

## Glass Transition in Ultrathin Polymer Films: Calorimetric Study

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The ultrasensitive differential scanning calorimetry is used to observe the glass transition in thin (1–400 nm) spin-cast films of polystyrene, poly(2-vinyl pyridine) and poly(methyl methacrylate) on a platinum surface. A pronounced glass transition is observed even at a thickness as small as 1–3 nm. Using the high heating (20–200 K/ms) and cooling (1–2 K/ms in glass transition region) rates which are typical for this technique, we do not observe appreciable dependence of the glass transition temperature over the thickness range from hundreds of nanometers down to 3 nm thick films. The evolution of calorimetric data with film thickness is discussed in terms of broadening of transition dynamics and loss of transition contrast.

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The glass transition in thin polymer films attracts tremendous experimental attention [1–5]. Numerous methods are being used to observe glass transition in films which are less than 100 nm thick. However, comparison of results given by different techniques, particularly concerning dependence of glass transition temperature on film thickness, is an actively discussed topic in the field.

The standard technique to observe the glass transition in bulk materials is differential scanning calorimetry (DSC) [4,6]. Calorimetry takes a special place among other methods. In addition to its simplicity and universality, the energetic characteristics (heat capacity  $C_p$  and its integral over temperature  $T$  — enthalpy  $\Delta H$ ), measured via DSC, have a clear physical meaning. The significant part of theoretical considerations and glass transition models are constructed on the basis of  $\Delta H(T)$  functions, which are obtained using calorimetry. Up to now, heat capacity data of thin polymer films have not been available because of the limited sensitivity of commercial DSC devices.

Here we report calorimetric measurements on extremely thin (< 10 nm) polymer films made possible with the development of the ultrasensitive thin-film DSC technique (nanocalorimetry) [7]. Our sensor (Fig. 1) consists of a thin  $\text{SiN}_x$  membrane (40–400 nm thick and several mm in height and width) supported by a Si frame. Sensors with a thick membrane are used for thick (70–80 nm and above) polymer films in order to resist the internal stress in the  $\text{SiN}_x$ /polymer system. A Pt heater strip (~ 50 nm thick) is deposited onto one side of the membrane. By inducing a short pulse of current through it, such a heater serves both to heat the membrane and to measure its temperature. The values of voltage and current across the heater are used for power and temperature calculations, and, finally, for the calculation of  $C_p(T)$  dependence. Very fast heating, varied from 20 to 200 K/ms, allows the sensor to operate in nearly adiabatic conditions.

Three types of monodispersed atactic polymer were investigated: polystyrene (PS),  $M_w = 120\,200$ ,  $M_w/M_n = 1.04$ , poly(2-vinyl pyridine) (PVP),  $M_w = 138\,000$ ,  $M_w/M_n = 1.30$ , and poly(methyl methacrylate) (PMMA),  $M_w = 105\,400$ ,  $M_w/M_n = 1.04$ . In order to observe the effects of different molecular weight, several experiments with high molecular weight polystyrene (PS-H),  $M_w = 10\,200\,000$ ,  $M_w/M_n = 1.22$  were made. All samples were obtained from Polymer Source, Inc. These glass-forming polymers are widely used for studies

