

Interfacial glass transition profiles in ultrathin, spin cast polymer films

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Interfacial glass transition temperature (T_g) profiles in spin cast, ultrathin films of polystyrene and derivatives were investigated using shear-modulated scanning force microscopy. The transitions were measured as a function of film thickness (δ), molecular weight, and crosslinking density. The $T_g(\delta)$ profiles were nonmonotonic and exhibited two regimes: (a) a sublayer extending about 10 nm from the substrate, with T_g values lowered up to $\sim 10^\circ\text{C}$ below the bulk value, and (b) an intermediate regime extending over 200 nm beyond the sublayer, with T_g values exceeding the bulk value by up to 10°C . Increasing the molecular weight was found to shift the $T_g(\delta)$ profiles further from the substrate interface, on the order of 10 nm/kDa. Crosslinking the precast films elevated the absolute T_g values, but had no effect on the spatial length scale of the $T_g(\delta)$ profiles. These results are explained in the context of film preparation history and its influence on molecular mobility. Specifically, the observed rheological anisotropy is interpreted based on the combined effects of shear-induced structuring and thermally activated interdiffusion. © 2004 American Institute of Physics. [DOI: 10.1063/1.1647047]

INTRODUCTION

Prescribed rheological properties and film stability are paramount to the development of polymer thin film and coating technologies, as found, for instance, in polymer-based thermomechanical data storage¹ and light emitting diodes.² In polymeric systems, the molecular mobility is of particular concern if length scales below ~ 200 nm are involved. Over the last few years, various groups have reported bulk-deviating structural and dynamic properties for polymers at interfaces.³⁻⁹ For example, reduced molecular mobility in ultrathin polystyrene films was reported based on forward recoil spectroscopy measurements.³ Furthermore, in secondary ion mass spectrometry (SIMS) and scanning force microscopy (SFM) studies of polystyrene and polyethylene-co-propylene systems, it was found that the degree of molecular ordering significantly affects dynamic processes at interfaces.⁴

An aspect that is ignored with classical mean-field theoretical considerations of thin films is the possibility of conformational changes due the film preparation process.⁹ In the past, one considered substrate effects to be confined to the pinning regime, typically on the order of a few nanometers. However, recent SFM experiments have revealed that the spin casting process alters the structural properties of polyethylene-co-propylene at silicon interfaces, leading to an anisotropic molecular diffusion process.¹⁰ Thermal annealing has been found inadequate to relax process-induced structural anisotropy in confined polymer systems because of insufficient *mixing* at the interface.¹⁰ Consequently, depending on the proximity to the substrate, i.e., film thickness, the

molecular mobility and relaxation properties of the polymer may be altered during the preparation process.

One parameter that is of particular interest in a discussion about molecular mobility of polymers is the glass transition temperature, T_g . For thin homopolymer films, it has been recognized that several factors are intricately responsible for the departure of the glass transition temperature from the bulk value,¹¹⁻³⁰ e.g., the proximity of a free surface, substrate interactions, and process-induced rheological anisotropy. Here, we address the effect of spin casting on the glass transition of amorphous atactic polystyrene films in the close vicinity to their silicon substrates. Furthermore, the use of chemical crosslinking as a stabilizing mechanism for spin cast thin films is investigated, and the rheological repercussions are discussed.

EXPERIMENT

Monodisperse, atactic polystyrene (PS) and polystyrene-vinylbenzocyclobutene (PS-BCB) homo- and co-polymer films were spin cast from cyclohexanone solutions onto silicon wafers (001) and thermally annealed at 134°C under vacuum. The film thicknesses ranged from ~ 3 to 275 nm. The molecular weights (M_w) were 12.0 kDa for PS and 17.5 and 21.0 kDa for PS-BCB, with 1.7 and 4.8 mole % BCB, respectively. The BCB served as a latent crosslinking agent, and one possible reaction mechanism is illustrated in Fig. 1. The crosslinking action of BCB is known commercially in adhesion promotion;³¹ its incorporation into linear hydrocarbon polymers has been more recent.^{32,33} The crosslinks are provided by an *o*-xylylene unit that is generated *in situ* from ring opening of the vinylbenzocyclobutene component on application of heat. The reactive diene (*o*-xylylene) then couples with species on adjacent polymer chains, resulting in

