Temperature-Modulated Ellipsometry: A New Probe for Glass Transition in Thin Supported Polymer Films

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Temperature modulation (TM) is a modification of various instrumental techniques, where the parameter of interest is monitored while the temperature of the sample oscillates. TM effectively separates reversible from irreversible processes. Selective ac amplifiers and lock-in detectors ensure high sensitivity of TM methods.[1] TM is particularly useful in combination with scanning techniques for separation of overlapping transitions. Temperature-modulated differential scanning calorimetry (TMDSC) is well-known method in material characterization,[2] although many other TM methods exist: TM thermomechanical analysis,[3] TM dilatometry,[1] TM dielectric analysis (TMDA),[4] to name a few.

In this work we introduce temperature-modulated ellipsometry (TMEll) in combination with temperature scanning of a supported thin film sample. TMEll selectively filters out irreversible thermal transitions that do not follow repetitive changes in temperature. In contrast, standard ellipsometry records reversible processes (for example, glass transition) as well as irreversible ones. Here we demonstrate the advantages of TMEll for probing glass transition in thin supported films of model polymer glass-formers: atactic polystyrene (PS) and poly(methyl methacrylate) (PMMA).

The experimental system and conditions are described in detail elsewhere.[5] Probing of thin films requires an extremely clean environment. Oxidation, uptake of water, and other contaminants alter the interfacial part of a sample. Since a substantial part of a thin film sample is comprised of interface layers, experiments in this field are sensitive to the quality of the environment. In our experiments we use an ellipsometer coupled with a vacuum chamber where the sample is situated. Both the primary and secondary vacuum pumps are oil-free. The chamber has a liquid nitrogen trap in the sample's vicinity to reduce water uptake. Residual gas pressure is kept below 10^{-7} Torr during a typical experiment. A working vacuum ionization gauge can affect the polymer sample.[5] Elevated temperature of the sample increases the effect. The gauge left off during a temperature scan and switched on for a few minutes before and after the scan, when the sample was at room temperature, to monitor the vacuum level in the chamber. PS ($M_w = 212$ kg/mol, $M_w/M_n = 1.05$) and PMMA ($M_w = 159$ kg/mol, $M_w/M_n = 1.09$) are obtained from Polymer Source, Inc. Supported polymer films are made by spin-coating of filtered polymer solutions in toluene on polished silicon wafers in a class 100 clean room. Annealing of the samples is performed in situ at the maximal temperature T_{max} achieved in the experiment ($T_{max} = 160$ °C for PS and $T_{max} = 180$ °C for PMMA) for at least 6 h.

Experiments in the regular scanning mode are performed by heating the sample up to T_{max} and cooling down to 20 °C linearly. Both heating and cooling rate in this mode are equal to 1 K/min. The ellipsometric angle Δ is monitored during the temperature change. Data are represented in the form of $d\Delta/dT$ vs temperature T function. In the TM scanning mode, the linear dependence of T on time t is modulated by means of pulse-width modulation of the heater power. The period of the modulation t_P is constant, and the duty cycle either increases in the heating regime or decreases during cooling. Typical values of t_P are 300 and 600 s. The peak-to-peak temperature amplitude T_{P-P} slightly varies throughout the scan. T_{P-P} is close to 10 K for $t_P = 300$ s and to 20 K for $t_P = 600$ s for the greater part of the scan. The average temperature of a cycle T_{AV} changes with time at a rate of 0.1 K/min—much slower than in the regular mode. The experimental data are represented as a slope of the $\Delta(T)$ curve for each modulation cycle, $(d\Delta/dT)\,|_{TM}$, plotted against T_{AV}.

The glass transition on a $d\Delta/dT(T)$ plot (for both TM and regular scanning modes) appears as a steplike feature, as demonstrated in Figures 1d and 2. The glass transition temperature T_g is computed using limiting fictive temperature concept.[5,6]

TM implementation as presented here is primitive and does not require any changes in the system hardware. More advanced TM methods typically use sinusoidal modulation, and phase shifts of the signals are taken into account in the data analysis.[2] Nevertheless, even the simplistic TM realization discussed here shows remarkable results in glass transition observation in thin films.

