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Effect of Low Surface Energy Chain Ends on the Glass Transition Temperature of Polymer Thin Films

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Introduction. Many polymer thin film applications are intimately related to the chemical functionality of the chain end groups. For example, use of hydrophilic end groups is a common strategy to end-graft hydrophobic polymer chains onto high-energy substrate surfaces;[1] introduction of polar end groups to the polyfluoroalkyl ether improves its ability to protect a computer hard disk against wear;[2] using high molecular weight end-functionalized chains as additives can improve the durability of polymer thin films against deweting;[3] polymer surfaces that are modified by thermodynamically segregated low-energy chain ends can be exploited to make “self-healing” surfaces.[4] Previous experiments showed that polymer surfaces enriched with segregated chain ends exhibit higher molecular mobility,[5−7] which are consistent with theoretical predictions[8] assuming the generally larger free volume associated with chain ends compared to chain segments. A local interfacial layer with higher molecular mobility has been attributed to be the cause of a global reduction in the T_g of polymer thin films observed recently.[9−14] In this study, we investigate the T_g of thin films of PS with low surface energy fluoroalkylsilyl (R^f) termination on both ends (α,ω-PS-$(R^f)_2$). Results show that the amount of reduction in the T_g found in thin films of α,ω-PS-$(R^f)_2$ with decreasing film thickness is about twice of that found in thin films of *sec*-butyl-initiated-proton-terminated PS (H-PS).

Experimental Section. The α,ω-PS-$(R^f)_2$ (M_n = 47.8K Da, $M_w/M_n = 1.18$, T_g^{DSC} = 376 K) was synthesized by living anionic polymerization using potassium naphthalene as a bifunctional anionic initiator and (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane as a terminator. The H-PS, synthesized by anionic polymerization using *sec*-butyllithium as the initiator, had been purchased from Scientific Polymer Products (abbreviated com. H-PS,[15] M_n = 530K Da, $M_w/M_n = 1.04$, T_g^{DSC} = 382 K) and also self-made in our own laboratory (abbreviated home H-PS, M_n = 52K Da, $M_w/M_n = 1.05$, T_g^{DSC} = 372 K). Thin films of the polymers with different thicknesses (~8−200 nm) were prepared by spin-coating solutions of the polymers in toluene (0.3−4 wt %) onto cleaned silicon substrates[16] covered with a ~1.2 nm thick native oxide layer. Upon spin-coating, the α,ω-PS-$(R^f)_2$ thin films were kept under vacuum at ambient temperature for 3 days to remove the residual solvent. Before measurement, all samples were annealed at or above 120 °C for 5−9 h inside a vacuum oven to relax the polymer, whereupon they were allowed to cool to room temperature under vacuum. Spectroscopic ellipsometric measurements over wavelengths 350−1300 nm were carried out in a J.A. Woollam (Lincoln, NE) variable-angle spectroscopic ellipsometer (VASE). A home-built hot-stage with temperature controllable to within ±1 °C was incorporated to heat the sample in situ. To obtain the temperature scans, both the wavelength and incident angle of incoming light were fixed at settings empirically found to optimize the VASE signal;[9] the ellipsometric angles, δ and ξ, which are directly related to the film thickness and sample refractive index,[9] were recorded as a function of temperature, T, at a constant heating rate of 2 K/min. The T_g of a polymer film was determined as the temperature at which slope of its the temperature dependence data displays a discontinuity.

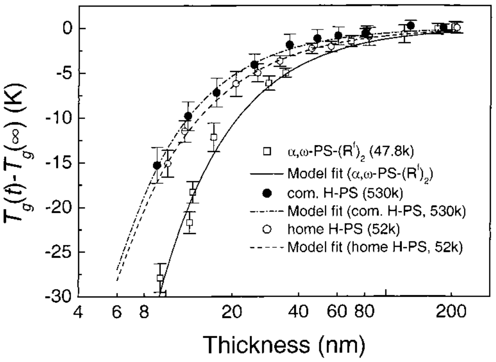

Figure 1. $T_g(t) - T_g(\infty)$ vs thickness, t, for thin films of PS with different M_n and chain ends. Smooth lines through the data are fits to the phenomenological expression discussed in the text.

