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Probing the the Glass Transition of Atactic Polystyrene Thin Films Using Fiber Optic Refractometry

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Summary: An high resolution optical technique based on the film fiber optic refractometer has been used to investigate the effect of the thickness on the glass transition dynamic of Atactic Polystyrene films in the range 20–120 nm. The thermo-optic behavior of a set of layers dip coated onto the fiber has been analyzed upon cooling from long term equilibrated melt state. The glassy transition temperature is observed to be thickness-independent as did both the width and the lower and upper bounds of the transition itself. At lowering the thickness of the film the relevant effect is the reduction of the "contrast" between the melt equilibrium phase and the glassy state. A double layers model where a surface soft layer (3.9 nm at 418 K) do not contribute to the glass dynamic retaining liquid features even at temperature well below the glass transition, while the core layer shows a bulk glass transition, is able to quantitatively reproduce reflectance experimental data.

Keywords: fibre optic; glass transition; thin film

Introduction

In recent times a large number of experimental studies have been devoted to the analysis of glass transition of polymeric thin films because both this geometrical configuration provide a simple tool for studying the confinement effects on glass transition dynamic and their wide use in technological applications. The Atactic Polystryrene, aPS, has been used as a model for polymeric glass-forming materials. Investigations made on freely standing films[1–4] revealed all a large decrease of the glass transition temperature for decreasing thickness. The same results have been obtained, with a number of techniques, also for aPS thin films supported by both polymer-interacting[5–8] (non polar) and non interacting[2,9–11] (polar) substrates, so that, apparently the transition dynamics are not sensitive to the nature of the interactions between the polymer and the substrate. However, up shifts of the glass transition have been observed for aPS films cast on hydrogen passivated silicon by scanning probe microscopy[12] and by X-Ray reflectivity.[13] Recent studies made by Efremov et al.[14,15] by differential scanning calorimetry and by Lupascu et al[16] by ac-calorimetry, dielectric spectroscopy and capacitive dilatometry did not show any dependence of the calorimetric glass transition temperature for aPS films supported by polar substrates, down to 4nm thickness, supporting, thus, the earlier findings of Ge et al. by Shear Modulated Force Microscopy.[17] Furthermore an indirect study, by probe diffusion measurements, of transition dynamics of thin aPS films show no change of the Tg in respect to the bulk value even for freely standing films.[18] However, a marked reduction of the contrast of the transition, given by the difference between the thermal expansion coefficient of the glassy and melt state, for

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film thickness lowering to nanoscale has been always observed. Finally, a progressive broadening and, in some case shifting,[6] of the transition region has been recorded for decreasing film thickness. Some reviews on the status and the perspectives of the research in the field highlighted that a) there is an evidence of a reduced Tg at the nanometer size scale,[19] b) however different behaviors of such dependence have been observed for the same material leaving unclear if the effect is due to confinement effect, size effect or sample preparation,[19] c) experimental techniques give low strength signals due to the reduced sample volumes,[20] d) the always observed reduction of the contrast between the melt and glassy phases at reducing thickness increases the difficulty of the glass transition identification.[20]

In this work the fiber optic refractometer has been used to probe the glass transition of Atactic Polystyrene thin films due to the high resolution of this experimental technique.[21] The effect of the reducing thickness on the glass transition dynamics in aPS films cast on the silica surface has been investigated upon cooling at fixed rate (10 K/min) from long term equilibrium melt. The glass transition temperatures as well as the width and strength of the transition (i.e. contrast) have been evaluated for a set of film samples with nominal thickness lowering from 120 nm to 20 nm.

Experimental Part

Material

The aPS used in the work has been purchased by Aldrich and presents an average molecular weight (GPC) of 230.000 g/mol, specific density 1.04 and calorimetric glass transition temperature of 374 K (at 10 K/min).[21]

Fiber Optic Refractometer

An optical technique based on the principle of the film fiber optic refractometer (FFOR) has been used to monitor the changes of the optical reflectance of the polymer films upon cooling at constant rate. Basically, the technique[22] consists in lighting the fiber optic with a broadband light source (2 mW over 40 nm bandwidth) centered at 1310 nm. A 2 × 2 in fiber coupler provides the necessary connections between the light source, the sensing interface and two receiving channels, for reflected signal and for power monitoring respectively, and the recorded output signal I is the ratio between these two signals.

