Study on the Glass Transition Temperature of Polymer Brushes on Silicon Wafer

Jintao Yang, Bin Zhu, Weibin Zha and L. James Lee

Department of Chemical and Biomolecular Engineering, The Ohio State University, Columbus, OH 43202

Hongmin Chen and Y. C. Jean

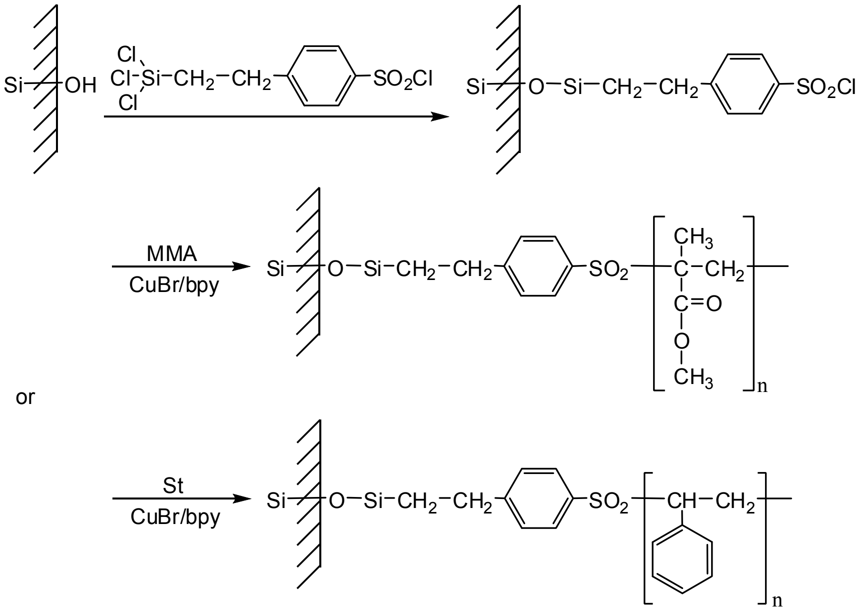
Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO, 64110

Introduction

The glass transition temperature (T_g) of the polymer thin film near the surface of inorganic material may increase or decrease depending on the interaction between polymer chains and the substrate surface. Generally, if the inorganic materials surface are compatible with the polymer, the $\mathrm{T_g}$ of the polymer near the interface will be higher than the polymer's bulk $\mathrm{T_g}$, otherwise it will be lower than bulk $\mathrm{T_g}$ [1, 2]. A better understanding about the interaction effect from substrate surface on the T_g of polymer can be helpful for the surface modification of nanoparticles and the preparation of nanocomposites. The polymer thin film-substrate system with a high specific interfacial area is a good model for analyzing the $\mathrm{T_g}$ of the polymer in interface. Some studies have used this technique to simulate the situation of the interface, showing that the T_g of the thin film can be lower or higher than bulk T_g depending on the interaction between the polymer and substrate [3~5]. Bansal et al [6] for the first time correlated the thermalmechanical properties of polymer nanocomposites with that of planar polymer films. By drawing a direct analogy between film thickness and interparticle spacing, the T_g changes in the nanocomposites are quantitatively equivalent to the corresponding thin film data. Torkelson et al [7] proposed a model nanocomposite, confining the polymer thin films between silica slides and using fluorescence method, to investigate the T_g and physical ageing in confined polymer. The T_g and physical ageing changes caused by varying interlayer distance can be used to explain the corresponding changes occurred in the real nanocomposites. However, as we know that most studies focus on choosing different polymers spin coated on substrates such as silicon wafer to investigate the different interaction effect from the substrate. In the real cases, the nanoparticles were sometimes surface modified with organic molecules, surfactant or polymer brush in order to enhance the compatibility with the polymer matrix. If the polymer chain is covalent bonded on the substrate, is the T_g different from that of the same polymer but spin coated on the substrate? In this paper, we report the first study of the effect of the covalent constraint on the T_g of the polymer brush using the well defined thin film model.

