Nanomechanical Thermal Analysis of the Glass Transition of Polystyrene Using Silicon Cantilevers

Namchul Jung,[†] Hyejung Seo,[†] Dongkyu Lee,[†] Chang Y. Ryu,[‡] and Sangmin Jeon*,[†]

Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, Korea, and Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy, New York 12180

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The glass transition temperature (T_g) is an important characteristic of amorphous polymers. It can be interpreted microscopically as the onset of long-range, coordinated molecular motion. From a thermodynamic point of view, amorphous polymers above and below T_g are considered to be in equilibrium and nonequilibrium states, respectively. If polymer melts are cooled below T_g over a period that is shorter than the time required for molecular rearrangements to accommodate the temperature changes, the vitrified polymer chains are kinetically trapped in a nonequilibrium state. If the cooling is arrested at a temperature below T_g (or if the polymer is annealed at a temperature below T_g), excesses in thermodynamic quantities such as the specific volume and the enthalpy will be present in the amorphous polymer, and these excesses will drive the polymer toward an equilibrium state and induce reductions in the volume and enthalpy. The reductions continue until the vitrified polymer reaches a near-equilibrium state at the aging temperature. This time-dependent approach toward equilibrium is known as physical aging or structural relaxation.[1]

A number of studies have been performed to investigate the physical property changes near T_g using differential scanning calorimetry (DSC)[2−4] and dilatometry.[5,6] However, these methods are not sensitive enough to directly investigate the interaction between the excesses in thermodynamic quantities and mechanical properties such as creep and stress relaxation.[1] In contrast, cantilever sensors are extremely sensitive to changes in the volume or stress of a material coated onto the cantilever due to their miniaturized bimaterial structure but have mainly been used for the detection of gases and biomolecules.[7−10] When a silicon cantilever coated with any material is heated or cooled, the difference between the volume expansion coefficients of the material and silicon induces the cantilever to bend. In addition, the temperature-dependent modulus change of the coated material induces the shifts in the resonance frequency of the cantilever. Finally, samples of a few nanograms are sufficient for measurements with cantilever sensors, leading to fast thermal equilibrium even for polymers with low thermal conductivity.

A few studies have used cantilevers as miniaturized calorimeters.[11−13] Berger et al. used cantilevers to study the phase transitions of paraffins,[11] and Nakagawa et al. showed that similar measurements could be carried out with a sample mass of 7 pg.[12] However, these studies focused on the melting of paraffins by carrying out deflection measurements rather than on the glass transitions of polymers. Further, the paraffin-coated cantilever was used only as a calorimeter, so they did not relate the mechanical properties of the paraffin to its thermodynamic properties, which is the most important advantage of cantilever sensors. In this study, we coated rectangular silicon cantilevers with polystyrene (PS) to investigate its glass transition behavior. We measured not only T_g but also the in situ changes in volume of the PS induced by physical aging.

PS was purchased from Aldrich (Saint Louis, MO); as indicated by the manufacturer, the weight-average molecular weight and polydispersity were 979 800 g/mol and 1.03, respectively. Toluene was purchased from Aldrich and used without further purification to prepare a 0.5 wt % PS solution. Rectangular silicon cantilevers with a triangular free end were obtained from Nanoworld (Neuchatel, Switzerland). Each cantilever was 500 μm long, 100 μm wide, and 1 μm thick and had a spring constant of ~0.03 N/m. One side of the cantilever was coated with PS by using an inkjet printing method (Cantion, Denmark). The average film thickness was measured to be ~0.4 μm with atomic force microscopy (Veeco, Santa Barbara, CA).

The PS-coated cantilever was mounted on a thin aluminum holder, and its temperature was controlled using a resistance heater with a programmable temperature controller (Hanyoung, Inchon, Korea). After the temperature had been increased from 65 to 155 °C at a rate of 5 °C/min, the heater was switched off, and the cantilever was cooled to 65 °C. The typical cooling time was about 30 min. The heating and cooling cycle was repeated several times to relieve the stress developed during polymer coating. The cantilever deflection and resonance frequency were then measured as functions of temperature with an optical beam technique.[10] The absolute deflection of the cantilever was calibrated using a Wyko NT1100 (Veeco, Santa Barbara, CA).

