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Authors	Wang, Tong; Yan, Jinsong; Yuan, Hailin; Xu, Jianquan; Lam, Ho Yi; Yu, Xuanji; Lv, Chao; Du, Binyang; Tsui, Kwan Chui
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T_g Confinement Effect of Random Copolymers of 4-*tert*-Butylstyrene and 4-Acetoxy styrene with Different Compositions

Tong Wang¹, Jinsong Yan¹, Hailin Yuan¹, Jianquan Xu,¹ Ho Yi Lam², Xuanji Yu,³ Chao Lv⁴, Binyang Du⁴, Ophelia K. C. Tsui^{1,*}

¹*Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong.*

²*Department of Chemical and Biological Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong.*

³*Division of Materials Science and Engineering, Boston University, Boston, MA 02215, USA.*

⁴*Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China.*

Abstract. We observe that T_g confinement effect of polymer films can saturate with polymer-substrate interaction. Thickness dependences of glass transition temperature, $T_g(h_0)$, of random copolymer films of 4-*tert*-butylstyrene (TBS) and 4-acetoxy styrene (AS) supported by silica (SiOx) were measured for different TBS concentrations, X_{TBS} . For $0 \leq X_{TBS} \leq 0.47$, $T_g(h_0)$ displays identical enhancements independent of X_{TBS} . For $X_{TBS} > \sim 0.66$, however, $T_g(h_0)$ decreases steadily with X_{TBS} . The $X_{TBS} > 0.66$ result is in keeping with expectations that TBS interacts less strongly with SiOx than AS does, and weaker polymer-substrate interaction renders greater dominance of the air surface over substrate surface on T_g , and thereby T_g reduction. We propose that saturation in $T_g(h_0)$ found for $X_{TBS} \leq$

0.47 is caused by maximization in polymer-substrate specific bonds formation. Further experiment and a calculation support this proposition.

1. INTRODUCTION

A variety of recent technologies employ polymer nanometer films. These include nanoimprinting, photolithography and polymer photovoltaics. On decreasing the film thickness, h_0 , below ~ 100 nm, T_g of polymer films often displays departures from the bulk value, T_g^{bulk} , but details can vary. Some systems, such as polystyrene (PS) on silica (SiOx), display decreasing T_g with decreasing h_0 .¹⁻³ But other systems, such polymethylmethacrylate (PMMA)^{1, 4-6} and poly(2-vinylpyridine) (P2VP)^{6, 7} on silica display the opposite $T_g(h_0)$ dependence. One broadly accepted explanation to the different $T_g(h_0)$ dependences is that different systems have different polymer-substrate and/or polymer-air interfaces. It has been found that dynamics of polymers near the free surface are faster than bulk.⁸⁻¹⁰ On the other hand, a substrate surface can have neutral or enhancing effect on T_g .^{9, 10} For polymer films containing both T_g -depressing and T_g -enhancing components, such as random copolymer films of styrene and MMA (P(S-*r*-MMA))^{6, 11} or 2VP (P(S-*r*-2VP))⁶, it has been reported that as the styrene content of the films increased from zero, $T_g(h_0)$ changed steadily from enhanced to suppressed, as expected. These findings support the ideas that T_g of polymer films arise from competitions between the substrate and free surfaces that are continuously adjustable. The idea that surface effect is continuously adjustable is frequently employed in computer simulations. Specifically, it is common to introduce a polymer-surface interaction parameter and vary it to produce different T_g confinement effects observed in experiment.¹²⁻¹⁵

In this paper, T_g confinement effect is studied for P(TBS-*r*-AS) (i.e., random copolymers of 4-*tert*-butylstyrene and 4-acetoxystyrene) films on SiOx with different TBS contents, X_{TBS} . It had been found that T_g of PTBS films is strongly suppressed,¹⁶ but after

prolonged heating above T_g , the extent of T_g suppression lessens and is eventually erased.¹⁷ Based on the fact that PAS contains ester groups (inset of Figure 1A) that can form strong bonds with the hydroxyl groups (Si-OH) of silica,¹⁸⁻²⁰ we anticipate T_g of the films with sufficiently high AS content to be enhanced.^{4, 21, 22} On the other hand, TBS does not form strong bonds with SiOx, so renders lower polymer-substrate interactions if its concentration in the copolymer is higher. By varying X_{TBS} we anticipate the average polymer-substrate interaction strength to be adjusted continuously. To our surprise, T_g of the films does not decrease with X_{TBS} from 0 to 1. Instead, it starts to decrease with X_{TBS} only when X_{TBS} is increased above ~0.47. This finding shows that substrate effect on T_g could saturate. We propose that it is caused by saturation in the acetoxyl-hydroxyl interactions. Accordingly, in describing substrate effects, one may need to consider the density of interactions.