Experimental

Polystyrene (PS) and polymethyl methacrylate (PMMA) brushes were graft polymerized on the silicon wafer by a “grafted from” route depicted in Scheme 1. The oxidized silicon wafer was placed in a dehydrated flask heated for a period of time under vacuum. A dehydrated toluene (20mL) solution of initiator, 2-(4-chlorosulfonylphenyl) ethyltrichlorosilane (CTCS) (60 μL), was injected into the flask. The immobilization was carried out at the ambient temperature for 12 hrs. Then, the wafer was taken out and cleaned by ultrasonification in toluene and tetrahydrofuran (THF) for 3 times of each.



Scheme 1.

The graft polymerization was carried out in a Schlenk flask equipped with a magnetic stirring bar. A typical formulation is: a mixture solution of methyl methacrylate (MMA, 20mL) or styrene (St, 20mL), CuBr (15 mg) and 2,2'-bipyridine (bpy, 32 mg) was added into a flask and stirred for 12 hrs at ambient temperature for dissolving CuBr. Then, the modified silicon wafer, *p*-toluenesulfonyl chloride (15 mg, free initiator) and the above solution were added into a Schlenk flask followed by three times of vacuum-nitrogen gas cycles. The ATRP was carried out at 90 °C (MMA) or 110 °C (St) for different periods of time in order to get different thicknesses of polymer brush films. The polymer grafted wafer was rinsed by ultrasonification in toluene and THF to remove the free polymer. The rinsed wafers were transferred into a vacuum oven and annealed at 135°C for 12 hrs. The free polymer was dissolved in THF and passed through a column of alumina to remove the residual catalyst. A toluene solution of free polymer was spin coated on the silicon wafer. The thicknesses of the thin films were controlled by adjusting the concentration of the solutions.

Results and discussion

The thicknesses of polymer brushes measured by ellipsometry can be plotted as a function of the reaction time, as shown in Figure 1. The linear increase in film thickness with the increasing reaction time is observed for both polymer brushes, implying a good control over the propagation of polymer from the substrate, which can also be proved by the smooth surface imaged by atomic force microscopy (AFM). The presence of the polymer brushes are also confirmed by FT-IR spectroscopy, the infrared spectrums are shown in Figure 2. For the PS brush, the peak around 1500cm^{-1} is attributed to the C-C aromatic bond stretching vibration. In the spectrum of PMMA brush, the characteristic absorption peaks, ν(C=O) at 1725 cm^{-1} and δ(C-CH$_3$) at 1435 cm^{-1}, are observed.

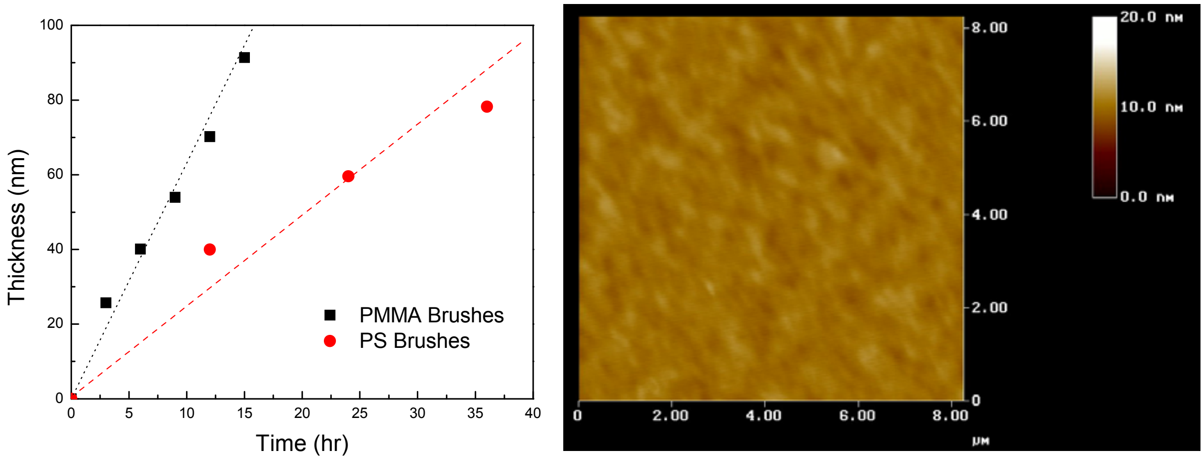


Figure 1. Thicknesses of PS and PMMA brushes as a function of reaction time and the AFM image of the surface