Figure 1 shows the variations in the resonance frequency of a PS-coated cantilever during three independent cycles of heating and cooling. The measurements were conducted three times and identical responses were found, indicating that these measurements are highly reproducible and reversible. The resonance frequency of the cantilever (f) is a function of its spring constant (k) and effective mass (m), i.e., $f = (1/2\pi)(k/m)^{1/2}$. Since the mass of the coated cantilever is constant during the measurements, the change in resonance frequency is directly proportional to the square root of the spring constant, which is related to the effective Young's modulus of the cantilever (E):[14]

$$k = \frac{Ewt^3}{4l^3} \tag{1}$$

where t, l, and w are the thickness, length, and width of the cantilever, respectively. Note that the spring constant (or the resonance frequency) of the cantilever can be affected by the surface stress effect due to the PS coating, but the change with temperature in the frequency is caused by the variations in the Young's modulus of PS.

A typical viscoelastic response for glass polymers was found and is shown in Figure 1: a gentle decrease in the glass region (~100 °C), a steep decrease in the glass transition region (~130 °C) where the Young's modulus of PS is known to decrease by a factor of 1000, and a rubbery plateau region (>130 °C).[15] The inset in Figure 1 shows the variation with temperature in the resonance frequency of an uncoated silicon cantilever, which is almost constant, indicating that the changes in the Young's modulus of PS are responsible for the changes in the

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* To whom correspondence should be addressed. E-mail: jeons@postech.ac.kr.
[†] Pohang University of Science and Technology.
[‡] Rensselaer Polytechnic Institute.

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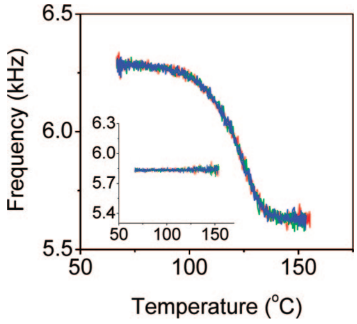

Figure 1. Variations in the resonance frequency of the cantilever during three thermal cycles (blue, first; green, second; red, third). The inset shows the variation in the resonance frequency of an uncoated silicon cantilever with temperature.

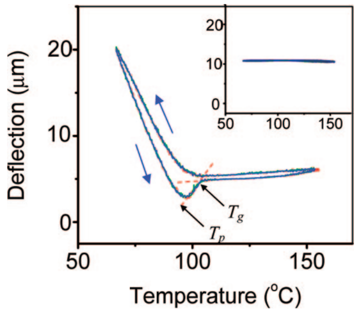

Figure 2. Variations in the deflection of the cantilever with temperature (measured at the same time as the resonance frequency in Figure 1). The inset shows the variation in the deflection of an uncoated silicon cantilever with temperature.

resonance frequency of the PS-coated cantilever.

The deflections of the PS-coated cantilever were measured at the same time as the resonance frequency, confirming the reproducibility and reversibility of the measurements. Three characteristic regimes were reproducibly observed for the variation in the deflection of the PS-coated cantilever upon the heating and cooling cycles, as shown in Figure 2, and these regimes are different from the viscoelastic regimes in Figure 1. The inset in Figure 2 shows a control experiment of the deflection of the uncoated silicon cantilever, which is almost constant with temperature in spite of the slight change in the deflection possibly due to the desorption of water from the cantilever upon heating. This strongly supports that the changes in the deflection of the PS-coated cantilever are induced by the differential thermal expansion/contraction between the PS and silicon cantilever. A decrease in the deflection of the cantilever implies an expansion of the PS volume. As the PS-coated cantilever was heated from 65 °C, the PS volume increased for temperatures up to ~90 °C (regime I) and then *decreased* for temperatures up to ~102 °C (regime II). The temperature at which the PS volume starts to decrease upon heating from the glassy state is denoted T_p. Further heating to 155 °C resulted in almost constant deflection (regime III).

T_g was determined to be 103 °C from the intersection of the tangents to the curves in regimes II and III, which is close to the value obtained from DSC measurements.[16] Although the volume expansion with temperature of PS above T_g is known to be larger than that below T_g,[6] the deflection is almost constant in regime III. This result can be understood in terms of the substantial changes in the modulus of PS during the glass transition shown in Figure 1. Since the Young's modulus of a silicon cantilever is ~170 GPa and the modulus of polystyrene below and above T_g are ~3 GPa and ~0.002 GPa, respectively,[15] above T_g the PS is too soft to deflect the silicon cantilever.

