Effect of Sample Preparation on the Glass-Transition of Thin Polystyrene Films

Z. FAKHRAAI,[1] J. S. SHARP,[2] J. A. FORREST[1]

[1]Department of Physics and Guelph–Waterloo Physics Institute, University of Waterloo, 200 University Ave. W., Waterloo, Ontario, Canada, N2L 3G1

[2]School of Physics and Astronomy, University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

ABSTRACT We have investigated the effect of sample preparation on the glass-transition temperature (T_g) of thin films of polystyrene (PS). By preparing and measuring the glass-transition temperature T_g of multilayered polymer films, we are able to assess the contribution of the spincoating process to the reduced T_g values often reported for thin PS films. We find that it is possible to determine a T_g even on the first heating cycle, and that by the third heating cycle (a total annealing time of 15 min at $T = 393$ K) the T_g value has reached a steady state. By comparing multilayered versus single layered films we find that the whole T_g depends only on the total film thickness, and not on the thickness of the individual layers. These results strongly suggest that the spincasting process does not contribute significantly to T_g reductions in thin polymer films. © 2004 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 42: 4503–4507, 2004

INTRODUCTION

There has been a significant amount of interest in recent years in the physical properties of very thin polymer films.[1–3] In particular, in a number of cases the properties of thin films display significant deviations from that of the bulk material, or even that of much thicker films. Of particular interest is the glass transition temperature (T_g). For many different polymers, measurements of the T_g in thin films have revealed large differences from the bulk value. Of these polymers, the most well studied material is atactic polystyrene (PS). Since the original study by Keddie et al.[4] showing thin film T_g values lower than that of the bulk, there have been many studies aimed at quantifying this behavior.[5] A recurring concern about these and other studies of thin polymer films involves the effect of sample preparation.[6, 7] Such films are typically spin cast from dilute solutions of polymer in a good solvent (such as toluene in the case of PS) and then annealed above the bulk T_g value for a time usually ranging from a few hours to a few tens of hours. During the process of spincasting, the chains may be in configurations not typical of those in equilibrium melts. In addition, even though the films are annealed, in many cases (depending on the substrate on which they are prepared) they are very different from the equilibrium state of a fully dewetted film. This concern is often dismissed, although there is not yet any proof that it is valid to do so. Although a definitive explanation to the observed T_g reductions has not yet emerged, there is compelling evidence that it is related to the presence of the free surface.[8] One way to distinguish between an effect due to the free surface

and one due to sample preparation is to make films with the same thickness (and hence the same relative contribution of the free surface) but different sample preparation history (i.e., solvent concentration and spin speed). The most effective way to implement such a comparison is the use of layered samples. The T_g values of layered samples also have relevance in supporting the conclusion of recent studies by Ellison and Torkelson where layered samples with one labeled layer were used as a way to quantify the depth-dependent T_g value in thin films.[9] In this study, we investigate the relative effect of sample preparation and the free surface by preparing and measuring the T_g value of a series of layered polymer films with up to four constituent layers. We show that it is possible to identify a T_g in all cases, and that after a single heating cycle (393 K for 15 min), the measured T_g of a multilayered sample depends only on the *total* film thickness rather than the thickness of the constituent layers.

EXPERIMENTAL

PS solutions of weight-average molecular weight (M_w) = 641 K, M_w/[number average molecular weight (M_n)]M_N = 1.11, polymer source) were spincast onto either Si (100) substrate (for the first layer) or on single crystal sodium chloride (NaCl) optical windows (Crystaltechno) for the second, third, and fourth layer of each film. The individual layer thicknesses were between 3 nm ≤ h ≤ 150 nm for the one and two layer films and 5 nm ≤ h ≤ 10 nm for three and four layer films. All layers in each sample were made using the same solution, and with the same spin speed. The layers were then separately annealed at 393 K [T_g(bulk) = 370 ± 1K] for 9 h under nitrogen to remove the solvent and relax the polymer chains. This is similar to the annealing conditions used for thin film T_g studies and assures that each layer has the same thermal history and, as a consequence, a similar chain conformation. These layers were then used to make samples in the following manner: a layer supported on NaCl was placed upside down on top of the layer supported on a Si substrate. A drop of deionized water placed on the edge of the salt substrate partially dissolved the salt and placed the second layer on top of the first layer. Once the second layer is placed on top of the first layer, the layers are pulled into contact by surface forces. The two layer film was then washed with deionized water