2. EXPERIMENT

P(TBS-r-AS) copolymers with $X_{TBS} = 0.95, 0.85, 0.66$ and 0.47 were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization (see the SI for details). The number-average molecular weight (M_n) and polydispersity indices (PDI), as determined by proton nuclear magnetic resonance (^1H NMR) and gel permeation chromatograph (GPC), respectively, are 13.5 kg/mol and PDI 1.10, 12 kg/mol and PDI 1.13, 10.3 kg/mol and PDI 1.23, and 10.3 kg/mol and PDI 1.15, respectively. For control experiment, we also synthesized PTBS and PAS for which $M_n = 8.33$ kg/mol and PDI = 1.16, and $M_n = 20.3$ kg/mol and PDI = 1.11, respectively.

Thin films of the copolymers were spin-coated on silicon covered by a native oxide (SiO_x) layer as detailed in the SI. Film thickness, h_0 , was determined by ellipsometry (Gaertner Scientific Corporation, LSE Stokes Ellipsometer). In each T_g measurement, the sample temperature was raised to 180 °C in 5 min then maintained for 7 min to erase thermal history and remove any adsorbed water. Afterward, the temperature was lowered at a steady rate of 2.2 K/min as h_0 was monitored at 5-second intervals. T_g was determined to be the temperature where h_0 vs. T display a change of slope.

3. RESULTS AND DISCUSSIONS

Figure 1 displays thickness versus temperature, $h(T)$, of P(TBS-*r*-AS) films with $X_{\text{TBS}} = 0.95$ and different starting thicknesses, h_0 , but a fixed pre-annealing time of 5 h (Figure 1A), and different pre-annealing times, but a fixed h_0 of 35 nm (Figure 1B). As one can see, all $h(T)$ display a temperature where slope of the curve changes qualitatively that we identify to be T_g . For the three largest h_0 (= 86, 123 and 156 nm), T_g is approximately independent of h_0 , equal to 132 ± 1 °C. We define the constant T_g displayed by thick films to be T_g^{bulk} or bulk T_g . For the films with $h_0 < 86$ nm, T_g decreases with decreasing h_0 . At the lowest h_0 studied (= 35 nm), $T_g = 128 \pm 2$ °C, or 4 °C below T_g^{bulk} . We find that the amount of T_g reduction is noticeably affected by the duration of pre-annealing (all conducted at 150 °C). As Figure 1B illustrates, T_g obtained from films with $h_0 = 35$ nm and $X_{\text{TBS}} = 0.95$ increases decidedly from 124 ± 2 °C to 132 ± 1 °C as pre-annealing time increases from 1 to 9 h. This finding is consistent with the T_g measurement of Perez-de-Eulate et al. for pure PTBS films on SiO_x.¹⁷ The

workers attributed the T_g increase with pre-annealing to stabilization of polymer chains on substrate surface that tends to reduce chain mobility.

Next, we investigate if T_g confinement effect of our films varies with X_{TBS} . To fix the effect of pre-annealing, we used the same pre-annealing time of 5 h. The main result is shown in Figure 2A as T_g deviation ($\equiv T_g - T_g^{\text{bulk}}$) versus h_0 for various X_{TBS} . To characterize individual curves, we fit each to an expression based on the empirical relation proposed by Keddie et al.:

$$T_g(h_0) = T_g^{\text{bulk}} \left[1 \mp \left(\frac{A}{h_0} \right)^\delta \right] \quad (1)$$

In here, A is a characteristic length and δ is the fitting exponent. We adopt the negative or