TM mode is useful to observe glass transition in unannealed films. It can be valuable for samples that lose their characteristic structure or composition after heating beyond the glass transition. The examples are 3-D structures and samples containing volatile components. Figure 1f demonstrates the first heating scan of a freshly prepared 170 nm thick PMMA film, performed in the regular scanning mode. The large broad feature on the plot masks entirely the glass transition step which should appear at about 120–130 °C. The feature corresponds to well-described decrease of as-spun PMMA film thickness in the vicinity of T_g.[7–9] Suggested reasons of this phenomenon include residual solvent evaporation,[7,8] structural relaxation,[8] and disappearance of the low-density surface layer.[9] In contrast to the regular scanning mode, the first heating scan on the similar sample performed in the TM mode shows a well-shaped glass transition (see Figure 1d, circles). For the experiment shown (TM mode and 170 nm thick PMMA film), T_g calculated for the unannealed film (first heating) and for the film after annealing (second heating) are very close to each other: 123.4 and 126.6 °C, respectively. The corresponding TM scans for the annealed film are shown in Figure 1d by triangles.

Another TM mode application is the separation of glass transition and accompanied overlapping processes that are repeated at each regular (linear) scan. For example, above 100 nm thick PMMA films demonstrate a shoulder on the low-temperature side of the glass transition feature. For ~200 nm thick films this shoulder often has the shape of a straight line segment, as shown on Figure 1d (solid lines). T_g calculated out of the cooling curve is equal to 122 °C, while the bulk T_g

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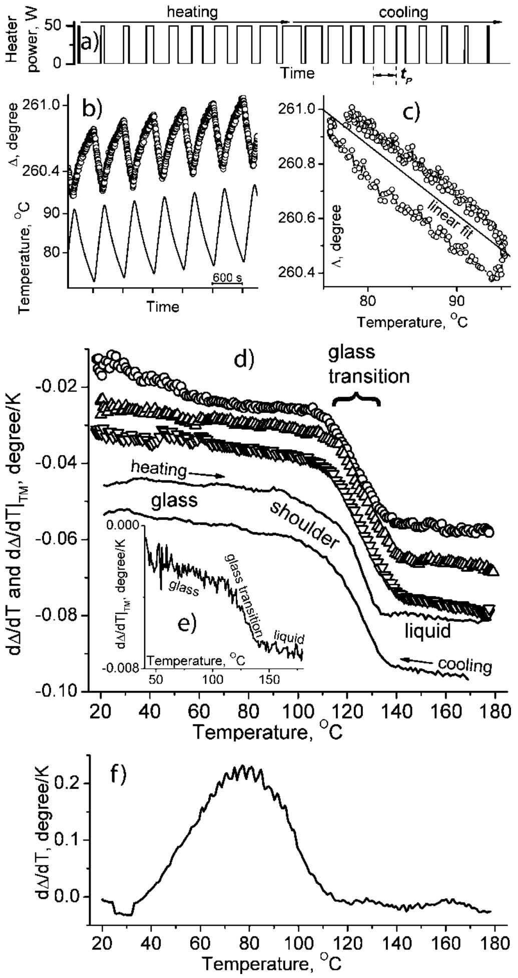

Figure 1. Temperature-modulated ellipsometry. (a) Regulation of the sample temperature by means of the pulse-width modulation of the heater power. (b) Part of the modulated temperature curve, solid line, and corresponding ellipsometer response, circles, 170 nm thick PMMA sample. $t_P = 600$ s. (c) Response vs temperature plot for one modulation cycle, 170 nm thick PMMA sample. $t_P = 600$ s. (d) Typical TMEll experimental curves for 170 nm thick PMMA sample. Circles: the first heating scan of unannealed film. The first cooling and the second heating scans for the annealed sample are shown by down-triangles and up-triangles, respectively. $t_P = 600$ s. For comparison, the average heating and cooling curves obtained by the regular scanning mode for the annealed sample are shown by the solid line, upper and lower curve, respectively. The data are offset for clarity. (e) The second heating TM scan for an 11 nm thick PMMA film. (f) The first heating scan for 170 nm unannealed PMMA sample obtained in the regular scanning mode.