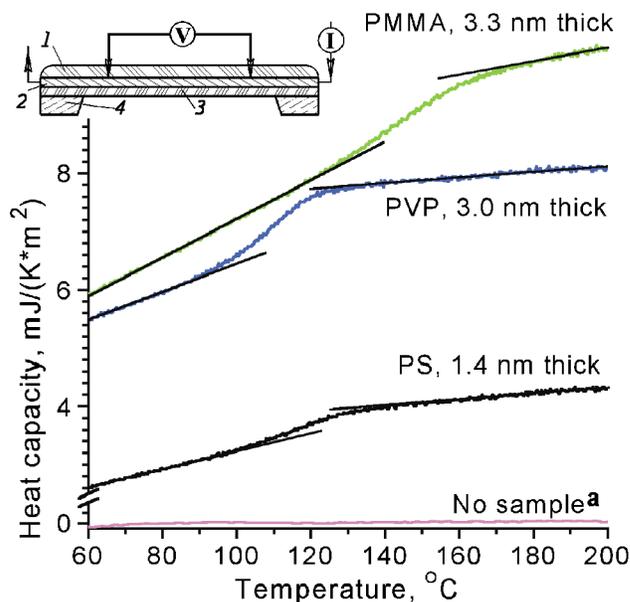


FIG. 1 (color).  $C_p(T)$  curves for 1–3 nm thick films. Straight lines denote glass and liquid  $C_p(T)$  functions. The heating rate is 30–40 K/ms (at the glass transition region – 100–160 °C).  
a— control experiment using a pure solvent for the film deposition. Inset: nanocalorimetry sensor, cross-section view (not to scale): 1 — polymer film, 2 — Pt heater/thermometer, 3 —  $\text{SiN}_x$  membrane, and 4 — Si frame.

of glass transition in thin films [4]. The films were formed by the spin-cast method from polymer solutions on the Pt heater of the sensor. The solvent used for PS and PMMA is toluene and for PVP is *n*-butanol. Film thickness was controlled both by varying the concentration of solution and the speed of rotation. The average thickness of film on the heater was calculated from  $C_p(T)$  at room temperature, using specific heat capacity for bulk substance. Additionally, the local film thickness on the heater at 15 different spatial points was measured (both before and after calorimetric measurement) *ex situ* by focused ellipsometry (Focus Ellipsometer FE-III, Rudolph Technologies, Inc.) with spot size  $12 \times 24 \mu\text{m}$ . The deviation of any local thickness from average value does not exceed  $\pm 10\%$  except the thickest (56 nm) PS-H sample. The agreement between average thickness obtained by ellipsometry and the one obtained by calorimetry in 90% of cases is better than  $\pm 10\% \pm 0.2 \text{ nm}$ . The roughness of selected samples of PS, PVP, and PMMA on sensors was measured by atomic force microscopy (AFM) (Digital Instruments Dimension 3000) after all calorimetric and ellipsometric measurements. The roughness of the thinnest films (1–2 nm) on the heater is equal to the roughness of the bare heater itself—about 1.5 nm of rms value. The roughness of thicker films decreases gradually with thickness. The AFM measurements show that the polymer film on the Pt heater is uniform to the level of 1.5 nm.

After spin casting and ellipsometry measurements, the samples were annealed in vacuum for 1000 s at  $140^\circ\text{C}$  for PS and PVP and at  $160^\circ\text{C}$  for PMMA. After annealing,  $C_p(T)$  curves demonstrate remarkable reproducibility through the whole experiment. Then DSC scans were performed under UHV ( $1\text{--}4 \times 10^{-8}$  torr) starting from room temperature up to  $240^\circ\text{C}$  for PS and PVP, and up to  $260^\circ\text{C}$  for PMMA. The scans were performed at eight different heating rates in the range of 20–200 K/ms. After reaching the maximum temperature during each scan, the sample was passively cooled at a rate of 1–2 K/ms over the 200– $100^\circ\text{C}$  range (where the glass transition occurs). The calorimetric data used in this Letter are averages of 300 consecutive scans taken at 1 s time intervals.

We observe a pronounced glass transition in films with thickness down to the level of 1–3 nm for all investigated polymers. Figure 1 shows the  $C_p(T)$  curves for the thinnest PS (1.4 nm), PVP (3.0 nm), and PMMA (3.3 nm) samples. To our knowledge, this is the first direct evidence that glass transition exists at such a small thickness.

The glass transition temperature,  $T_g$ , is assigned using the concept of limiting fictive temperature ( $T'_f$ ) [8]. It is defined as the temperature of intersection of the extrapolated equilibrium liquid and glass  $\Delta H(T)$  curves. Use of this definition minimizes the influence of complex relaxation effects in the vicinity of the glass transition on the assignment of  $T_g$ .

Figure 2 shows  $T'_f$  as a function of film thickness. As expected,  $T'_f$  for thickest (bulklike) films are 10–20 K