Figure. 1 (A) Comparison of the thickness versus temperature plots of $X_{\text{TBS}} = 95\%$ P(TBS-*r*-AS) films with different h_0 , of (from top to bottom) 156, 123, 86, 58, and 35 nm. The films had been pre-annealed for 5 h. The inset shows the chemical structure of the polymer where $m : n = 95 : 5$. **(B)** Comparison of the thickness versus temperature plots of $X_{\text{TBS}} = 95\%$, $h_0 = 35$ nm films undergone different pre-annealing times as marked. In both panels, the plots had been shifted vertically for ease of comparison.

positive sign if T_g displays suppression or enhancement, respectively. In performing the fit, δ was kept equal to 1.8, same as that reported by Keddie et al.¹, while A was varied. Figure 2B shows the fit result as A versus X_{TBS} . As seen, when X_{TBS} is increased from 0 to 0.47, A hardly changes. But when X_{TBS} exceeds 0.47, A increases with X_{TBS} clearly. Moreover, A switches from being negative (enhanced T_g) to positive (depressed T_g) at around $X_{\text{TBS}} = 0.80$. While adoption of other values of δ in fitting the data causes the fit value of A to change, it does not alter the qualitative dependence of A on X_{TBS} . We deliberate why the value of A (and correspondingly T_g confinement effect) is independent of X_{TBS} for $X_{\text{TBS}} \leq 0.47$.

Figure. 2 (A) Thickness dependence of $T_g - T_g^{\text{bulk}}$ of P(TBS-*r*-AS) films with various X_{TBS} as marked after pre-annealing for 5 h. Dashed lines are the best fits to Eq. (1) with δ held fixed to 1.8 and A alone varied. (B) A plot of the hence obtained best-fit values of A versus X_{TBS} .

Compared to TBS, AS interacts more strongly with SiO_x due to its ability to form specific ester-hydroxyl bonds.^{18-20, 22, 23} We thus contemplate the observed variations of $T_g - T_g^{\text{bulk}}$ versus h_0 with X_{TBS} to be caused by increasing dominance of substrate surface on the

dynamics of P(TBS-*r*-AS) as X_{TBS} decreases. However, Figure 2B shows that such a straightforward consideration only applies to $X_{\text{TBS}} > 0.47$. For smaller X_{TBS} , T_g confinement effect saturates to that of pure PAS. According to Perez-de-Eulate et al.,¹² upon prolonged pre-annealing, T_g reduction of PTBS-SiOx films lessened.¹² Below, we utilize this finding to explore the origin of the saturation in T_g confinement effect observed.

Shown in Figure. 3A are T_g versus X_{TBS} of $h_0 = 35$ nm films after pre-annealing for 1, 5 and 9 h, respectively, and that of bulk films after pre-annealing for 5 h (red circles). The solid line represents the best fit of the bulk-film data to the Gordon-Taylor equation:²⁴

$$T_g = \frac{w_{\text{AS}}T_{g,\text{AS}} + kw_{\text{TBS}}T_{g,\text{TBS}}}{w_{\text{AS}} + kw_{\text{TBS}}} \quad (2)$$

Here, $T_{g,\text{AS}} = 113.7$ °C and $T_{g,\text{TBS}} = 132$ °C is T_g^{bulk} of PAS and PTBS, respectively; w_{TBS} is the weight fraction of TBS, given by $X_{\text{TBS}}M_{\text{TBS}}/[X_{\text{TBS}}M_{\text{TBS}} + (1 - X_{\text{TBS}})M_{\text{AS}}]$ and $w_{\text{TBS}} (\equiv 1 - w_{\text{AS}})$ is that of AS; $M_{\text{TBS}} = 160$ g/mol and $M_{\text{AS}} = 162$ g/mol is the monomer molar mass of TBS and AS, respectively; $k = \Delta\alpha_{\text{PTBS}}/\Delta\alpha_{\text{PAS}} = 0.8 \pm 0.1$, where $\Delta\alpha_i$ is the difference in thermal expansion coefficient between the rubbery and glassy states of species i . Good agreement between the fit line and data suggests that assumption of volume additivity of monomer units applies to the bulk films. For the 35 nm films, however, only data obtained from the films after pre-annealing for 9 h can be fit to Eq. (2) provided $T_{g,\text{AS}} = 120$ °C, $T_{g,\text{TBS}} = 130$ °C and $k = 1.0 \pm 0.1$ (Fit-line not shown.) The higher $T_{g,\text{AS}}$ found indicates T_g enhancement of the PAS films. Similarity between T_g of the bulk film and the 9-h pre-annealed 35 nm film at $X_{\text{TBS}} = 1$ indicates that T_g of the latter becomes bulklike after 9-h

