

# Chemical Modification of Polystyrene by Low-Energy (<100 eV) Electron Irradiation Studied by Mass Spectrometry

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**ABSTRACT:** Dip-coated thin films of polystyrene were chemically modified (degraded) by low-energy electron irradiation (0–100 eV). The resulting degradation was studied by mass spectrometry with variable electron energy. In the negative-ion mode, H<sup>-</sup> was observed and was associated with two phenomena. The resonant structure at  $9.1 \pm 0.4$  eV was associated with dissociative electron attachment. The energy of the resonance peak agreed with the results obtained for organic molecules. At a higher energy, a monotonic rise of the emission yield was observed and was associated with nonresonant dipolar dissociation. More mass fragments were observed in the positive-ion mode. The predominant ion was H<sup>+</sup> at 100 eV of electron irradiation, and alkyl ions were detected at higher masses. Emission thresholds were

measured for the most predominant positive ions. The shape of the emission curve showed that there was no resonant process in the formation of these ions. The energy threshold was measured at about 20 eV, and this meant that the carbon structure of the polymer broke with a recombination of the degradation products with hydrogen atoms before the emission occurred. Below 19 eV, there was only hydrogen loss; this implied that the possible degradation mechanisms did not break the general carbon structure of the material, leading to cross-linking. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3163–3168, 2008

**Key words:** degradation; electron beam irradiation; mass spectrometry; polystyrene

## INTRODUCTION

The surface modification of polymers has attracted considerable attention in the past several decades.<sup>1</sup> Many techniques such as wet-chemical,<sup>2</sup> plasma,<sup>3</sup> and corona-discharge treatments<sup>4</sup> have been developed to modify polymer surfaces for practical applications, particularly in medicine and in microelectronics.<sup>5,6</sup> In the beginning, polymers were modified by radiation processing. The irradiation of polymers with ionizing radiation ( $\gamma$ -rays,<sup>7</sup> X-rays,<sup>8</sup> high-energy electrons,<sup>9</sup> and ion beams<sup>10</sup>) leads to the formation of very reactive and complex intermediates, free radicals, ions, and excited states.<sup>10</sup> These intermediates can follow several reaction paths that result in hydrogen abstraction, rearrangements, and/or the formation of new bonds.<sup>11</sup> Precise control of the radiation modification

processes still remains a challenge. To overcome this problem, a mass-separated, low-energy ion-beam treatment has been developed.<sup>10,12</sup> The use of a light-mass ion (e.g., H<sup>+</sup>) offers advantages and efficiency in modifying the polymer surface, but the use of a H<sup>+</sup> beam could be problematic for a polymer that does not contain hydrogen atoms, such as polytetrafluoroethylene. In fact, the use of such beams can contaminate the polymer surface by ion implantation.<sup>13</sup> Another approach to the problem could be the development of low-energy electron (LEE) sources for the irradiation of polymers. Below 100 eV, these electrons have a high linear energy transfer (i.e., comparable to that of light ions of higher energy) and can induce specific reactions via processes such as dissociative electron attachment (DEA).<sup>14</sup>

To investigate the possibility of developing a versatile apparatus for LEE irradiation of polymers, we chose polystyrene (PS) as a model compound. PS is an important material in academic research and industry that is relatively easy to mechanically process. Moreover, PS has a relatively simple structure consisting of phenyl groups and saturated aliphatic chains. In this work, we study the response of the degradation of PS thin films induced by the impact of 0–100 eV

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electrons. These studies will help us to determine the conditions for the modifications of this polymer and to understand the mechanisms of degradation of this material when it is bombarded with LEEs.

