ACS Macro Letters
Letter
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Effect of Long Range Interactions on the Glass Transition Temperature of Thin Polystyrene Films

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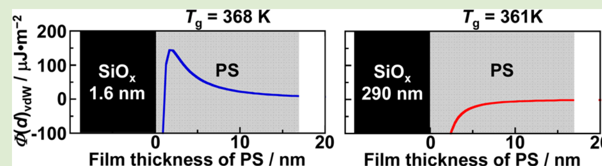
ABSTRACT: The glass transition temperature (T_g) of thin polystyrene (PS) films supported on silicon wafers with oxide layers of varying thickness was characterized by the temperature dependence of the film thickness using ellipsometry. This allowed us to uncover how a long-range interaction affects the T_g of polymer films. As previously reported using a variety of methods, the T_g decreased with decreasing film thickness. However, the extent was not the same among the reports. In this study, we found that the T_g attenuation of a PS film of a given thickness was dependent on the oxide layer thickness of the silicon wafer via the long-range interaction.



Thin polymer films have been used in a wide variety of applications such as lithography, selective membranes, organic sensors and devices, medical coatings, and so on.[1−3] When a film becomes thinner, the aggregation states and dynamics of the polymer chains will change from those in the bulk phase due to surface and interfacial effects.[4−6] Thus far, it has been widely accepted that those segments in the vicinity of the free surface are more mobile than those in the corresponding bulk phase.[7−16] On the other hand, although it appears that the segmental motion of the polymer chains at the substrate interface is less mobile than in the bulk phase,[17−26] the current understanding of this issue is far from clear, especially in comparison with surface dynamics.

To obtain better insight into the segmental motion at a solid interface, the effect of the surface chemistry of the substrate on the glass transition temperature (T_g) of thin polymer films has been investigated. For example, when a polymer has a strong attractive interaction with the substrate surface, chain mobility is attenuated at the substrate interface.[27−35] The interaction discussed here is regarded as a short-range one. However, the chemistry beneath the surface, which may impact the physical properties of the polymer layer, is mostly overlooked. In other words, the long-range interaction between the polymer and the substrate is generally disregarded. Previous studies on the dewetting of polymer films on solid substrates demonstrated that long-range van der Waals interactions altered the dewetting behavior of polymer films.[36−41] To the best of our knowledge, however, few or no studies have taken into account the effect of long-range van der Waals interactions on the glass transition behavior of thin polymer films. In this study, the T_g of thin polymer films coated onto silicon wafers with oxide layers of varying thickness was measured to examine the long-range van der Waals interactions on thin film dynamics.

Figure 1 shows a typically temperature dependence for the thickness of a polystyrene (PS) film spin-coated onto a native oxide substrate. The thickness increased with increasing temperature. The slope of the line in Figure 1, corresponding

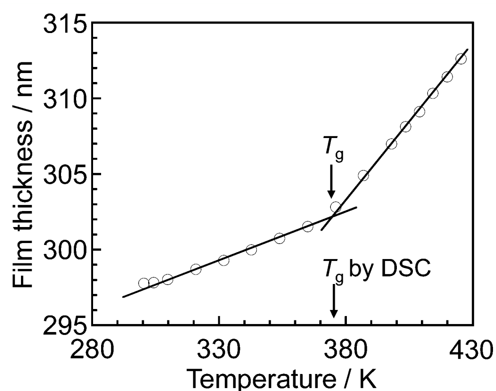


Figure 1. Temperature dependence of the thickness of a PS film with an original thickness of 297 nm.

to thermal expansion, was found to change at 376 K. The inflection point related to the slope is in good accord with the bulk T_g of 376 K measured by differential scanning calorimetry (DSC). Therefore, this temperature-dependent thickness measurement allows us to determine the T_g for thin PS films, as many researchers have previously reported.