Figure. 3 (A) Composition dependence of T_g of $h_0 = 35$ nm films pre-annealed for various times of 9 h (up-side-down triangles), 5 h (upright triangles) and 1 h (squares). The corresponding data of bulk-like films with $h_0 > 100$ nm and a pre-annealing time of 5 h are displayed by red circles. The solid line passing through the bulk film data is the best fit to Eq. (2). The dotted lines are guides-to-the-eye only. **(B)** Composition dependence of $T_g^{9h} - T_g^{1h}$, i.e., difference in T_g between 1-h pre-annealed and 9-h pre-annealed films with the same thickness h_0 of 35 nm.

pre-annealing. This finding qualitatively agrees with that of Perez-de-Eulate et al.¹² that prolonged annealing erases T_g confinement effect of PTBS films. For films pre-annealed for shorter times of 5 and 1 h, however, T_g versus X_{TBS} exhibits clear deviations from the 9-h data and cannot be described by Gordon-Taylor equation. More notably, ΔT_g changes from being constant 6 °C, for $X_{TBS} < 0.47$ to varying with X_{TBS} . At some $X_{TBS} (> 0.47)$, ΔT_g changes sign from positive to negative, departing from the positive or near zero values found of the 9-h pre-annealed films. These findings suggest that elevation of X_{TBS} above 0.47 causes the films to deviate from the steady state (presumed to be that of the 9-h pre-annealed films) even after the films had been pre-annealed for 5 h. Such a slow relaxation toward the steady state is

typical of polymer chains adsorbed on solid substrates where there is no specific polymer-substrate interactions.^{17, 25, 26}

Fujii et al.²⁵ reported that polymers, even without specific interactions with the substrate surface (e.g. PS on SiOx), can form an irreversible adsorbed layer on the substrate upon extensive annealing above T_g^{bulk} , and the process was slow. At an annealing temperature ~ 50 °C above T_g^{bulk} , the adsorbed layer did not reach 90% of the steady-state thickness until after ~ 10 h. For PTBS on SiOx, Perez-de-Eulate et al.¹⁷ found that thickness of the adsorbed layer also required ~ 10 h to stabilize upon similar annealing condition. Concomitantly, T_g of the films evolved toward T_g^{bulk} with time at a similar rate.¹⁷ By using x-ray and neutron reflectivity, Gin et al.²⁷ found that adsorbed layers of PS on SiOx are made of loosely packed outer chains and inner flattened, densely packed chains. With short pre-annealing, we believe that the outer adsorbed chains may take up sites that should be occupied by flattened chains in the steady- T_g state, thereby lessens the substrate confinement effect.

For $X_{\text{TBS}} \leq 0.47$, however, our data exhibits no variations in T_g with pre-annealing (Figure 3B). This suggests that adsorbed layers of these films are able to relax quickly. We attribute the fast relaxation to the large interaction energy, ΔE (~ -12 kcal/mol), of ester-silanol bonds²³ and findings that hydrogen bonds are dynamics and have lifetimes $\ll 1$ s.²⁸⁻³⁰ Large ΔE means that entropic contributions to the system energy is insignificant, while high dynamics of the ester-silanol bonds means that the near substrate chains can quickly seek the lowest energy state. However, large ΔE and high bond dynamics may not always lead to rapid attainment of the steady- T_g state. If the density of ester groups in the polymer is not high, the density of polymer-substrate bonds will also be not high. Then

non-specific polymer-substrate bonds may form easily in between. This would allow polymer chains to adopt a greater variety of conformations including the less stable ones when they come into contact with the substrate surface. If these conformations involve greater free volume, which is probable given that non-specific bonds are weaker than specific ones, the scenario portrayed may explain why the $X_{\text{TBS}} > 0.47$ films relax slowly while the higher AS contents ones relax quickly (Figure 3A).