## EXPERIMENTAL

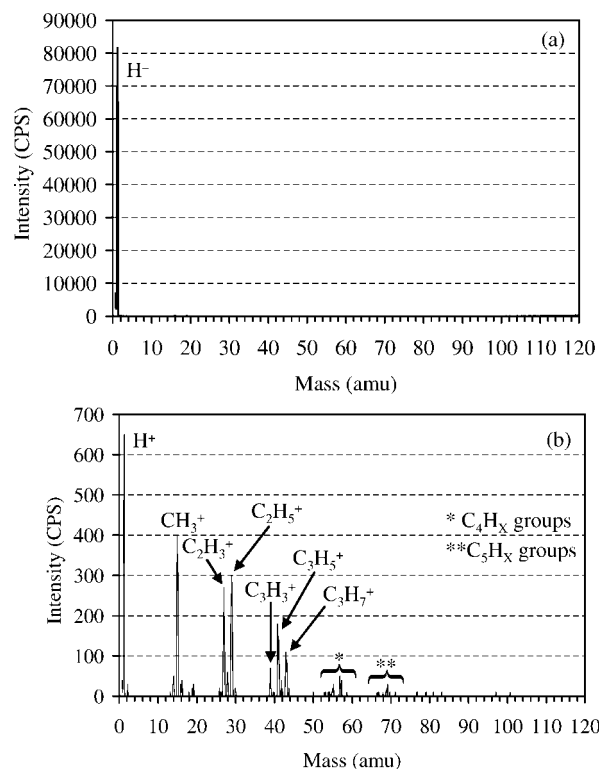
### Sample fabrication

The sample fabrication consisted essentially of two steps: the preparation of the substrates and the deposition of the films. The substrates had to be metallic to avoid charge accumulation during electron bombardment.<sup>15,16</sup> Molybdenum (Mo) was chosen because of its low tendency to oxidize at room temperature<sup>17</sup> and the relative ease of handling. Mo foils from Alfa Aesar (Ward Hill, MA) ( $100 \times 100 \text{ mm}^2$ , 1.0 mm thick, purity of 99.95%) were cut in the form of disks of about 14 mm. Each substrate was then cleaned with acetone in an ultrasonic bath for 10 min before polishing. The polishing was done in the first part with 600- and 150-grit sandpaper to obtain a uniform surface. Then, polishing was accomplished with a monocrystalline diamond suspension (0.5  $\mu\text{m}$ ) and a perforated Pellon polishing cloth, both from Anamet (Colborne, Canada). This level of polishing allowed us to maximize the uniformity of the added layer of the polymer film. After the polishing, the Mo substrates were cleaned in an ultrasonic bath with ethanol and acetone. For each solvent, the cleaning was 15 min long. The substrates were then dried for 24 h in a vacuum of about  $10^{-3}$  Torr at the ambient temperature.

The deposition of the PS films was done by dip-coating.<sup>18,19</sup> PS pellets (Aldrich, Oakville, Canada; weight-average molecular weight  $\approx 280,000$ , glass-transition temperature =  $100^\circ\text{C}$ , density ( $d$ ) = 1.047) were dissolved in tetrahydrofuran at a concentration of 0.25% (w/w). For each solution of 200 mL, only five films were made to ensure that the concentration was constant. The coating was done with a home-made dip coater at a constant withdrawal speed of  $40 \pm 2 \text{ mm/min}$ . The substrates were then dried for 24 h in a vacuum of about  $10^{-3}$  Torr at the ambient temperature and sheltered from the light to prevent possible degradation.<sup>20,21</sup> The PS film thickness was measured to be  $15 \pm 5 \text{ nm}$  by DekTak profilometry with a half-coating of PS.

### LEE degradation experiments

The LEE impact apparatus has been completely described elsewhere.<sup>22</sup> It consists of a load-lock chamber with a multisample holder and a main chamber equipped with a rotary target holder. The sample surface is placed perpendicularly to an Extrel 150-QC quadrupole mass spectrometer (Pittsburgh,