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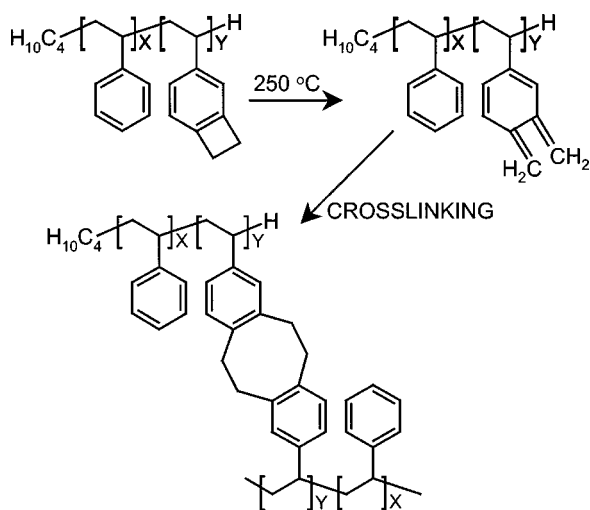


FIG. 1. Polystyrene–vinylbenzocyclobutene crosslinking mechanism.

a crosslinked matrix. The degree of crosslinking is controlled by the percentage of BCB incorporated during polymerization, and the crosslinking reaction is accomplished by heating the pre-cast films at 250 °C for 1 h under dry nitrogen.

The quality of the spin cast PS films is illustrated in Fig. 2(a), a SFM image which exhibits a smooth topography with a rms roughness of 0.6 nm. Figure 2(a) is representative of the quality of all tested films, with the exception of the thinnest crosslinked films. The onset of partial dewetting was found after crosslinking films thinner than the bulk radius of gyration (R_G) of 4 nm, illustrated in Fig. 2(b) for a 4 nm crosslinked 21 kDa PS-BCB film. Thus, we can conclude that the stress imposed on films with a thickness on the order of R_G or less is sufficient to thermally activate dewetting instabilities during the crosslinking process at 250 °C.

Near surface glass transition temperatures were acquired using shear-modulated scanning force microscopy (SM-SFM). Details of this technique are reported elsewhere.²⁷ Briefly, the SM-SFM method involves a nanometer sharp SFM cantilever tip (NanoSensors, normal spring constant of 0.13 N/m) that is sinusoidally modulated in lateral direction while in contact with the polymer surface. The modulation frequency was 4.3 kHz, the applied load was ~ 100 nN, and the ratio of the modulation amplitude to the tip diameter was ~ 1.8 (no slip condition). Below the glass transition temperature, the probing depth of the SM-SFM is on the order of 1 nm, which allows *substrate-independent* measurements down to film thicknesses of a few nanometers. Any surface effects less than 1 nm in depth, for example the *mobile surface layer* proposed by de Gennes,¹⁵ cannot be addressed under these loading conditions. The very slow creeping process above T_g is documented elsewhere.²² The measurements were conducted in a dry nitrogen environment with a relative humidity of less than 10%.

For the PS-BCB samples, T_g values were obtained before and after crosslinking. A representative example of the SM-SFM results is reported in Fig. 3 for an uncrosslinked, 140 nm, 17.5 kDa PS-BCB film. The glass transition temperature is indicated by the discontinuity in the slope of the amplitude response, i.e., the onset of creep.

