Secondary molecular ion emission from aliphatic polymers bombarded with low energy ions: Effects of the molecular structure and the ion beam induced surface degradation

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Abstract

The influence of the molecular structure on the secondary ion production is studied for three saturated aliphatic polymers (low-density polyethylene, polypropylene and polyisobutylene) bombarded with low energy ions. These polymers differ only by the presence and nature of the pendant group. The intensities of the most characteristic secondary molecular ions are followed as a function of the primary ion dose in the (10^{12} ions/cm^2–10^{14} ions/cm^2) range for two primary ion bombardment conditions (4 keV Xe$^+$ and 15 keV Ga$^+$). The results show that there is a direct relationship between the polymer degradation and the emission of molecular fragments. No truly "static" conditions are found, rather, the polymer surface undergoes a continuous transformation under ion beam bombardment. The most spectacular effect is its dehydrogenation. By rationalizing the competition between the two related processes, surface degradation and molecular ion production, a kinetic model is proposed in order to explain the behavior of molecular fragments belonging to the C8 cluster.

1. Introduction

Large molecular ions are emitted when a polymer is bombarded with low energy ions in the low fluence regime. These ions are characteristic of the polymer molecular structure and their detection (after mass discrimination) constitutes the basis of the Static SIMS technique for polymer surface analysis [1,2]. However, the mechanisms of the molecular ion emission are not yet fully understood. Several models have been invoked to explain the origin of secondary molecular ions in polymers [3,4]. In the precursor model, large molecular ions are believed to be produced only at some distance from the primary ion impact point, where the deposited energy from the collision cascade is limited [5]. However, the inelastic contribution to the ion sputtering is unclear. Part of the primary ion energy deposition is transformed into electronic and vibrational excitations leading to bond breaking and polymer chains fragmentation with the production of radicals and ions. The polymer molecular structure is modified during SIMS analysis even when using low dose levels ($< 10^{13}$ ions/cm^2) as evidenced by several authors [6–14].

In this work, a detailed study of the surface degradation mechanisms related to the molecular structure of the poly-

mer chains is presented in order to (i) gain a better understanding of the secondary ion formation in these systems; (ii) look at upper limit of the ion dose for which the molecular information can still be obtained with the SIMS technique. A series of saturated aliphatic polymers only differing by the pendant group (polyethylene, polypropylene, polyisobutylene) is investigated.

2. Experimental

2.1. Samples

Three saturated aliphatic polymers have been studied: low-density polyethylene (LDPE), polypropylene (PP) and polyisobutylene (PIB). LDPE and PP were in the form of films provided by Shell-Louvain-la-Neuve (B) and were analysed as received. PIB was purchased from Aldrich

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Table 1
Polymer structure

Polyethylene, PE	Polypropylene, PP	Polyisobutylene, PIB
$(-CH_2-CH_2-)_n$	$(-CH-CH_2-)_n$ $\mid$ CH_3	CH_3 $\mid$ $(-C-CH_2-)_n$ $\mid$ CH_3

Chemie, dissolved in a solution containing 2% of polymer and then spin-coated on Si wafers to produce thin films. The polymer molecular structures are given in Table 1. The samples' cleanliness and purity was tested by XPS (SSI-X-Probe) analysis and contamination was not detected except in the case of LDPE which showed ~ 1 at.% of oxygen on the surface.

2.2. SIMS analyses

The samples were bombarded and analyzed in two different systems. The first system consists of a time-of-flight SIMS microprobe-microscope (Charles Evans & assoc.) using a (5 kHz) pulsed Ga^+ beam (15 kV, 400 pA dc) [15]. The ion dose (D) for one spectrum acquisition is $\leq 10^{12}$ ions/cm^2. A pulsed electron beam and a stainless steel grid are used for charge compensation. For polymer surface degradation studies, alternated sequences of ToF-SIMS analysis periods (pulsed beam, $D = 10^{12}$ ions/cm^2) and continuous bombardment ($5 \times 10^{12} \leq D \leq 2 \times 10^{14}$ ions/cm^2) are utilized. In the second system, a Xe^+ (4 keV, 10 nA) ion beam is used and rastered on a 0.3 cm^2 surface area and the secondary ions are mass analyzed by means of a quadrupole spectrometer (Riber-Q156). For SIMS spectrum acquisition, the ion dose D is kept lower than 10^{13} ions/cm^2. Charge compensation is achieved by the use of a electron flood gun (2 A, 150 eV).