Briefly, the system output I is proportional to the reflectance R which, in turn, is proportional to both effective refractive index n and the actual thickness d of the polymeric film. A more detailed description of the optoelectronic set up and the complete analysis of the system output is reported elsewhere.[23]

Probe Preparation

The experimental probe was prepared cleaving with a precision cleaver the distal end of a standard glass single-mode optical fiber, 125 μm diameter and 9 μm core, and then dip-coating the fiber tip with aPS/toluene solutions with concentrations ranging from 4% to 0.5% b.w in order to obtain films with reducing size. In this way, films thick from 120 nm down to 20 nm have been produced. The evaluation of the films thickness, d, was made at 418 K by a broad band interrogation made with an optical spectrum analyzer that provided a separate evaluation of both the effective refractive index and the thickness of the polymer layer, as reported in detail in ref.[23]. The film sample was held at a constant temperature (418 K) till the signal stabilization in order to allow the attainment of the equilibrium before the thickness measurements. Films with thickness lower than 20 nm has not been produced due to melt instability and dewetting of the polymer during the equilibration procedure.

Cooling Down Experiments

Glass transition measurements have been then carried out by monitoring the change in reflectance as the temperature was lowered from 418 K to 308 K at constant

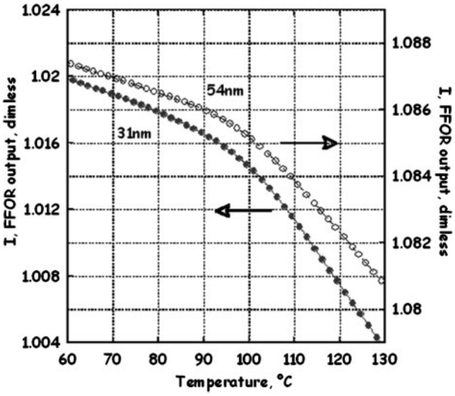

Figure 1.
Typical output of a cooling down tests. (In the case of 31 and 54 nm).

cooling rate of 10 ± 0.08 K/min, assured by a Peltier effect heat pump controller.

Each sample has been tested three times in order to estimate the reproducibility of the response for a given thickness. An example of the optical system output I as a function of temperature is reported in Figure 1. The curves, corresponding to two film samples, respectively 31 and 54 nm thick, present two well defined linear regions, very low scatter of data and exhibit a pronounced change in the slope at the glass transition.

Results and Discussion

Glass Transition Evaluation

Glass transition is a “pseudo” second order phase transition: it is experimentally marked by a quasi-discontinuity in the second derivative of the Gibbs free energy. In other words it manifest itself as a discontinuity upon heating or cooling at a given rate of the specific heat or the thermal expansion coefficient as a function of the temperature or of related properties such as in this case refraction index. So, in this work the glass transition of the aPS films has been studied by analyzing the second derivative of the optical signal with respect to temperature.[21] This method providing the glass transition temperature, by the extremum of the second derivative, allows an easy retrieval of the onset and end point of the transition that have been measured at the 50% of the transition peak.

Data for Tg together with the upper and lower limit of the transition for all the films have been reported as a function of the film thickness in Figure 2. No appreciable effect due to decreasing thickness on the glass transition temperature can be observed Tg = 372.6 ± 2.4 K. A negligible broadening or shifting (see Figure 2) toward lower temperatures of the transition region has been observed (Transition_onset = 381.2 ± 3.2; Transition_end = 364.4 ± 3.5 K). In the present study longer time scales have been investigated, for instance cooling rate of 1 ± 0.09 K/min, still resulting in negligible dependence of the glass transition on the film size (Tg = 370.0 ± 3.3K; Transition_onset = 378.7 ± 2.2K; Transition_end = 361.1 ± 4.5 K) The same results (not reported here) have been found when the Tg was identified by the fictive temperature procedure.