to make sure there is no salt left on the film and then annealed again for at least 12 h at 343 K to make sure that there is no water left on the film or between the layers. This annealing temperature is well below the bulk T_g and other possible reduced T_gs and therefore no chain relaxation will occur during the final annealing stage. If desired, a third or fourth layer was placed on the film using the above method. This procedure provides samples that are well annealed, in that all of the solvent should have been removed, but the chain conformations will be characteristic of the layer thickness rather than the total film thickness.

The multilayer films made by this method were then placed on a Linkam hot-stage and mounted on the sample stage of an Exacta 2000 fast-nulling ellipsometer (Waterloo Digital Electronics). The films were heated rapidly (90 K/min) to 403 K and held at that temperature for 5 min. The films were then cooled to 313 K with a cooling rate of 1 K/min to measure the T_g. This annealing time at 403 K is much less than a typical annealing time in this study and other studies, and less than that expected to result in significant interface formation at this temperature.[3] The T_g of each film was measured three times during three different heating cycles to examine the effect of annealing time on the T_g. Ellipsometric measurements were performed using a wavelength of 633 nm and an angle of incidence of 60 ± 0.1°. The ellipsometric angles P and A were measured during cooling. Because the values of P and A depend linearly on the film thickness before and after the transition, the inversion of P and A to actual thickness was not necessary and the P and A values and their temperature derivatives were enough to determine the T_g. The T_g can be determined by the constructions of two straight lines, fitted to the high and low temperature ranges (Figure 1) or by calculating their numerical derivatives, and finding the midpoint between the low temperature limit (T_-) and the high temperature limit (T_+).[10] Figure 1 shows the plots of P and A and their temperature derivatives versus temperature for a one-layer film with a thickness of 40 nm. This set of plots shows how the T_g can be defined and that any of the quantities can be used to determine the same value of T_g within the experimental error. This is an important point because in some cases for the multilayer films, the T_g is not discernible in all data types.
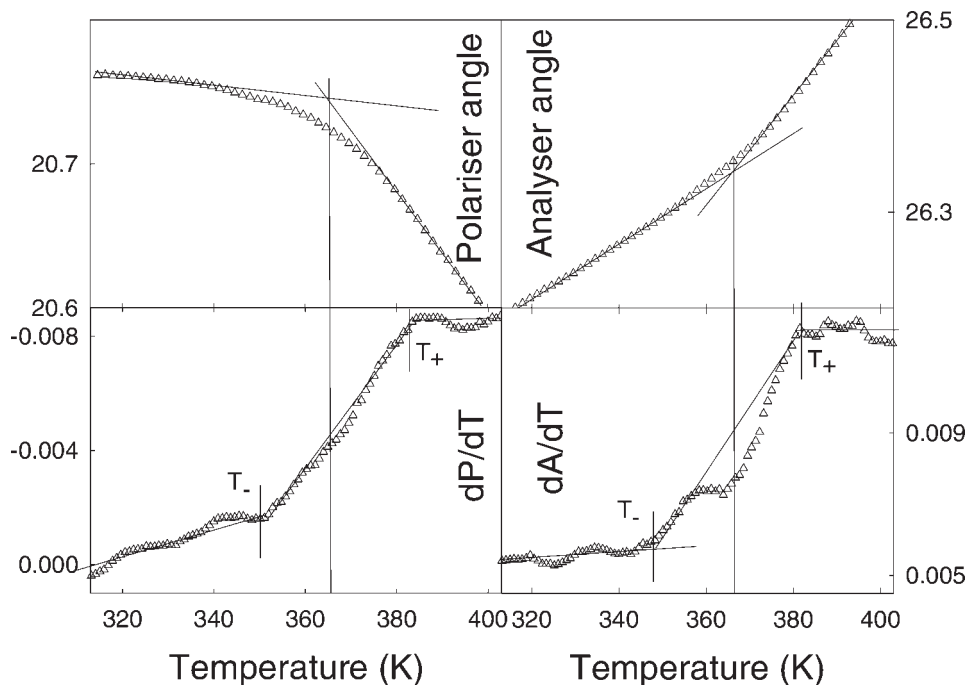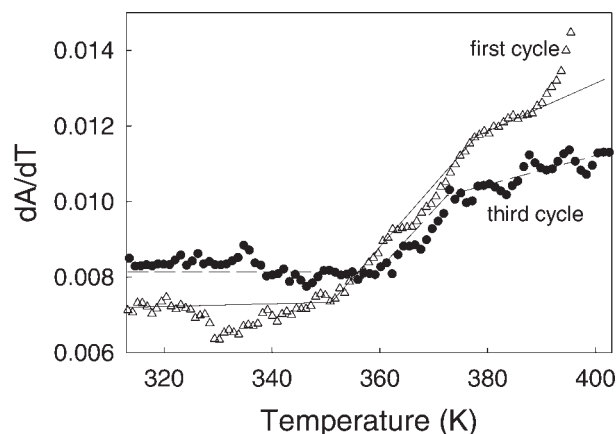
Figure 1 *P, A, dA/dT,* and *dP/dT* versus temperature of a 40 nm one-layer film. Solid lines show the T_g value. The T_g values are the same regardless of what data is used in the determination of the T_g.