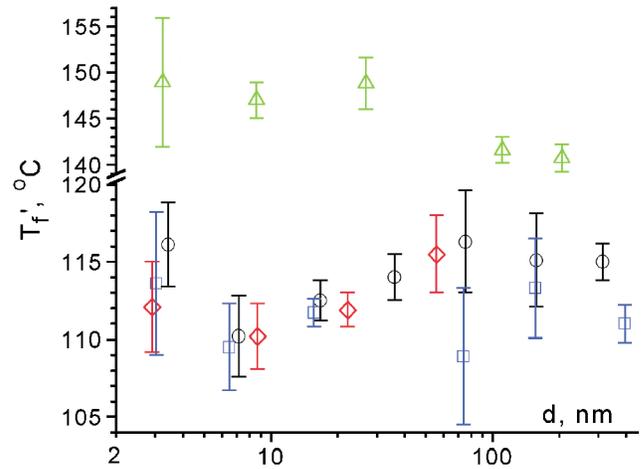


FIG. 2 (color).  $T'_f$  as a function of film thickness.  $\circ$  for PS;  $\diamond$  for PS-H;  $\square$  for PVP;  $\triangle$  for PMMA. Error bars denote the standard deviation of eight measurements with different heating rates.

higher than values obtained from conventional DSC [9] due to the fast cooling used in our technique [8].

Our data show no appreciable dependence of  $T'_f$  on film thickness from about 3 nm up to several hundred nanometers for all investigated polymers (Fig. 2). The fact of constancy of  $T'_f$  over a wide range of thickness is consistent with the conclusion [1] that  $T_g$  depression for thin films, measured by some other methods, is caused primarily by the broadening of the glass transition. It is also possible that the absence of  $T_g$  size dependence may be related to the high heating/cooling rates, which are inherent in our technique. This is consistent with the recent dielectric measurements of [10] on isotactic PMMA which indicate that there is no size dependence of  $T_g$  on the millisecond time scale—a time scale which corresponds to our high heating/cooling rates.  $T'_f$  for the thinnest (1–1.5 nm thick) PS and PS-H films (not shown) appears to be 10–15 K larger than the average value for PS.

Figure 2 demonstrates no significant difference in  $T_g$  among polystyrene of a different molecular weight, PS, and PS-H. For comparison, the radius of gyration, estimated from the formula  $R_g = 0.028(M_w)^{0.5}$  (nm) [11], is equal to 10 nm for PS and 90 nm for PS-H. So, if a noticeable  $M_w$  effect exists, it should appear in the shown range of thickness. The absence of the effect is in agreement with the conclusion of [1].

The broadening of the glass transition in our experiments indeed takes a major contribution in the evolution of the shape of calorimetric curves with decreasing of film thickness for all investigated polymers. This trend is illustrated in Fig. 3 for selected PS samples, using normalized heat capacity  $C_p^N(T)$ . Normalization means linear transformation of  $C_p(T)$  curves so that the  $C_p$  for glass is equal to 0 and the  $C_p$  for liquid is equal to 1. The broadness of the transition can be characterized by the

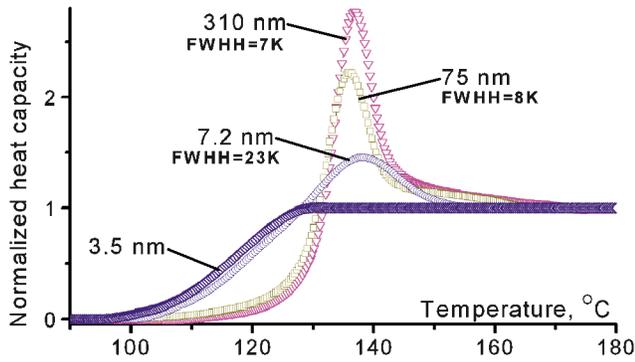


FIG. 3 (color). Normalized  $C_p(T)$  curves for PS films of different thicknesses. Heating rate — see Fig. 1 caption.

width of the “overshooting” peak, where the full-width-on-the-half-height (FWHH) value can be calculated from normalized  $C_p^N(T)$  curves, taking  $C_p^N_{\text{maximal}}/2$  as the half height on the low temperature side of the peak and  $(C_p^N_{\text{maximal}} - 1/2)$  as the half height on the opposite side. As the thickness decreases, the width of the overshooting peak increases, and the height of the peak decreases. For very small thickness (3 nm and less) an obvious overshooting peak is not observed (see Fig. 1).

In terms of relaxation models, the broadening of glass transition can be expressed as widening of the characteristic relaxation time spectrum. For the commonly used stretched exponent form of relaxation function  $\phi(t) = \exp[-(t/\tau)^\beta]$ , where  $t$  — time,  $\tau \in ]0, \infty[$ , and  $\beta \in ]0, 1[$  are constants, the value of  $\beta$  characterizes the broadness of the spectrum: the smaller  $\beta$  the broader the time distribution.

