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Glass transition of thin films of poly(2-vinyl pyridine) and poly(methyl methacrylate): nanocalorimetry measurements

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Abstract

Glass transitions were observed in thin films of poly(2-vinyl pyridine) (P2VP) and poly(methyl methacrylate) (PMMA) using a scanning nanocalorimetry technique which has both high sensitivity (10^{-9} J/K) and high scan rates (10^4–10^5 K/s). Samples were deposited by the spin-cast method. The thickness of samples was 100–400 nm. Glass transition temperature, obtained by nanocalorimetry, is shifted toward higher temperatures by 10–20 K and activation enthalpy of glass transition is shifted to lower values by factor of 2–4. The glass transition characteristics of both polymers are discussed in terms of the standard Tool–Narayanaswamy–Moynihan (TNM) multi-parameter model.

Keywords: Nanocalorimetry; Glass transition; Poly(2-vinyl pyridine); Poly(methyl methacrylate); Calorimetry

1. Introduction

There is great interest in the thermophysical properties of polymers especially with respect to the effect of the size and thickness on the glass transition characteristics of ultrathin films [1–4]. The measurement of the glass transition in polymer films below 100 nm continues to be a challenge to experimentalists. Calorimetry is a preferred measurement technique of choice for glass transition studies [4–6], since it yields absolute values for thermodynamic properties of the films. Unfortunately, conventional differential scanning calorimetry (DSC) systems are limited in their use for such studies of thin films. This is because the sample size is so miniscule that the required level of sensitivity for the measurement is usually beyond the limits of conventional DSC instruments.

In our previous work [7] on polystyrene (PS), we demonstrated the utility of a nanocalorimetry device for characterization of spin-cast thin film polymers. This thin-film differential scanning calorimetry device is based on MEMS technology and shows potential for studies of glass transition for films having nanometer-range thickness. The earlier experiments on poly-dispersed PS show that the key glass transition characteristics (i.e. glass transition temperature and activation enthalpy) were significantly different from results using the traditional DSC technique. These differences are attributed to the unusually high cooling (10^3 K/s) and heating rates (10^5 K/s), which are inherent in the nanocalorimetry technique.

In this paper, we present our initial nanocalorimetry results of an investigation of two other glass-forming

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polymers: poly(2-vinyl pyridine) (P2VP) and poly (methyl methacrylate) (PMMA). In order to compare these results with those of the previous study of 80 nm thick PS, we limited our study to relatively thick polymer films (100–400 nm), which are expected to have characteristics that are consistent with bulk samples [4].

2. Experimental

The operation and fabrication of the nanocalorimetry device and technique are described in detail elsewhere [7–12]. Here we give an abridged description of the technique. The nanocalorimeter is a MEMS micro-fabricated sensor as shown in cross-section in the schematic diagram in Fig. 1. The sensor consists of a SiN_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 thermometer. Platinum is used as a material of choice for the metal strip due to the superior stability of its electrical resistance. The Pt heater/thermometer, the SiN_x membrane directly beneath it, and a sample film deposited on either the Pt or SiN_x surface, form the calorimetric sensor. The extremely low thickness of the Pt strip and SiN_x membrane provides a mass addenda that is small enough to measure the heat capacity (C_P) of nanometer-thick films. This type of sensor has the capability of measuring incremental changes in sample thickness of the order of 0.004 nm [12]. It should be noted that in previous nanocalorimetry experiments involving thin metal films, [9–12], the thickness of the membrane was about 30–50 nm. The sensors used in this work have a 10-fold increase of membrane thickness. These sensors were made specifically for the current investigations in order to withstand the increased internal stress that is generated by thick polymer films during spin-cast deposition. In order to obtain the high sensitivity for our measurements we employ a differential technique, which is achieved by using a second sensor (reference) that is identical to the polymer-coated sample sensor, but has no material on it [11]. In order to determine the temperature response of the sensors, the resistance of both sensors is calibrated against the value of an RTD in a three-zone tube vacuum furnace system.

The sample is heated during the measurement by supplying a short pulse (1.5–16 ms) of electric current (20–100 mA) to the Pt strip, which rapidly increases the temperature of the entire calorimetry sensor, including the sample, by Joule heating. The entire apparatus is situated in a vacuum environment ($\sim 10^{-6}$ Pa) which not only eliminates the influence of the ambient gas with the sample, but also reduces heat loss via convection. The high heating rate υ_{heat} (10–200 K/ms) provides near-adiabatic conditions. Both the voltage across the heater and the current are monitored in real-time during the pulse and are used for calculation of electrical power (P) and resistance (R) of metal strip. In order to obtain the temperature of the system, the temperature (T) is calculated using an $R(T)$ temperature coefficient of resistance (TCR) function. Using P and T as functions of time, the $C_P(T)$ function is obtained.

