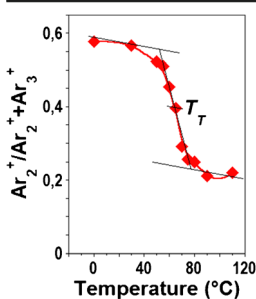


SHORT COMMUNICATION

Temperature Dependence of Ar_n^+ Cluster Backscattering from Polymer Surfaces: a New Method to Determine the Surface Glass Transition Temperature

Claude Poleunis, Vanina Cristaudo, Arnaud Delcorte

Institute of Condensed Matter and Nanosciences (IMCN), Surface Characterisation Platform (SUCH), Université catholique de Louvain (UCL), Place Louis Pasteur 1, box L4.01.10B-1348, Louvain-la-Neuve, Belgium



Abstract. In this work, time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to study the intensity variations of the backscattered Ar_n^+ clusters as a function of temperature for several amorphous polymer surfaces (polyolefins, polystyrene, and polymethyl methacrylate). For all these investigated polymers, our results show a transition of the ratio $\text{Ar}_2^+ / (\text{Ar}_2^+ + \text{Ar}_3^+)$ when the temperature is scanned from -120 °C to $+125$ °C (the exact limits depend on the studied polymer). This transition generally spans over a few tens of degrees and the temperature of the inflection point of each curve is always lower than the bulk glass transition temperature (T_g) reported for the considered polymer. Due to the surface sensitivity of the cluster backscattering process (several nanometers), the presented analysis could

provide a new method to specifically evaluate a surface transition temperature of polymers, with the same lateral resolution as the gas cluster beam.

Keywords: ToF-SIMS, Glass transition temperature (T_g), Polybutadiene (PIB), Polystyrene (PS), Polymethyl methacrylate (PMMA)

Received: 31 August 2017/Revised: 24 October 2017/Accepted: 25 October 2017/Published Online: 27 November 2017

Introduction

Ion beams have been used for structural and chemical characterization of materials for decades. Mega-electronvolt ion beams provide access to compositional and structural information from the surface towards the depth of solid targets via the backscattering of the projectile (He^+) after collision with the atoms of the sample (Rutherford backscattering spectroscopy, RBS) [1]. The atomic composition of the sample is deduced from the energy lost by the backscattered ion after elastic collision in the solid and the structural information is obtained via the blocking and channeling effects occurring in crystalline materials. In contrast, the penetration depth of kiloelectronvolt ions is limited to the surface region. The backscattering of keV monoatomic ions of noble gas, at the origin of low-energy ion scattering spectroscopy (LEIS, also known as ISS), provides structural and elemental information about the extreme surface of the sample (top atomic layer)

because low energy ions have a very high neutralization probability when they penetrate the solid [2]. Another technique using keV ions is secondary ion mass spectrometry (SIMS). As the name suggests, SIMS collects the atomic, fragment, and molecular secondary ions emitted from the surface as a result of the energy deposited by a primary ion in the solid, in order to form a mass spectrum of the interrogated surface. With the use of very well-focused beams, state-of-the-art SIMS instruments provide chemical images with submicronic resolution and a depth resolution of the order of the nanometer [3]. Recently, large gas cluster ion beams (GCIB) have attracted a strong interest because they can desorb surface molecules from organic materials with minimal damage to the sample, provided that their kinetic energy per atom (E/n) is sufficiently low [4]. GCIB have opened the door to less fragmented mass spectra such as in matrix-assisted laser desorption ionization (MALDI-MS) or electrospray ionization (ESI-MS) and to depth profiling with retention of the molecular information. In turn, GCIB using $\text{Ar}_{500-5000}^+$ clusters have now become the reference for the chemical and molecular analysis of organic coatings and films (organic electronics multilayers [5], plasma-treated surfaces [6], cells and tissues [3, 7], etc.)

In a recent article, Mochiji et al. have studied the distributions of small Ar_n^+ clusters appearing in the secondary ion

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s13361-017-1840-7>) contains supplementary material, which is available to authorized users.

