471d The Diffusion Behavior of Polymer Ultrathin Films: Fundamental Insights and Molecular Weight Effects

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The effect of nanoscale confinement in modifying the physical properties of polymer thin films has recently received significant attention, particularly in the areas of polymer film glass transition temperatures (Tg). Depending on the nature of the interaction between the polymer and the substrate, both large increases and decreases in the polymer Tg have been observed. Our recent work has added further support to the idea that polymer chain dimensions are critical in controlling the length scale over which these effects are observed, and we have also shown the dramatic impact of nanoscale confinement on the coefficient of thermal expansion of supported polymer thin films. The focus of this paper is our expanded study of other important polymer physical properties that are modified due to nanoscale thin film confinement. In particular, the influence of thin film confinement on the diffusion coefficient of small penetrant molecules in polymer thin films has been studied in detail and will be presented. Changes in the diffusion behavior of small molecules in polymer thin films due to confinement has implications in a variety of fields including membranes, drug delivery, and semiconductor processing.

The influence of film thickness and molecular weight on the diffusion coefficient of water, low molecular weight organic solvents, and various acids in a series of polymers including poly(p-hydroxystyrene), substituted polynorbornenes, and PMMA has been studied using techniques such as quartz crystal microbalance (QCM) sorption experiments. It was observed that the diffusion coefficient is a strong function of film thickness and decreases drastically as film thickness is reduced below a critical thickness value. This critical thickness value is found to be a function of both the type of polymer and its molecular weight. Recent studies have focused on determining if this anomalous diffusion behavior is the result of film aging and densification, and the results of these studies will be presented. Recent simulation data suggests that differences in the free volume distribution of films of different thickness may be responsible for the observed differences in film diffusion behavior. Experimental data directed at probing the free volume distribution will also presented to further elucidate the possible factors controlling the observed behavior.