To understand the observed variations of T_g confinement effect with X_{TBS} (Figure 2A), we deliberate how the maximum attainable ester-silanol interactions might vary with X_{TBS} . By using temperature-modulated DSC and MD simulations, Mortazavian et al.²³ studied similar ester-silanol interfacial bonds found in poly(vinyl acetate) (PVAc) adsorbed on silica. They found that a portion of the adsorbed PVAc, referred to as “tightly bound amount”, exhibited T_g above T_g^{bulk} . This portion increased with the total adsorbed amount, and ultimately reached a plateau value corresponding to an areal density of the ester groups in the tightly bound amount, σ_{ester} , of 4.6 nm^{-2} . That this value agrees with the areal density of Si-OH on silica, $\sigma_{\text{Si-OH}}$ ($= 4.4\text{--}4.9 \text{ nm}^{-2}$ ^{31, 32}) suggests that the maximum attainable ester-silanol interactions are attained upon the intuitive condition, $\sigma_{\text{Si-H}} = \sigma_{\text{ester}}$. For P(TBS-*r*-AS), we estimate σ_{ester} (or σ_{acetoxy}) by:

$$\sigma_{\text{acetoxy}}(X_{\text{TBS}}) = h_{\text{b}}(X_{\text{TBS}}) \frac{\rho N_{\text{A}}}{M_0} \quad (3a)$$

$$\text{where} \quad h_{\text{b}}(X_{\text{TBS}}) = \min \left(h_{\text{b,saturate}} = \frac{\sigma_{\text{Si-OH}} M_0}{\rho N_{\text{A}} (1 - X_{\text{TBS}})}, R_{\text{g}} \right) \quad (3b)$$

Here, N_{A} is the Avogadro number, ρ is mass density of the polymer, M_0 is the average monomer molecular weight, R_{g} is the polymer radius of gyration, which we approximate by

assuming the Kuhn length of PS, ³³ and $h_{b,saturate}$ denotes the hypothetical thickness of the saturated tightly bound amount had it a uniform thickness. The factor $1/(1 - X_{TBS})$ takes into account the fact that when the AS content is lower, $h_{b,saturate}$ needs to be bigger for the tightly bound layer to contain the same amount of acetoxy groups needed to saturate the silanol groups. However, the actual thickness of the bound layer, h_b , should have a physical limit. As discussed above, adsorbed polymers (even weakly interacting) can be so adherent that they cannot be washed off the substrate with a good solvent. Therefore, it is unlikely for the tightly adsorbed chains to desorb and give way for the farther removed chains to overcome steric hindrance to bond tightly with the substrate. We thus propose that h_b has an upper limit of $\sim R_g$. Calculation using Eq. (3b) gives $h_b \sim 1$ to ~ 2.6 nm (Table 1). That these h_b values are $\gg 0.2$ nm - the range of ester-silanol bonds ²³ - means that effects of these bonds can be mediated much beyond their physical locations. One possible realization of this situation is that at any given moment, only a portion of the ester groups form physically bonds with the silanol groups. But in short durations, a new set of ester groups (with the same average number as

Table. 1 Estimated values of $h_{b,saturate}$, h_b and $\sigma_{acetoxy}$ of our P(TBS-*r*-AS) films

X_{TBS}	$h_{b,saturate}$ (nm)	h_b (nm)	$\sigma_{acetoxy}$ (nm ⁻²)
1.00	∞	2.00	0.00
0.95	23.40	2.55	0.48
0.85	7.81	2.40	1.35
0.66	3.45	2.22	2.83
0.47	2.22	2.22	4.40
0.00	1.18	1.18	4.90

before) form bonds with a new set of silanol groups. Such a picture is probable because it allows more ester groups than those instantaneously in contact with the substrate to participate in bond formation. It is also in line with Mortazavian et al.'s finding that not all (but equal fractions of ~ 0.3 To ~ 0.4) of ester and silanol groups form bonds with large ΔE in a simulation snapshot.²³ Figure 4 portrays the polymer-substrate interactions contemplated above. Importantly, our calculation (Table 1) shows that σ_{acetoxy} increases as X_{TBS} is decreased from 1, but on reaching $X_{\text{TBS}} = 0.47$ or below, it becomes $\approx \sigma_{\text{Si-OH}}$. Saturation of acetoxy-silanol interactions for $X_{\text{TBS}} \leq 0.47$ (Figures 4A and 4B) could explain why ΔT_g saturates to the maximum value of $\sim +6$ °C over this range of X_{TBS} as found in Figure. 3A.