RESULTS AND DISCUSSION

Figure 2 shows plots of *P* and *A* values versus temperature for a three-layer film made of 10 nm layers in the first (open symbols) and third (filled symbols) cooling cycle. There are a number of noteworthy points about these plots. In the first case, one can see that the value of the polarizer angle *P* during the third cooling is larger than that in the first cooling cycle. The most likely reason for this difference is that the film thickness decreases slightly during the successive heating and cooling cycles. Once the sample is heated above the T_g for the first time, the layers start to anneal into each other and the interface starts to disappear. This causes the difference between *P* and *A* values in different cooling cycles. The other notable aspect of the plots is the significant curvature in the high temperature region of the *P(A)* versus the temperature plot. This curvature is a result of the convolution of the temperature dependence of *P* and *A* as the sample is cooled with the time dependence of *P* and *A* as the interface in the multilayered samples heal with time. It is easiest to make a quantitative analysis by looking at the temperature derivatives, and we use *dA/dT* in this case. Figure 3
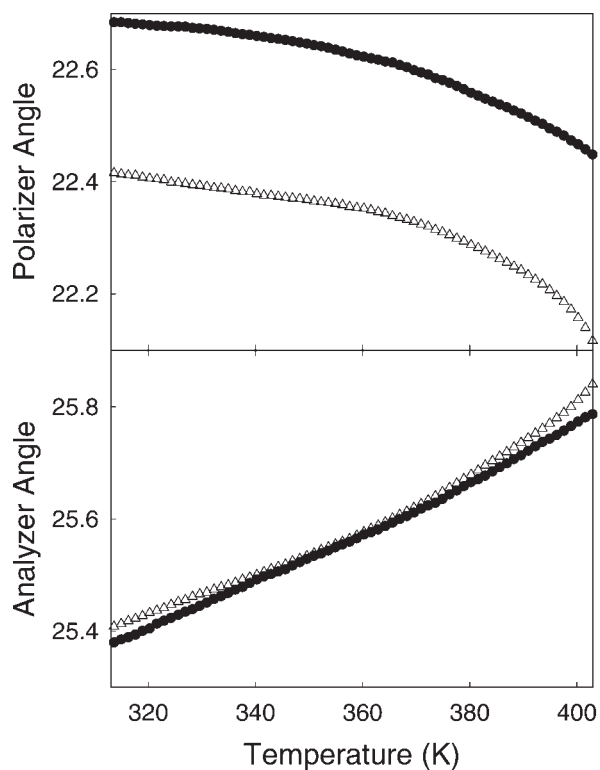
Figure 2 *P* and *A* versus temperature of a three-layer film made of 10 nm layers in the first ($\triangle$) and third ($\bullet$) cooling cycles.