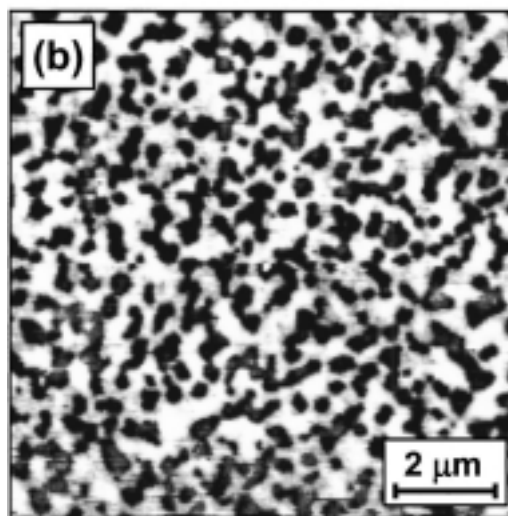
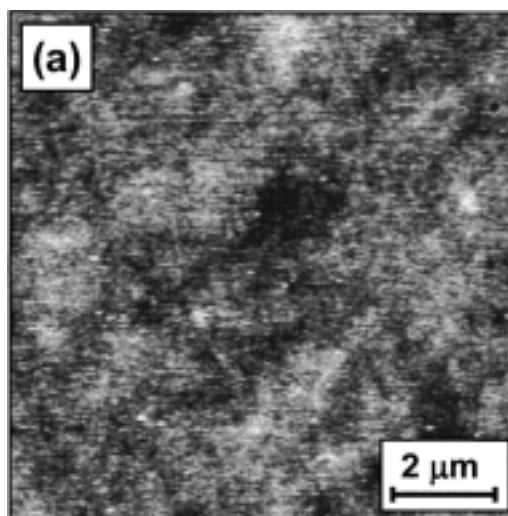


FIG. 2. (a) Representative SFM topography image of a smooth, thin PS film with a rms roughness of 0.6 nm (dynamic range of grayscale 3.4 nm), measured at 27 °C. (b) Crosslinked PS-BCB film of 4 nm thickness reveals dewetting instability. SFM topography image measured at 27 °C (dynamic range of grayscale 9 nm).

RESULTS AND DISCUSSION

In Fig. 4, glass transition values are presented for the homopolymer PS films over a film thickness (δ) range of 5 to 240 nm. For $\delta > 200$ nm, the transition values correspond to the bulk T_g value of 95 °C.¹¹ However, bulk-deviating values were found for $\delta < 200$ nm. From a qualitative perspective, there are two findings: (a) adjacent to the substrate interface, T_g values are depressed relative to the bulk value within a *sublayer* with a thickness on the order of the unperturbed R_G , which exceeds the persistence length predicted by Brogley³⁴ by one order of magnitude; and (b) between the sublayer and the bulk phase lies an *intermediate regime* within which T_g values exceed the bulk T_g .

This unexpected, nonmonotonic $T_g(\delta)$ relationship can be interpreted considering two competing processes that affect the relaxation dynamics: (a) shear-induced structuring and (b) interdiffusion.^{8,10,35} Shear-induced structuring creates an interfacial region where the spin casting shear stresses

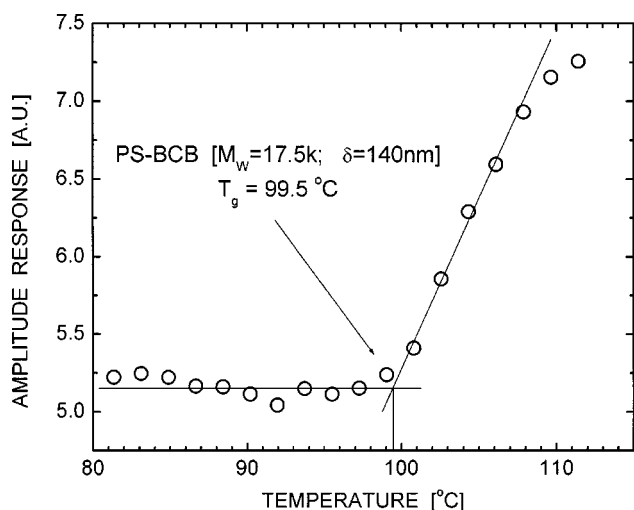


FIG. 3. Near surface T_g measurement in thin PS films using shear-modulated SFM. The amplitude response to the modulation force indicates a T_g value of 99.5 °C on an uncrosslinked, 140 nm thick PS-BCB film ($M_w = 17.5$ kDa).

induce polymer stretching and or disentanglement. This process will hereafter be referred to as polymer deformation. The second process involves the interdiffusion between the entropically cooled interfacial region and the unperturbed bulk phase.