Figure. 4 (color online) Illustrations of the interactions between P(TBS-*r*-AS) copolymer chains and SiOx substrate surface for different X_{TBS} , where $\sigma_{\text{acetoxy}} > \sigma_{\text{Si-OH}}$ (A), $\sigma_{\text{acetoxy}} \approx \sigma_{\text{Si-OH}}$ (B) and $\sigma_{\text{acetoxy}} < \sigma_{\text{Si-OH}}$ (C). The brown and yellow chain segments represent sections where TBS and AS are, respectively. Red bumps on the substrate surface represent Si-OH groups. Dotted lines denote the dynamic bonding between acetoxy and silanol groups.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.XXXXXXX. It contains descriptions of how to synthesize the P(TBS-*r*-AS) copolymers and make the films.

AUTHOR INFORMATION

Corresponding Author

* Email: oketsui@ust.hk

Notes

The authors declare no competing financial interest.

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REFERENCES

1. Keddie, J. L.; Jones, R. A. L.; Cory, R. A., Interface and surface effects on the glass-transition temperature in thin polymer films. *Faraday Discussions* **1994**, *98*, 219-230.
2. Tsui, O. K. C.; Zhang, H. F., Effect of Chain Ends and Chain Entanglement on Glass Transition Temperature of Polymer Thin Films. *Macromolecules* **2001**, *34*, 9139-9142.
3. Tsui, O. K. C.; Russell, T. P.; Hawker, C. J., Effect of Interfacial Interactions on the Glass Transition of Polymer Thin Films. *Macromolecules* **2001**, *34*, 5535-5539.
4. Li, R. N.; Chen, F.; Lam, C.-H.; Tsui, O. K. C., Viscosity of Polymethylmethacrylate on Silica: Epitome of Systems with Strong Polymer–Substrate Interactions. *Macromolecules* **2013**, *46*, 7889-7893.
5. Geng, K.; Tsui, O. K. C., Effects of Polymer Tacticity and Molecular Weight on the Glass Transition Temperature of Poly(methyl methacrylate) Films on Silica. *Macromolecules* **2016**, *49*, 2671-2678.
6. Park, C. H. K.; J. H.; Ree, M.; Sohn, B. -H.; Jung, J. C.; Zin, W. -C., Thickness and composition dependence of the glass transition temperature in thin random copolymer films. *Polymer* **2004**, *45*, 4507-4513.
7. van Zanten, J. H.; Wallace, W. E.; Wu, W.-L., Effect of strongly favorable substrate interactions on the thermal properties of ultrathin polymer films. *Physical Review E* **1996**, *53*, R2053-R2056.
8. Fakhraai, Z.; Forrest, J. A., Measuring the Surface Dynamics of Glassy Polymers. *Science* **2008**, *319*, 600-604.

9. Yang, Z.; Fujii, Y.; Lee, F. K.; Lam, C.-H.; Tsui, O. K. C., Glass Transition Dynamics and Surface Layer Mobility in Unentangled Polystyrene Films. *Science* **2010**, 328, 1676-1679.
10. Ellison, C. J.; Torkelson, J. M., The distribution of glass-transition temperatures in nanoscopically confined glass formers. *Nature Materials* **2003**, 2, 695-670.
11. Mundra, M. K. E., C. J.; Behling, R. E.; Torkelson, J. M., Confinement, composition, and spin-coating effects on the glass transition and stress relaxation of thin films of polystyrene and styrene-containing random copolymers: Sensing by intrinsic fluorescence. *Polymer* **2006**, 47, 7747-7759.
12. Torres, J. A.; Nealey, P. F.; de Pablo, J. J., Molecular simulation of ultrathin polymeric films near the glass transition. *Physical Review Letters* **2000**, 85, 3221-3224.
13. Hanakata, P. Z.; Douglas, J. F.; Starr, F. W., Interfacial mobility scale determines the scale of collective motion and relaxation rate in polymer films. *Nature Communications* **2014**, 5, 4163.
14. White, R. P.; Price, C. C.; Lipson, J. E. G., Effect of Interfaces on the Glass Transition of Supported and Freestanding Polymer Thin Films. *Macromolecules* **2015**, 48, 4132-4141.
15. Simmons, D. S. An Emerging Unified View of Dynamic Interphases in Polymers *Macromolecular Chemistry and Physics* [Online], 2015.
16. Ellison, C. J.; Mundra, M. K.; Torkelson, J. M., Impacts of Polystyrene Molecular Weight and Modification to the Repeat Unit Structure on the Glass Transition-Nanoconfinement Effect and the Cooperativity Length Scale. *Macromolecules* **2005**, 38, 1767-1778.

