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Structural and thermal behavior of polystyrene thin films using ATR–FTIR–NanoDSC measurements

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Abstract Most studies report a depression of the glass transition temperature in thin polymer films. To gain insight into this behavior, we have simultaneously investigated the structure of materials and their thermal behavior by developing an ATR–FTIR–nano-differential scanning calorimeter (nanoDSC) hybrid instrument consisting of a ZnSe ATR crystal upon which the sample and a DSC-on-a-chip rests. FTIR spectra showed property changes with film thickness; nanoDSC did not. The relative absorbance of an IR peak at 797 cm^{-1} was found to correlate with aging time in thin films, suggesting that conformational structure of thin films is critical to their thermal behavior.

Keywords FTIR · Glass transition · Nanocalorimetry · Thin films

Introduction

Numerous studies report that thin films show a depression of the glass transition temperature (T_g) compared to bulk samples [1–3] implying a change in the physical aging properties. Several reports have shown such variations in T_g with film thickness using Brillouin light scattering [4], position annihilation lifetime spectroscopy (PALS) [5], X-ray or neutron spectroscopy [6], ellipsometry [1, 7, 8], and interferometry [9]. Most studies reveal a relatively sharp change once the film thickness is below about 50–100 nm.

It is clear that the physical properties of polymer samples vary not only with time, as in physical aging, but also with sample thickness, which has generated a great deal of interest [1, 10, 11]. Two major hypotheses have been suggested to explain the effect of sample size: in a first hypothesis, Keddie et al. suggested that the observed changes could be due to the presence of a layer of increased mobility at the air/polymer interface [12]. Some experimental evidence supports this latter hypothesis [13, 14].

A second hypothesis involves the amount and type of interactions between the polymer and the support. As the polymer thickness decreases, the relative influence of these interactions on the physical properties of the sample increases. Various reports showed evidence that the variation of T_g with thickness depended strongly on interactions between substrate and polymer as a relation between type of support and extent or sign of the depression was observed [15–18], showing that the affinity between support and samples plays an important role in this phenomenon. This conclusion was confirmed in an experiment conducted in our lab that showed the change in melting temperature of thin polyethylene films with various surface coverage of substrate particles [19]. However, Forrest et al. reported that unsupported material showed a decrease in T_g at low film thicknesses so that the presence of interactions is not the only component responsible for the change of physical properties of thin films. Other hypotheses have been examined. Variations in T_g have also been associated with constraints on the motion of segmental units of relatively small dimensions [20]. Changes in the alignment of these segments either parallel or perpendicular to the plane of the film could be hindered or favored by such constraints leading to variations in segmental motion freedom and therefore in the observed value of T_g [20].

There has been a considerable amount of effort to model thin polymer films with the objective of understanding the effect of size and to help experimenters gain insight into

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the problem [21–23]. Binder et al. obtained results of particular interest when they performed molecular dynamic simulations of supercooled liquids next to rough and smooth walls [24]. They reported important differences in relaxation times between the two surfaces, which decreased as the distance between the liquid and the walls increased. Several other investigators attempted to reduce the thin film problem into a confinement model by adding an excess volume parameter, which accounts for the reduced space in thin films [22, 23]. The observations presented above suggest that the variation in T_g with film thickness is the result of a combination of effects. However, none of these models perfectly satisfies all the experimental data. Therefore, the key roles of free volume and chain mobility in the glass transition phenomenon must be understood.

In bulk systems, it is well established that the glass transition temperature is dependent on the methodology as similar samples may display different T_g depending on the time frame of the experiment; since its well documented that T_g can only be modeled using more than one mechanism of relaxation, i.e., with different relaxation times, each type of experiment may favor some mechanism of relaxation compared to others. The different methods used in the literature to explore T_g, may probe different components of the phenomenon and therefore lead to different estimations of T_g in thin films as well as in bulk samples. In fact, a several groups using nano-calorimetry have reported that no change in T_g with decreasing thicknesses was observed in polymer thin films, a puzzling result [25–27]. A methodology capable of exploring the thermal and structural behaviors of the thin polymer films may shed new light on the problem.