Correspondence to: Claude Poleunis; e-mail: claudio.poleunis@uclouvain.be

mass spectra of metallic surfaces as a result of the backscattering of the projectile fragments [8]. They demonstrated that the intensity ratio of $Ar_2^+/\Sigma Ar_n^+$ ($2 \leq n \leq 7$) could be correlated to the impulsive stress caused by the impact of the cluster at the metal surface, which depends only on the projectile velocity, the Young moduli of the cluster and of the metal, and their densities (assuming an initially elastic interaction). Therefore, their analysis gives access to the local Young's modulus of an unknown surface, since the surface nature can be identified with the mass spectrum.

In this work, we show that large gas cluster fragmentation is also sensitive to the physical state of polymer surfaces. In particular, the intensity of backscattered Ar cluster fragment ions displays a pronounced and reproducible variation at the surface transition temperature (T_T), in relationship with the bulk T_g of the investigated polymers.

Experimental

Samples

Amorphous polymers were supplied by Sigma-Aldrich Inc (Overijse, Belgium). The investigated polymers were high molecular weight polydisperse polyisobutylene (PIB), polystyrene (homodisperse; $M_w = 4000$ Da, PS 4K), and polymethyl

methacrylate (homodisperse; $M_w = 2000$ Da, PMMA 2 K and 150,000 Da, PMMA 150 K). Solutions of each polymer in toluene (Sigma-Aldrich, >99.7% purity) were prepared and spin-coated onto clean Si wafers of 1×1 cm² at 5000 rpm with acceleration 20,000 rpm/s for 60 s. The wafers were sonicated in isopropanol prior to the coating and then dried under N₂ flux. The solution concentrations (from 20 to 35 g/l) were chosen in order to obtain ≈ 100 nm thick films. Thicknesses were evaluated via calibration curves previously established for these polymers [9]. Low density polyethylene (LDPE) additive-free film was supplied by Goodfellow (Cambridge, United Kingdom).

DSC Measurements

Differential scanning calorimetry (DSC) measurements were performed with a Mettler Toledo DSC821 for all PS and PMMA samples and with a Mettler Toledo DSC822 for the PIB sample. Scans consisted to heat, cool down, and heat again from 30 °C up to 150 °C at a rate of 10 °C/min, for PS and PMMA; and from -120 °C up to 100 °C at a rate of 10 °C/min, for PIB.

ToF-SIMS Instrumentation

ToF-SIMS spectra were collected using a TOF.SIMS 5 (ION-TOF GmbH, Münster, Germany) time-of-flight secondary ion mass spectrometer. The instrument is equipped with an Ar gas