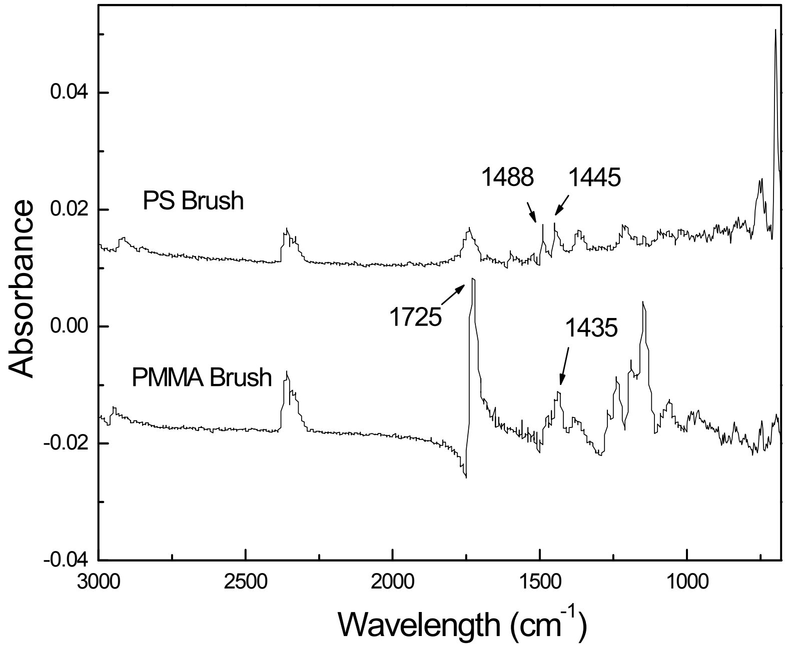


Figure 2. Infrared spectrums of PS and PMMA brushes on silicon wafer, the thickness of sample layer was around 80nm

For the polymer brushes grafted from the surface, one important concern is the density of the polymer. Herein, the positron annihilation lifetime spectroscopy (PALs) is applied to measure the free volume, i.e. density, of the polymer brushes. Since the ortho-Positronium (o-Ps, the triplet Positronium) is preferentially trapped in the subnanoscale free volume, PALs has the capacity to determine the atomic level free volume in polymer [8~10]. Through adjusting the incident energy of the beam, the positron can be implanted into different depth in the polymer film, and hence, the profile of the free volume along the depth can be obtained. Using positron annihilation spectroscopy, we obtained Doppler broadening energy spectra as a function of positron incident energy and expressed the results in terms of S parameter, which is defined as a ratio of integrated counts near 0.511 MeV at the central part to the total counts. The S parameter has been employed to indicate the relative free-volume quantity in polymeric materials since it is mainly derived from para-Ps (p-Ps, the singlet Positronium) annihilation in molecular systems. Figure 3 shows the variation of the S-parameter measured at room temperature as a function of mean depth (top x-axis) calculated from the positron energy according to the established equation for the PS and PMMA brushes (the thicknesses are around 100nm and 120nm, respectively) on the silicon wafer. The curves of spin-coated films with the same thickness are also presented for the comparison. It is clear that the PMMA brush has a similar curve with the spin-coated thin film, meaning no free volume or density difference between them. However, for the PS, a higher S parameter of brush in the interfacial region (from around 80nm depth) is observed, indicating a higher free volume or a larger interfacial region. Moreover, the S parameter data are useful to determine the layer structures of polymer thin films or brushes. Using a computer program VEPFIT, the data can be fitted into the three-layer model (polymer, polymer/Si interface and Si). The value of thickness and the density of each layer were obtained. The fitting results for the S parameter data of brushes and spin-coated thin films are given in Table 1. It is found that the polymer brushes synthesized by ATRP have almost the same layer structure as the spin-coated thin films except a lager interfacial layer thickness in the PS brush.

