Communications to the Editor

Thin-Film Differential Scanning Calorimetry: A New Probe for Assignment of the Glass Transition of Ultrathin Polymer Films

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Glass transition in ultrathin polymer films is the subject of intense interest due to theoretical and experimental issues regarding size-dependent effects in finite systems.[1,2] The small sample size presents unique challenges to experimentalists, and subsequently a variety of techniques have been utilized[1−5] with varying results. The standard technique for glass transition studies[6,7] is differential scanning calorimetry (DSC), which is of special interest in this field because it yields absolute thermodynamic properties such as heat capacity. However, it is difficult to use conventional DSC systems on ultrathin samples because of the insufficient sensitivity. In this paper we demonstrate a recently developed MEMS-based thin-film differential scanning calorimetry (TDSC) device (also referred to as nanocalorimetry) which shows potential for studies of glass transition for films with nanometer-range thickness. In our previous work in polyethylene[8] and metals[9−11] we have measured the heat capacity, heat of fusion, and melting temperature for discontinued films with average thickness of less than 1 nm.

The TDSC technique is described in detail elsewhere.[8−11] In brief, TDSC uses a microfabricated sensor shown in Figure 1 as a calorimetric cell. The sensor consists of a Si_3N_x membrane supported at the perimeter by a Si substrate. A 500 μm wide metal strip is deposited on the membrane and functions both as a heater and as a

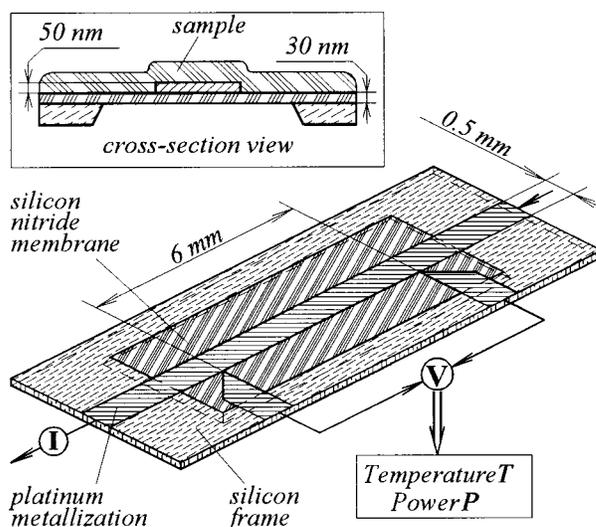* Corresponding author. E-mail: L-ALLEN9@uiuc.edu.

Figure 1. MEMS-based calorimetric sensor for TDSC (not to scale).

thermometer/RTD. Platinum is used as a material of choice for the metal strip due to its enhanced time stability of electrical resistance. The Pt heater/thermometer, the Si_3N_x membrane directly beneath it, and a sample film deposited on either the Pt or Si_3N_x surface form a sample calorimetric cell. The extremely low thickness of the Pt strip (50 nm) and Si_3N_x membrane (30 nm) provides a mass addenda, which is small enough to measure the heat capacity (C_p) of nanometer-thick films. The high-sensitivity differential mode is achieved by using the second reference sensor which is identical to the polymer-coated sample sensor but has no material on it.[11] Before the experiment, the resistance of both sensors is calibrated against the temperature in a three-zone tube vacuum furnace.

The measurement is initiated by supplying a short pulse of electric current to the Pt strip. This rapidly increases the temperature of the cell by Joule heating. The vacuum environment ($10^{-7}−10^{-8}$ Torr) and high
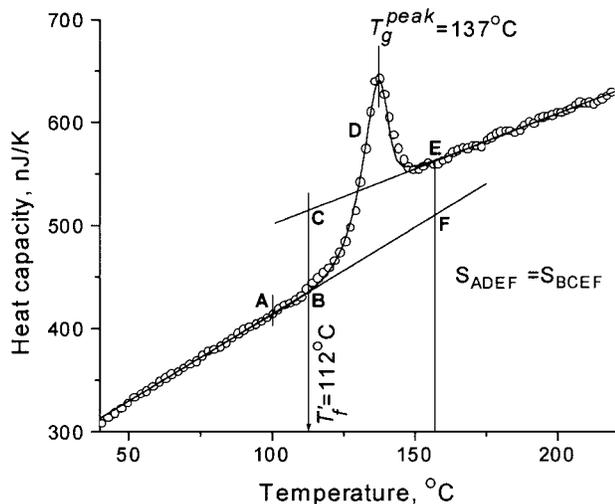
Figure 2. Calorimetric curve for 80 nm thick polystyrene on platinum, scanning rate 25 K/ms. Values of T_g^{peak} and T_f' are shown. To calculation of T_f': points A and E lie on the linear part of the curve.

