Pattern formation in thin polystyrene films induced by an enhanced mobility in ambient air

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(Received 24 November 2004; revised manuscript received 11 February 2005; published 1 June 2005)

Thin polystyrene films (prepared in a sandwich geometry between two aluminum electrodes) develop a characteristic pattern in ambient air when kept above the glass-transition temperature, whereas they remain unchanged in vacuum or in a pure nitrogen atmosphere. Measurements by broadband dielectric spectroscopy, capacitive dilatometry, and AC calorimetry reveal that the pattern formation is initiated in ambient air by an increase in the average relaxation rate of the dynamic glass transition, which results in a corresponding reduction of the glass-transition temperature. Infrared measurements evidence that this is caused by a shift of the molecular weight distribution to lower values as a consequence of oxygen-induced chain scissions.

DOI: 10.1103/PhysRevE.71.061801 PACS number(s): 36.20.−r, 64.70.Pf, 68.60.Dv

Dynamics in thin polymeric films is an actual topic for fundamental research, as well as for technological applications. The observations of a shift of the glass-transition temperature T_g in confinement [1–7] have stimulated many efforts in understanding the origin of the glass-transition phenomenon [8–11], a still open challenge in contemporary physics [12,13]. Nevertheless, the overview emerging from the data reported in the literature is controversial, since there are many studies indicating no shifts of T_g in thin polymeric films [14–22]. For example, Efremov *et al.* investigated the glass-transition temperature T_g of polystyrene (PS) thin films on a time scale of milliseconds using nanocalorimetry and found no T_g reductions down to a thickness of 3 nm [14]. Shortly after, the authors reported another study in which they modified their technique in order to investigate the glass transition on a time scale of seconds rather than milliseconds and found no T_g reductions as well [15]. The mobility of polymers, whose change in confinement underlies the shifts of the glass-transition temperature, appears to be a key factor in the development of periodic patterns, as reported in the literature for polymeric films capped between two metal layers [23–25].

Here we demonstrate that thin polystyrene films exhibit in ambient air a reduction of the glass-transition temperature caused by a decrease of the average molecular weight as a consequence of oxygen-induced chain scissions. This effect causes an enhanced mobility and allows for the development of a specific pattern.

Thin films of polystyrene (molecular weight $=700\,000$ g/mol, polydispersity 1.05) were prepared by spin-coating from a toluene solution on a glass plate, onto which an aluminum electrode (0.5 mm width, 60 nm height) had been previously evaporated. The samples were annealed for more than 12 h at 150 °C in high vacuum (10^{-5} mbar), followed by the evaporation of a perpendicularly oriented second aluminum counterelectrode. Atomic force microscopy revealed a typical roughness of 2–3 nm for the aluminum electrodes, which assures a rather narrow thickness distribution (having a half-width of 4 nm) and practically parallel interfaces (deviations less than one degree). The thickness, adjusted by varying the concentration of the polymer solution, was determined by measuring the sample capacity at low temperatures (30 °C) and high frequencies (0.1 MHz), a spectral regime where no dielectric dispersion is observed.

When kept at 180 °C in air, thin PS films undergo a gradual change of their initially flat geometry, which ends up with the formation of a specific pattern. A typical example is given in Fig. 1, for a film thickness of 239 nm: after 4 h at 180 °C in air, the initial sample geometry [Fig. 1(a)] is changed and an undulated pattern is developed [Fig. 1(b)], with a well-defined lateral wavelength. The insets in Figs. 1(a) and 1(b) show the corresponding surface topographies, measured by atomic force microscopy. With a typical initial value of 2–3 nm, the root-mean-square roughness increases

