Polymer communication

Calorimetric glass transition of ultrathin poly(vinyl methyl ether) films

Huajie Yin, Andreas Schönhals*

BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, D-12200 Berlin, Germany

ARTICLE INFO

ABSTRACT

Specific heat spectroscopy in the frequency range typically from 1 Hz to 1 kHz with a sensitivity of pJ/K was employed to study the glass transition behavior of ultrathin poly(vinyl methyl ether) (PVME) films with thicknesses ranging from 218 nm down to 12 nm. The amplitude and the phase angle of the complex differential voltage as a measure of the complex heat capacity were obtained as a function of temperature at a given frequency simultaneously. Both spectra are used to determine the dynamic glass transition temperature as a function of both the frequency and the film thickness. As main result no thickness dependence of the dynamic glass transition temperature was observed down to a film thickness of 12 nm within the experimental uncertainty of ± 2 K. Further the width of the glass transition is independent of the film thickness which indicates that the extent of the cooperativity is essentially smaller than 12 nm.

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1. Introduction

From a technological point of view, the glass transition of ultrathin polymer films characterized by the glass transition temperature T_g is of great interest in a broad variety of fields like coatings, membranes, organic electronic devices, etc. From the scientific point of view, ultrathin polymer films provide an ideal sample geometry for studying the confinement effects on the glass transition of polymers because the confining dimension (film thickness) can be easily tuned by spin coating [1].

There is growing consensus that in polymer films supported by a non-attractive substrate, a T_g depression is observed [2]. This T_g depression is discussed to originate as a result of a free surface having a higher molecular mobility than the bulk [3]. In the case of polymer films supported by substrates having a strong interfacial interaction, T_g may increase with the reduction of film thickness [4]. In the most studies, a thermodynamic property (or an associated quantity) is measured during a temperature scanning experiment and a change in the temperature dependence is interpreted as thermal glass transition where a T_g can be extracted. Recently, techniques that directly detect the time scale of segmental dynamics like broadband dielectric spectroscopy [5,6], optical photobleaching technique [7], and differential AC chip calorimetry [8–11] are also applied to study the glass transition of ultrathin polymer films. For various polymers like polystyrene [5–8],

poly(methyl methacrylate) [5,9], polycarbonate [11], the dynamic glass transition temperature in the specific frequency range of the employed method was found to be independent of the film thickness down to several nm. Compared for instance to dilatometric techniques, dynamic methods work in the linear regime, where the spontaneous fluctuations associated with the segmental relaxation are probed at temperatures usually above the thermal T_g discussed before. Thus, they directly measure the intrinsic segmental dynamics of the glass former in the supercooled liquid-like state.

Although PVME is widely used in chemical, pharmaceutical and textile applications and moreover blended with various polymers to form different types of adhesives or for coating applications, there are only few investigations with regard to the confinement effects on its glass transition behavior. This is partially due to the low T_g value and thermal sensitivity which leads to difficulties in the preparation and measurement of thin PVME films. In the present study, the thickness dependence of the molecular dynamics of PVME films supported on a silicon dioxide layer with one free surface was investigated by specific heat spectroscopy using differential AC chip calorimetry. With this method the heat capacity can be measured in a wide frequency range as a direct proof of the glass transition. Moreover this also allows a discussion of the extent of the cooperativity as discussed in ref. [11]. As main result no thickness dependence of the dynamic glass transition temperature of PVME films is observed down to a film thickness of 12 nm. Also the width of the glass transition is independent of the film thickness which indicates that the extent of the cooperativity is essentially smaller than the lowest film thickness of 12 nm.

* Corresponding author. Tel.: +49 30 8104 3384; fax: +49 30 8104 1637.
E-mail address: Andreas.Schoenhals@bam.de (A. Schönhals).

2. Experimental section

PVME was purchased as in aqueous solution (50 wt%) from Aldrich Chemical Company Inc. with a M_w of 60,000 g/mol and a PI of 3. PVME was dried under vacuum at 40 °C for 96 h. The glass transition temperature was estimated to be −26 °C by DSC (10 K/min, second heating run) in accord with literature data [see ref. 12].