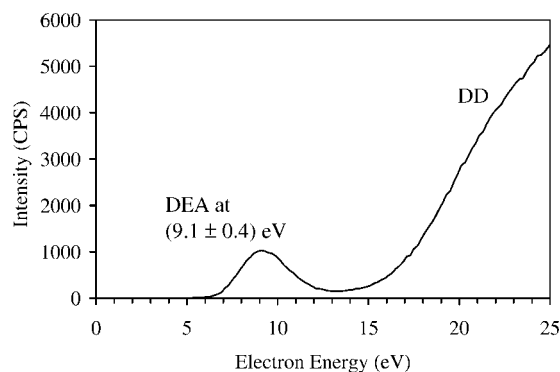


**Figure 1** Mass spectra of (a) negative and (b) positive ions emitted from PS irradiated with a 100-eV electron beam.

PA) and a modified commercial LEE gun, with its axis oriented at an incident angle of  $70^\circ$  with respect to the sample surface normal. The spectrometer has a mass resolution (ratio of the ion mass on the difference in mass between two resolvable peaks) of 400 in the mass range of 1–120 amu, permitting measurements in counts per second of positive and negative ions during LEE irradiation. The LEE gun has an estimated energy resolution of  $\sim 0.4 \text{ eV}$  at a current of  $\sim 0.35 \text{ nA}$  for an energy of 10 eV. The LEE degradation experiments were performed under a pressure of  $\sim 10^{-9}$  Torr and at about 300 K.

## RESULTS AND DISCUSSION

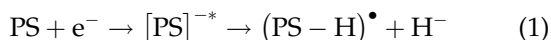
Figure 1 exhibits mass spectra obtained from a 100-eV incident electron beam onto PS films. The beam current for the measurements was  $\sim 0.3 \text{ nA}$  in the negative-ion mode and  $\sim 30 \text{ nA}$  in the positive-ion mode because of the poor emission rate of cations. As seen in the negative-ion-mode mass spectrum [Fig. 1(a)],  $\text{H}^-$  is the only anion signal of significant magnitude. More mass fragments were observed in the positive mode, as shown in Figure 1(b). Positive mass fragments consist only of C and H atoms, proving the purity of the samples. The predominant ion is  $\text{H}^+$ . At higher masses, the presence of hydrocarbon ions is detected, and one can see  $\text{C}_n$  ion



**Figure 2** Energy dependence of the  $\text{H}^-$  ion yield with 5–25-eV electron bombardment.

groups at  $\sim 15$  ( $\text{CH}_x^+$ ,  $x = 2-4$ ),  $\sim 29$  ( $\text{C}_2\text{H}_x^+$ ,  $x = 2-6$ ),  $\sim 41$  ( $\text{C}_3\text{H}_x^+$ ,  $x = 3-7$ ),  $\sim 57$  ( $\text{C}_4\text{H}_x^+$ ), and  $\sim 69$  amu ( $\text{C}_5\text{H}_x^+$ ) with a decrease in the intensity as the number of carbon atoms increases. The most predominant ions are identified in Figure 1(b); they are  $\text{H}^+$  (1 amu),  $\text{CH}_3^+$  (15 amu),  $\text{C}_2\text{H}_3^+$  (27 amu),  $\text{C}_2\text{H}_5^+$  (29 amu),  $\text{C}_3\text{H}_3^+$  (39 amu),  $\text{C}_3\text{H}_5^+$  (41 amu), and  $\text{C}_3\text{H}_7^+$  (47 amu).

The incident electron energy dependence of the  $\text{H}^-$  ion yield (i.e., the yield function) is shown in Figure 2 with approximately 0.3 nA of electron irradiation. The electron energy range was scanned from 5 to 25 eV. Two phenomena were observed in this energy range. At an electron energy of  $9.1 \pm 0.4$  eV, there is the appearance of a resonant structure that is associated with DEA:<sup>23–26</sup>



The resonant structure at 9.1 eV was previously observed for other organic molecules. Prabhudesai et al.<sup>23</sup> reported DEA of  $\text{H}^-$  ions for acetic acid and propanoic acid at 9.1 eV. Moreover, LEE bombardment of solid films composed of saturated hydrocarbons ranging from  $\text{CH}_4$  to  $\text{C}_9\text{H}_{20}$  produced  $\text{H}^-$  yield functions exhibiting a broad peak near 9 eV due to DEA.<sup>27</sup> Finally, from electron-impact experiments on thin films of methanol, it was concluded that C–H cleavage occurs via DEA above 9 eV with the production of  $\text{C}\cdot\text{H}_2\text{OH}$  radicals.<sup>28</sup>