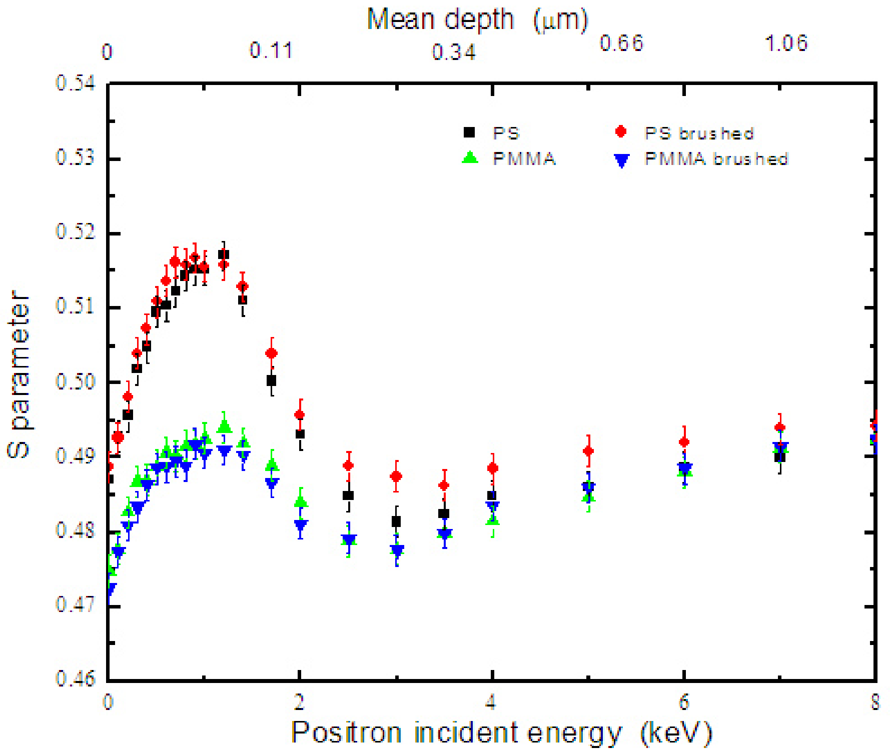


Figure 3. S parameter as a function of positron incident energy (depth) in PS and PMMA brushes and spin-coated thin films

Table 1. Thickness and density of bulk layer and interface layer in the polymer brushes and spin-coated thin films determined by PALS

	PS brush		Spin-coated PS film		PMMA brush		Spin-coated PMMA film	
	Bulk layer	Interface layer	Bulk layer	Interface layer	Bulk layer	Interface layer	Bulk layer	Interface layer
Thickness(nm)	97.8	25.7	86.9	12.2	95	18.4	104.1	15.3
Density(g/cm^{-1})	1.1	0.9	1.1	0.9	1.2	0.9	1.2	0.9

To investigate the effect of interaction between the polymer chains and substrate on T_g of the supported thin film, the T_g s of the polymer brushes and the corresponding spin-coated thin films are measure by ellipsometry. Figure 4 shows a typical experimental scan. It is observed that the thickness of the polymer thin film increases with the temperature. By linearly fitting the thickness expansion in glass and rubber regions, the point of intersection is defined as the T_g of the thin film.