Figure 2 shows the thickness dependence of the T_g for PS films supported on silicon wafers with native and thermal oxide layers. The solid and dotted lines are the best fits to the data using Keddie's empirical equation:[42]

$$T_g(d) = T_g^{\infty}(1 - (A/d)^{\delta}) \quad (1)$$

where T_g^{∞} is the bulk T_g, A is a characteristic length, d is the film thickness, and δ is the fitting exponent. Furthermore, the shaded area denotes the region where data have been reported by other research groups.[43−46] The T_g for both films decreased

Received: July 29, 2012
Accepted: October 19, 2012
Published: October 25, 2012

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dx.doi.org/10.1021/mz300391g | ACS Macro Lett. 2012, 1, 1317−1320

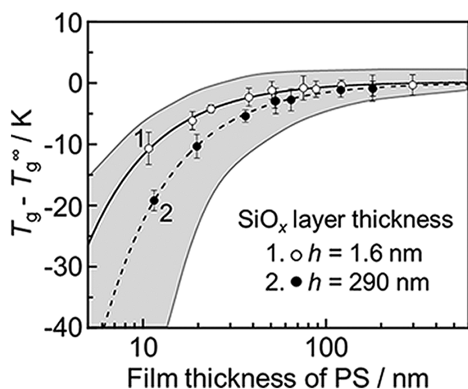

Figure 2. Thickness dependence of the T_g of PS films on silicon wafers with 1.6 and 290 nm thick oxide layers. The gray area indicates the region where published data from different groups are available.

with decreasing thickness when the film became thinner than approximately 100 nm. The thickness dependence of the T_g was more striking for the thermal oxide substrates than for the native oxides. Although the two substrates possessed the same chemical nature, namely, silicon wafers with a silicon oxide layer, the thickness of the oxide layer was not the same between the two substrates. The results obtained suggested that long-range van der Waals interactions may account for the different mobility of the two PS films. Also, it is noteworthy that both data sets lie within the region where data have been previously reported by other research groups.

Here, the effective interfacial potential against the film thickness, $\Phi(d)$, given by eq 2 is introduced.[47]

$$\Phi(d) = \frac{C}{d^8} + \Phi(d)_{\mathrm{vdW}} \tag{2}$$

where C is a constant related to the short-range interaction strength and the second term characterizes the long-range interactions by the van der Waals potential. The $\Phi(d)_{\mathrm{vdW}}$ for a system composed of air/PS/SiO$_x$/Si is expressed by

$$\Phi(d)_{\mathrm{vdW}} = -\frac{A_{\mathrm{SiO}_x}}{12\pi d^2} + \frac{A_{\mathrm{SiO}_x} - A_{\mathrm{Si}}}{12\pi(d+h)^2} \tag{3}$$

where A_{SiO_x} and A_{Si} are the Hamaker constants for air/PS/SiO$_x$ and air/PS/Si systems.

Figure 3 shows the effective interfacial potential as a function of the thickness for PS films coated onto silicon wafers with

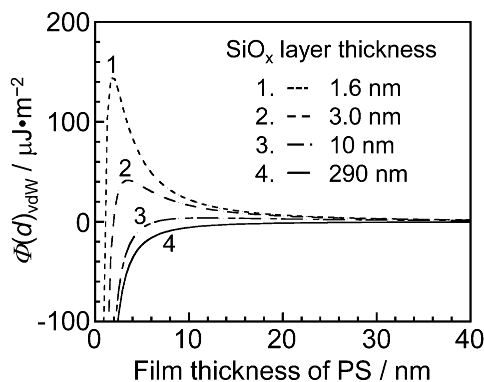

Figure 3. PS film thickness vs long-range effective interfacial potential as a function of the SiO$_x$ layer thickness.

SiO$_x$ layers of varying thickness. Here, an A_{SiO_x} value of 1.8 × 10^{-20} and an A_{Si} of −2.2 × 10^{-19} J were used.[47] As shown in Figure 3, the relationship between the PS thickness and the long-range interactions was strongly dependent on the thickness of the oxide layer (h). For example, in the case of h = 1.6 nm, the $\Phi(d)_{\mathrm{vdW}}$ increased slightly with decreasing PS thickness, abruptly increased at around 10 nm, and then suddenly dropped at around 2 nm. On the other hand, the $\Phi(d)_{\mathrm{vdW}}$ kept decreasing with decreasing PS thickness for h = 290 nm. These two extreme cases correspond to the two sets of samples in Figure 2. As shown in eq 2, the stability of a thin film is governed by the $\Phi(d)_{\mathrm{vdW}}$, which is a function of the film thickness. When the $\Phi(d)_{\mathrm{vdW}}$ is positive, the air and the substrate prefer not to come in contact with each other, resulting in a relatively stable film of PS. In contrast, a negative $\Phi(d)_{\mathrm{vdW}}$ represents an attraction between the air and the substrate, leading to the PS film on the thermal oxide layer becoming less stable and/or mobile at a given film thickness of PS.