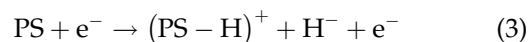
Above the energy threshold for electronic excitation, the DEA resonant process is principally characterized by the formation of a temporary excited molecular anion or arises from a core-excited resonance<sup>23,26,29</sup> consisting of a one-hole two-electron state, that is, two electrons trapped in excited orbitals by a core hole.<sup>30,31</sup> The dissociative anion state occurs at a specific resonance energy corresponding to a given orbital configuration. According to results obtained from thymine and adenine,<sup>26</sup> the anion formation can be attributed to electron capture by the

electron affinity of excited states involving excitation of the lone pair:  $n \rightarrow \sigma^*$ ,  $\pi \rightarrow \pi^*$ , and/or  $\sigma \rightarrow \sigma^*$ . When the lifetime of this resonance is of the order of, or longer than, the nuclear motion vibrational period ( $\sim 10^{-14}$  s),<sup>32</sup> the temporary excited molecular anion can dissociate into radical and anion fragments, as shown in eq. (1), if at least one of the fragments has a positive electron affinity.<sup>33,34</sup> Because DEA occurs in vibrational timescales, there is relatively little energy redistribution. Because of the localization of energy, the fragmentation occurs at the site of core excitation, and the excess charge is carried away by the detected fragment.<sup>23</sup> The energy balance is given by<sup>35,36</sup>

$$E_k = (1 - \beta)(E_i - E^* - E_B + EA + E_{\text{pol}}) \quad (2)$$

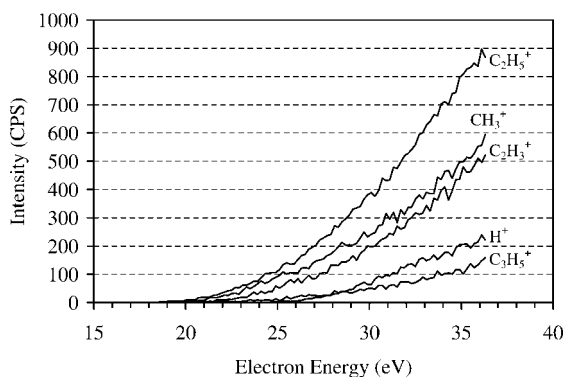
where  $E_k$  is the kinetic energy of the emitted anion,  $\beta$  is the anion mass ratio,  $E_i$  is the field-free energy of the incident electron,  $E^*$  is the total internal energy of the fragments following the dissociation,  $E_B$  is the bond cleavage energy, EA is the electron affinity of the fragment with which the electron combines, and  $E_{\text{pol}} (<0)$  is the induced polarizing potential at the surface that the emitted ion must overcome.<sup>35</sup>

In the 13–25-eV electron energy range, there is a monotonic rise of the emission yield of  $\text{H}^-$  ions (Fig. 2). In this energy range, direct dipolar dissociation (DD) is the only nonresonant mechanism that can produce a significant signal of stable anions with sufficient energy ( $\geq 1$  eV) to escape the induced polarization potential at the surface.<sup>37–39</sup> The DD process is described as follows:<sup>24,28</sup>



DD is a nonresonant electronic excitation dissociative process that results in the production of a stable anion and cation from a neutral excited state ( $\text{PS}^*$ ) of the initial molecule. In our case, the energy transfer via inelastic scattering of the incident electron to the polymer breaks the C–H bond, resulting in the production of the  $\text{H}^-$  anion. The dissociation limits of the neutral excited states involved in the DD process usually lie at much higher energies than the neutral and anion ground-state dissociation limits. Thus, transitions to excited states leading to the formation of ion pairs are usually not observed below the first ionization threshold.<sup>28,32</sup>

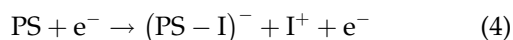
We note that below 13 eV, only a single negatively charged species is formed ( $\text{H}^-$ ) via DEA. In this case, no charge compensation occurs such as in DD. Because  $\text{H}^-$  anions are expected in an amorphous solid to be emitted equally in all directions, a considerable number of  $\text{H}^-$  ions should remain in the film after LEE bombardment and charge it negatively, as