Contrast Evaluation

Further investigations of the transition dynamics have been carried out by analyzing the features of the excess function δ that describes the actual status of the system I

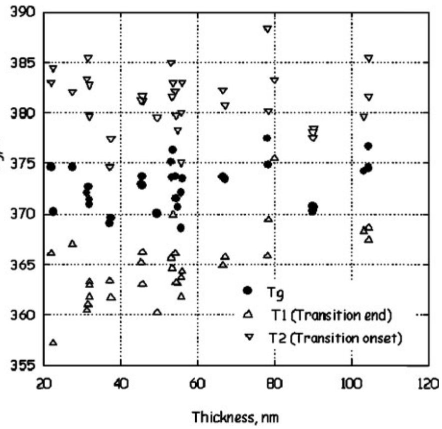

Figure 2.
Glass transition temperature Tg and limits of transition as a function of the thickness d.

with respect to the equilibrium melt state I_{eq}, as

$$\delta(T,d) = \frac{I_{eq} - I}{I_{eq}} = \frac{R_{eq} - R}{R_{eq}} \qquad (1)$$

where the equilibrium curve has been considered as the linear fit of the sensor output I in the temperature range 408–418 K. Figure 3 shows the course in temperature of the excess function for four films with thicknesses reducing from 21 to 105 nm. Below the glass transition, the slope of the excess function decreases with the thickness. In Figure 4 the absolute value of temperature derivative of the excess function evaluated in the glassy zone δ_T^{glass}, i.e. the contrast between the glass and the equilibrium regime, has been reported as a function of the film thickness d (experimental data in the range 120–220 nm have been added to better estimate the onset of the bulk behavior).

A strong depression of the contrast of the transition for decreasing thickness is observed. Such a decrease in the transition strength has been observed in almost all the experimental investigations and has been commonly explained as due to the presence of an enhanced mobility layer at the free surface of the film.[24] As a consequence, the thinner is the film the bigger is the effect of this layer on the properties of the film on a thermal scan.

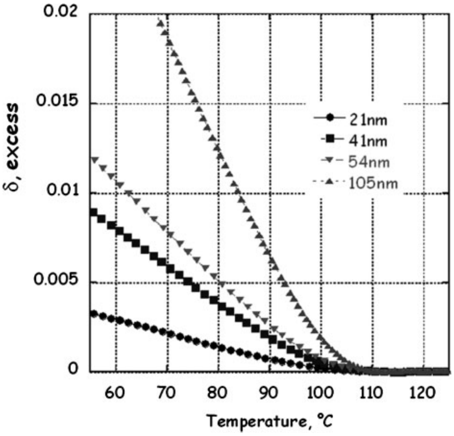

Figure 3.
Excess function course upon cooling for four different thicknesses (21, 41, 54 and 105 nm).

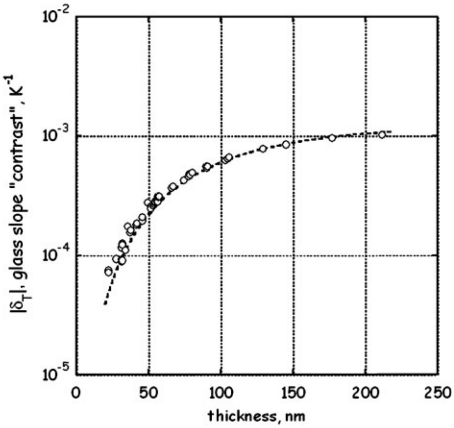

Figure 4.
Absolute value of transition "contrast" vs. thickness with double layer reflectance model predictions.

Transition Function

To analyze the effect of the contrast reduction upon the glass transition dynamic the transition function Tr(d,T) has been defined as

$$Tr(d,T) = \frac{\delta_T(d,T)}{\delta_T^{glass}(d)} \qquad (2)$$

by a scaling of the temperature derivative of the excess function to the "contrast" δ_T^{glass}.

Figure 5 shows that an intrinsic transition dynamic exists not sensitive to the film thickness. Such independent variables decoupling suggests the hypothesis that the external enhanced mobility layer does not contribute to the global glass transition dynamic of the film: in this case the cooperative dynamic of the aPS thin films can be assigned to the core layer that shows essentially a bulk dynamic.