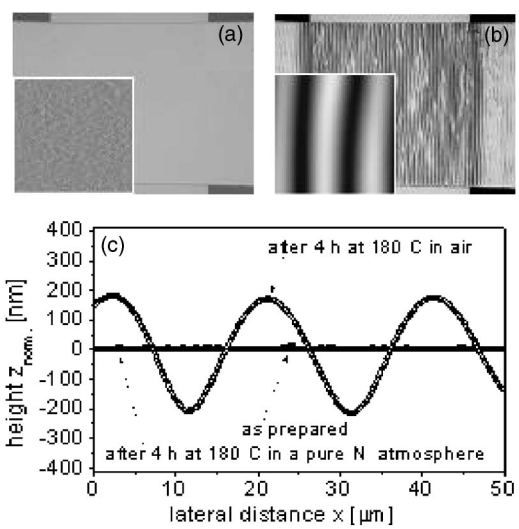

FIG. 1. (a) Optical image (1×1 mm^2) of a 239 nm thin PS film between two aluminum electrodes, as prepared. (b) The sample after 4 h at 180 °C in air. The insets in (a) and (b) represent measurements of the corresponding surface profiles by atomic force microscopy (50 μm$\times$50 μm). (c) The vertical surface profile of the sample, as prepared, after 4 h at 180 °C in a nitrogen atmosphere and after 4 h at the same temperature in air.

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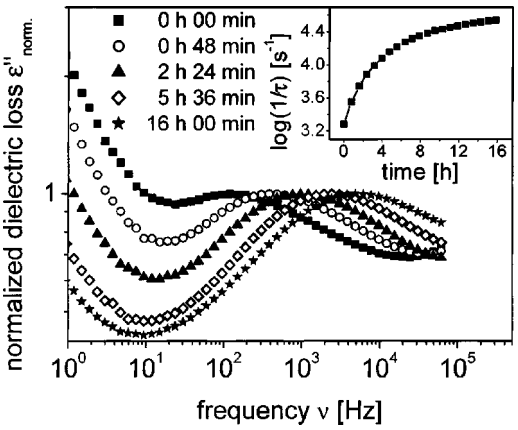

FIG. 2. Dynamic glass transition (α relaxation) at 123 °C in ε'' vs frequency for a film thickness of 75 nm after different annealing times at 180 °C in air, as indicated. Inset: the corresponding relaxation rate in dependence on the annealing time at 180 °C in air.

steeply and reaches 129 nm after the formation of the pattern. As explained in the literature [23,25], the pattern development is caused by the compressive stress originating from the difference in the thermal-expansion coefficients between the polymer and the upper metal layer. In contrast to the measurements performed in air, in a pure nitrogen atmosphere, under the *same* experimental conditions, *no* pattern is developed: both optical microscopy and atomic force microscopy reveal in these cases similar results as in Fig. 1(a), thus no deformations of the sample geometry. This is clearly illustrated in Fig. 1(c), which shows the vertical surface profiles measured by AFM for the sample of 239 nm as prepared and after 4 h at 180 °C in a nitrogen atmosphere and in air, respectively. This finding suggests that the mobility of thin PS films is enhanced in ambient air in comparison to that in a pure nitrogen atmosphere.

In order to analyze the molecular dynamics of PS thin films, broadband dielectric spectroscopy [26] is employed. The average relaxation rate of the α relaxation process increases in time by more than one decade when the sample is kept in air at 180 °C (Fig. 2). Using the usual fitting procedure [26], the relaxation rate as a function of inverse temperature is extracted (Fig. 3). While unchanged in a nitrogen atmosphere, the dynamic glass transition becomes faster in air, which corresponds to a shift to lower temperatures of the maximum position of the α relaxation peak (inset in Fig. 3). This causes a reduction of the glass-transition temperature, which was measured by dilatometry as well (Fig. 4). Its principle is schematically illustrated in the inset of Fig. 4: the kink in the temperature dependence of ε' reflects a change in the thermal-expansion coefficient from a glassy to a liquid state and by that marks the position of the glass-transition temperature. The usual algorithm calculates the value of T_g as the intersection point of two linear dependencies. However, if the accuracy of the measurements permits, a much