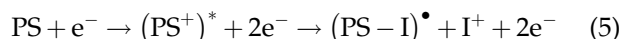
**Figure 3** Dependence of the positive-ion emission with electron bombardment between 16 and 36 eV.

has been clearly shown in the case of *n*-hexane films.<sup>40</sup> Such charges can modify the properties of the dielectric. In fact, it has been shown that the dielectric aging of high-voltage cables made of polyethylene is partially caused by the accumulation of negatively charged species produced by DEA of weakly trapped electrons that are released and accelerated by the presence of the high electric field.<sup>32</sup>

Emission thresholds were measured for the most predominant positive ions observed in Figure 1(b) ( $\text{H}^+$ ,  $\text{CH}_3^+$ ,  $\text{C}_2\text{H}_3^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$ ) with 16–36-eV electron bombardment (Fig. 3). The other detected ions, such as  $\text{C}_3\text{H}_3^+$  or  $\text{C}_3\text{H}_7^+$ , did not have a sufficient signal-to-noise ratio to obtain a significant accuracy in the threshold measurements. As shown in Figure 3, only a monotonic increase in the emission is observed for all the positive ions, showing the absence of a resonant structure in all desorption yields. This suggests that the degradation process can be associated with DD<sup>24,28</sup>



or with dissociative ionization:<sup>41</sup>



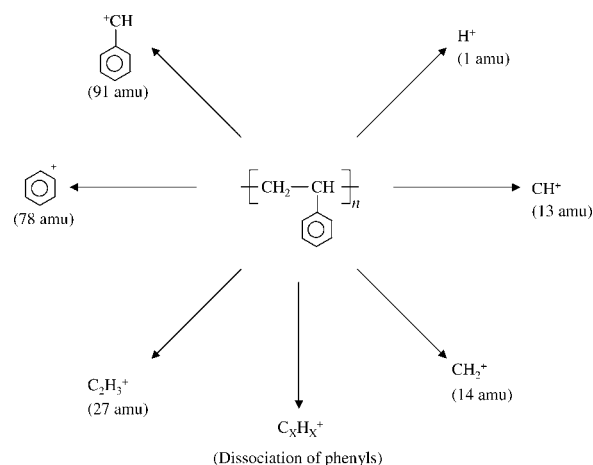
where PS is the polymer and  $\text{I}^+$  is the ion detected by mass spectrometry. Emission thresholds for the five main ions were evaluated and are presented in Table I. Intensity ratios are not the same in the mass spectrum in Figure 1(b) and in Figure 3 because of the difference in the energy of the incident electrons. In Figure 1(b), the most abundant ion is  $\text{H}^+$  with 100-eV electron irradiation, whereas the  $\text{H}^+$  signal is one of the less intense in Figure 3 with 35-eV electron irradiation. This suggests that positive-ion emission does not increase at the same rate for all the ions studied as electron energy increases.

Considering the structure of PS, we find that the main possible ions produced by direct impact are  $\text{H}^+$