The calculation of  $\beta$  is performed by the fitting of  $C_p(T)$  curves using the Tool-Narayanaswamy-Moynihan model, as described elsewhere [7]. Eight curves, obtained at different heating rates (20–200 K/ms) are fitted simultaneously. Figure 4 displays  $\ln(\beta)$  as a function of reciprocal thickness  $1/d$ . The linear dependence in these coordinates corresponds to the equation  $\beta = \beta_\infty \exp(-A/d)$  (where  $\beta_\infty$  and  $A$  are constants), which represents the natural extension to a small thickness of the linear form  $\beta = \beta_\infty(1 - A/d)$ , suggested by [12]. Parameter  $A$  has the meaning of a characteristic length scale for the broadening of the relaxation time spectrum. The exponential form gives non-negative  $\beta$  while  $d \leq A$ , and approximates the linear form while  $d \gg A$ .

Linear fitting of  $\ln(\beta)$  as a function of  $1/d$  for PS gives  $A_{\text{ps}} = (4.9 \pm 0.4)$  nm, which is in excellent agreement with the value  $(5.2 \pm 0.4)$  nm, given by [12]. The value for PVP is  $A_{\text{pvp}} = (4.9 \pm 0.5)$  nm, for PMMA  $A_{\text{pmma}} = (3.4 \pm 0.3)$  nm.

The ability of our technique to observe the glass transition in 1–3 nm thick films can be discussed in terms of the loss of glass transition contrast as the film thickness decreases — the difference between glassy and liquid

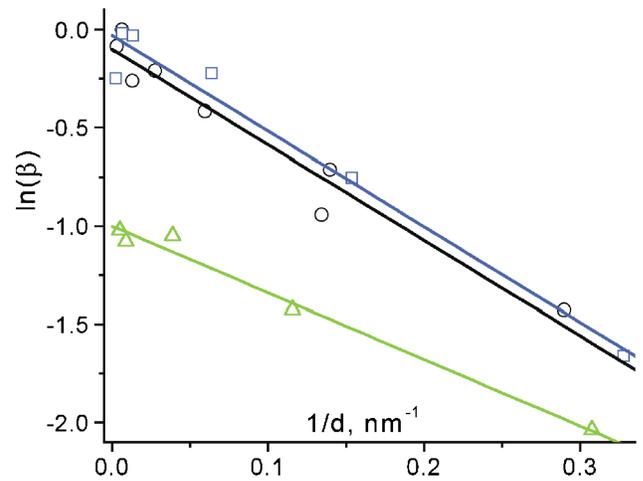


FIG. 4 (color). Logarithm  $\beta$  as a function of reciprocal film thickness. Lines represent a linear fit of data.  $\circ$  for PS;  $\square$  for PVP;  $\triangle$  for PMMA.

states vanishes. A natural gauge for the transition contrast loss in calorimetric experiments is the relative difference between  $C_p(T)$  of liquid and glass, extrapolated to the  $T_f'$ :  $\delta = [C_p^{\text{liquid}}(T_f') - C_p^{\text{glass}}(T_f')]/C_p^{\text{liquid}}(T_f')$ . Figure 5 displays  $\ln(\delta)$  as a function of  $1/d$ . The linear plot, as in the case of  $\beta$ , corresponds to the equation  $\delta = \delta_\infty \exp(-B/d)$  (where  $\delta_\infty$  and  $B$  are constants). In this case the slope  $B$  has the meaning of a characteristic length scale for the transition contrast loss. Linear fitting gives values for PS  $B_{\text{ps}} = (1.0 \pm 0.2)$  nm, for PVP  $B_{\text{pvp}} = (1.3 \pm 0.2)$  nm, and for PMMA  $B_{\text{pmma}} = (2.0 \pm 0.1)$  nm. The significant difference between  $A$  and  $B$  suggests that the two corresponding effects, broadening of transition dynamics and loss of transition contrast, probably have