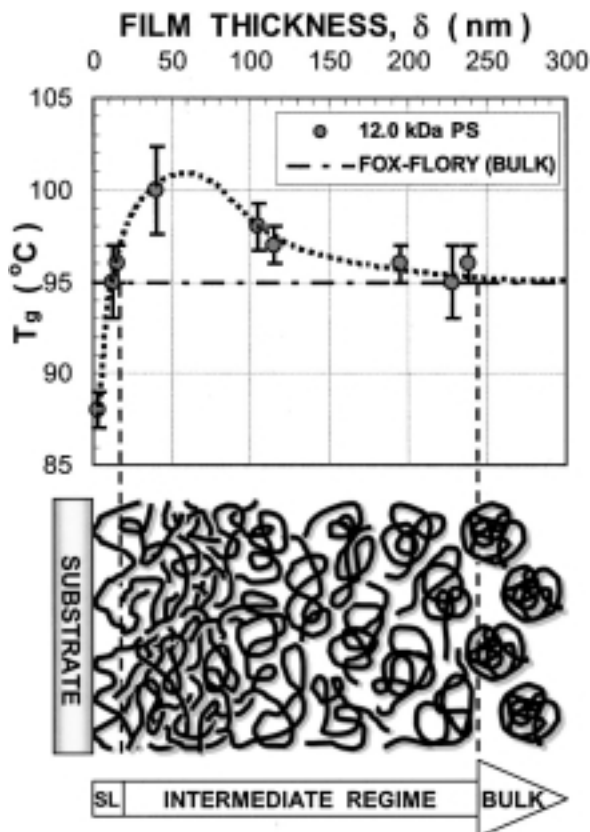


FIG. 4. (Top) film thickness dependence of the glass transition temperature on polystyrene films ($M_w = 12$ kDa) compared to the bulk T_g value predicted from Fox-Flory theory. (Bottom) rheological anisotropy model describing the observed T_g relationship (SL = sublayer).

Considering shear-induced structuring, computational fluid dynamics (CFD) simulations of Newtonian flow over a rotating disk indicate that the shear stress increases with distance from the interface until a maximum is reached at a distance approximately corresponding to the momentum boundary layer thickness.³⁶ Further from the interface, the shear stress asymptotically decays to zero at a distance approximately ten times the momentum boundary layer thickness. This shear stress profile is qualitatively similar to the $T_g(\delta)$ profile in Fig. 4, and suggests that the extent of polymer deformation may be related to the shear stresses experienced during spin casting. Interdiffusion of the deformed chains occurs during annealing, and diffusion generated entanglements are formed. Conformational relaxation during annealing is hindered by the entanglements, which results in residual internal stresses, schematically illustrated as the intermediate regime in Fig. 4. The entanglement density and internal stress profiles follow the shear stress profile during spin casting, with the residual internal stresses presenting an additional barrier to the relaxation associated with the glass transition. Hence, it is surmised that the sequential combination of deformation followed by interdiffusion contributes to the observed $T_g(\delta)$ profile.

Because the spin casting of polymer solutions exhibits a non-Newtonian behavior, direct correlation of the shear stress length scales from the CFD simulations to those of Fig. 4 is not possible. However, experimental studies of polymer solutions under shear flow^{37–39} have indicated that shear-induced structure formation is a common phenomenon in polystyrene solutions.³⁸ Given sufficient shear stress and shearing rate, laminar flow-induced anisotropic structuring has been observed in polystyrene solutions both with and without entanglements. Furthermore, depending on the solution concentration, the shear-induced structuring becomes an irreversible process.³⁹ With this strong precedence for shear structuring in polystyrene solutions, it is reasonable to propose that the effects of the spin casting process extend from the silicon substrate, over both the sublayer and intermediate regime, to the boundary with the unperturbed bulk phase.