17. Perez-de-Eulate, N. G. S., M.; Cangialosi, D.; Napolitano, S., Irreversible Adsorption Erases the Free Surface Effect on the Tg of Supported Films of Poly(4-tert-butylstyrene). *ACS Macro Letters* **2017**, *6*, 354-358.
18. Yu, X.; Yiu, P.; Weng, L.-T.; Chen, F.; Tsui, O. K. C., Effects of Molecular Weight on the Mobility and Dynamic Heterogeneity of a Surface Mobile Layer. *Macromolecules* **2019**, *52*, 877-885.
19. Yu, X.; Yiu, P.; Weng, L.-T.; Chen, F.; Tsui, O. K. C., Tuning the Effective Viscosity of Polymer Films by Chemical Modification. *Macromolecules* **2019**, *52*, 3499-3505.
20. Mortazavian, H.; Fennell, C. J.; Blum, F. D., Surface Bonding Is Stronger for Poly(methyl methacrylate) than for Poly(vinyl acetate). *Macromolecules* **2016**, *49*, 4211-4219.
21. Grohens, Y.; Brogly, M.; Labbe, C.; Marie-Odile, D.; Schultz, J., Glass Transition of Stereoregular Poly(methyl methacrylate) at Interfaces. *Langmuir* **1998**, *14* (11), 2929-2932.
22. Geng, K.; Katsumata, R.; Yu, X.; Ha, H.; Dulaney, A. R.; Ellison, C. J.; Tsui, O. K. C., Conflicting Confinement Effects on the Tg, Diffusivity, and Effective Viscosity of Polymer Films: A Case Study with Poly(isobutyl methacrylate) on Silica and Possible Resolution. *Macromolecules* **2017**, *50*, 609-617.
23. Mortazavian, H.; Fennell, C. J.; Blum, F. D., Structure of the Interfacial Region in Adsorbed Poly(vinyl acetate) on Silica. *Macromolecules* **2016**, *49*, 298-307.

24. Gordon, M.; Taylor, J. S., Ideal Copolymers and the Second-Order Transitions of Synthetic Rubbers. I. Non-Crystalline Copolymers. *Journal of Applied Chemistry* **1952**, *2*, 493-500.
25. Fujii, Y.; Yang, Z.; Leach, J.; Atarashi, H.; Tanaka, K.; Tsui, O. K. C., Affinity of Polystyrene Films to Hydrogen-Passivated Silicon and Its Relevance to the T_g of the Films. *Macromolecules* **2009**, *42*, 7418-7422.
26. Chen, F.; Takatsuji, K.; Zhao, D.; Yu, X.; Kumar, S. K.; Tsui, O. K. C., Unexpected Thermal Annealing Effects on the Viscosity of Polymer Nanocomposites. *Soft Matter* **2017**, *13*, 5341-5354.
27. Gin, P.; Jiang, N.; Liang, C.; Taniguchi, T.; Akgun, B.; Satija, S.; Endoh, M. K.; Koga, T., Revealed Architectures of Adsorbed Polymer Chains at Solid-Polymer Melt Interfaces. *Physical Review Letters* **2012**, *109* (26), 265501.
28. Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W., Reversible Polymers Formed from Self-Complementary Monomers Using Quadruple Hydrogen Bonding. *Science* **1997**, *278*, 1601-1604.
29. Tamai, Y.; Tanaka, H.; Nakanishi, K., Molecular Dynamics Study of Polymer-Water Interaction in Hydrogels. 2. Hydrogen-Bond Dynamics. *Macromolecules* **1996**, *29*, 6761-6769.
30. Zhou, C.; Li, X.; Gong, Z.; Jia, C.; Lin, Y.; Gu, C.; He, G.; Zhong, Y.; Yang, J.; Guo, X., Direct observation of single-molecule hydrogenbond dynamics with single-bond resolution. *Nature Communications* **2018**, *9*, 807.