One method to confirm the presence of T_g is to follow the physical aging of a sample. Physical aging, the associated phenomenology that occurs when the temperature of a sample is allowed to drop and remain below its glass transition temperature (T_g), is associated with a decrease in volume and enthalpy and results in an increase in the brittle failure of polymers [28–31]. Figure 1 summarizes the physical aging process. A liquid at a temperature T_i is cooled to a temperature T_a, below its glass transition temperature T_g. As it crosses T_g, its changes in volume and enthalpy no longer follow the equilibrium liquid line (dashed line) but follow a glassy line. Once at the temperature T_a, the material attempts to return to an equilibrium state by decreasing its volume or enthalpy, the phenomenology of physical aging. This aging can be followed by measuring the relative volume changes δ or the enthalpy changes and is often discussed in terms of the relaxation time τ, which is the time the chains take during their return to equilibrium. While the phenomenology of this effect is well documented, the mechanisms involved are still a source of debate [32], as is evidenced by the fact that well known models of physical aging such as the Tool–Narayanaswamy–Moynihan (TNM), the Kovacs–Aklonis–Hutchinson–Ramos (KAHR), and Ngai's coupling models have been repeatedly found to be inadequate [10, 33, 34].

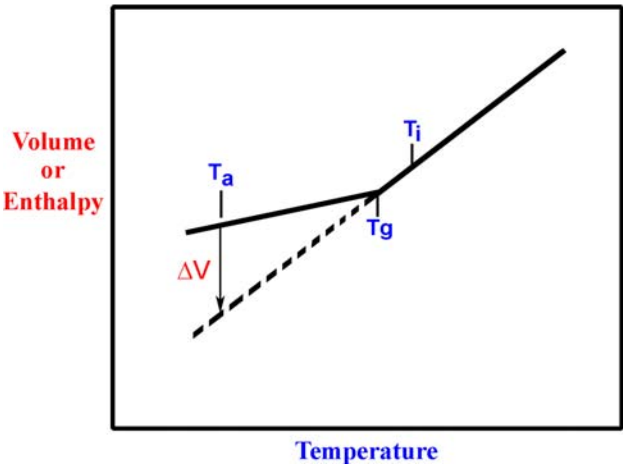

Fig. 1 The physical aging process. A liquid at a temperature T_i is cooled to a temperature T_a, below its glass transition temperature T_g. As it crosses T_g, its volume and enthalpy changes no longer follow the equilibrium liquid line (*dashed line*) but follow a *glassy line*. Once at the temperature T_a, the material attempts to return to an equilibrium state by decreasing its volume, the phenomenology of physical aging

Because relaxation dynamics are a function of time and temperature it is more difficult to model and predict this type of behavior. Hence, investigating physical aging and T_g is a more robust test of any methodology. Since the absolute values of τ and T_g may vary depending on the methodology, their simultaneous evaluation using two completely different methods can prove or disprove the validity of each method. To assess the thermal and structural properties related to the glass transition phenomena of thin PS films, we developed a hybrid instrument infrared spectrometer–nanoDSC, and used this instrument to simultaneously probe the molecular structural changes physical aging of thin polymer films as well as the changes in heat capacity of the material during these changes. In addition, as mentioned above, studies using the nanoDSC methodology have reported observing no changes in T_g with polymer film thickness while infrared spectrometry has [9, 19, 25–27].