For this study, we choose poly(2-vinyl pyridine) and poly(methyl methacrylate) with $\bar{M}_w = 138,000$ and 105,400 g/mol, respectively, obtained from Polymer Source, Inc. Both types of samples are monodispersed with $\bar{M}_w/\bar{M}_n = 1.30$ and 1.04, respectively. The thin films of polymer were deposited onto the sensor via standard spin-casting technique at a spin rate of rotation of 3000–10,000 rpm. Solutions of P2VP in n-butanol and PMMA in toluene were used for

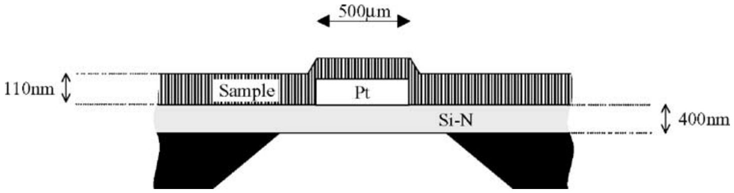

Fig. 1. Cross-section of the nanocalorimetry sensor which is a MEMS-based calorimetric device used to measure thin-film material. The polymer samples are spin-cast onto the silicon nitride membrane (400 nm thick) that supports the thin-film Pt micro-heater, which is 50 nm thick.

deposition. The uniformity of the polymer on the Pt was excellent with a variation in the thickness of only ±10% from the average value on the active part of the metal strip. Focused ellipsometry (FOCUS^{TM} ellipsometer FE-III, Rudolph Technologies, Inc.) with a spot size of 12 μm × 24 μm was used to measure the local film thickness. Two independent values of thickness of the sample are obtained: (1) by the ellipsometry technique and (2) by the change in the baseline heat capacity the ΔC_P of the calorimeter, which occurs with the addition of the polymer film to the calorimeter (assuming bulk values of the density and specific heat for the thin film). The values of both methods agree to within 10%.

Nanocalorimetry scans were performed from room temperature up to 240 °C for P2VP and up to 260 °C for PMMA. After reaching the maximum desired temperature, the current was halted and the sample was allowed to passively cool to the ambient temperature. The cooling rate v_{cool} was the same for all measurements on a given sample. A typical average value for v_{cool} was 0.8 K/ms in the temperature range of 100–160 °C (approximately the glass transition region). This cooling rate is several orders of magnitude greater than in conventional DSC.

Each experiment consisted of a series of identical heat pulses. As expected, the first scan of the as-deposited samples produced a $C_P(T)$ curve which is significantly different from the subsequent scans. This is due to the outgassing of solvent residue. Prior to the main part of calorimetric measurements, all samples were annealed in vacuum for 1000 s at 140 °C for P2VP and 160 °C for PMMA. After the annealing, scans showed remarkable reproducibility. The final calorimetric curves are the result of averaging of 300 scans taken at 1 s time intervals. It should be noted that the very first scan in each series deals with the initial state of polymer film, which somewhat differ from initial states for all consecutive scans. Due to this reason, the data of the first 10 scans in each series are not used.

3. Results and discussion

The results of our measurements are given in Fig. 2(a), and show the heat capacity data $C_P(T)$ measurements for 160 nm thick P2VP (sample P2VP-160) and 110 nm thick PMMA (sample PMMA-110). The glass transition temperature T_g is the standard parameter of the glass/liquid transition region and is assigned using the concept of the limiting fictive temperature T_f' [13,14]. T_f' is defined as the temperature of intersection of the extrapolated equilibrium liquid and glass enthalpy versus temperature curves, as illustrated in Fig. 2(b). The measured values for the polymers used in this study were $T_f' = 112\,°C$ (sample P2VP-160) and 141 °C (sample PMMA-110). Conventional DSC measurements of used substances give $T_f' = 94\,°C$ for P2VP and $T_f' = 128\,°C$ for PMMA.[1] Nanocalorimetry