obtained by DSC for bulk sample upon cooling is higher by 4 °C (see Table 1). This supports the assumption that the shoulder is not the part of the glass transition. A more solid argument can be obtained by the TM scan, shown in Figure 1d. The shoulder is much less pronounced for the TM scan, even for the large modulation amplitude that naturally broadens the transition. Also, as shown in Table 1, T_g calculated out of the TM experiment, bulk T_g obtained by TMDSC, and bulk T_g obtained by regular DSC are close to each other within 2 °C. Regarding the possible nature of the shoulder, relaxation of thermal stress can be considered. Thus, generation of compressive thermal stress upon heating slightly below T_g with subsequent relaxation has been observed for supported glassy polymer films.[10] The relaxation can increase apparent thermal coefficient of expansion and create a shoulder on the low-temperature side of the glass transition feature.

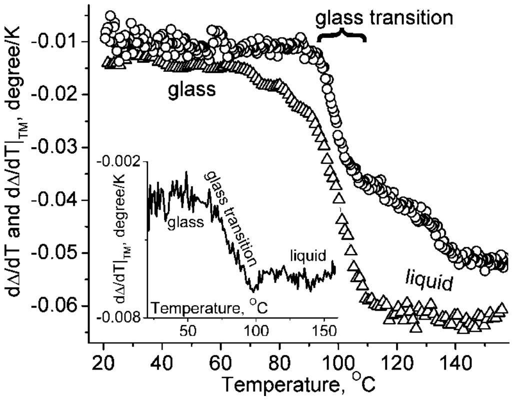

Figure 2. TM ellipsometry (circles) vs regular mode ellipsometry (triangles) for 160 nm thick PS sample. The cooling curves are shown. The data are offset for clarity. Inset: TM scan for thin (5 nm thick) PS sample, the heating curve.

Table 1. T_g of PS and PMMA Obtained by DSC and Ellipsometry

method[a]	T_g for PS, °C	T_g for PMMA, °C
DSC,[b] regular scan,[c] bulk sample	99.3 ± 1.1	125.7 ± 0.9
DSC,[b] ac mode,[d] bulk sample	102.6 ± 0.3	127.4 ± 0.2
ellipsometry, regular scan,[c] thick film[e]	97	122
ellipsometry, ac mode,[f] thick film[e]	97 ± 2	127 ± 2

[a] T_g are calculated for scans upon cooling; errors are standard deviations of individual measurements. [b] Q100 DSC (TA Instruments). [c] Cooling rate is 1 K/min. [d] Cooling rate is 1 K/min, modulation amplitude is ±3 K, and period is 200 s. [e] 160 nm thick PS film and 170 nm PMMA film are used. [f] Cooling rate is 0.1 K/min, modulation amplitude is up to ±10 K, and period is 300−600 s.

It is worth to note that thick PS samples demonstrate nonlinear liquid line on the plots obtained by TM scans, while a regular scan shows flat dependence (see Figure 2). Thin PS films also demonstrate practically constant dΔ/dT for the liquid state in the TM mode. Appearance of the feature on TM scans of thick PS films requires additional investigation; at this time we cannot exclude instrumental origin.

Further exploration of this method involves probing of glass transition in ultrathin polymer films. Our data show a well-shaped glass transition for ~10 nm thick PMMA films and ~5 nm thick PS films; see examples shown in Figure 1e and in the Figure 2 inset. Previously glass transition was demonstrated by ellipsometry in polystyrene films as thin as 5.5 nm[11] and as thin as 10 nm.[12]

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