Figure 4 shows the T_g attenuation for 16 nm thick PS films supported on substrates with different oxide layer thicknesses.

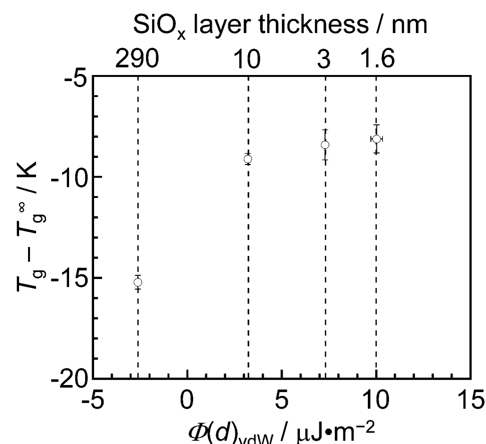

Figure 4. T_g attenuation of a 16 nm PS film supported on silicon wafers with oxide layers of varying thickness.

The T_g value decreased with an increasing oxide layer thickness of the substrate. Hence, long-range van der Waals interactions can affect the T_g of the thin PS film. Given that the thickness of the oxide layers of the silicon substrates would differ in different groups over the world, the effects of these long-range interactions on the T_g of thin polymer films on silicon wafers should also differ. Thus, it is noteworthy to mention that in using different kinds of substrates such as silicon wafers without oxide layer, glass slides, gold, aluminum, and so on, not only the short but also the long-range interactions between the polymer and the substrate should be taken into account to understand the glass transition behavior in thin films.

The thickness range of a PS in which the long-range van der Waals forces become significant is up to approximately 20 nm. Nevertheless, as shown in Figure 2, even at a PS film thicker than 20 nm, the extent of the T_g attenuation was not the same for PS films on substrates with 1.6 versus 290 nm thick oxide layers. This apparent inconsistency might be explained in terms of a gradient of long-range interactions in the film along a direction normal to the surface. This leads to the observation that the T_g attenuation for a PS film much thicker than 20 nm is dependent on the thickness of the oxide layer on the silicon

substrate. Furthermore, the gradient of chain mobility in close proximity to the substrate interface should also be a function of the thickness of the silicon oxide layer. This will be investigated in the near future.

We finally come to alternative possibilities to explain the results that the T_g depression for the thin films was a function of the thickness of the silicon oxide layer. Taking into account that polymers in a thin film are far away from an equilibrium state,[26] the aggregation states are also affected by the long-range interactions, leading to the alteration of the segmental dynamics of polymers. Second, the network structure of SiO_x will not be well developed in a thin layer of a few nanometers, even more so in a thick layer where there is a structural gradient along the depth direction.[48,49] The structural difference between native and thermal oxide layers was actually observed in their electrical properties such as in their band gaps.[50] Thus, the oxide layer in various substrates may not be the same in terms of structure. If this is the case, then the short-range interactions in addition to the long ones are also a function of the thickness of the silicon oxide layer. This, of course, results in the change of the segmental dynamics of polymers.

In conclusion, we measured the T_g of PS films supported on silicon wafers with oxide layers of varying thickness using spectroscopic ellipsometry. We observed that the glass transition temperature decreased with decreasing thickness of the PS films. Interestingly, the thickness dependence of the T_g was more striking on thermal oxide substrates than on the native oxides. When we fixed the thickness of the PS films, the T_g decreased with increasing oxide layer thickness. These data provide compelling evidence that long-range van der Waals interactions can affect the glass transition behavior of polymer thin films.

■ EXPERIMENTAL SECTION

As a sample, monodispersed polystyrene (PS) with a number-average molecular weight (M_n) of 73.5k was used. The bulk T_g measured by differential scanning calorimetry (DSC) was 376 K. The PS films were prepared by a spin-coating method from toluene solutions onto silicon wafers. To control the long-range van der Waals forces, we chose substrates with oxide layer thicknesses (h) of 1.6 nm (native oxide) and 290 nm (thermal oxide). The as-purchased substrate was submerged into a piranha solution, that is, H_2SO_4/H_2O_2 (7:3), preheated to 363 K for 1 h, rinsed thoroughly in excess deionized water, and dried under nitrogen. This process removes all organic contaminants, leaving the silicon surface a native oxide layer covered with Si−OH groups. The film thickness was controlled by varying the concentration of the PS solution. The PS films were annealed under vacuum at 393 K for at least 48 h to remove the residual solvent and preparation history. The T_g of the thin PS films was then determined based on the temperature dependence of the film thickness measured by ellipsometry. The films were heated by a custom-built hot stage which was assembled for ellipsometry. The heating rate was 0.5 $K{\cdot}min^{-1}$.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was partly supported by a Grant-in-Aid for Scientific Research (B; No. 24350061) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

