Ion crater healing and variable temperature ellipsometry as complementary probes for the glass transition in thin polymer films

Y. Grohens\textsuperscript{1}, R.M. Papaléo\textsuperscript{2}, and L. Hamon\textsuperscript{3}

\textsuperscript{1} Laboratoire Polymères et Procédés, Université de Bretagne Sud, rue St Maudé, BP 92116, 56325 Lorient Cedex, France
\textsuperscript{2} Faculty of Physics, Catholic University of Rio Grande do Sul, Av. Ipiranga 6681, C.P. 1429, 90619-900 Porto Alegre, RS, Brazil
\textsuperscript{3} IUT d’Evry, Département des Sciences, rue du Père Jarland, 91025 Evry Cedex, France

Received January, 2003
Published online November 5, 2003 © EDP Sciences / Società Italiana di Fisica / Springer-Verlag 2003

Abstract. Poly(methyl methacrylate) (PMMA) thin films of various tacticity and thickness were bombarded at grazing angles by 20 MeV Au ions at different temperatures. The shape of the tracks was investigated by scanning force microscopy (SFM) after annealing for various time at different temperatures and constant quenching rate. The thickness dependent glass transition temperature, \(T_g(h)\), was estimated from the temperature of relaxation of ion-caused nanodeformations in the films. \(T_g(h)\) obtained from the thermal healing of the holes and hillocks is found in good agreement with the one determined by variable temperature ellipsometry for PMMA film thickness of 80 nm and corresponds to the \(T_g\) of each bulk PMMA stereoisomer. Below this thickness, some significant divergences are observed between the \(T_g\) measured by the two techniques. We propose that the healing of ion crater hillock and the kink in the thermal expansion arise from the different nature of chains motions which are perturbed to different extents according to the main polymer chain preferential orientation in the thin film. This can be tentatively interpreted by a so-called “anisotropic” character of the glass transition.

PACS. 05.70.NP Interface and surface thermodynamics – 34.50.Dy Interactions of atoms and molecules with surfaces; photon and electron emission; neutralization of ions

1 Introduction

Many experimental observations have shown that the glass transition of thin polymer films strongly differs from (usually below for PS and above for PMMA and P2VP) the glass transition temperature of the bulk polymer, \([1,2,3,4,5,6,7,8,9,10]\). This is a fascinating recent feature exhibited by homopolymers in confined geometry, namely supported films, freely standing films and polymers in nanoporous minerals.

Many attempts have been undertaken to explain these observations, mostly by considering microscopic models of the inner structure of the films. Long \textit{et al.} have envisaged the freezing of the film as a percolation of rigid domains \([11]\), mediated by thermal fluctuations \([12]\). De Gennes recently suggested that collective motions, so-called sliding motions, would dominate in thin films because chain end effects might be negligible. Other models assume a layered structure of the film, with a particularly mobile region close to the free surface of the film \([13]\). Within this framework, Forrest \textit{et al.} \([14]\) have recently proposed a model which makes use of the so-called cooperativity length, which plays a major role in a whole class of theoretical concepts of the glass transition based on the Mode Coupling Theory (MCT) or Cooperatively Rearranging Region (CRR) \([15,16]\). A major drawback is that whilst relatively well established theory exists in the case of bulk polymers no relevant model exists for thin films. Furthermore, as a consequence of the multi-layer structure of the film, it is not completely clear why there should not be two glass transitions, rather than a single one shifted in temperature. Very recently, Ngai \([17]\) suggested that anisotropy in the orientation of polymer chains in thin films that has previously been proposed \([18]\), might be responsible for the modifications of \(T_g\) through a change in the intermolecular coupling. Analogy with dynamics in the mechanically deformed glassy polymers \([19]\) accounts for the above mentioned assumption.

An alternative way to probe thermal relaxation of polymer chains in thin films is to produce corrugated surfaces and to study the temporal evolution of the roughness at various temperatures. Kerle \textit{et al.} \([20]\) presented a fascinating work in which they showed that only partial relaxation of the surface asperities can be achieved for temperatures below the bulk \(T_g\) and that complete relaxation only occurs above \(T_g\). Moreover, they realised the
importance of the interfacial free energy in the relaxation process. Using the same idea, we produced tracks from individual energetic ions impacting a solid and followed the healing of the craters as a probe of the $T_g$ of the polymer film [21]. For 100 nm thick films the estimated $T_g$ of atactic PMMA is in good agreement with the bulk $T_g$. In previous papers we have shown that the $T_g(h)$ of thin films of isotactic PMMA increased significantly for thickness lower than 50 nm whereas a decrease of the $T_g(h)$ was observed for syndiotactic PMMA [22]. Therefore, in the present study, we investigated the thermal healing of tracks created on stereoregular PMMA films thinner than 100 nm and compare these results with the thickness dependent $T_g$ measured by ellipsometry.

