

Surface Oxidation of Styrene Butadiene Copolymers: Study by Laser Ablation and Secondary Ion Mass Spectrometry

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Received 21 February 2002; accepted 24 May 2002

ABSTRACT: The capabilities of ion bombardment and laser ablation coupled to mass spectrometry as independent techniques to investigate the surface thermooxidative stability of polystyrene, polybutadiene polymers, and styrene butadiene rubber (SBR) copolymers were investigated. Surface chemical modifications were detected according to the polymeric structure. The degradation products detected by static secondary ion mass spectrometry appeared at m/z 29, 43, and 55. Their compositions were related to the general formulae $C_nH_mO^+$ with $n = 1-3$ and $m = 1-3$ for polybutadiene and styrene butadiene copolymers, whereas polystyrene was not affected by the aging treatment. The $C_nH_mO^+$ ions result from butadiene unit degradation. The laser ablation ionization Fourier transform ion cyclotron resonance

mass-spectrometry results confirmed the detection of $C_nH_mO^+$ ions. Finally, it may be considered that the surface thermooxidative process of SBR copolymers begins with butadiene unit degradation. The development of butadiene unit oxidation showed a dynamic oxidation phase, which coincided with a loss of unsaturation. The influence of the polymer conformation (blocked, branched, and random) on the surface oxidation for 30% styrene SBR compounds was also studied. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1910–1917, 2003

Key words: polystyrene; polybutadiene; styrene butadiene copolymer; static secondary ion mass spectrometry

INTRODUCTION

¹The stability of polymer materials is very important for their practical use and processing. That is the reason why the investigation of their thermooxidative stability is primordial.

Mass spectrometry (MS) can potentially be useful to characterize surface thermooxidative degradation. Because of its high molecular specificity and surface sensitivity, static secondary ion MS (S-SIMS) and laser ablation MS (LA-MS) have already been used to determine the mass of the repeat unit, the fragmentation within the polymer, or the molecular weight distribution.^{1–4} The association of these two techniques may be interesting because of their different areas of application. Indeed, the S-SIMS technique is a very sensitive spectrometry of the topmost material surface. The information depth was measured to be below 1 nm for molecular ions. Thus, the S-SIMS technique is a surface characterization technique and it can be devoted

to the study of surface modifications.⁵ The LA ionization Fourier transform ion cyclotron resonance MS (LA-FTICRMS) technique supplies information on deeper layers (10–50 nm) and may give information from the bulk.⁶

Useful targets for chemical modifications are unsaturated polymers, especially the styrene butadiene rubber copolymer (SBR) diene polymers, which are susceptible to thermooxidative degradation.⁷

In this article the thermooxidative stability of SBR was investigated. The surface chemical modifications occurring by thermooxidative degradation were followed by MS.

Our aim is to determine if S-SIMS and LA-FTICRMS can be used as independent techniques to investigate the surface thermooxidative stability of polystyrene (PS), polybutadiene (PB), and SBR copolymers and if the surface phenomena that occur during oxidation agree with the results already obtained by more conventional methods of analysis.⁸

Using model PS, PB, and a random SBR system, we first characterized the surface thermooxidative stability of these polymers. The spectral information showed that styrene as butadiene units had a different sensibility on thermal degradation. Then we used

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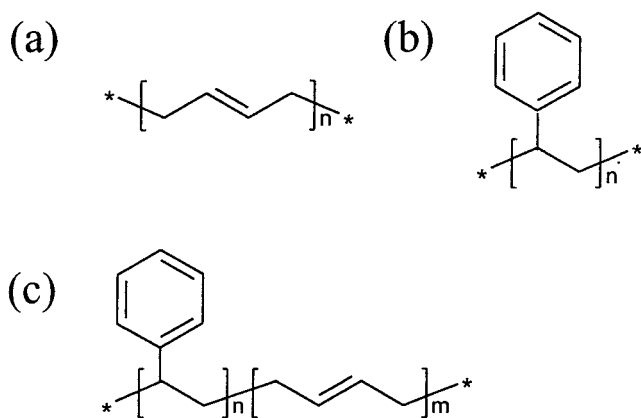


Figure 1 The polymer molecular structure of (a) polybutadiene (PB), (b) polystyrene (PS), and (c) styrene butadiene copolymer (SBR).

blocked and branched SBR copolymers to investigate the oxidation effects on the copolymer repeat unit sequences. According to the different conformations, differences in the overall thermal behavior can be expected.

EXPERIMENTAL

Materials and sample preparation

The PS, PB, and SBR polymers (Fig. 1) studied in this work are all commercial. Various SBR copolymers were prepared by emulsion or solution polymerization with different percentages of styrene (23 and 30%). The bulk composition was determined by $^1\text{H-NMR}$ (Table I). The samples were dissolved in toluene (>99%, 30 mg/mL, Merck), and thin films were prepared by spin coating a drop of this solution onto a silicon wafer.

Aging treatment

For the aging experiments, thin film polymers prepared by spin coating were exposed to the atmosphere in an oven at 75°C . The exposure time was varied between 20 min and 400 h.

