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Role of neighboring domains in determining the magnitude and direction of T_g-confinement effects in binary, immiscible polymer systems☆

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ABSTRACT

The glass transition temperature (T_g) of a polystyrene (PS) nanolayer is shown to be strongly tuned by the presence of neighboring immiscible polymer layers over a 100 °C range spanning temperatures above and below the bulk PS T_g. Fluorescence spectroscopy is used to measure the glass transition temperature (T_g) of the ultrathin dye-labeled PS layers at specific regions within multilayer films of immiscible polymers. The T_g of a 14-nm-thick PS layer is 45 °C atop poly(n-butyl methacrylate) and 144 °C atop poly(4-vinyl pyridine). Additionally, the T_g of an 11- to 14-nm thick PS layer is shown to be the same as that reported by a near-infinitely-dilute PS blend component [Evans and Torkelson *Macromolecules* **2012**, *45*, 8319] with the same neighboring polymer, which indicates a common physical origin of T_g perturbations in both systems. The magnitude of T_g-confinement effects depends not only on the T_g of the neighboring domain but is also strongly correlated with neighboring domain fragility, a fundamental property of glass formers which provides a link between medium-range structural order and dynamics.

1. Introduction

The glass transition temperature (T_g) of a polymer is important in defining the conditions required for thin films used in microelectronics [1], large-scale polymer processing [2,3], and polymer electrolytes used in batteries [4]. In bulk glass-formers, T_g is associated with the cooperative motions of many segments [5–15]. Although experimentally well defined, the fundamental nature of the glass transition remains a major unresolved issue in condensed matter physics [6,9–11]. One approach for improving the understanding of glass formation is to investigate systems where T_g can be substantially perturbed and tuned. In such cases, the fundamental parameters governing T_g should become more apparent.

It is known that neighboring polymer domains can substantially perturb the T_g of one another, e.g., in selected binary miscible polymer blends where a distinct T_g can be resolved for each component [8,16,17]. The component T_gs are perturbed away from their bulk values towards the T_g of the other species. Similar behavior is observed in multilayer films of immiscible polymers where the T_g of a sub-100 nm layer is perturbed towards the T_g of the second polymer [2,3]. Studies of near-infinitely-dilute (0.1 wt%) polystyrene (PS) blend components have demonstrated that PS T_g can be perturbed over a 150 °C range depending on its immiscible blend partner [18]. The strengths of these perturbations have been rationalized in terms of the dynamic fragility (m) of the blend partner. Fragile glasses have little medium-range structural order and a non-Arrhenius temperature (T) dependence of alpha-relaxation times above T_g [6,15]. Strong glasses have more robust structure and a nearly Arrhenius T-dependence of alpha-relaxation times [6]. Dudowicz et al. [19] have probed the relationship between polymer structure and fragility and found that polymers with stiff side groups or backbones behave as fragile glasses because they encounter greater packing frustration. Higher fragility blend partners pack less efficiently about their own units and the units of a 0.1 wt% PS component, and are weaker perturbers of PS T_g [18].

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Significant deviations from bulk T_g are often observed with glass-formers in nanopores [20], ultrathin films [21–38], nanospheres [39–41], and nanocomposites [42–44]. Some studies of dynamics or mobility have also reported substantial confinement effects [38,40,45–48]. The magnitude of confinement effects depends on the exact quantity being measured as demonstrated recently by Preistley and co-workers who studied PS nanospheres via dielectric spectroscopy [40]. They reported substantial T_g reductions with decreasing sphere diameter as defined by a change in the T-dependence of dielectric strength. When the T of the dielectric loss maximum was characterized, no substantial change was observed with diameter. However, the emergence of a new relaxation mode occurred upon confinement in sub-200 nm diameter spheres.

The T_g-confinement effect is frequently explained in terms of interfacial perturbations which become increasingly important to average film behavior as thickness decreases. Free surfaces are understood to reduce requirements for cooperative segmental relaxation and decrease T_g [22–24,27,33,35,49]; attractive interactions with a substrate hinder cooperative mobility and increase T_g [23,24,29,44]. Studies using fluorophore-labeled layers within multilayer polymer films (or brushes) have measured T_g at targeted locations [22–25,27,29,50], indicating that T_g-confinement effects in PS films supported on silica or glass originate from a reduced free-surface layer T_g. In contrast, with poly(methyl methacrylate) (PMMA) films there is a competition between the effects of the free surface (reducing T_g) and the substrate interface (increasing T_g) where ester side-groups form hydrogen bonds with substrate-surface hydroxyl groups. Using labeled layers, T_g perturbations were shown to propagate tens of nanometers into the film [22,23,27]. In confined polymers, fragility can be substantially reduced from bulk values [48,51,52], suggesting that it is fundamental property that may be related to T_g-confinement effects in polymer films lacking significant, attractive interactions with a substrate. In fact, Evans et al. [28] found that the magnitude of T_g depressions in confined, supported, single-layer films of linear polymers shows a one-to-one correlation with the dynamic fragility of the polymer species, i.e., increasingly fragile polymers exhibit larger T_g-confinement effects.

Studies of neighboring domains and confined polymers raise several intriguing questions: To what extent can T_g be tuned by a neighboring layer? Over what length scale can the T_g of one polymer layer be affected by a neighboring layer? Are T_g perturbations in multilayer films related to those in near-infinitely-dilute polymer blends? What fundamental properties govern the strength of T_g-confinement effects?