An alternate mechanism responsible for the observed anisotropy proposes the shear structuring effects associated with spin casting extend only through the sublayer, and that interdiffusion alone is responsible for the conformational restructuring within the intermediate regime. The sublayer can be pictured as highly disentangled with a free volume in excess of that of the bulk. This is consistent with neutron reflectivity measurements on PS films that have indicated, for $\delta < R_G$, the film density is less than that of the bulk polymer, and that the density continues to decrease as the film thickness decreases.³⁵ The mobility of the PS chains is limited by the propagation of *holes*, or packets of free volume, which facilitate conformational rearrangements of the chains.⁴⁰ For molecular weights less than the entanglement molecular weight, a moving boundary diffusion process is encountered during annealing, where molecules from the bulk phase diffuse toward the interface into the less dense sublayer, leaving behind holes in which molecules from the adjacent outer *shell* diffuse. The diffusion front propagates

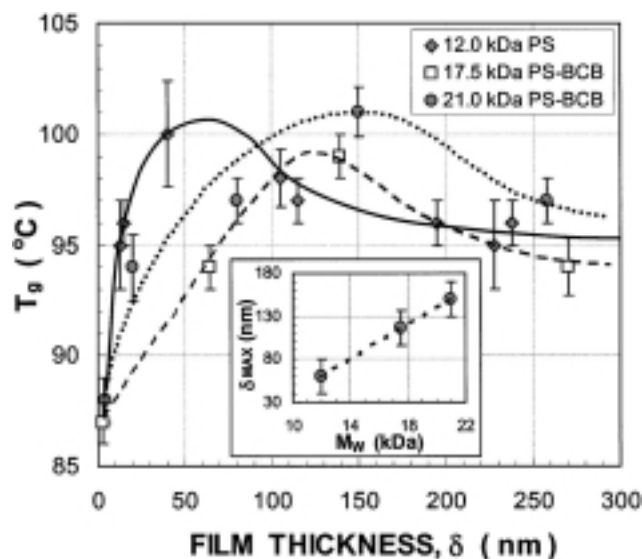


FIG. 5. The effect of molecular weight on $T_g(\delta)$ profiles for polystyrene. (Inset: film thickness corresponding to maximum T_g , δ_{MAX} , as a function of molecular weight.)

from the sublayer a finite distance out into the bulk phase, creating the intermediate regime.

To investigate the effect of the radius of gyration on the $T_g(\delta)$ profile, $T_g(\delta)$ studies have been performed for PS and uncrosslinked PS-BCB samples as a function of molecular weight (12.0, 17.5, and 21 kDa). As seen in Fig. 5, the $T_g(\delta)$ profile for each molecular weight follows the same qualitative behavior as discussed above in Fig. 4. The most significant difference between each molecular weight is the film thickness corresponding to the maxima in the $T_g(\delta)$ profiles. Figure 5 indicates that, with an increase in molecular weight, the maximum in the $T_g(\delta)$ profile is shifted further from the substrate. The film thickness values at the T_g maxima (δ_{MAX}), interpolated from the three curves in Fig. 5, are plotted together in the inset of Fig. 5. The apparent linear dependence on molecular weight in Fig. 5 (inset) yields an approximate δ_{MAX} shift of 10 nm/kDa over the range of molecular weights considered. For all three molecular weights, the bulk T_g values are recovered beyond ~ 250 nm.