The instrument used slightly modified Fourier Transform infrared spectrometer (FTIR) allied with the attenuated total reflectance (ATR) sampling technique since it can accommodate the nanoDSC, which fits on top of it sandwiching the polymer sample. Figure 2 shows a schematic representation of the setup. A most important factor in this method is the use of a nanocalorimeter since several studies using nanoDSC noted that no decrease in T_g was observed with decreasing film thickness. This surprising result suggests large disparities in the measurement methodologies. One possible explanation consists in the fact that measurements of nanoDSC cannot follow the expected

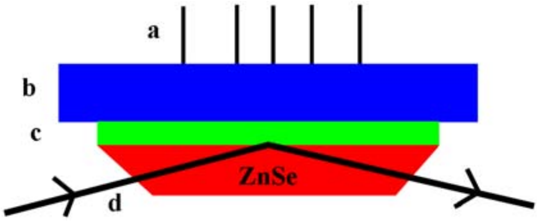

Fig. 2 Schematic diagram of the ATR–FTIR–nano-calorimeter. The sample (c) is placed on the zinc selenide crystal of the ATR (d). The membrane of the calorimeter on a chip (b) rests in thermal contact with the sample. Micron size thermocouples and heating elements (a) are connected to the membrane and their values are controlled and read via computer

changes due to fast temperature ramps. While this has been debated more investigations should be attempted. The hybrid FTIR–nanoDSC is an effective method to differentiate and possibly establish what individual spectroscopic and calorimetric method measure when considering the glass transition phenomenon.

The dual goals of our experiment are (a) to investigate if the nanoDSC methodology is capable of determining a change in T_g with the film thickness and (b) to demonstrate the capability of a hybrid instrument to explore the glass transition phenomenon of nano-thin polymer films. In this paper, we report preliminary results of the T_g and physical aging measurements using FTIR–nanoDSC on thin polystyrene (PS) films.

Experimental

Materials and sample preparation

Polystyrene (PS) of $Mw = 223{,}200$ g mol^{-1} as well as *o*-xylene with served as a solvent, were acquired from Aldrich (St. Louis).

Thin films were prepared using the floating method in which one or more drops of a solution of polystyrene in *o*-xylene were deposited on water. The resulting films were dried in air at room temperature for at least 24 h and then annealed at 60 °C for 2 h prior to all measurements. The ATR ZnSe crystal was used as the support. Film thickness was controlled primarily by varying the concentration of the solutions between 0.1 and 3.0% (W/W). Sample thickness was determined using an interferometric method [9]. Optical microscopy (1,000×) revealed no inhomogeneities at the surface of the films.

ATR–infrared spectroscopy–nanoDSC hybrid measurements

The simultaneous use of a nanoDSC on-a-chip housed in a Thermo Electron Nexus 470 FTIR spectrometer was used in ATR mode. In order to improve the contact between the ZnSe crystal and the sample a pressure estimated to be around 5 psi was applied. Spectra were recorded using one scan at a resolution of 4 cm^{-1} so that each spectrum corresponds to a narrow range of temperature. Each scan takes less that 3 s to record and is therefore an average measure of the sample structure over 5 °C using a heating rate of 100 °C min^{-1}. Before each series of experiments, the instrument was purged with nitrogen gas for about 10 min. The nanoDSC consist in a calorimeter on a chip (Xensor). The sample rests on a thin membrane connected to thermocouples and heating elements. An identical membrane is setup next to that containing the sample and serves as the reference. A heat sink maintained at 30 °C and consisting of a mesh wire was placed surrounding the ATR crystal. Water was used as the calibration standard. Heating was provided solely by the nanoDSC. Heating and cooling rates of 100 and 60 °C min^{-1}, respectively, were used in all experiments. Aging experiments consisted in heating the sample above T_g and maintaining that temperature for 5 min than cooling and staying at a temperature 15 °C below T_g for a set period of time, and finally recording the subsequent heating ramp. The complete instrument was controlled through Labview™ custom made software.

