to arise from end segregation effects.

Recently, several groups have reported direct experimental evidence for the surface localization of chain ends.[16–18] Zhao et al.[16] performed neutron reflectivity investigations on a $6.5 \times 10^4$ mol wt polystyrene labeled at each end with ~2% deuterated polystyrene. A 2 times excess of chain ends at the free surface was found to best describe the experimental data. Botelho do Rego et al.[17] also investigated end segregation in isotopically end-labeled polystyrene using HREELS, a vibrational spectroscopy technique that employs low-energy incident electrons with a penetration depth of one or two monomer layers. For a $1.0 \times 10^4$ molecular weight polystyrene with about two deuterated units at each end, a 2-fold enrichment of chain ends was indicated within the first ~10 Å of the polymer surface. In another recent study Affrossman et al.[18] employed static secondary ion mass spectroscopy to quantify end segregation in the same triblock material and in a second triblock of comparable molecular weight (~$10^4$) but with the inverse labeling scheme. The surface end concentration was indicated to be ~300% of the bulk value for the H–D–H copolymer and ~400% for the corresponding D–H–D material, suggesting that the segregation of chain ends is not principally an isotope effect.

There has been comparatively little work examining the influence of surface on the glass transition. In a recent study Meyers et al.[19] observed pattern formations on the surface of amorphous polystyrenes examined by atomic force microscopy. The characteristic spacing of the surface modulations was noted to be molecular weight dependent. The authors suggested these findings as evidence of an elasticlike region at the near-surface of polystyrene. Jackson and McKenna[20] studied the glass transitions of organic liquids confined to nanometer-scale pores in porous silica glasses. A depression in the glass transition relative to bulk values was observed that became more pronounced with decreasing pore size. A reduction in the density of the liquids due to packing constraints in the pores was suggested to account for the reduction in $T_g$. These results lend support to the present work, which predicts a similar depression in the surface glass transition of polymers from a reduction in density caused by end localization. It should be noted, however, that end enrichment at the polymer surface will also give rise to an adjacent depletion region over a distance $\sim R_0$ from the surface, where the glass transition should approach $T_{g,\infty}$.

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