■ REFERENCES

(1) Yampolskii, Y.; Pinnau, I.; Freeman, B. D. *Materials Science of Membranes for Gas and Vapor Separation*; John Wiley & Sons, Ltd.: England, 2006.
(2) Stamm, M. *Polymer Surfaces and Interfaces: Characterization, Modification and Applications*; Springer-Verlag: New York, 2008.
(3) Schaefer, H. E. *Nanoscience: The Science of the Small in Physics, Engineering, Chemistry, Biology and Medicine*; Springer-Verlag: Germany, 2010.
(4) Jones, R. A. L.; Richards, R. W. *Polymers at Surfaces and Interfaces*; Cambridge University Press: Cambridge, 1999.
(5) Karim, A.; Kumar, S. *Polymer Surfaces, Interfaces and Thin Films*; World Scientific: Singapore, 2000.
(6) Tsui, O. K. C.; Russell, T. P. *Polymer Thin Films*; World Scientific: Singapore, 2008.
(7) Mansfield, K. F.; Theodorou, D. N. *Macromolecules* **1991**, *24*, 6283−6294.
(8) Meyers, G. F.; DeKoven, B. M.; Seitz, J. T. *Langmuir* **1992**, *8*, 2330−2335.
(9) Forrest, J. A.; Dalnoki-Veress, K.; Stevens, J. R.; Dutcher, J. R. *Phys. Rev. Lett.* **1996**, *77*, 2002−2005.
(10) Tanaka, K.; Takahara, A.; Kajiyama, T. *Macromolecules* **2000**, *33*, 7588−7593.
(11) Wallace, W. E.; Fischer, D. A.; Efimenko, K.; Wu, W. L.; Genzer, J. *Macromolecules* **2001**, *34*, 5081−5082.
(12) Kim, H.; Rühm, A.; Lurio, L. B.; Basu, J. K.; Lal, J.; Lumma, D.; Mochrie, S. G. J.; Sinha, S. K. *Phys. Rev. Lett.* **2003**, *90*, 068302.
(13) Morita, H.; Tanaka, K.; Kajiyama, T.; Nishi, T.; Doi, M. *Macromolecules* **2006**, *39*, 6233−6237.
(14) Fakhraai, Z.; Forrest, J. A. *Science* **2008**, *319*, 600−604.
(15) Yang, Z.; Fujii, Y.; Lee, F. K.; Lam, C. H.; Tsui, O. K. C. *Science* **2010**, *328*, 1676−1679.
(16) Paeng, K.; Swallen, S. F.; Ediger, M. D. *J. Am. Chem. Soc.* **2011**, *133*, 8444−8447.
(17) Wallace, W. E.; van Zanten, J. H.; Wu, W. L. *Phys. Rev. E* **1995**, *52*, R3329−R3332.
(18) Weber, R.; Zimmermann, K. M.; Tolan, M.; Stettner, J.; Press, W.; Seeck, O. H.; Erichsen, J.; Zaporojtchenko, V.; Strunskus, T.; Faupel, F. *Phys. Rev. E* **2001**, *64*, 061508.
(19) Efremov, M. Y.; Warren, J. T.; Olson, E. A.; Zhang, M.; Kwan, A. T.; Allen, L. H. *Macromolecules* **2002**, *35*, 1481−1483.
(20) Pham, J. Q.; Green, P. F. *Macromolecules* **2003**, *36*, 1665−1669.
(21) Tanaka, K.; Tateishi, Y.; Okada, Y.; Nagamura, T.; Doi, M.; Morita, H. *J. Phys. Chem. B* **2009**, *113*, 4571−4577.
(22) Fujii, Y.; Yang, Z.; Leach, J.; Atarashi, H.; Tanaka, K.; Tsui, O. K. C. *Macromolecules* **2009**, *42*, 7418−7422.
(23) Napolitano, S.; Wübbenhorst, M. *Nat. Commun.* **2011**, *2*, 260.
(24) Koga, T.; Jiang, N.; Gin, P.; Endoh, M. K.; Narayanan, S.; Lurio, L. B.; Sinha, S. K. *Phys. Rev. Lett.* **2011**, *107*, 225901.
(25) Inoue, R.; Kawashima, K.; Matsui, K.; Nakamura, M.; Nishida, K.; Kanaya, T.; Yamada, N. L. *Phys. Rev. E* **2011**, *84*, 031802.
(26) Tsuruta, H.; Fujii, Y.; Kai, N.; Kataoka, H.; Ishizone, T.; Doi, M.; Morita, H.; Tanaka, K. *Macromolecules* **2012**, *45*, 4643−4649.
(27) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Faraday Discuss.* **1994**, *98*, 219−230.
(28) Wu, W. L.; van Zanten, J. H.; Orts, W. J. *Macromolecules* **1995**, *28*, 771−774.
(29) van Zanten, J. H.; Wallace, W. E.; Wu, W. L. *Phys. Rev. E* **1996**, *53*, R2053−R2056.
(30) Porter, C. E.; Blum, F. D. *Macromolecules* **2000**, *33*, 7016−7020.
(31) Fryer, D. S.; Nealey, P. F.; de Pablo, J. J. *Macromolecules* **2000**, *33*, 6439−6447.