Results and discussion

Infrared spectroscopy component

The first step of our investigation is to determine the capability of the FTIR component of the system. In order to determine any structural changes of PS during the heating ramp, the sample was sandwiched between the nanoDSC and an ATR-crystal within a FTIR spectrometer. IR scans and nanoDSC traces were recorded simultaneously. As expected the IR of the thin PS films did not present large changes with temperature. However, a region in the spectra associated with CH bending of the benzene ring hydrogen atoms, did show a band which is solely observed in PS films of thicknesses smaller than 150 nm. This band was found to be sensitive to the temperature of the sample. Figure 3a shows the IR spectra in the mid-IR region while Fig. 3b presents the IR spectra of PS thin films as a function of increasing temperature in the 820–780 cm^{-1} region. The figure shows that as the temperature increases the band at 797 cm^{-1} decrease. The reversibility of this phenomenon is dependent on the heating rate, i.e., is the heating/cooling rates are high the bands will increase upon cooling the film, whereas if the heating/cooling rates are low the band will not increase upon cooling. Heating at a lower rate (1 °C min^{-1}) did not significantly change these observations but did modify the temperature at which the band

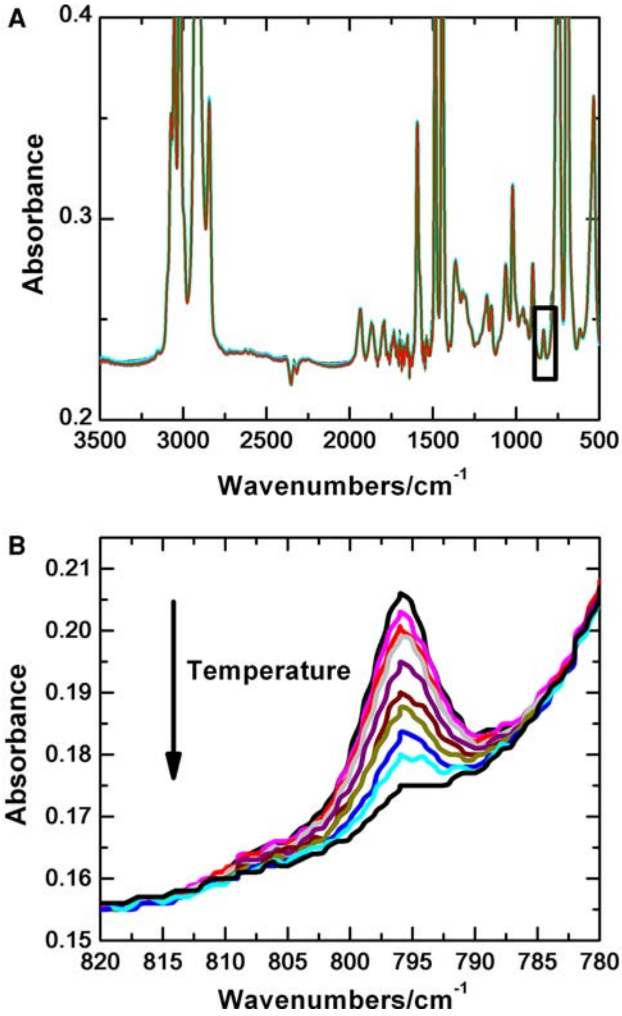

Fig. 3 ATR–IR spectra of a PS thin film of 62 nm thickness, recorded simultaneously with the nanoDSC trace. **a** Complete mid-IR region. **b** Region of interest

disappeared. However, at this time the nanoDSC cannot heat at rates lower than 60 °C min^{-1}.

Figure 4 shows the plot of the ratio of the 795 cm^{-1}/3,026 cm^{-1} bands as a function of temperature. The 3,026 cm^{-1} band is associated with the asymmetric stretching of the C–H group involving hydrogen atoms not in the benzene ring. This band was used as an internal standard as it is not expected to vary with temperature or aging time. Figure 4 shows that the decrease in the absorbance at 797 cm^{-1} with temperature follows a pattern that may help to determine T_g independently. In this method, the disappearance of the band implies few or no significant amount of interactions within the time scale of the experiment. This can then be construed as the definition of the liquid state. Figure 4 implies that the T_g of thin PS films of 62 nm thickness is depressed by 12 °C compared to that of the bulk.