3. Results and discussion

3.1. Molecular structure

Fig. 1 shows the positive ToF SIMS spectra obtained with 1.1×10^{12} Ga^+ ions/cm^2 on pristine PE, PP and PIB samples (see their molecular structures in Table 1). These spectra are similar to those reported in the literature [1,2]. Although the molecular structures of the monomers differ only by the presence of methyl pendant groups, the spectra are clearly different in the relative intensities of some ions in the different carbon clusters (a cluster "Cx" refers to the ions having the same number (x) of carbon atoms, the number of hydrogen atoms varying from 0 to $2x + 1$). The maximum intensity is observed for the deprotonated monomer $(M-H)^+$ at 27 amu for PE, 41 amu for PP and 55 amu for PIB. The pendant methyl group contributes to the high relative intensities of the characteristic fragments at masses 55 and 69 amu for PP and PIB, and the double pendant methyl group of PIB accounts for the peaks at 83 and 97 amu. Their molecular structures have been previously discussed by Van Ooij and Briggs [16,17]. Another significant difference between these spectra is the contribution of the C8 cluster which increases with the branching level: the mean values of the normalized intensities $I(\Sigma C_8H_y)/I_{Tot}^*$ are respectively 0.42×10^{-2} for PE, 1.05×10^{-2} for PP, and 2.47×10^{-2} for PIB (the stan-
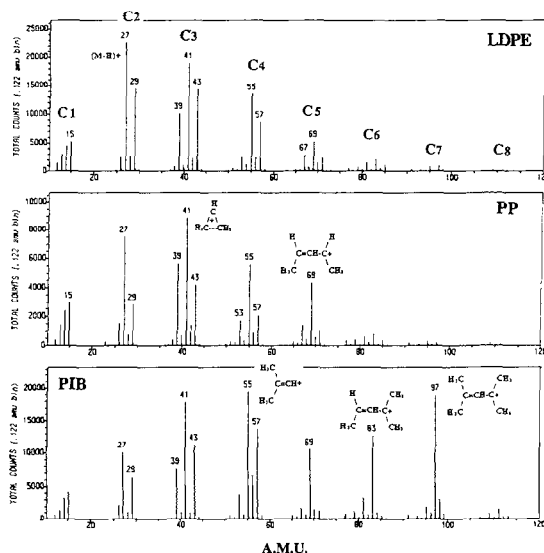

Fig. 1. Positive ToF SIMS spectra obtained with 1.1×10^{12} Ga^+ ions/cm^2 on pristine PE, PP and PIB samples.

dard deviation is about 1×10^{-3}). I_{Tot}^* is the total integrated intensity minus the hydrogen intensity which is barely reproducible. The explanation for this effect is related to the higher stability of branched ions as compared to the linear ones [16].

3.2. Surface degradation

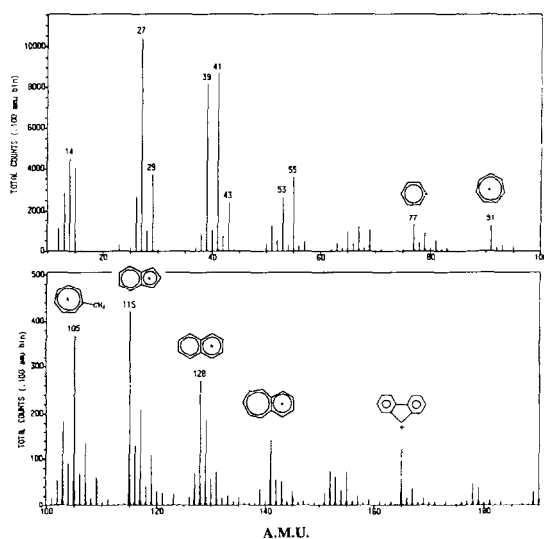The influence of the ion dose on the spectrum is stressed in Fig. 2 where a PP spectrum obtained with

Fig. 2. Positive ToF SIMS spectrum obtained with 1.1×10^{12} Ga^+ ions/cm^2 on a PP sample previously bombarded with 2×10^{14} Ga^+ ions/cm^2 ion dose.