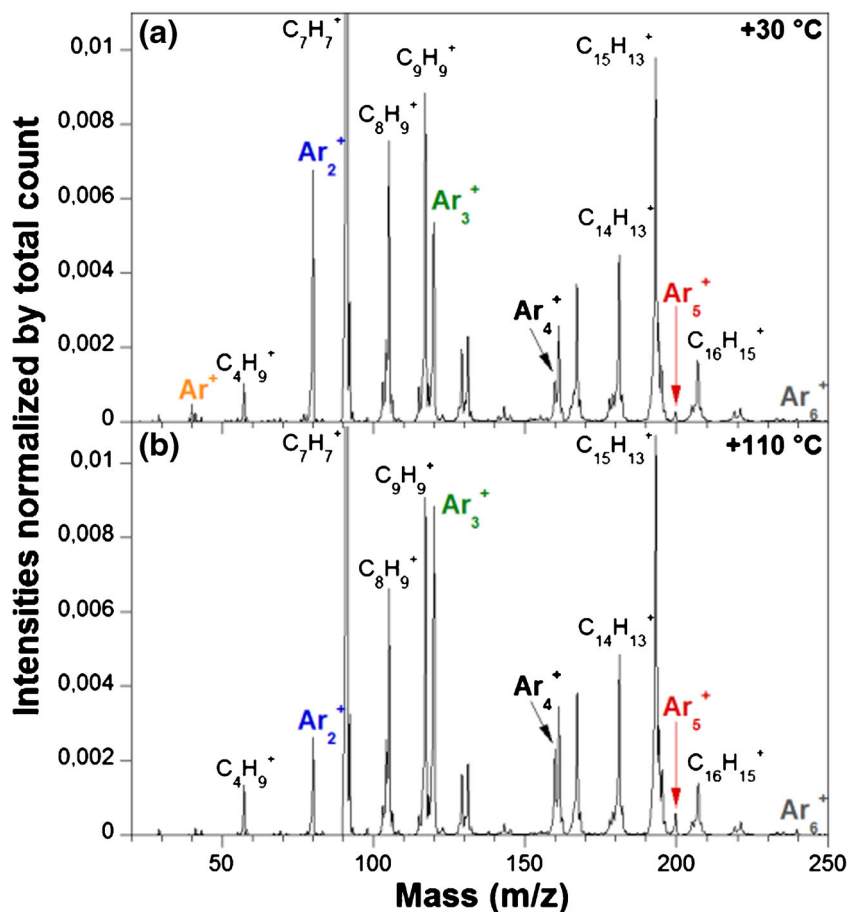


Figure 1. Positive ToF-SIMS spectra of PS 4K measured at (a) +30 °C, and (b) +110 °C

cluster ion beam (Ar-GCIB) mounted at 45° with respect to the sample surface. It was used both as sputtering and analytical source. The time-of-flight mass analyzer is perpendicular to the sample surface. The Ar-GCIB ion source was operated at 10 keV and the cluster distribution was centered on Ar₃₀₀₀⁺. For the spectral analyses, an AC target current of 0.037 pA with a bunched pulse width around 70 ns was used. A raster of 128 × 128 data points over an area of 500 × 500 μm² was used. The total primary ion beam dose per unit area for each analyzed region was kept below 8 × 10¹¹ ions·cm⁻², ensuring static conditions. Only positive secondary ion species were analyzed. Mass resolution $m/\Delta m \approx 280$ at 67 m/z (corresponding to C₅H₇⁺) was maintained for spectra acquisition. Charge compensation was ensured using a very low energy electron flood gun ($E_k = 5$ eV). All the data analyses were carried out using the software supplied by the instrument manufacturer, SurfaceLab (ver. 6.5). Temperature was controlled with a special sample holder called “Holder G” (ION-TOF GmbH, Münster, Germany). This holder allows maintaining any temperature from -150 °C to +600 °C through a combination of simultaneous heating and cooling, with an accuracy of ± 1 °C. The temperature was stabilized for 20 min before each analysis. Prior to analysis, a pre-sputtering of 2×10^{13} Ar₃₀₀₀⁺/cm² over an area of 1000 × 1000 μm² was also conducted with the Ar-GCIB in DC mode. This mandatory procedure was done in order to eliminate all the surface contaminations.

Results and Discussion

Figure 1 shows the positive secondary ion mass spectra measured on a PS 4K surface at +30 °C (a) and +110 °C (b). These temperatures have been chosen in order to be well in the glassy state and the rubbery states of PS 4K, respectively (bulk $T_g \approx +83$ °C).

In the case of PS 4K, argon clusters up to Ar₇⁺ (m/z 280), are detected. Backscattered Ar⁺ is only detected below T_T , but with a low intensity. In addition, because of the possible interference with ⁴⁰Ca⁺ at the same nominal mass (due to poor mass resolution), the interpretation of this peak is subject to caution.

Figure 2a displays the behavior of the backscattered Ar_n⁺ peaks ($1 \leq n \leq 5$) for PS 4K as a function of the temperature. The intensities are normalized first by the total counts of the related spectrum, then by the maximum of the curve of the considered cluster. A clear transition is observed for the Ar⁺ curve. The inflection point of this curve is lower than the bulk T_g of PS. The Ar₂⁺ curve presents a transition too, but less pronounced than the one of Ar⁺. Unlike Ar⁺, the intensity of the Ar₂⁺ peak stabilizes after the transition and never levels off. Furthermore, the Ar₂⁺ peak intensity is always higher and there is no interference with other contributions at the same mass, in contrast with Ar⁺. The other Ar_n⁺ backscattered clusters also show a transition around T_T , but unlike Ar⁺ and Ar₂⁺, their intensities increase with T° at the transition.