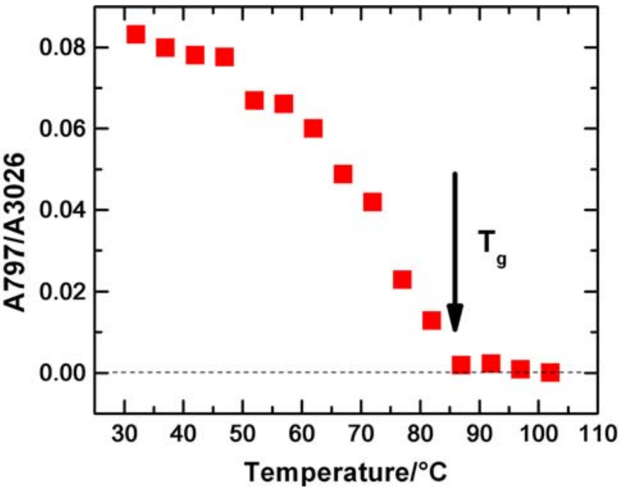

Fig. 4 Evolution of the band at 797 cm^{-1} with temperature from Fig. 3. The absorbance has been standardized using the peak at 3,026 cm^{-1}. The glass transition temperature is taken as the temperature at which the band reaches zero

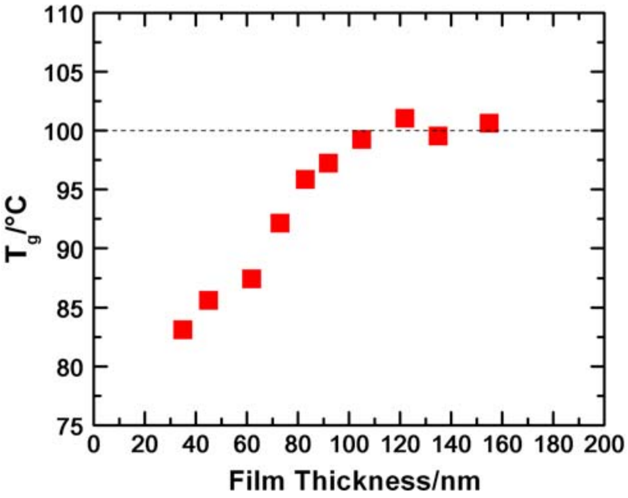

Fig. 5 Evolution of the glass transition temperature with film thickness as determined by FTIR from Fig. 3

Using this methodology and analysis on PS samples of varying thicknesses, a plot of the variation of T_g with film thickness was obtained (Fig. 5). The figure clearly shows that as sample thickness falls below 100 nm the T_g determined by infrared spectroscopy decreases. For thicker samples, the 797 cm^{-1} band is not observed. These observations lead to the hypothesis that the band may be strongly related to chain–chain interaction between benzene rings that are preferentially aligned in a specific structure at the surface of the sample. This hypothesis could be supported by following the 797 cm^{-1} band as a function of aging time. Figure 6 presents the correlation of the IR band at 797 cm^{-1} with the aging time for two films of different thicknesses. A linear relation is observed for both samples, which supports the hypothesis that the simultaneous ATR–IR–nanoDSC can offer a method of following the physical aging of thin PS films in both a thermodynamic method and a structural point of view. The aging time for both samples is 82 °C which is 6 °C lower than the experimental T_g using FTIR for the thin film but 18 °C lower that T_g for the thick film the aging time for this latter should therefore be about three orders of magnitude larger. The figure shows that from an IR spectroscopy point of view, the aging temperature is lower for the thin film compared to that of the thick film. If the T_g observed for the thin film is an artifact depending on the method used, both curves on Fig. 6 would be expected to have the same slope. The figure also shows that, as the thickness of the film increases, the absorbance of the 797 cm^{-1} band decreases and the correlation between the band and the aging time becomes less evident. For thick films, no 797 band is observed, possibly due to the large amount of bulk chain assembly which distorts the interaction. While the surface ordering will always be present, the relative importance of this ordering compared to other vibrations will decrease. Hence, when the absorbance of the band at 797 cm^{-1} is normalized by that of the band at 3,026 cm^{-1} a decrease is observed. The amount and strength of these chain–chain interactions, as represented by the 797 peak, could be analyzed in terms of heats of the overshoot determined by the simultaneous nanoDSC measurement. This supports the hypothesis that nanoDSC measures a different aspect of the phenomenology of the glass transition. Further investigations upon the nature of these differences are underway.