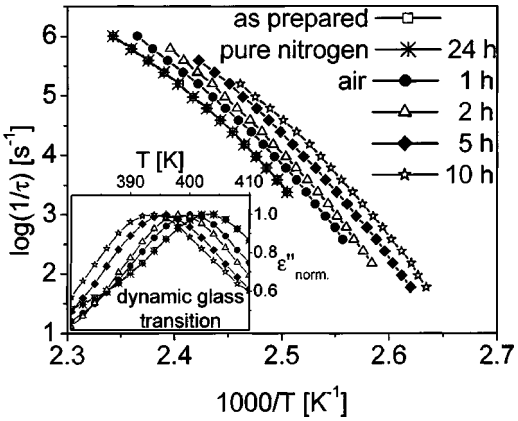

FIG. 3. Relaxation rate vs inverse temperature for a 63 nm thin film as prepared, after 24 h annealing at 180 °C in a pure nitrogen atmosphere, and after 1, 2, 5, and 10 h annealing at the same temperature in air (the logarithm is in decimal base). Inset: the corresponding α relaxation at 1.2 kHz in ε'' vs temperature. If not specified otherwise, the errors are comparable with the size of the symbols.

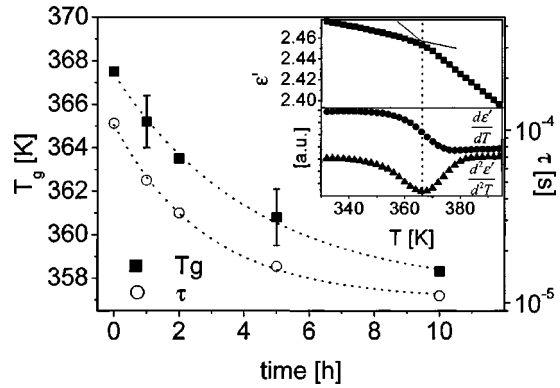

FIG. 4. Glass-transition temperature T_g (determined by dilatometry) and relaxation time τ at 404 K as a function of annealing time in air at 180 °C for a film thickness of 63 nm. The dotted lines serve as guidance for the eyes. Inset: dilatometric determination of the glass-transition temperature. Upper: ε' vs temperature at 10^6 Hz (the solid lines represent linear dependencies, the dotted line marks the position of the glass-transition temperature). Lower: the corresponding first and second derivative of ε' (in arbitrary units) as a function of temperature.

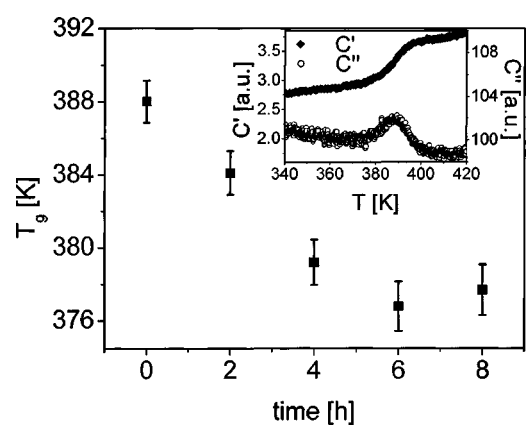

FIG. 5. Glass-transition temperature T_g (determined by temperature modulated calorimetry at 20 Hz) for a film thickness of 93 nm in dependence on the annealing time at 200 °C in ambient air. Inset the real and the imaginary part of the complex heat capacity (in arbitrary units) at 10 Hz as a function of temperature.

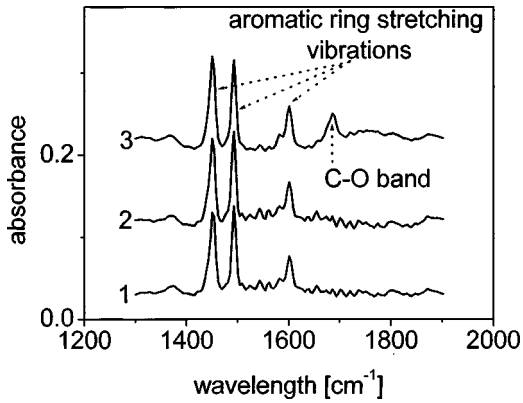

FIG. 6. Infrared spectra (spectral resolution of 8 cm^{-1}) for a PS film of 4 μm: (1) as prepared, (2) after 24 h at 200 °C in a pure nitrogen atmosphere, (3) after 24 h at 200 °C in air. The curves are vertically shifted for clarity.