In order to probe the effect of modifying the polymer's relaxation behavior on the $T_g(\delta)$ profiles, covalent crosslinks were introduced to the polymer structure (see Experiment section). Figure 6 provides $T_g(\delta)$ plots of PS-BCB films ($M_w = 21$ kDa) before and after crosslinking. The $T_g(\delta)$ profiles exhibit a similar qualitative behavior before and after the reaction, suggesting that the rheological anisotropy, illustrated in Fig. 4, remains even after heating the polymer films $\sim 150^\circ\text{C}$ above the bulk T_g value to the crosslinking temperature of 250°C . However, the crosslinking yields an overall T_g increase of $7 \pm 3^\circ\text{C}$. In contrast to the molecular weight dependence of δ_{MAX} shown in Fig. 5, no significant shift is found in the peak values of the $T_g(\delta)$ profiles on crosslinking, which are located at $\delta_{MAX} \approx 150$ nm. The lack of shift in δ_{MAX} on crosslinking is surprising, given the increase in molecular weight that accompanies crosslinking. However, since crosslinking occurs after spin coating, the spin casting dynamics that create the shift in δ_{MAX} are not

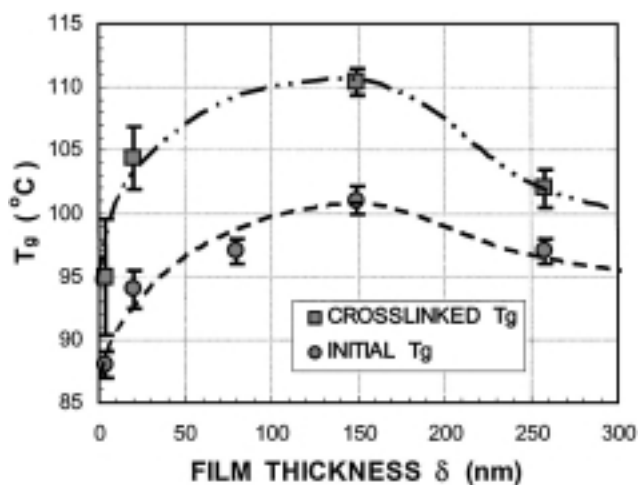


FIG. 6. The effect of crosslinking on the T_g of PS-BCB thin films (21 kDa PS-4.8 mol % BCB, crosslinked at 250°C under N_2 for 1 h).

present. The $T_g(\delta)$ profile is impacted differently for each of the two conditions of higher molecular weight because of the sequential film preparation process.

CONCLUSIONS AND OUTLOOK

SM-SFM glass transition measurements of ultrathin spin cast PS films revealed a molecularly restructured and thermally stable boundary layer that extends over 200 nm from the substrate interface, i.e., two orders of magnitude beyond the persistence length. The glass transition temperature, measured as a function of the distance from the substrate, was found to deviate nonmonotonically, by as much as $\pm 10^\circ\text{C}$, from the bulk value. The $T_g(\delta)$ profiles exhibited (a) increased molecular mobility in a sublayer adjacent to the substrate ($\delta \sim R_G$), and (b) reduced molecular mobility in a wide intermediate zone ($R_G < \delta < \sim 200$ nm) between the sublayer and the bulk phase. We attribute the localized increase and decrease in the T_g value to the coupled effects of shear-induced restructuring during spin casting and anisotropic relaxation and transport constraints during annealing.

It was qualitatively and quantitatively illustrated how the $T_g(\delta)$ profiles can be controlled either by adjusting the molecular weight or by crosslinking. On one hand, an increase in the molecular weight was found to cause the boundary constraints to extend further away from the substrate interface. Crosslinking, on the other hand, was found to affect the absolute T_g value without shifting the boundary constraints. The different rheological outcome for crosslinking versus increasing the molecular weight is correlated with the sequence of events during thin film preparation: molecular weight changes are introduced during solution preparation, prior to spin casting, while crosslinking occurs in a post-spin casting annealing step. The effect of molecular weight is manifested, through spinning, in the resulting anisotropic boundary layer, whereas pre- and post-crosslinked films share the same spin casting history.

In summary, very specific material engineering involving ultrathin spin cast polymer films can be achieved through an understanding of polymer dynamics at the polymer-substrate

interface. Modified relaxational properties and enhanced conformational stability may be achieved through control of the molecular weight, crosslinking density, and film thickness. In this regard, the measurement and control of interfacial glass transition profiles become increasingly important, as nanotechnological thin film applications, such as terabit thermomechanical data storage,¹ rely on very specific relaxation, transition, and transport properties within the sub-100 nm regime.

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