31. Zhuravlev, L. T., Concentration of Hydroxyl Groups on the Surface of Amorphous Silicas. *Langmuir* **1987**, 3 (3), 316-318.
32. Barbier, D.; Brown, D.; Grillet, A.-C.; Neyertz, S., Interface between End-Functionalized PEO Oligomers and a Silica Nanoparticle Studied by Molecular Dynamics Simulations. *Macromolecules* **2004**, 37 (12), 4695-4710.
33. Tanaka, K.; Takahara, A.; Kajiyama, T., Film Thickness Dependence of the Surface Structure of Immiscible Polystyrene/Poly(methyl methacrylate) Blends. *Macromolecules* **1996**, 29, 3232-3239.

Tg Confinement Effect of Random Copolymers of 4-tert-Butylstyrene and 4-Acetoxystyrene with Different Compositions

Tong Wang¹, Jinsong Yan¹, Hailin Yuan¹, Ho Yi Lam², Xuanji Yu,³ Chao Lv⁴,
Binyang Du⁴, Ophelia K. C. Tsui^{1,*}

Supporting Information

T_g Confinement Effect of Random Copolymers of 4-*tert*-Butylstyrene and 4-Acetoxystryrene with Different Compositions

Tong Wang,[†] Jinsong Yan,[†] Hailin Yuan,[†] Jianquan Xu,[†] Ho Yi Lam,[‡] Xuanji Yu,[§]

Chao Lv,^{//} Binyang Du,^{//} Ophelia K. C. Tsui*,[†]

[†]*Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong*

[‡]*Department of Chemical and Biological Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong*

[§]*Division of Materials Science and Engineering, Boston University, Boston, Massachusetts 02215, United States*

^{//}*Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China*

*Corresponding author: Email: oketsui@ust.hk

Method to synthesize the P(TBS-*r*-AS) copolymers

4-*tert*-butylstyrene (TBS, 90% purity) and 4-acetoxystyrene (AS, 98% purity) were purchased from J & K Scientific Ltd. and purified by chromatography with an alkaline alumina column (100-200 mesh particle size). Azobis(isobutyronitrile) (AIBN, 98% purity) was purchased from Aladdin Chemical Co., Ltd. and purified by recrystallization twice from methanol. 4-cyano-4-(thiobenzoylthio) pentanoic acid (CTA, > 97% purity, purchased from Sigma-Aldrich) was used as received. All other reagents, such as tetrahydrofuran (THF) and absolute methanol were of analytical grade and used as received.

P(TBS-*r*-AS) with different X_{TBS} from 0 to 1 were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. Typically, suitable amounts of TBS, AS, CTA and AIBN were sequentially added into an ampoule bottle of 50 mL in an N₂ environment. The mixture was degassed with three freezing-evacuation-thawing cycles. After sealing, the mixture was heated to 50 or 80 °C in an oil bath where polymerization took place. The reaction lasted for various amounts of time depending on the feeding of monomers, and was terminated by quenching with liquid N₂. The reaction product was diluted with THF and precipitated with absolute methanol thrice. After drying at 50 °C under vacuum for 12 h, P(TBS-*r*-AS) copolymers in powder form resulted.

Method to prepare the substrates and polymer films

Silicon covered by a native oxide (SiO_x) layer was used as substrate for the films, and prepared as follows. Firstly, silicon wafers were sonicated in deionized water for 15 min, then

immersed in a piranha solution at 90 °C for 20 min to remove the organic contaminants. Afterward, the wafers were sonic rinsed in deionized water four times, 5 min each time. After rinsing and nitrogen-drying, the wafers were further cleaned by oxygen plasma for 20 min. Polymer films were prepared by spin-coating solutions of polymer in toluene with concentrations of 0.5-10.0 wt % onto cleaned substrates at a spinning speed of 4500 rpm. Afterward, the films were annealed at 150 °C under a vacuum of ~1 Pa for various times of 1, 5 or 9 h.