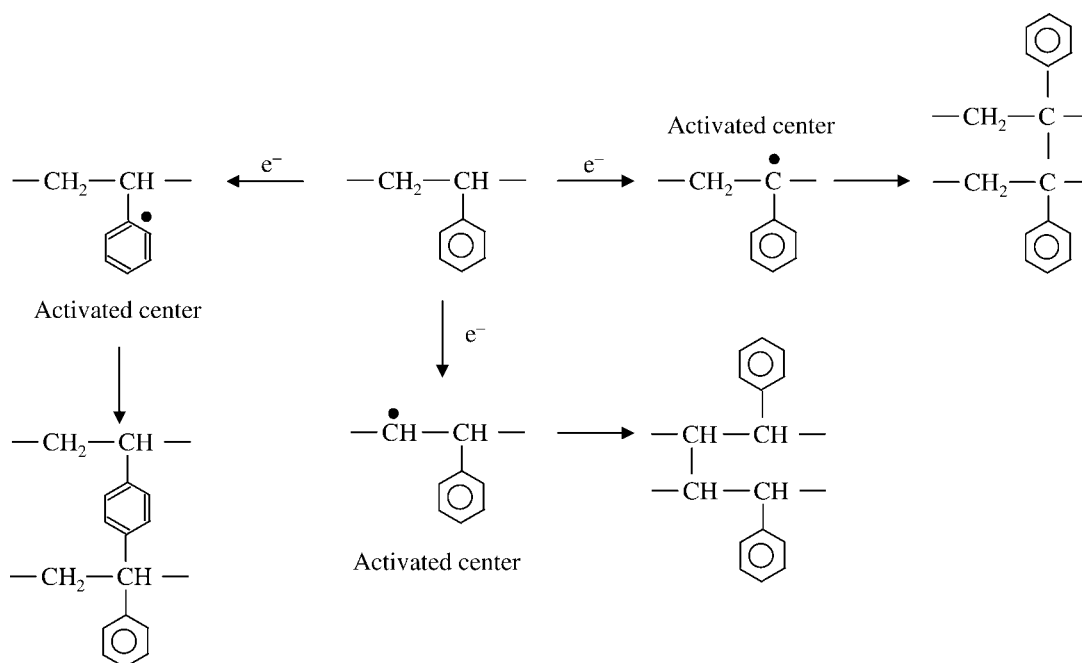
**TABLE I**  
Positive-Ion Emission Threshold Energies with LEE Bombardment on PS

Ion	Threshold energy (eV)
$\text{H}^+$	$25.9 \pm 0.5$
$\text{CH}_3^+$	$19.9 \pm 0.5$
$\text{C}_2\text{H}_3^+$	$21.5 \pm 0.5$
$\text{C}_2\text{H}_5^+$	$19.9 \pm 0.5$
$\text{C}_3\text{H}_5^+$	$23.1 \pm 0.5$

(1 amu),  $\text{CH}^+$  (13 amu),  $\text{CH}_2^+$  (14 amu),  $\text{C}_2\text{H}_3^+$  (27 amu), phenyl (78 amu), and  $\text{C}_7\text{H}_6^+$  (91 amu), as shown in Figure 4. Other massive ions (e.g., phenyl- $\text{CH}^+$ ) can possibly be created as immediate products, but these are not considered here. Cleavage of phenyl groups is also possible, giving aliphatic  $\text{C}_x\text{H}_x^+$ . These predicted ions were determined by bond cleavage of certain chemical bonds and without chemical recombination with other products of degradation. The main detected ions in Figure 1(b) present chemical structures similar to saturated hydrocarbons ions that are different than those predicted in Figure 4, except for  $\text{H}^+$  and  $\text{C}_2\text{H}_3^+$  ions. This suggests that the other ions detected cannot be produced directly by the LEE beam (i.e., they are not the immediate products of LEE impact). Chemical recombination of degradation products with hydrogen atoms before emission is the only mechanism that can explain the observed ions in Figure 1(b). Chemical recombination also explains why the emission of  $\text{H}^+$  is a few electronvolts higher than that of the other ions studied (Table I). Above 25.9-eV electron irradiation, cleavage of the C–H bond according to eq. (4), with  $\text{I}^+ = \text{H}^+$ , happens with enough kinetic energy for the  $\text{H}^+$  ion to escape the polymer matrix without recombination with other products from electron bombardment. As the incident



**Figure 4** Major predicted products of the direct degradation of PS.



**Figure 5** Some chemical mechanisms of stabilization of PS after less than 19-eV electron degradation.

electron energy increases, the ratio of hydrogen ions on recombined hydrogen increases to the point at which the detected 1-amu signal is the most intense signal, as shown in Figure 1(b). Below the  $H^+$  energy threshold of 25.9 eV, cleavage of the C—H bond is possible, but there is not enough energy for the ions to be emitted; this permits the chemical recombination with direct products of degradation. Therefore, it appears that as the LEE impact energy increases,  $H^+$  ions with increasing energy are produced, thus diminishing the interaction time of  $H^+$  with its surroundings; this in turn decreases the reaction of  $H^+$  with the polymer or its degradation products. The decrease in the reaction rate of  $H^+$  results in an increase of the ratio of hydrogen ions to those resulting from chemical recombination. In Figure 1(b), no phenyl group was detected in a significant way. This suggests cleavage of the aromatic group,<sup>10,42</sup> giving  $C_xH_x$  groups (e.g.,  $C_2H_2^+$  or  $C_3H_3^+$ ; see Fig. 4). Detected ions, such as  $C_3H_5^+$  or  $C_3H_7^+$ , are also products of the recombination of direct products of phenyl degradation with hydrogen atoms.