Here, we demonstrate a newly discovered nature of the T_g-confinement effect in linear PS: The T_g of a top, ultrathin PS layer in a bilayer film can be tuned over a ~100 °C range by changing the underlayer polymer. Additionally, the T_g of an ultrathin PS layer within a multilayer film can increase relative to its bulk T_g if the neighboring layer T_g exceeds that of PS. We use a multilayer/fluorescence technique with a pyrene-labeled PS ultrathin layer; this method of measuring T_gs in single-layer films yields excellent agreement with T_gs measured by other techniques [22,26,27,29]. Furthermore, we show that the strong tunability of T_g of a near-infinitely-dilute (0.1 wt%) PS blend component dispersed at the molecular level [18] is intimately linked to T_g perturbations observed for an ultrathin PS layer sandwiched between bulk neighboring layers. Under extreme confinement, the T_g reported by a 14-nm-thick PS layer and a 0.1 wt% PS blend component are identical for a given polymer pair. This equivalence indicates a common physical origin of perturbations which correlates with neighboring polymer fragility.

2. Experimental

Polymers were purchased or synthesized: poly(4-vinyl pyridine) (P4VP) [Polymer Source, $M_n = 130{,}000$ g/mol, $M_w/M_n = 1.24$, reported by supplier, $T_g = 140$ °C] in the bilayers or [Sigma–Aldrich, $M_n = 160{,}000$ g/mol, reported by supplier, $T_g = 150$ °C] in the trilayers; polycarbonate (PC) [Scientific Polymer Products, $M_n = 17{,}300$ g/mol, $M_w/M_n = 1.66$, reported by supplier, $T_g = 141$ °C]; poly(methyl methacrylate) (PMMA) [Pressure Chemical, $M_w = 255{,}000$ g/mol, $M_w/M_n \leq 1.15$, reported by supplier, $T_g = 120$ °C] in the bilayers or [Scientific Polymer Products, $M_n = 56{,}000$ g/mol, $M_w/M_n = 1.08$, reported by supplier, $T_g = 125$ °C] in the trilayers; poly(2-vinyl pyridine) (P2VP) [Scientific Polymer Products, $M_v = 200{,}000$ g/mol, reported by supplier, $T_g = 101$ °C]; polystyrene (PS) [free radical polymerization (FRP), $M_n = 419{,}000$ g/mol, $M_w/M_n = 1.73$, $T_g = 102$ °C); poly(isobutyl methacrylate) (PiBMA) [FRP, $M_n = 399{,}000$ g/mol, $M_w/M_n = 1.41$, $T_g = 63$ °C); and poly(n-butyl methacrylate) (PnBMA) [FRP, $M_n = 270{,}000$ g/mol, $M_w/M_n = 1.64$, $T_g = 27$ °C]. Free radical polymerization of styrene with trace levels of 1-pyrenyl butyl methacrylate (BPy) or 1-pyrenyl methyl methacrylate (MPy) was used to synthesize BPy-labeled PS [$M_n = 464$ kg/mol, $M_w/M_n = 1.57$, $T_g = 102$ °C, 0.3 mol% label content] or MPy-labeled PS [$M_n = 800$ kg/mol, $M_w/M_n = 1.31$, $T_g = 103$ °C, 0.8 mol% label content]. All M_n and M_w/M_n values for synthesized samples were determined by gel permeation chromatography (GPC) (Water 2410 RI detector, Styragel columns, tetrahydrofuran as eluent at 30 °C). Label content determined by UV–Vis absorbance (Perkin Elmer Lambda 35) [18]. Labeled polymers were dissolved/precipitated in toluene/methanol seven times to remove residual monomer and dye and placed in a vacuum oven at ~60 °C for 24 h.

Individual layers were made by spin coating [53], and layer thickness was measured individually by ellipsometry [26] (J.A. Woollam Co., Inc. M-2000D). Bilayer and trilayer geometries were fabricated by sequential floating of layers onto water and then onto glass slides [28,29]. Individual layers were annealed separately at $T_g + 20$ °C for 12 h under vacuum to remove residual solvent prior to floating. Solutions of 0.1 wt% MPy-labeled PS (800 kg/mol) were prepared by codissolution and solvent casting with a blend partner as previously described [18]. Multilayer films and blends were annealed at $T_g + 20$ °C (of the higher T_g material) for at least 4 h in a vacuum oven before measurement.

The PS layer T_g is determined by a pseudo-thermodynamic approach involving a change in the T-dependence of fluorescence intensity (BPy label [18,22–25,27,29,44,50]) or the intensity ratio of the third vibronic peak to the first vibronic peak (I_3/I_1) of the pyrene emission spectrum (MPy-label [18,27,54]) measured upon cooling. (It is well known that I_3/I_1 values of the pyrene emission spectrum are sensitive to local polarity [55], and our group previously determined that its T dependence can be used to determine T_g in supported and free-standing polymer films [27,54,56].) In bulk polymers, these labels report T_gs in agreement with differential scanning calorimetry (DSC) [18,22,25,26,44]. Steady-state fluorescence was performed for BPy-labeled PS (SPEX Fluorolog II, 4.0–9.0 nm bandpass excitation, 4.0–9.0 nm bandpass emission) and MPy-labeled PS (Photon Technology International fluorimeter, 1.0–3.0 nm bandpass excitation, 2.0 nm bandpass emission). Temperature was controlled by a mica heater on a flat aluminum plate. A glass slide with the sample film was placed directly on top of a thin aluminum plate with the film side facing away from the plate and clamped in place. The excitation wavelength was set to 324 nm, and emission intensity was monitored at 360–460 nm (BPy-labeled PS) or 370–405 nm (MPy-labeled PS). After holding the sample at $T_g + 40$ °C for at least 20 min to remove thermal history, T_g measurements were obtained on cooling from the