Double-Layer Reflectance Model

A double-layer reflectance model [25] where the polymer film is constituted by an external soft layer and a core layer that suffers the glass transition has been set up. Figure 6 shows the physical model. The expression of the double-layer reflectance

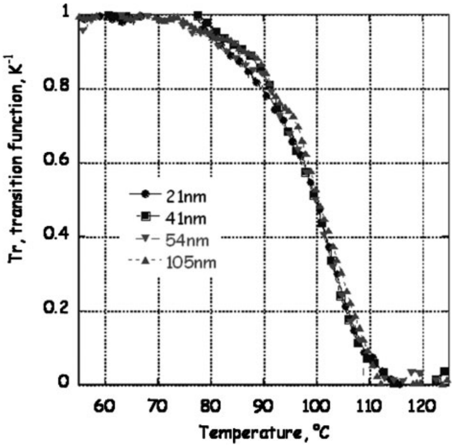

Figure 5.
Transition function, for the four films already reported in Figure 4.

is:

$$R = \left| \frac{r_{12} + r_{23}e^{i\beta_2} + r_{34}e^{i(\beta_2+\beta_3)} + r_{12}r_{23}r_{34}e^{i\beta_3}}{1 + r_{12}r_{23}e^{i\beta_2} + r_{12}r_{34}e^{i(\beta_2+\beta_3)} + r_{23}r_{34}e^{i\beta_3}} \right|^2$$

$$r_{i,i+1} = \frac{n_i - n_{i+1}}{n_i + n_{i+1}} \qquad \beta_i = \frac{4\pi n_i d_i}{\lambda} \tag{3}$$

Where n_i and d_i are the refractive index and thickness of the i layer. The excess function, δ, for a given nominal thickness d, can be evaluated from its temperature derivative (Equation 2) by integration from a generic melt-equilibrium temperature T_{eq},:

$$\begin{aligned} \delta(d,T) &= \int_{T_{eq}}^{T} \delta_T^{glass}(d) \cdot Tr(T) \\ &\cong \delta_T^{glass}(d) \cdot (T - T_g) \end{aligned} \tag{4}$$

Figure 6.
Scheme of the double layer physical model.

Finally Equation 4 relates the experimental data for "contrast" δ_T^{glass} to the excess function δ and by using Equation 1 to the double-layer reflectance equation (Equation 3). Figure 4 shows the best fitting to the experimental data for "contrast" δ_T^{glass}. The model accounts for the simultaneous variation with the temperature of both the layers refractive indexes n_2, n_3 and thicknesses d_2, d_3.

As measured in separate experiments the refractive index of the bulky aPS at 388K is $n = 1.5686$, the melt thermo optic coefficient is $\delta \ln(n)/\delta T|_{eq} = -2.34 \times 10^{-4}$ 1/K and the melt linear expansion coefficient is $\delta \ln(d)/\delta T|_{eq} = 6.00 \times 10^{-4}$ 1/K (5.8–7.2×10^{-4} 1/K for 275 000 Mw aPS [6]). Model adjustable parameters are: the thickness of the liquid layer $d^{liq} = 3.9$ nm at 388 K; the ratio $\alpha_n = 3.1$ between the thermo-optic coefficient of the equilibrium and glassy phases (1.3–2.9 for 120 000 Mw bulky sample aPS;[26] and the ratio $\alpha_d = 2.3$ between the linear expansion coefficient of the equilibrium and glassy phases that is agreement with bulky values 2.1–3.5.[26]

Conclusion

An high resolution optical technique has been used to investigate the effect of the thickness in the range 20–120 nm on the glass transition temperature of aPS (230.000 g/mol) films. Very high signal to noise ratio characterise the experimental data. Cooling down experiments from stabilised melt equilibrium temperature showed that, in this case, not only the glass transition temperature is unaffected by the film nominal thickness but also an intrinsic transition dynamic tested at cooling rate of 10 K/min exists, while the "contrast" between liquid and glassy phase δ_T^{glass} reduces at the film thickness reduction. The double-layer hypothesis with an external film layer (estimated of 3.9 nm at 388 K) that maintains its liquid feature even at temperatures well below the glass transition temperature, while the internal layer experiences the bulk transition has been tested by the implementation of the probe reflectance model.

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