2×10^{14} Ga$^+$ ions/cm^2 is shown. Increasing the ion dose gives rise to several differences: (i) the intensity of the peak at 69 amu, which is the most characteristic of the PP structure, decreases strongly; (ii) the cluster Cn with the maximum intensity is shifted to a lower value, the cluster C2 is becoming predominant; (iii) in every Cn cluster, unsaturated peak intensities increase at the expense of the more saturated ones; and (iv) new peaks of ions with an aromatic structure (at 77, 91, 105, 115, 128 amu [16]) become very intense (similar peaks are observed in polystyrene). The same trends are also observed on the other polymers. The decrease in the intensity of the most characteristic peaks of PP and PIB is shown in Fig. 3 as a function of the cumulated ion dose as described in the experimental section. For PIB, the decrease with the ion dose of characteristic fragments at 83 and 97 amu is already initiated at the first point of measurement while for PP, the peak at 69 amu increases first to a maximum before decreasing. These results show the close relationship between the secondary molecular ion production and the polymer degradation under ion beam bombardment [13]. The direct loss of intensity for the most characteristic ions observed in the investigated ion dose is related to the degradation of the precursor. The maximum observed for the 69 amu peak in PP indicates the competition between two processes: the degradation and the ion formation which may be induced by a previous degradation. Looking at the intensity variation of the less characteristic peaks in the different Cn clusters, a direct loss is always observed for the most saturated fragments and this cannot result from a previous degradation of the surface. In order to investigate more deeply this effect, continuous bombardment and secondary ion intensity measurements were done on PP for specific ions using a quadrupole mass spectrometer and a Xe$^+$ (4 keV, 10 nA) ion beam. The results obtained for the different ions of the C8 cluster are shown in Fig. 4. Special attention was paid to this cluster because
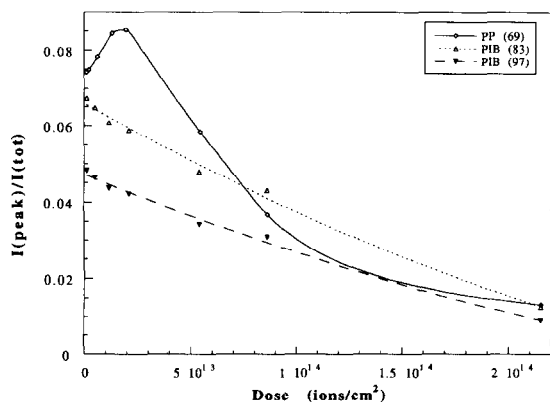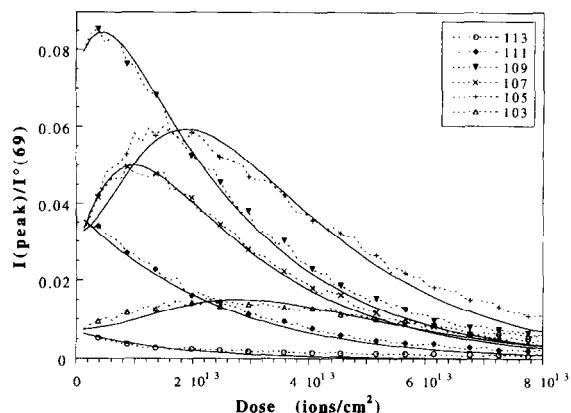

Fig. 4. Quad-SIMS intensities of C8 cluster (C$_8$H$_y^+$) as a function of the cumulated Xe$^+$ (4 keV) ion dose for PP. The intensities are normalized to the initial value of the peak at 69 amu.

it does not contain fragments highly characteristic of the polymer structure. It is striking to see in Fig. 4, the regularity of the (SIMS intensity versus ion dose) curves succession, from the most saturated ion (C$_8$H$_{17}^+$ at 113 amu) to the less saturated one (C$_8$H$_7^+$ at 103 amu). This shows that the degradation is always greater for saturated peaks than for unsaturated ones. Moreover, the curves show a variation in shape and intensity which suggests a dehydrogenation reaction affecting the surface of the polymer. Indeed, only dehydrogenation is able to produce such a continuous transformation into fragments of increasing unsaturation.