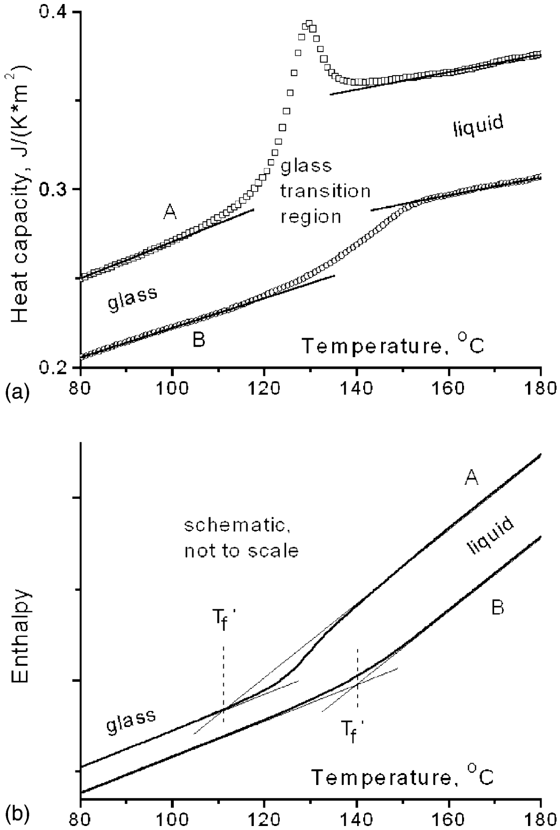

Fig. 2. Typical calorimetric curves (a) and their integrals over temperature, shown schematically (b). (A) P2VP, 160 nm thick; (B) PMMA, 110 nm thick. Heating rate is 16–18 K/ms through the glass transition temperature range (100–160 °C).

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[1] T_f' is measured using Perkin-Elmer DSC7, calibrated against melting temperature of In and Ga. Polymer samples are 5–10 mg. Data are collected during heating, preceded by cooling from the liquid state. Both heating and cooling rates are 3 K/min.

values are significantly higher (10–20 K) than those obtained by the conventional DSC of bulk samples, as was also the case reported in our previous results of the PS investigation [7]. The increase in T_g is expected, because the high cooling rate leads to a less stable glass state, which corresponds to an increase of the glass transition temperature [13,14].

More detailed analysis of the experimental data is made using Tool–Narayanaswamy–Moynihan (TNM) multi-parameter model [14]. Experimental calorimetric curves were fitted using an algorithm described elsewhere [15]. A commonly used stretched exponential is used as a relaxation function, both in the explicit form and expressed as a weighted sum of exponentials [15]. The parameters of this model (stretch exponent β, non-linearity parameter x, activation enthalpy Δh^*, and the exponent coefficient A) are found by simultaneously fitting data over a range of heating rates υ_{heat}. The values for these parameters are optimized from the experimental data via the set of methods (Levenberg–Marquardt, Gauss–Newton, simplex, quasi-Newton) implemented in the Optimization Toolbox of MATLAB software (release 12) [16]. At the final stage of fitting, the temperature step ΔT did not exceed 0.1 K. The iteration scheme ensures that, for each step, the change in fictive temperature ΔT_f does not exceed the maximal ΔT (0.1 K on the final stage) for more than 50%.

Best-fit parameters for the samples P2VP-160 and PMMA-110 are shown in Table 1. While the values for the TNM parameters for P2VP are not available in the literature, we expect them to be close to those of PS (see Table 1) due to the similar structure of these polymers [17]. In fact, the previous data for PS, obtained by nanocalorimetry technique are quite close to the values obtained in this work for the P2VP. From the same table in [15], the typical parameters for PMMA are also shown in Table 1. Obviously, only the parameter β is in satisfactory agreement between nanocalorimetry and conventional DSC measurements. The activation enthalpy Δh^* is significantly (2–4 times) lower for nanocalorimetry, which suggests possibly less cooperative nature of the glass transition at the extremely high heating rates. At the same time, it should be pointed out that correspondence of parameters for all three investigated polymers for the nanocalorimetry technique is similar to that of conventional DSC. The T_g parameter for P2VP is equal to the T_g of PS and is less than the T_g of PMMA, both for nanocalorimetry and for conventional calorimetry. The calorimetric curves for P2VP are expected to be similar to those for PS [17], and they are, both for nanocalorimetry and for conventional DSC. The Δh^* of PMMA exceeds the Δh^* of PS by 40% in nanocalorimetry experiments and on average by 70% in regular DSC measurements (calculated from the table in [15]).

Table 1
Comparison of TNM parameters

Sample	$\Delta h^*/R$[a] (kK)	β	$A \ln s$	x	Reference
P2VP-160	24	1.0	−68	0.9	This work
PMMA-110	39	0.4	−99	1.0	This work
PS	53–110	0.55–0.71		0.44–0.52	[15]
PS[b]	28	1.0	−76	0.8	[7]
PMMA	135–150	0.35		0.19–0.20	[15]

[a] R is the gas constant.

[b] Using nanocalorimetry technique.

4. Conclusions

The data shown here represent, to our knowledge, the first direct calorimetry measurements of the glass transition phenomenon for thin films of P2VP and PMMA. The ultra-sensitive DSC technique—nanocalorimetry—is used characterized by high cooling and heating rates, which are several orders of magnitude higher than those in the conventional DSC method. Glass transition temperature, obtained by nanocalorimetry, is shifted toward higher temperatures by 10–20 K and activation enthalpy of glass transition is shifted to lower values by factors of 2–4.

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