Results and Discussion. Shown in Figure 1 are the measured results plotted as $T_g(t) - T_g(\infty)$ vs t, where t is the film thickness and $T_g(\infty)$ is the asymptotic T_g in the limit of large t. The data exhibit a monotonic reduction in $T_g(t)$ with decreased t, in accordance with previous measurements.[9−14] A number of models have been proposed to explain this behavior.[9,11−14] While they may differ by the physical process involved, all these models are based on the idea that a nanometer scale mobile (or lower T_g) region exists, whose influence on the T_g of the film increases as the film thickness is decreased, and end in the same phenomenological expression: $T_g(t) = T_g^{\infty}[1 - (\xi_0/t)^{\nu}]$, where ξ_0 is the length scale of the mobile region and ν a constant. We have model-fitted our data to this expression and found excellent agreement (smooth lines). From Figure 1, one may also notice that data points of the two H-PS fall within each other’s experimental error bars (or 1σ confidence interval) and hence are indistinguishable. On the other hand, the T_g of the α,ω-PS-$(R^f)_2$ thin films are noticeably more reduced (by ~2 times, which amounts to a sizable difference of ~3.5σ on average). According to Table 1, the fitted value of ν and ξ_0 are within the range of values obtained previously.[9,13] Comparing between polymers, the fitted values of ν vary only by

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Table 1. Comparison between Fitted Parameters for $T_g(t) - T_g(\infty)$ vs t Data of Figure 1 by Using the Phenomenological Expression Discussed in the Text

sample	ξ_0 (nm)	ν	$T_g(\infty)$ (K)
α,ω-PS-(R^f)$_2$	1.46 ± 0.23	1.37 ± 0.1	375 ± 0.9
com. H-PS ($M_n = 530$K)	0.86 ± 0.12	1.35 ± 0.06	373.5 ± 0.2
home H-PS ($M_n = 52$K)	0.72 ± 0.06	1.22 ± 0.03	372.2 ± 0.3

~10%. However, the fitted value of ξ_0 for the α,ω-PS-(R^f)$_2$ films is about 2 times larger than those of the H-PS films, suggesting a doubling in the length scale of the mobile region in the former. In the following, we will try to understand these different results in terms of the degree of surface segregation of chain ends and surface molecular motion in these two kinds of PS.

In H-PS, numerous measurements showed that the *sec*-butyl end groups preferentially segregated to the polymer surface.[5,17] The preferential segregation of surface chain ends is attributable to the enhanced surface molecular motion found in H-PS by scanning viscoelasticity microscopy (SVM)[5] and lateral force microscopy (LFM),[6] as a later finding[7] showed that no enhanced surface molecular mobility was present in PS with higher surface energy chain end groups, namely α,ω-PS-(COOH)$_2$ and α,ω-PS-(NH$_2$)$_2$.

In the fluoroalkylsilyl-terminated PS, angle-dependent X-ray photoelectron spectroscopy (ADXPS) and neutron reflectivity revealed that the polymer surface was ~5 times more concentrated with the fluoroalkylsilyl end groups than the bulk,[18] which is about 2.5 times bigger than that found in H-PS.[4] In PS terminated with both kinds of end groups, i.e., α-H-PS-ω-(R^f), the fluoroalkylsilyl end group had been found to dominate at the free surface.[17] LFM study also revealed that surface relaxations began to be discernible at a much lower temperature (~140 K) in α,ω-PS-(R^f)$_2$ than in H-PS (~300 K). It is thus justifiable to presume that the degree of segregation of chain ends to the free surface and the surface molecular mobility are substantially larger with the fluoroalkylsilyl termination than with the *sec*-butyl-initiated proton termination.

These previous findings enable useful insights to the understanding of data displayed in Figure 1. The notably lower T_g found in α,ω-PS-(R^f)$_2$ than in H-PS thin films reveals that when the surface of a polymer is sufficiently plasticized, the reduction in the T_g of the polymer confined in thin films may be promoted. To inspect whether this conclusion can be generalized to any kind of chain end that causes a lowering in the T_g of the surface, we examine data of the two H-PS displayed in Figure 1. Clearly, the same degree of depression in T_g prevails in thin films of both polymers despite their notably different M_n. This is consistent with previous experiments on the T_g of similar system, namely uncapped H-PS supported on Si substrates, where no M_n dependence was discernible for $M_n = 12.4-2900$ kDa.[9,19,20] Correlating these findings with results of ref 6 showing that the surface molecular motions of H-PS with $M_n < \sim 30$K Da are enhanced, one may conclude that existence of a plasticized surface layer does not always warrant a promotion in the depression of T_g in supported polymer films.

In conclusion, we have measured the T_g of thin films of PS with *sec*-butyl-initiated proton terminations and those with the lower energy fluoroalkylsilyl termination. In comparison, the latter exhibit a drastically higher reduction in the T_g with decreasing film thickness. The present result evidences the first time that a surface layer sufficiently plasticized by segregated chain ends may have a global effect on the T_g of a polymer film.

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