heating rates v_{heat} (20–100 K/ms) provide near-adiabatic conditions. The voltage across the heater and current through it are monitored in real time during the pulse and are used for calculation of the electrical power (P) and resistance (R) of the metal strip. The temperature (T) is calculated using an $R(T)$ function. Using P and T as functions of time, the $C_p(T)$ function is expressed.

As a model polymer system, we choose polydispersed polystyrene (PS) with $\bar{M}_w$ = 280 000 g/mol, obtained from Aldrich Chemical Co., Inc. The PS film on the sensor was formed by a standard spin-casting technique with speed of rotation of about 10 000 rpm. Toluene solutions of the polymer with concentration ranging from 0.1 to 3% generated films with thickness ranging from 2 to 100 nm. The spin-cast method produces PS films with variation in the thickness of about 10% on the working part of the Pt strip. Film thickness was measured by focused ellipsometry (FOCUS ellipsometer FE-III, Rudolph Technologies, Inc.) which has a spot size of 12 μm × 24 μm. Furthermore, the ellipsometry thickness agrees with the measured change in the heat capacity of the calorimeter due to the addition of the PS film.

TDSC scans for PS samples were performed from room temperature up to 240 °C. After heating, the sample cell was passively cooled. The cooling rate v_{cool} was fixed for given calorimetric cell. A typical value for v_{cool} was 1 K/ms at a temperature of 100 °C (temperature within the glass transition region) which was several orders of magnitude greater than in conventional DSC.

Heating during the first scan of as-deposited PS sample produced a $C_p(T)$ curve that was different from data of the subsequent scans. Noticeable endothermic effects can be caused by releasing of solvent residue; the aging process can also take place. After the initial bake-out, the calorimetric curves are remarkably reproducible even through several thousand scans. This means that once heated and quenched the film remains stable during subsequent temperature scans, which allows us to obtain the resultant calorimetric curve consisting of an average of 1000 scans.

Typical $C_p(T)$ data for 80 nm thick polystyrene film are shown in Figure 2. The peak in the plot (hysteresis peak) is characteristic for experiments where v_{heat}/v_{cool}

$\gg 1$.[12] The last condition is essential for TDSC in order to achieve a near-adiabatic regime.

The conventional characteristic parameter of the glass/liquid transition region—the glass transition temperature T_g—is expressed on the plot by the peak temperature T_g^{peak} (137 °C) and the limiting fictive temperature T_f' (112 °C). This last term is defined as the temperature of intersection of the extrapolated equilibrium liquid and glass enthalpy vs temperature curves.[12,13] The practical way of the T_f' calculation is shown in Figure 2. These values are significantly higher than those obtained by the conventional DSC experiments of bulk samples. A high cooling rate leads to a less stable glass state, which corresponds to increasing of the glass transition temperature. In addition, since $v_{heat} \gg v_{cool}$, the hysteresis peak is well-defined and shifted toward higher temperatures.[12,13] Conventional DSC measurements of samples with similar molecular weight (for v_{heat} = (5–150) × 10^{-3} K/s and v_{heat}/v_{cool} = 0.5–10^3) report values of T_g^{peak} to be in the range of 103–110 °C and T_f' to be in the range of 92–103 °C.[14,15]