Instrumentation

S-SIMS Analysis

The polymers were analyzed by means of a ion time of flight (ToF) S-SIMS III spectrometer using an Ar^+ electron impact ion source combined with a pulsed 90° deflector for beam chopping and primary ion mass separation, followed by an axial buncher for pulse compression. The resultant mass-separated primary ion pulses have a typical pulse length of <1 ns and a variable spot diameter between 5 and $50\ \mu\text{m}$.

Secondary ions are accelerated at 3 keV. In the following 2-m flight path, an Einzel lens and reflectron optics are integrated for focusing the secondary ion beam and for energy compensation, respectively. To achieve high detection efficiency, in particular to large molecular ions in the high mass range, the ions can be postaccelerated to 10 keV, where they are then detected by a channel plate–scintillator–photomultiplier combination.

During the analysis the target was bombarded by a 10-keV Ar^+ beam with an average pulsed primary ion current of 0.5–1.0 pA for a total collection time of 150 s. The fluence was less than 10^{12} ions cm^{-2} (static conditions). A typical resolution ($m/\Delta m$) was 5000 at m/z 41. No charge neutralization was needed.

LA-FTICRMS Analysis

Analyses were performed using a modified laser microprobe Fourier transform mass spectrometer.^{9,10} This instrument is differentially pumped with a dual-cell Nicolet FTMS 2000 instrument (Thermoquest, Madison, WI), operated at a 3.04-T magnetic field and coupled to a reflection laser interface and special sample manipulation hardware. The viewing system (inverted Cassegrain optics design) allows the visualization of the sample with a $300\times$ magnification.^{9,11} The ionization step was performed using an excimer laser (Lamba Physik, Göttingen, Germany) for an ArF mixture at 193 nm (pulse duration = 23 ns, output energy = 250 mJ). The laser beam diameter can be adjusted from 15 to $\sim 500\ \mu\text{m}$ on the sample, which is placed inside the source cell, by means of several internal lenses and an external adjustable telescope. This configuration corresponds to a power density that is easily adjustable in the 10^5 – 10^{10} W cm^{-2} range.

The experimental sequence used for these analyses is the following. Ions are formed by laser-induced ionization in the source cell (residual pressure = 10^{-6} Pa). During the ionization event, the conductance limit plate between the two cells (source and analyze) is kept at the trap potential (typically + 0.75 V) to con-

TABLE I
Bulk Compositions of Polymers Determined by $^1\text{H-NMR}$

Sample	Styrene	1,2 (Vinyl)	<i>cis</i> 1,4	<i>trans</i> 1,4
Homopolymers				
PS	100	0	0	0
BR	0	9	36	55
		Styrene	Confirmation	
Styrene butadiene copolymers				
SBR1		23	Random	
SBR2		30	Blocked	
SBR3		30	Branched	
SBR4		30	Random	