(32) Ellison, C. J.; Kim, S. D.; Hall, D. B.; Torkelson, J. M. *Eur. Phys. J. E* **2002**, *8*, 155−166.
(33) Priestley, R. D.; Ellison, C. J.; Broadbelt, L. J.; Torkelson, J. M. *Science* **2005**, *309*, 456−459.
(34) Lipson, J. E. G.; Milner, S. T. *Eur. Phys. J. B* **2009**, *72*, 133−137.
(35) Nguyen, H. K.; Labardi, M.; Capaccioli, S.; Lucchesi, M.; Rolla, P.; Prevosto, D. *Macromolecule* **2012**, *45*, 2138−2144.
(36) Mirnik, M.; Težak, B.; Overbeek, J. T. G.; Derjaguin, B. V.; Verwey, E. J. W.; Fowkes, F. M.; Osmond, D. W. J.; Napper, D. H. *Discuss. Faraday Soc.* **1966**, *42*, 14−22.
(37) Herminghaus, S.; Jacobs, K.; Mecke, K.; Bischof, J.; Fery, A.; Ibn-Elhaj, M.; Schlagowski, S. *Science* **1998**, *282*, 916−919.
(38) Reiter, G.; Sharma, A.; Casoli, A.; David, M.; Khanna, R.; Auroy, P. *Langmuir* **1999**, *15*, 2551−2558.
(39) Craster, R. V.; Matar, O. K. *Rev. Mod. Phys.* **2009**, *81*, 1131−1198.
(40) Xue, L.; Han, Y. *Langmuir* **2009**, *25*, 5135−5140.
(41) Bäumchen, O.; Jacobs, K. *J. Phys.: Condens. Matter* **2010**, *22*, 033102.
(42) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys. Lett.* **1994**, *27*, 59−64.
(43) Fukao, K.; Miyamoto, Y. *Phys. Rev. E* **2000**, *61*, 1743−1754.
(44) Alcoutlabi, M.; McKenna, G. B. *J. Phys.: Condens. Matter* **2005**, *17*, R461−R524.
(45) Forrest, J. A.; Dalnoki-Veress, K. *Adv. Colloid Interface Sci.* **2001**, *94*, 167−196.
(46) Kawana, S.; Jones, R. A. L. *Phys. Rev. E* **2001**, *63*, 021501.
(47) Seemann, R.; Herminghaus, S.; Jacobs, K. *Phys. Rev. Lett.* **2001**, *86*, 5534−5537.
(48) Tang, M.; EvansLutterodt, K. W.; Higashi, G. S.; Boone, T. *Appl. Phys. Lett.* **1993**, *62*, 3144−3146.
(49) Ohwaki, T.; Takeda, M.; Takai, Y. *Jpn. J. Appl. Phys.* **1997**, *36*, 5507−5513.
(50) Pic, N.; Glachant, A.; Nitsche, S.; Hoarau, J. Y.; Goguenheim, D.; Vuillaume, D.; Sibai, A.; Autran, J. L. *J. Non-Cryst. Solids* **2001**, *280*, 69−77.