### 2 Experimental

The PMMA polymers used have been purchased from Polymer Source Inc. Their characteristics are given in Table 1. These polymers were spin cast from chloroform solutions on (111) silicon surfaces treated by H$_2$O plasma prior to polymer deposition. Silicon wafers covered by vacuum evaporated aluminum were also used. The films were studied after annealing 30 °C above $T_g$ for at least 10 hours followed by cooling at constant rate. We used a FT-IR spectrometer (Bruker IFS-66) equipped with a mercury-cadmium-telluride (MCT) detector. Experiments were performed with a Specac specular reflectance element used in polarized reflection-absorption mode (RAIR). The incidence angle, $\theta$, was set to 82°. The experimental reflectivity is measured at each incidence angle and compared to the theoretical reflectivity obtained from the Kramers-Kronig equations. According to the methodology developed in reference [18], the ratio of these two reflectivities obtained at different angles of incidence and polarization allows the calculation of the orientation of the backbone chain axis as well as the persistence length of the orientation in the thin film. Spectroscopic ellipsometry experiments were performed by using a Sopra ES4M apparatus working in a range of wavelength from 0.4 to 0.8 μm. The film thickness was calculated from the fit of the ellipsometric angles tan $\phi$ and cos $\Delta$ in this range of frequencies. The so-called kinetic ellipsometric scans were performed by focusing on only one wavelength (0.75 micrometers) and with a heating rate of 2 °C/min. The same heating rate was used for DSC experiments.

The films were bombarded with individual 20 MeV Au ions at very low doses. The ion fluence, around $10^9$ ions/cm$^2$, is reached in less than 2 s with a scanned beam of approximately 1 nA/cm$^2$. Immediately after the irradiation the films were quenched with cooling water if the temperature was above the room temperature. The topology of irradiated targets was characterised in air by Nanoscope IIIa (Digital Instruments) scanning force microscopy in the Tapping Mode. The damping of the free oscillation of the cantilever was kept to a minimum value. Each individual ion leaves a tiny hole (crater) and a deformed raised region (bump) around the point of ion impact. The dimensions of the impact features were extracted from the cross-sectional profiles using the AFM software and mean values were calculated from data collected from 50 impact sites. The length of the craters and hillocks are measured along the direction of the ion impact. At temperatures close to $T_g$ the relaxation rate of the deformed region is fast and the deformed region relaxes (disappears) before large scale movements are frozen by cooling. Previous values on a-PMMA, indicated a relaxation temperature very close to $T_g$ (i.e., we are identifying the temperature of bump relaxation with $T_g$). The uncertainties on the $T_g$ determination is calculated to be in the range of ±5 °C.

### 3 Results and discussion

The present challenge to develop tools for nanometer-scale characterization of surfaces has rekindled interest in the field of MeV-GeV ion track production. When a fast particle penetrates a solid a large amount of energy is rapidly pumped into the material in a small nanometer region around the ion path [23]. Initial stages of ion track formation are complex and dynamic, involving fast conversion of the electronic excitation energy into atomic motion. In spite of this complexity, the main features of surface track formation in molecular solids have been described relatively well by simple hydrodynamic mechanisms [24]. The nanometer-sized craters and/or raised regions (hillocks) around the point of ion impact are observed by Scanning Force Microscopy (SFM). In previous papers [21] it has been shown that the size of the craters created in a PMMA thin film was independent of the temperature at which it has been bombarded in a range of −196 to 80 °C. Above this temperature, the crater dimensions increases steeply and no hillock is observed around the crater. This can be observed in Figure 1 for a-PMMA film of 40nm thickness on which the nanodeformation relaxation time is above 30 s for temperature of 90 °C which is close to the $T_g$ of this isomer at 105 °C. The same method was applied to stereoregular PMMA. Since the works of Karasz et al. [25] it well known that the bulk PMMA stereoisomers show a large difference in $T_g^{bulk}$, ranging between 40 and 130 °C for $i$-PMMA and $s$-PMMA, respectively. It is worth noting that the origin of this discrepancy in $T_g^{bulk}$, usually related to structural parameters, is still not fully understood. The level of coupling between backbone and side-chain motions was recently proposed to explain the differences in the $T_g$ of the PMMA stereoisomers [26].