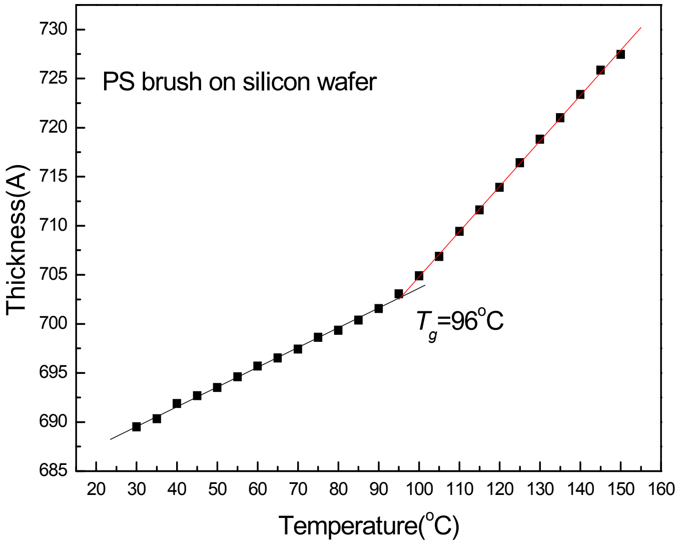
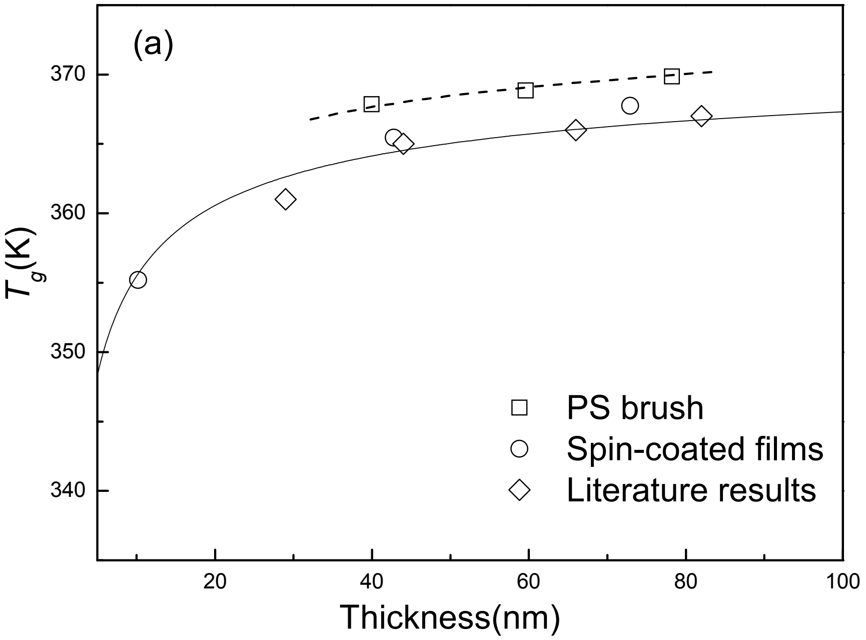


Figure 4. Typical plot of thickness versus temperature of polymer brush on silicon wafer

Figure 5a shows the T_g s of the PS brushes and the spin-coated films with different thickness as well as some results from literature. In a supported thin film system, the mobility of the polymer chains can be affected by two interfaces: the polymer-air interface (free surface) and the polymer-substrate interface. In general, the former enhances the chain mobility by increasing the free volume while the latter can enhance or reduce the chain mobility depending on the interaction between the polymer chains and the substrate [11]. Therefore, any T_g measured by ellipsometry is determined by these two factors. Figure 5a indicates that the T_gs of PS spin-coated films decrease continuously with the thickness, which can be attributed to the enhanced chain mobility caused by both interfaces. One of our initial concerns is to elevate the T_g of the supported thin film by building up a covalent bounding between the polymer and the substrate. Our experimental results, however, just show a slight increase in the T_gs of the polymer brushes instead of a dramatic increase as we expected. The reason can be explained as the following. It has been proved that the polymer chains are substantially stretched from the surface in the thickness range from 40nm to 80nm. In other words, the covalent bonding constraint can only affect the chains very close to the substrate but not the chains far from the interface. We speculate that the T_g can be higher when the polymer brush is so short that the covalent constraint effect become dominant. Matyjaszewski et. have found that the T_g s of the polystyrene-grafted silica hybrid nanoparticles have no difference with the pure polymer when the molecular weight of the brushes is above 30,000g/mol [12], which is apparently consistent with our speculation. The same mechanism can be applied to interpret the T_g data of PMMA brushes (Figure 5b) which also show a slight enhancement over that of the corresponding spin-coated films.

In summary, the PS and PMMA brushes covalently bounded on the silicon wafers were successfully synthesized by ATRP. FT-IR, AFM and PALs demonstrated that the same layer structure as the spin-coated polymer thin films was obtained. The covalent constraint can only affect the polymer chains close to the substrate and the polymer brushes just show a slight increase in T_g compared to the corresponding spin-coated thin films.