Figure 3 dA/dT versus Temperature of a three-layer film made of 10 nm layers in the first ($\triangle$) and third ($\bullet$) cooling cycles.

shows the dA/dT data that are derived from the data in Figure 2. The high temperature range (temperatures greater than 380 K) shows the extent of the high temperature annealing effect, and as we anneal the film for a longer cumulative time, this high temperature effect diminishes. This dynamical effect is investigated more carefully using two-layer films and will be published separately. The results of simulation and experiments on those films confirm that the changes in the P and A values at high temperatures are due to interface annealing. Although this dynamical process exists at high temperatures, we are still able to define the T_g because of the existence of a plateau at temperatures low enough so the dynamical effect is not observed on the time scale of the experiment, and yet high enough to be above the T_g value. This plateau is clearly seen in Figure 3. A careful analysis of the data in Figure 3 reveals that the T_g values in the third cycle are slightly higher than the T_g values in the first cycle. This effect exists in the measurements of all multilayer films, and does not exist in the measurements of one layer films. The most likely reason for this is the healing of the PS–PS interfaces in the multilayer films. Since the individual layers have an initial surface roughness; the interfacial regions of the multilayer films will not start out with a density the same as the bulk polymer. Although this dynamical process exists, the measurements of the thickness before and after annealing the films shows that the changes in the film thickness are always less than 10% of the total thickness of the film. Since the effect of this dynamical process almost disappears at the end

of the third cooling cycle, the results of T_g measurements at this cooling cycle is used in the analysis. Further annealing of the samples was avoided to ensure that the total annealing time is still negligible in comparison with the total chain disentanglement time, which is of the order of 1000 min for PS at 390 K.[3]
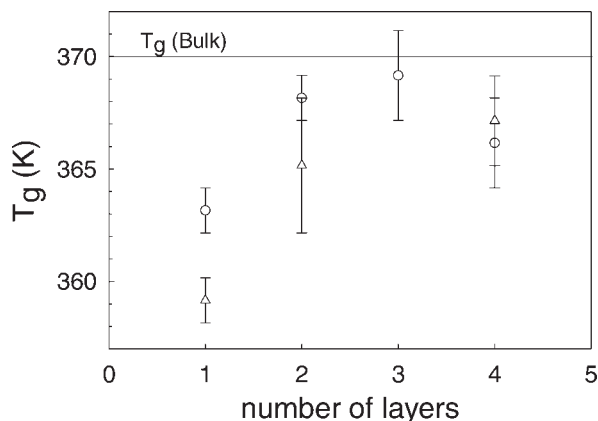
Figure 4 shows the plot of all T_g values at the third cooling cycle versus the total film thickness measured at the end of the cycle. In this figure, the final film thickness is determined from the final values of the P and A angles, and will be less than the sum of the thicknesses of the constituent layers. It can be seen from the plot that the T_g reduction of two, three, and four layer films are the same as the T_g reduction of one layer films with the same total thickness, within the experimental uncertainty. Although there is a noticeable scatter in the T_g values of Figure 4, it is not dissimilar from any other study of film thickness-dependent T_g values in PS films.[5] As a particular example, we can consider the case of the single layer film of 9.5 nm. The measured T_g of this film is 363 K. The T_g of a 28 nm film made of three 9.5 nm layers is 369 K. This value is similar to the T_g of a one layer 34 nm film (370 K) within the experimental error, and is very different from that of the original 9.5 nm layer. The main conclusion to draw from Figure 4 is that after only 15 min of annealing at 403 K, the multilayered films all take on a T_g value typical of a single film with the *same total thickness*. These films have not had enough annealing to relax the polymer chains from the conformations they adopted in the single layers, and so it is reasonable to say that the T_g
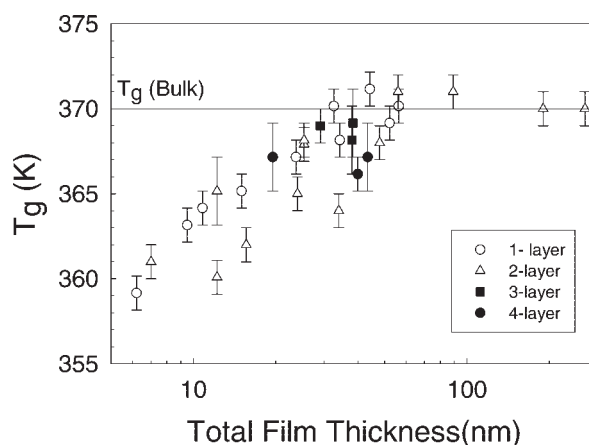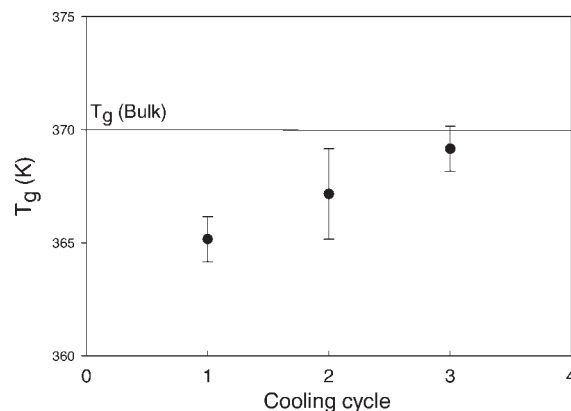