Calorimetric measurements on ultrathin polymer films have been achieved with the development of the ultrasensitive differential AC chip calorimetry [8–11]. Thin films with one free surface were prepared directly on the surface of the calorimeter chip (XEN-39390, Xensor Integration, Nl), which is used as measuring cell. Firstly, the sensor was cleaned by dropping a droplet of toluene to its center in order to remove dust and organic contaminants on the surface by spinning. This procedure was repeated three times, followed by annealing under vacuum at 473 K for 2 h. The annealing process is necessary to cure the epoxy resin completely, which was used to glue the chip to the housing. Secondly, thin films with various thicknesses were prepared by spin coating. PVME was dissolved in toluene (99.8%; Sigma−Aldrich) and the solution was spin coated on the central part of the sensor (3000 rpm, 1 min). The film thickness was varied by changing the concentration of the solution. After spin coating, all samples were annealed at 40 °C (66 K above the T_g of bulk PVME) in an oil-free vacuum for 72 h in order to remove the residual solvent and the stress induced by the spin coating procedure [13]. Moreover an identical and well-defined thermal history of all samples is ensured. The thickness of the so-prepared samples was verified by atomic force microscopy (AFM, Nanopics 2100). Because the thickness of the thin films cannot be directly measured on the sensor, a second set of films was prepared under identical conditions on a silicon wafer to estimate the film thickness. Since the silicon wafer has similar surface properties to the sensor, it can be assumed that under identical spin coating conditions the film on the silicon wafer has the same thickness as that on the sensor. AFM topography image also revealed no inhomogeneities at the surface of the films and a low surface roughness, as indicated in Fig. 1. The roughness in the central area of the empty sensor is about 3.5 nm rms [10]. The roughness of the film spin coated onto the surface of the sensor is lower and decreases with increasing film thickness. For a thickness of ca. 10 nm the roughness of the film on the sensor is comparable with that of a film prepared on a wafer [14].

In the calorimetric experiments the temperature-scan-mode was employed, which means that the frequency was kept constant while the temperature was scanned with a heating/cooling rate of 2.0 K/min. During the measurements the heating power for the modulation is kept constant at about 25 μW which ensures that the amplitude of the temperature modulation is less than 0.5 K [8]. Temperature calibration was carried out as described in ref. [13]. The frequency is varied between 1 Hz and 1000 Hz. As result of the measurement a complex differential voltage is obtained which is proportional to the complex specific heat capacity as function of frequency and temperature [8]. The real part of the complex differential voltage U_R increases stepwise at the dynamic glass transition where the phase angle φ shows a peak. A dynamic glass transition temperature can be determined as either the half step temperature of U_R or the peak temperature of the corrected phase angle signal. The T_g values obtained from different parts of measured thermopile signals are close to each other with uncertainty within ±2 K.

3. Results and discussions

In order to determine the film thickness dependence of the dynamic glass transition temperature, a series of measurements were carried out at the frequency of 640 Hz. The data were
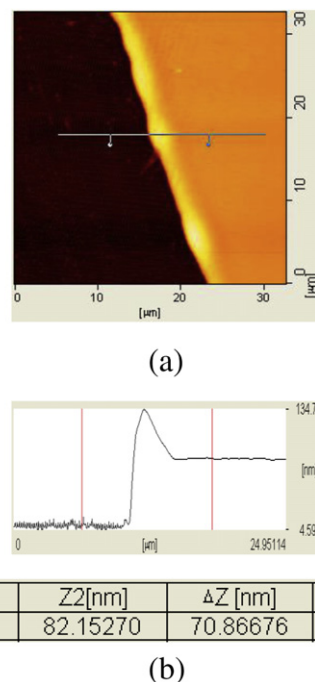

(a)

	Z1[nm]	Z2[nm]	ΔZ [nm]	Distance [μm]
■	11.28594	82.15270	70.86676	11.96288

(b)

Fig. 1. (a) AFM image of a scratch across the PVME film (ca. 70 nm) spin coated on a silicon wafer. (b) Sectional view of the scratch along the line in the AFM image.

collected during continuous heating and cooling at a rate of 2 K/min, where the second heating run is used for analysis. The data for the different film thickness are normalized for comparison (see Fig. 2). The real part of the complex voltage was scaled by its step height at the dynamic glass transition minus its value at T_g after normalization, $U_R/(U_{R,T=210\ K} - U_{R,T=330\ K}) - U_{R,T_g}^N$ (see Fig. 2a), where the corrected phase angle is normalized by its maximum value (see Fig. 2b). All rescaled data for the different thicknesses collapse into one chart for both the real part and the phase angle. This indicates that the temperature corresponding to half of the amplitude step as well as that of maxima of the phase angle of the complex differential voltage is independent of the film thickness down to 12 nm. In other words the dynamic glass transition temperature is independent of the film thickness down to 12 nm.

It is interesting to analyze the confinement effect on the cooperativity length scale ξ or the corresponding volume V_{CRR} at the dynamic glass transition for different film thicknesses. In the framework of a fluctuation approach, the theory of Adam and Gibbs was extended by Donth [16]. Within that approach, a correlation length ξ (or volume V_{CRR}) of dynamically correlated segments at the glass transition can be calculated to

$$\xi^3 \sim V_{CRR} = \frac{k_B T_g^2 \Delta(1/c_p)}{\rho\ \delta T^2} \tag{1}$$

where T_g is the dynamic glass transition temperature, ρ is the density at T_g and $\Delta(1/c_p)$ the step of the reciprocal specific heat capacity at the glass transition where $c_V \approx c_p$ was assumed. δT is the width of the glass transition and can be extracted experimentally from the temperature dependence of the specific heat capacity [17]. Recently, it became also possible to estimate δT from the phase angle estimated by specific heat spectroscopy [18–21]. According to Eq. (1), two main quantities, the specific heat capacity c_p and the mean temperature fluctuation δT should be taken into consideration for the estimation of the extent of cooperativity. In the present study specific heat capacity is found to be independent of the film