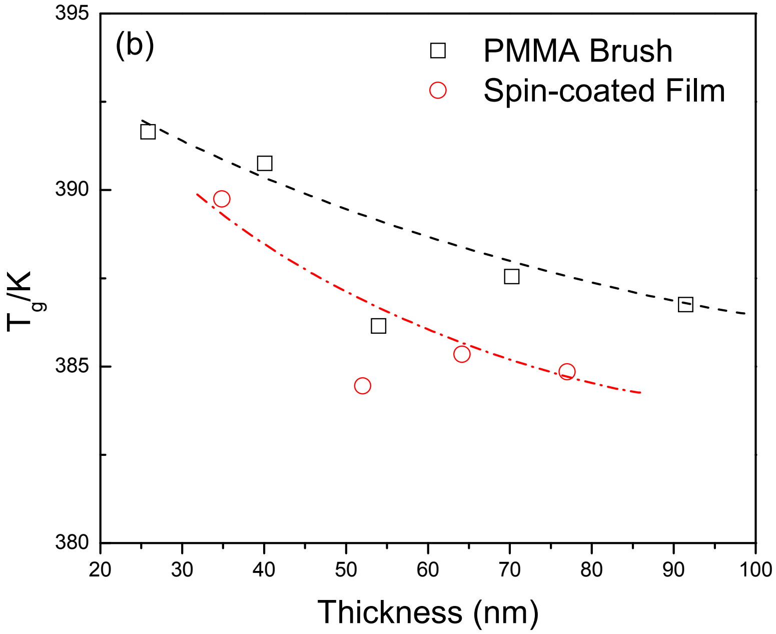


Figure 5. T_gs of PS (a) and PMMA (b) brushes and spin-coated thin films determined by ellipsometry

References

[1] Vaia, R. A.; Sauer, B.B.; Tse, O.K.; Giannelis, E. P. *J. Polym. Sci. Part B: Polym. Phys.* 35, 59-67(1998)

[2] Sanchez, C.; Julian, B.; Belleville, P.; Popall, M. J. *Mater. Chem*, 15, 3559-3592(2005)

[3] Zanten, J. H.; Wallace, W. E.; Wu, W. L. *Physical review E*, 1996, 53, R2053-R2056

[4] Wallace, W. E.; Zanten, J. H.; Wu, W. L. *Physical review E*, 1995, 52, R3329-R3332

[5] Fryer, D.S. *Macromolecules*, 34, 5627-5634(2001)

[6] Bansal, A.; Yang, H.; Li, C. Z.; Cho, K. W.; Benicewicz, B.C.; Kumar, S. K.; Schadler, L.S. *Nature Materials*, 4, 693-698(2005)

[7] Rittigstein, P.; Priestley, R.D.; Broadbelt, L. J.; Torkelson, J. M. *Nature Materials*, 6, 278-282(2007)

[8] J. J. Zhang, H. M. Chen, Y. Li, T. Suzuki, T. Ohdaira, Y. C. Jean, *Radiation Physics and Chemistry* 76, 172-179 (2007).

[9] H. Chen, W.S. Hung, C.-H. Lo, S. H. Huang, M. L. Cheng, G. Liu, K. R. Lee, J.-Y. Lai, Y.-M. Sun, C. C.Hu, R. Suzuki, T. Ohdaira, N. Oshima, Y.C. Jean, *Macromolecules* 40, 7542-7557

[10] Y.C. Jean, P.E. Mallon, D.M. Schrader, Eds. *Principles and Applications of Positron and Positronium Chemistry* (World Sci. Pub.: Singapore, 2003) Chapter 11

[11] Forrest, J. A.; Dalnoki-Veress, K.; Stevens, J. R.; Dutcher, J.R. *Phys. Rev. Lett.* 77, 2002-2005(1996)

[12] Savin, D. A.; Pyun, J.; Patterson, G. D.; Kowalewski, T.; Matyjaszewski, K. *J. Polym.Sci. Part B: Polym. Phys.* 40, 2667-2676 (2002)