In addition to temperature characteristics, a more detailed description of the glass transition can be obtained using modern relaxation models.[16] To demonstrate the application of the widely used Tool–Narayanaswamy–Moynihan (TNM) model,[13] calorimetric curves were fitted using an algorithm described elsewhere.[16] All four parameters of this model—activation enthalpy Δh^*, exponent coefficient A, stretch exponent β, and nonlinearity parameter x—are found by simultaneous fitting of several curves, obtained with different v_{heat}. Optimization is performed by the set of methods (Levenberg–Marquardt, Gauss–Newton, simplex, quasi-Newton) implemented in the Optimization Toolbox of MATLAB software (release 12).[17] The optimum fit of the curve presented in Figure 2 is shown on the same plot by a solid line. Best-fit parameters for 80 nm thick polystyrene films are $\Delta h^*/R$ = 28 kK, ln A (s) = −76, β = 1.0, and x = 0.8 (where R is the gas constant). To a certain extent, these values can be compared with results of conventional DSC studies. High values of β and x are typical for polystyrene (see table in ref 16) and have been reported even as high as 0.83 ± 0.1 and 0.64 ± 0.1, respectively.[18] However, we found that the value of $\Delta h^*/R$ is significantly smaller than reported values for conventional DSC (53–175 kK).[16]

We also investigated the glass transition in thin PS films using an alternative method by combining isothermal annealing with the TDSC scan of the sample following the annealing. This method more closely corresponds to the time scale used in conventional DSC. After cooling from a TDSC scan, the sample was isothermally annealed at a specific temperature T_{ann} for 60 s and then cooled to the ambient temperature slowly with cooling rate of 2K/s or less (the cooling rate did not depend on T_{ann}). The time scale for annealing should be significantly larger than the time of DSC scan (12 ms in this case) and was chosen in order to provide adequate statistics in a reasonable time of experiment, although there are no system-specific limitations for the annealing time. Then the TDSC measurement was performed. The first scan after annealing reveals a characteristic response, which depends on T_{ann}. We expect that in the first approximation the state of the isothermally annealed PS films would be invariant with T_{ann}, if $T_{ann} \gg T_g$. This is because ideally a liquid does not keep a memory of its thermal treatment. Conse-
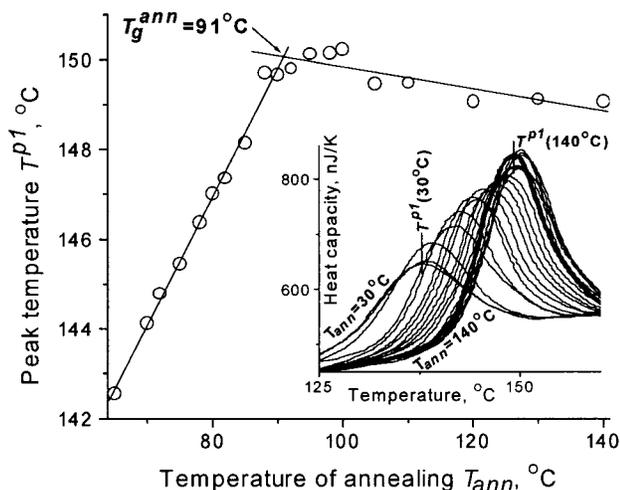
Figure 3. Calculation of T_g^{ann}. The sample is the same as in Figure 2. The set of the first run calorimetric curves after annealing at different temperatures is shown in the inset.

quently, the dependence of the first scan response on the T_{ann} would be negligible. In contrast, for films isothermally annealed at $T_{ann} < T_g$ the thermal history of the film effectively changes with the T_{ann}. In this case there would be a strong dependence of the first scan calorimetry response after annealing on the T_{ann}. It is worth noting that in this type of experiment the TDSC technique is used only as an indicator of the film state after annealing: whether or not it changes with T_{ann}. The peak temperature of the first-scan curve T^{p1} is a convenient measure of the change in the first scan calorimetry response with annealing due to its sensitivity to T_{ann} and stability with regard to the extraneous effects of the adsorption/desorption of the residual gases in the vacuum chamber (although the height of the peak and other characteristics could be used). The T^{p1} vs T_{ann} dependence is shown in Figure 3. During the experiment the T_{ann} was changed in both directions to ensure that there were no memory effects. The T_g for annealed samples (T_g^{ann}) is calculated as a temperature of break of $T^{p1}(T_{ann})$ function.

These data represent, to our knowledge, the first direct calorimetry measurements of the glass transition phenomenon for thin-film material. Detailed discussion of the calorimetric studies of polystyrene thin films for various thicknesses made by TDSC technique will be presented in future publications. Preliminary results shown here demonstrate the utility of the TDSC technique for studying the glass transition features in thin polymer films.

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