Figure 2b points out a ratio, defined as: $Ar_2^+/(Ar_2^+ + Ar_3^+)$, as a function of the temperature. The choice of this ratio is

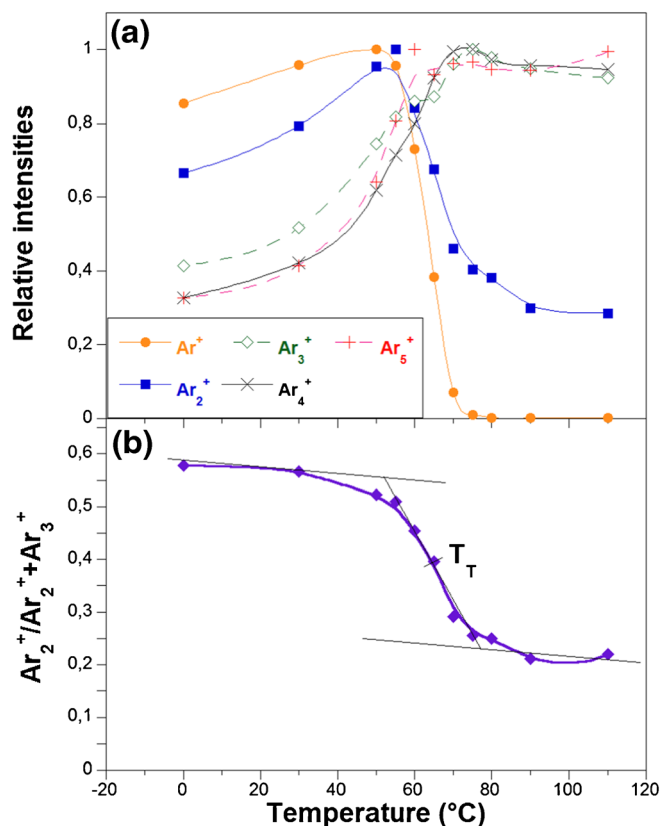


Figure 2. Temperature dependence of (a) the normalized intensities of the backscattered Ar_n⁺ peaks ($1 \leq n \leq 5$), and (b) the $Ar^+/(Ar_2^+ + Ar_3^+)$ ratio, for PS 4K

justified by the fact that the Ar₂⁺ and Ar₃⁺ peaks are the most intense in all cases, and no mass interference is encountered. Its variation is very similar to that of $Ar_2^+/\sum Ar_n^+$ ($2 \leq n \leq 7$), as defined in [8]. The reason not to use that ratio as such is that the number of detectable Ar_n⁺ species depend on the analyzed polymer and interferences occurring in some cases for $n > 3$. Dividing by $(Ar_2^+ + Ar_3^+)$ intensities enhances the variation of Ar₂⁺ and makes it independent of instrumental variations. As was the case with Ar⁺, the temperature of the inflection point of this curve is also lower than the bulk T_g reported for PS 4K (see Table 1). We propose to consider this ratio rather than the transition also observed on the Ar⁺ curves because of the low intensity of Ar⁺ and the possible interference with Ca⁺.

Other polymers, with different bulk T_g , have been investigated with the same methodology. The results are summarized in Table 1. It is remarkable that the temperatures measured at

Table 1. Bulk T_g (Measured by DSC) and T° Measured at the Inflection Point for The Different Polymers Tested in This Study

	Bulk T_g	T° measured at the inflection point for:	
		Ar ⁺	$Ar_2^+/(Ar_2^+ + Ar_3^+)$
PIB	-65 °C	-71 °C	-70 °C
PS 4K	+83 °C	+64 °C	+65 °C
PMMA 2K	+75 °C	+65 °C	+66 °C
PMMA 150K	+127 °C	+101 °C	+102 °C

the inflection points are always lower than the reported bulk T_g . These differences between bulk T_g and surface T_T were already described by Fu et al. for homodisperse PS [10] and for homodisperse PMMA [11], using a different approach based mainly on the secondary ion spectrum interpretation. No literature was found on this topic for PIB.

Another example of application is shown in Figure S1 in the Supplementary Information, where a droplet of PS 4K has been deposited onto an LDPE film surface. The image (a) displays the chemical contrast between both polymers, while the image (b) shows the ratio $Ar_2^+/(Ar_2^+ + Ar_3^+)$.

These images were taken at room temperature. The highest values of the ratio are found in the glassy PS 4K region, whereas the lowest corresponds to the rubbery LDPE (LDPE bulk $T_g < -100$ °C and PS 4K bulk $T_g = +83$ °C).