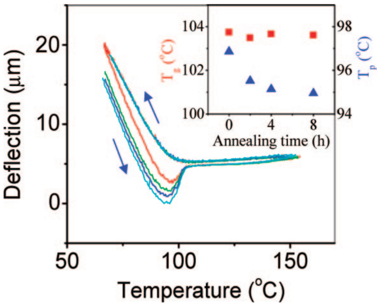

Figure 3. Variations in the deflection of the PS-coated cantilever with temperature after annealing at 65 °C for 0 h (red), 2 h (light green), 4 h (blue), and 8 h (sky blue). The inset shows the variations in T_g (square) and T_p (triangle) with annealing time.

However, the constant deflection in regime III does not mean that the cantilever is stress-free. On the contrary, this result implies that the PS-coated cantilever is still bent but that no further bending occurs during heating above T_g. The PS coating on the silicon cantilever induces the cantilever to bend toward the PS side, and the PS-coated cantilever experiences a tensile stress throughout the experiments as shown in Figure 2. Therefore, the plateau in regime III can be attributed to the balance between the volume expansion of PS and the tensile stress of the cantilever.

Once the temperature reached 155 °C, the heater was switched off, and the cantilever was cooled to 65 °C. Constant deflection was again observed in regime III. Further cooling below T_g resulted in a monotonous decrease in PS volume, and the deflection returned to its initial value at 65 °C. It is important to notice that a substantial hysteresis was observed in the deflection during heating and cooling, whereas no hysteresis was observed in the resonance frequency. We tentatively attribute the hysteresis to the physical aging of PS.

To investigate the influence of the time-dependent physical aging on the hysteresis, we annealed the PS-coated cantilever at two different sub-T_g temperatures for various lengths of time: (1) 65 °C ($T \ll T_p$) and (2) 90 °C ($T \sim T_p < T_g$). Figure 3 shows that the PS volume at 65 °C increases with annealing time, inducing a larger hysteresis in the subsequent heating and cooling cycle. Further, T_p decreases with the annealing time since the stress relaxation during the annealing facilitates the molecular rearrangements required for physical aging to occur. When the cantilever was heated above T_g after annealing, the subsequent deflections were found to be the same, regardless of how long the PS was annealed at 65 °C. This indicates that the annealing effect finally disappears once the polystyrene has undergone the glass-to-melt transition upon heating. The variation in the resonance frequency with the annealing time was also measured, but none was found, probably because of insufficient sensitivity. The inset in Figure 3 summarizes the variations in T_g and T_p for various annealing times. Note that T_g is almost constant with annealing time whereas T_p decreases.

In contrast, the annealing of the cantilever at 90 °C produces quite different results from annealing at 65 °C. The deflection of the PS-coated cantilever is minimum at ~90 °C, at which temperature PS has enough energy to induce physical aging (or local chain ordering). Figure 4 shows the variations in the deflections of the cantilever with temperature after annealing at 90 °C for various lengths of time. Each measurement was conducted after the cantilever had been subsequently cooled to 65 °C after annealing at 90 °C. Both T_p and T_g increase with

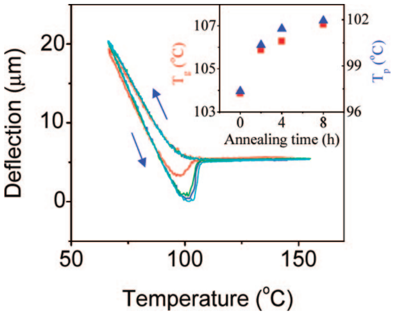

Figure 4. Variations in the deflection of the PS-coated cantilever with temperature after annealing at 90 °C for 0 h (red), 2 h (light green), 4 h (blue), and 8 h (sky blue). The inset shows the variations in T_g (square) and T_p (triangle) with annealing time.

the annealing time at 90 °C. This would be attributed to the local chain ordering of PS (or the decrease in the free volume in PS) via the physical aging that favors the formation of locally ordered chains with higher T_p and T_g. The inset in Figure 4 summarizes the variations in T_g and T_p for various annealing times at 90 °C. This effect disappears once the polystyrene has undergone the glass-to-melt transition.

In conclusion, we have used the PS-coated silicon cantilever to determine the thermomechanical and physical properties of the PS sample in the vicinity of the glass transition temperature. By measuring the variations of the resonance frequency and deflection of the cantilever with temperature, we obtained the temperature dependence of the effective modulus and volume change of the PS samples that have different physical aging history in the glassy state. These results indicated that the nanomechanical thermal analysis technique using polymer-coated silicon cantilevers could serve as a useful method to experimentally probe the volume expansion and contraction of the amorphous polymers in the glassy state upon heating. We are in the process of extending our studies to the polymer films at various thicknesses.

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