With LEEs of energy below the positive-ion energy thresholds (<19 eV), only the loss of hydrogen was measured (Figs. 2 and 3), and this indicates that the possible degradation mechanisms do not break the general carbon structure of the material. Because PS is a crosslinking-type polymer, the loss of hydrogen atoms leads to chemical stabilization mechanisms, such as those exemplified in Figure 5.<sup>10,43,44</sup> Other stabilization mechanisms involving crosslinking are possible from a mixture of the mechanisms shown in Figure 5, which involve crosslinking between ali-

phatic and aromatic carbon atoms. With LEEs above 19 eV, observation of hydrocarbon ions [Fig. 1(b)] suggests that the carbon structure of the polymer changes with the loss of carbon atoms. PS degraded by 19 eV (or higher energy) of electrons is not subject to the same chemical mechanisms as those discussed previously. Phenyl groups are cleaved by electron bombardment. Loss of fragments suggests that the ring fragmentation leads to aliphatic carbon chains. These activated hydrocarbon centers produced by the aromatic ring fragments can crosslink with other activated centers in the polymer matrix.

No measurements of film thickness were done after LEE irradiation. As the beam current was approximately 30 nA and lower, the emission rates were low (<700 cps) for ions resulting from destruction of the polymer structure (i.e., positive ions), as shown in Figure 1. This suggests that there is no significant etching of the surface from sputtering. Etching needs energetic beams. Electron beams of 10 keV and up are currently used for polymer etching;<sup>45–47</sup> this is 2 orders of magnitude larger than the energies used for this article.

## CONCLUSIONS

We have investigated the response of PS thin films bombarded with LEEs (0–100 eV). The electron-induced desorption of anions and cations from PS thin films was studied by mass spectrometry. Only the emission of  $H^-$  ion was detected in the negative-ion mode. Two phenomena were identified to produce  $H^-$ . At  $9.1 \pm 0.4$  eV, there is a resonant struc-

ture that is associated with DEA and characterized by the formation of a temporary excited molecular anion. The dissociative core-excited resonance state involves the excitation of the lone pair:  $n \rightarrow \sigma^*$ ,  $\pi \rightarrow \pi^*$ , and/or  $\sigma \rightarrow \sigma^*$ . The resonance peak at 9.1 eV is similar in energy and line shape to the one obtained from LEE-stimulated desorption from many other organic molecules. At higher energies, a monotonic rise of the emission yield of  $H^-$  ion is associated with nonresonant DD that results in the production of stable ions.

Considerably more mass fragments were observed in the positive-ion mode than in the anion mode. At an impact energy of 100 eV, the predominant ion is  $H^+$ , and hydrogen-loss saturated hydrocarbon ions are detected. Emission thresholds were measured for the most predominant positive ions. Only a monotonic rise of the yield function has been observed for all the positive ions, and this shows that the degradation process can be associated only with nonresonant processes with an energy threshold around 20 eV.

From the chemical structures of hydrogen-loss saturated hydrocarbons ions observed and the analysis of the immediate products formed by LEE impact, we suggest that a recombination of degradation products with hydrogen atoms occurs before cation desorption. Chemical recombination can also explain why the threshold energy for the emission of  $H^+$  is a few electronvolts higher than that of the other ions observed during LEE irradiation. Below electron energy of 19 eV, only loss of hydrogen was measured in the anion mode. This means that the possible degradation mechanisms do not break the backbone carbon structure of the material, leading to crosslinking. With LEEs above 19 eV, observation of hydrocarbon ions suggests that the carbon structure of the polymer breaks. During experiments, no significant signal from the phenyl group was detected, but  $C_xH_x^+$  masses were observed, suggesting cleavage of the phenyl groups.

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