NanoDSC component

Figure 7 shows the response of the nanoDSC for a thin PS films of 62 nm thickness at different aging times. A standard DSC measurement of a bulk sample of PS would result in a T_g of 96 °C. The nanoDSC measurement suggest that the T_g of thin PS films of 62 nm thickness is 82 °C, i.e., significantly lower than the bulk sample, which is similar to observations found by others [4–7]. The nanoDSC traces presented in Fig. 6 also show that the instrument is sensitive to the physical aging of thin films, as the overshoot increases with aging time. This method can therefore follow the changes that occur in thin films. Since the heating ramp is relatively fast, the observed phenomena must take please with in the experimental time scale. This suggests relatively fast kinetics of chain reorganization in thin films.

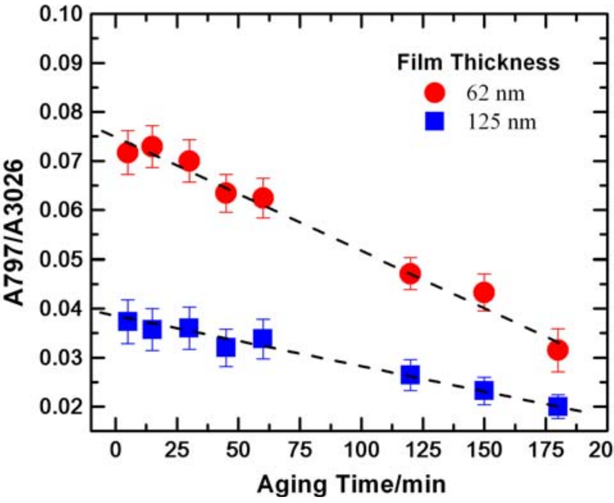

Fig. 6 Correlation between the standardized band at 797 cm^{-1} and the aging time. The linearity of the curve shows that this band can be used to follow the physical aging of PS thin films

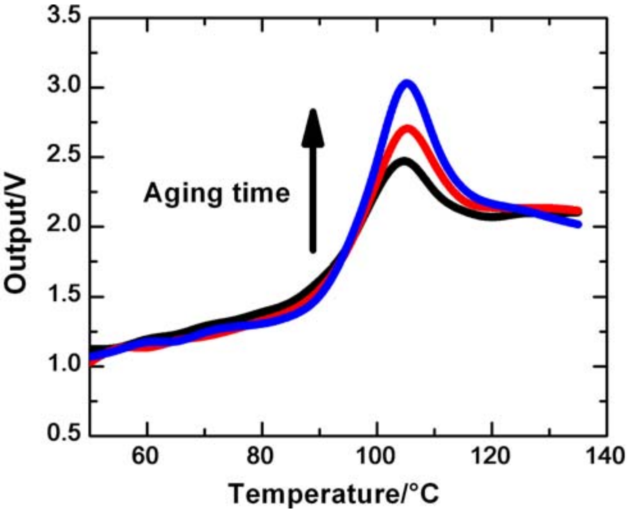

Fig. 7 NanoDSC trace of a PS thin film of 55 nm thickness at three different aging times. Aging time were 50, 120, and 180 min at 60 °C

Conclusion

A new method of analyzing the glass transition temperature and the physical aging of thin PS films was developed. The method involved simultaneous ATR–FTIR and nanoDSC measurements. While the infrared spectroscopy measurement showed a depression in T_g of about 12 °C for PS samples of a thickness of 62 nm no such depression in T_g was observed by the nanoDSC. This was confirmed by the physical aging experiments. These results show that the FTIR and nanoDSC probe different aspects of the glass transition phenomenon. In addition, this hybrid method helped assign the 797 cm^{-1} band to PS inter-chain phenomena and hence shows potential in characterizing thin polymer films.

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