We developed a kinetic model able to account for this intra-cluster phenomenon. It is related to the observation that decay of fragments with a given H content contributes to the production of fragments with lower H content. The model is based on the assumption of existence at the polymer surface of precursors for the given molecular ions. Then the intensity of a given ion i, I_i, is proportional to the surface concentration of its precursors C_i^*,

$$I_i = \varepsilon_i C_i^*, \tag{1}$$

where ε_i is a sensitivity factor related to the physics of the interaction and to the experimental conditions. The effect of ion beam degradation is to modify the precursor concentrations C_i^* with a decrease rate α_i and this contributes to the increase of the C_{i+x}^* concentration with a probability factor γ_{i+x} so that we obtain a set of coupled differential equations for the C_i^*:

$$dC_i^* = -\alpha_i C_i^* + \alpha_{i-1}\gamma_{i-1}C_{i-1}^* + \alpha_{i-2}\gamma_{i-2}^* C_{i-2}^* + \cdots. \tag{2}$$

If we assume that only the first two terms are dominant in the second part of Eq. (2), then

$$dI_i = -\alpha_i I_i + \alpha_{i-1}\gamma_{i-1}(\varepsilon_i/\varepsilon_{i-1})I_{i-1}, \tag{3}$$

Fig. 3. ToF-SIMS intensity dependence of the most characteristic peaks of PP (69 amu) and PIB (83 and 97 amu) as a function of the cumulated Ga$^+$ (15 keV) ion dose.

Table 2
Parameters for $C_8H_y^+$ intensity dose dependence

Mass [amu]	y	i	α_i [10^{-13} cm^2/ions]	β_i
113	17	1	0.58	0
111	15	2	0.50	1.0
109	13	3	2.0	10.5
107	11	4	2.23	0.7
105	9	5	1.0	0.63
103	7	6	1.0	0.28

or applied to the dehydrogenation of the C8 cluster:

$$dI(C_8H_y) = -\alpha_i I(C_8H_y) + \alpha_{i-1}\beta_{i-1}I(C_8H_{y+2}),$$
$$(4)$$

where $y = 2x + 1$, $4 \leq x \leq 8$ and $i = 9 - x$ (see Table 2) and

$$\beta_i = \gamma_i \varepsilon_{i+1}/\varepsilon_i. \qquad (5)$$

The α_i and β_i values giving the best fit between the model and the experimental results are presented in Table 2 and the calculated dependence of $I(C_8H_y)$ with the ion dose are represented by the full lines in Fig. 4. It is observed that the model describes correctly the experimental behavior and confirms the continuous loss of hydrogen from polymer surfaces bombarded with ions in the experimental conditions of the SIMS analysis. This transformation is already begun at the first point of measurement.

The $1/\alpha_i$ values give the characteristic ion doses for degradation and are in the $\sim 10^{13}$ ions/cm^2 range. They represent the upper limit for molecular SIMS analyses. The interpretations of the β_i values are not straightforward because they include the probability factors γ_i (≤ 1) and also the ratio of the SIMS sensitivity factors $\varepsilon_{i+1}/\varepsilon_i$ which can be greater than 1. Indeed, the information given by SIMS is not a direct image of molecules lying on the polymer surface. Several parameters, depending on exact physics and chemistry of the phenomenon, influence strongly the fragment intensities. First of all, the detected ions only represent a little fraction of emitted species and this fraction could depend on the mass and structure of the fragments and on their chemical stability. For example, aromatic or branched ions are favored compared to linear aliphatic fragments [16].

4. Conclusion

The degradation study shows that when bombarded with ion beams (Xe$^+$, Ga$^+$), saturated aliphatic polymer surfaces undergo a continuous transformation already initiated at very low doses. This transformation affects the whole spectrum and not only the highly characteristic SIMS peaks which are however the most sensitive to

degradation. This leads to the conclusion that there does not exist a real "static" regime for these polymers and that ion formation is intrinsically related to the degradation process. On the other hand, this study shows clearly, especially the $1/\alpha$ values in Table 2, that reproducible molecular information can be obtained from these polymers when analyzed with ion doses $< 10^{+13}$ ions/cm^2. One key phenomenon inducing polymer degradation has been identified: the dehydrogenation. But there is still work to be done to understand the modifications of the molecular structures leading to other phenomena such as segmentation, cross-linking and aromatic ion formation. A better understanding of secondary ions formation in polymers is also very desirable and would directly enlight such degradation mechanisms.

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