Figure 4 T_g versus film thickness at the end of the third cooling cycle, of one (o), two ($\triangle$), three ($\blacksquare$), and four ($\bullet$) layer films.

reductions of PS films supported on Si wafers are *not* related to chain conformation in the confined geometry of the thin film. Instead, the T_g values depend only on the total thickness of the film. Certainly the films in Figure 4 have had much less annealing than those in typical thin film T_g studies, and thus those studies are not strongly affected by chain conformations. Another way to look at this is to consider the T_g value of a single layer when it is incorporated into a particular sample type. Figure 5 shows the T_g value of 6 and 10 nm layers when they are part of a film of n layers ($1 \leq n \leq 4$) This clearly shows that the T_g values are monotonically increasing with n. This supports the above assertion that it is only the total sample thickness that determines the T_g value.

The high temperature behavior shown in Figure 3 was attributed to interface growth. If this is the case, then the initial multilayer film does have some excess free volume at the interface and one might reasonably expect a slightly lower T_g value. This is similar to what is observed in the interfaces of highly immiscible polymers.[11] To see if this is the case, we can look at the case of a 3 layer film (with 9.5 nm layers) as it is thermally cycled (Fig. 6). The first measurements of T_g has a value of 365 K. This T_g value increases with

Figure 6 T_g values of a three-layer film made of 9.5 nm layers in different cooling cycles.

each annealing cycle, and by the third cycle has a T_g characteristic of a single film of thickness of 3 $\times$ 9.5 = 28.5 nm.

In summary, we have considered the effect of sample preparation history on the T_g of thin PS films by making multilayer films of thin PS, and show that the only important parameter in defining the T_g reduction is the total film thickness, not the thickness of sublayers.

REFERENCES AND NOTES

1. Reiter, G.; Forrest, J. A. (Eds.) Eur Phys J E 2002, 8.
2. Forrest, J. A. Eur Phys J E 2002, 8, 261.
3. Jones, R. A. L.; Richards, R. W. Polymers at Surfaces and Interfaces; Cambridge University Press: Cambridge, 1999.
4. Keddie, J. L.; Jones, R. A. L.; Cory, R. A. Europhys Lett 1994, 27, 59.
5. Forrest, J. A.; Dalnoki-Veress, K. Adv Colloid Interface Sci 2001, 94, 167–195.
6. Frick, B.; Zorn, R.; Buttner, H. (eds.) J Phys 2000, 10, 7.
7. McKenna, G. B. Eur Phys J E 2003, 12, 191.
8. Sharp, J. S.; Forrest, J. A. Phys Rev Lett 2003, 91, 235701.
9. Ellison, C. J.; Torkelson, J. M. Nature Mater 2003, 2, 695.
10. Kawana, S.; Jones, R. A. L. Phys Rev E 2001, 63, 021501.
11. Forrest, J. A.; Dalnoki-Veress J Polym Sci Part B: Polym Phys 2001, 39, 2664.

Figure 5 T_g versus number of layers for films made of 6 nm (△) and 10 nm (o) layers.