The mechanistic interpretation of the observed variations, i.e., the explanation of the different distributions of backscattered fragment ions when going from the glassy to the rubbery state of the polymers, remains to be established. It is important to note that the range of variation of the ratio $Ar_2^+/(Ar_2^+ + Ar_3^+)$ is the same for all the polymers, showing a certain independence of the effect on the specific polymer chemistry. An interpretation based on the structural properties, resulting in smaller cluster fragments in the glassy state than in the rubbery state, is therefore reasonable. As mentioned earlier, mechanical properties were also the cause of similar variations for metallic surfaces (hardness) [8]. Concerning polymers, molecular dynamics simulations of cluster impacts on crystalline and amorphous polymeric samples [12] with varying free volume will be implemented in order to better understand the dependence of the cluster fragmentation on the polymer surface structure. At this point, it is impossible to completely rule out the influence of ionization or neutralization effects.

Conclusions

A new method to probe the surface mechanical properties of polymers at the molecular level (surface T_T) in relationship with the bulk T_g was demonstrated, using the impact of large noble gas cluster ions. Though the detailed mechanistic interpretation remains elusive at this stage, the fact that the method

indicates surface T_T for a series of polymers with diverse chemistries, in a range between -70 and $+130$ °C, demonstrates its efficacy and robustness. This new protocol should also be investigated for irreversible structural changes occurring in polymers and induced by heating, such as polymerization and cross-linking via sample curing.

References

1. Earwaker, L.G.: Rutherford backscattering and nuclear reaction analysis. *Vacuum*. **45**, 783–803 (1994)
2. Bertrand, P.G., Rabalais, J.W.: Ion scattering and recoiling for elemental analysis and structure determination. In: Rabalais, J.W. (ed.) *Low energy ion-surface interactions*, p. 55. Wiley, Chichester (1994)
3. Fletcher, J., Vickerman, J.C.: Secondary ion mass spectrometry: characterizing complex samples in two and three dimensions. *Anal. Chem.* **85**, 610–639 (2013)
4. Delcorte, A., Cristaudo, V., Lebec, V., Czerwinski, B.: Sputtering of polymers by keV clusters: microscopic views of the molecular dynamics. *Int. J. Mass Spectrom.* **370**, 29–38 (2014)
5. Mouhib, T., Poleunis, C., Wehbe, N., Michels, J.J., Galagan, Y., Houssiau, L., Bertrand, P., Delcorte, A.: Molecular depth profiling of organic photovoltaic heterojunction layers by ToF-SIMS: comparative evaluation of three sputtering beams. *Analyst*. **138**, 6801–6810 (2013)
6. Cristaudo, V., Collette, S., Tuccitto, N., Poleunis, C., Melchiorre, L.C., Licciardello, A., Reniers, F., Delcorte, A.: Molecular surface analysis and depth-profiling of polyethylene modified by an atmospheric Ar-D₂O post-discharge. *Plasma Process. Polym.* **13**, 1106–1119 (2016)
7. Shon, H.K., Yoon, S., Moon, J.H., Lee, T.G.: Improved mass resolution and mass accuracy in ToF-SIMS spectra and images using argon gas cluster ion beams. *Biointerphases*. **11**, 02A321.1–02A321.7 (2016)
8. Mochiji, K., Se, K., Inui, N., Moritani, K.: Mass spectrometric analysis of the dissociation of argon cluster ions in collision with several kinds of metal. *Rapid Commun. Mass Spectrom.* **28**, 2141–2146 (2014)
9. Cristaudo, V., Poleunis, C., Czerwinski, B., Delcorte, A.: Ar cluster sputtering of polymers: effects of cluster size and molecular weights. *Surf. Interface Anal.* **46**, 79–82 (2014)
10. Fu, Y., Lau, Y.T.R., Weng, L.T., Ng, K.M., Chan, C.M.: Evidence of enhanced mobility at the free surface of supported polymer films by in situ variable-temperature time-of-flight-secondary ion mass spectrometry. *Anal. Chem.* **85**, 10725–10732 (2013)
11. Fu, Y., Lau, Y.T.R., Weng, L.T., Ng, K.M., Chan, C.M.: Transition temperature of poly(methyl methacrylate) determined by time-of-flight secondary ion mass spectrometry and contact angle measurements. *J. Colloid Interface Sci.* **504**, 758–764 (2017)
12. Delcorte, A., Debongnie, M.: Macromolecular sample sputtering by large Ar and CH₄ clusters: elucidating chain size and projectile effects with molecular dynamics. *J. Phys. Chem. C*. **119**, 25868–25879 (2015)