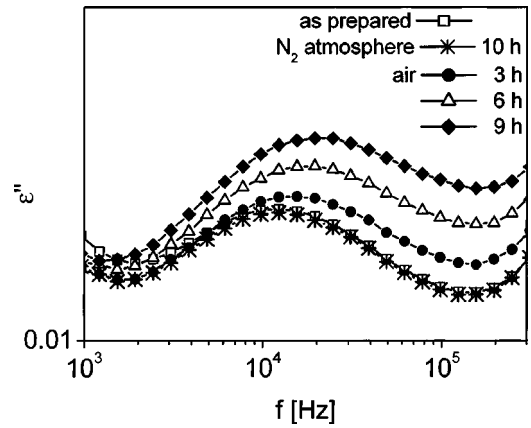

FIG. 7. The dynamic glass transition of an 86 nm thin PS film at a constant temperature of 414 K, as prepared, in a pure nitrogen atmosphere and in air as a function of time, as indicated.

better way is represented by the numerical calculation of the first and second derivative of ε' as a function of temperature. The position of the kink in the ε' versus temperature dependency corresponds to the minimum in the temperature dependence of $d^2\varepsilon'/d^2T$.

The aluminum electrodes appear to play no role in the observed T_g reductions. Measurements by ac calorimetry [27] for thin PS films prepared by spin coating on a SiN membrane and not covered by an upper aluminum layer reveal similar results as for the samples prepared in a sandwich geometry: a decrease in time of the glass-transition temperature in ambient air (Fig. 5).

The origin of the enhanced mobility is suggested by several studies investigating the viscosity of bulk PS at temperatures above 260 °C in high vacuum [28–30]: a pronounced decrease of the sample viscosity is observed in time, caused by a decrease of the average molecular weight induced by chain scissions. Since there is a significant dependence of the glass-transition temperature on the molecular weight of PS [31], a consequent T_g reduction and a corresponding faster dynamics is implied. In ambient air, this is expected to take place at much lower temperatures than in high vacuum because of the presence of oxygen, which diminishes the probability of chain recombination after scission. The effect should be even more pronounced in thin films, since the surface-to-volume ratio increases here by many orders of magnitude, which enhances strongly the exposure area per volume unit. This hypothesis has been checked by keeping PS thin films at 180 °C in a pure oxygen atmosphere: a similar pattern to that in Fig. 1(b) is developed after a few hours. Additionally, infrared measurements confirm the formation of the C-O band in the spectrum of a 4-μm-thick PS film kept 24 h in ambient air at 200 °C (Fig. 6), a clear proof of a chain scission effect, since oxygen is not present initially in the structure of the polystyrene macromolecule.

As a collateral aspect of our work, an increase of the average relaxation rate in thin PS films in air is also observed at much lower temperatures, i.e., 414 K (Fig. 7). Such temperatures are comparable with those currently reached in most of the studies investigating the T_g reductions in thin polystyrene films, many of them being performed in ambient air. It is of course not excluded that the effects reported in the present paper occur below 414 K, too, when the samples are exposed to the presence of oxygen. Besides this, even more pronounced effects are expected for thin films having a free interface, that is, not covered with a thin upper aluminum electrode. *Whether* and to what extent the results indicating a faster dynamics in thin films are caused by chain scissions in the presence of oxygen, as suggested in the present study, and especially whether there is a thickness dependence of this effect, is currently investigated and will be published in a separate paper.

In conclusion, we show that already at 140 °C the glass-transition temperature of thin polystyrene films decreases in time in the presence of oxygen because of chain scissions. This leads to an enhanced mobility, which allows for the development of a period pattern.

The authors thank Otto van den Berg for fruitful discussions.

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