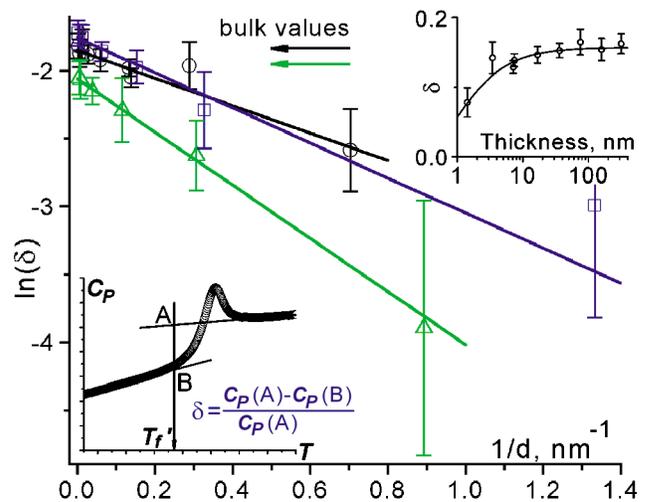


FIG. 5 (color). Logarithm  $\delta$  as a function of reciprocal film thickness. Lines represent a linear fit of data.  $\circ$  for PS;  $\square$  for PVP;  $\triangle$  for PMMA. Error bars — see the Fig. 2 caption. Bulk values for  $\delta$  are calculated using  $C_p(T)$  [6] and bulk  $T_f'$  [9]. The upper inset shows  $\delta$  as a function of thickness for PS.

different origins. It should be noted that our measurements allow us to make a clear separation between these two effects: we determine  $\beta$  and  $A$  using  $C_p(T)$  data in the vicinity of glass transition; however,  $\delta$  and  $B$  are calculated from the  $C_p(T)$  values of the liquid and glass, which are far away from the transition region.

The effect of the loss of transition contrast is used in literature to estimate parameters of layer models [1,2,4,11–14]. These models assume that polymer films may contain special layers at their interfaces with vacuum (air) and substrate, where the glass transition does not occur. These layers can act as a permanent liquidlike (L) layer or as a dead (D) layer with almost no molecular mobility. The total thickness  $d_{(D+L)}$  of such (D + L) layers is estimated to be about 10 nm [11–14] for PS. Obviously, these models predict that  $\delta$  would be the linear function of  $1/d$ :  $\delta = \delta_\infty(1 - b/d)$ , where  $d_{(D+L)} = b$ . The fitting of our data by this equation gives for PS  $b_{ps} = (0.8 \pm 0.1)$  nm, for PVP  $b_{pvp} = (0.6 \pm 0.1)$  nm, and for PMMA  $b_{pmma} = (0.9 \pm 0.1)$  nm, which are at least an order of magnitude less than values of  $d_{(D+L)}$ . The simple evidence of the negligible amount of (D + L) layers in our experiments is the clear glass transition in 1–3 nm thick films, demonstrated in Fig. 1.

The linear relationship between glass transition contrast data and  $1/d$  was used to characterize the loss of contrast in ellipsometric [14,15] and x-ray reflectivity studies [16] of polystyrene films. The characteristic length scales are  $b_{ps}^{E1} = (8.0 \pm 0.8)$  nm,  $b_{ps}^{E2} = 6$  nm, and  $b_{ps}^X = 40$  nm, respectively (the last two values are estimated from the plot in [2]). While characteristic lengths for ellipsometric studies are close to each other ( $b_{ps}^{E1}$  and  $b_{ps}^{E2}$ ), the difference between two extreme values ( $b_{ps}$  and  $b_{ps}^X$ ) is more than 1.5 order of magnitude. It is reasonable to suppose that loss of transition contrast strongly depends on the type of experimental parameters used for glass transition observation rather than reflects layered structure of the films. It is worth noting that since good contrast is the essential condition for a successful observation of glass transition, the reported calorimetric technique, characterized by small  $b$ , is also attractive in terms of transition contrast as a glass transition probe in thin polymer films.

In conclusion, we observe a pronounced glass transition for films of PS, PVP, and PMMA with thicknesses as small as 1–3 nm. Using the high heating (20–200 K/ms) and cooling (1–2 K/ms in glass transition region) rates which are typical for this technique, we do not observe an appreciable dependence of  $T_g$  over the thickness range from hundreds of nanometers (bulklike films) down to 3 nm thick films. In addition, no appreciable effect of

molecular weight on the  $T_g$  for PS is registered. Experimental data for all used polymers demonstrate both broadening of glass transition and loss of transition contrast effects while film thickness decreases.

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