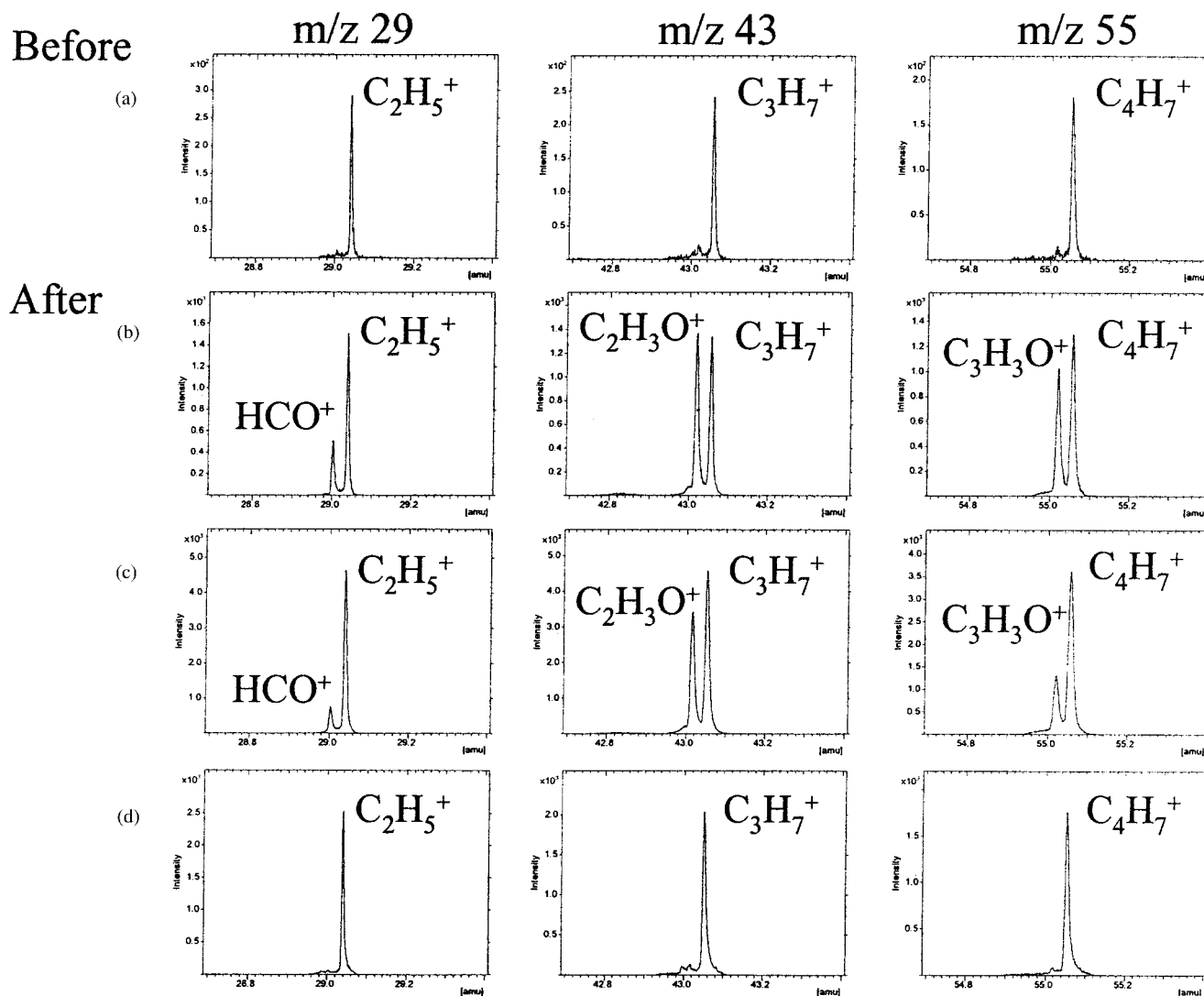


Figure 2 The positive time of flight SIMS spectra (a) before and (b–d) after aging treatment for (b) PB, (c) SBR1, and (d) PS polymers after a 72-h aging treatment.

fine positive ions to the source side. A variable delay period follows, during which ion and molecule reactions can occur. Ions are then excited by a frequency excitation chirp and the resulting image current is detected, amplified, digitized, apodized (Blackman–Harris, three terms), and Fourier transformed to produce a mass spectrum.¹²

RESULTS AND DISCUSSION

Surface chemical modifications characterized by S-SIMS: Chemical structure influence

The positive S-SIMS spectra of SBR1, PB, and PS obtained after a 72-h aging treatment was not significantly modified if it was compared to its standard fingerprints.¹³ Nevertheless, several ions appeared. Figure 2 reports three mass ranges for SBR1, PB, and PS before and after aging treatment. Before treatment,

whatever the studied polymers, only hydrocarbon ions were detected: $C_2H_5^+$, $C_3H_7^+$, and $C_4H_7^+$ at m/z 29, 43, and 55, respectively. After treatment, other peaks appeared at m/z 29, 43, and 55 for SBR1 and PB polymers. By taking advantage of the high mass resolving power and accuracy from the TOF analyzer, it is possible to identify these ions as HCO^+ , CH_3CO^+ , and $C_2H_3O^+$ species (Table II). There is no evidence of $C_xH_yO_2^+$ carboxylic functionality ions.

The presence of $C_nH_mO^+$ seems to indicate the slight oxidation of the polymer surface. These results were in agreement with what was expected: a heat and air treatment is known to introduce chemical modifications for this kind of compound, especially because of the oxygen reactivity. The temperature increase led to polymeric chain breaks. Oxygen molecules, which were physisorbed on the polymer surface, reacted and created oxidized groups such as

TABLE II
Measurement and Ion Assignment of Oxygenated Ions
in S-SIMS Spectrum of SBR1

Ions	Measured	Calculated	δm (ppm)	Resolution
CHO ⁺	29.0021	29.0027	20.7	4571
C ₂ H ₃ O ⁺	43.0180	43.0184	9.2	4949
C ₃ H ₃ O ⁺	55.02056	55.0198	12.7	5283

carbonyl ones. These results are in agreement with those of Galuska.¹⁴ He reported in particular the formation of methyl carbonyls, which induces the formation of C₂H₃O⁺, in the study of ethylene-propylene-diene monomer (EPDM) terpolymers.¹⁴ In addition, he observed smaller contributions from C₂H₅O⁺, C₃H₅O⁺, C₃H₇O⁺, C₄H₅O⁺, C₄H₇O⁺, and C₅H₉O⁺, which were directly associated with particular types of EPDM oxidation products.

Figure 2 also shows that the polymer reactivity was greatly influenced by their chemical structure. The results obtained in the study of PS confirmed its unreactivity to oxygen species at this temperature. In SBR copolymers, it is well known that the butadiene and styrene units have a different sensibility to thermal degradation.⁷ Consequently, the C_{*n*}H_{*m*}O⁺ ions observed in the SBR1 mass spectrum were directly associated with butadiene unit oxidation. The degradation of SBR seemed to finally be initiated in the butadiene portion whereas styrene degradation appeared to be inhibited. Therefore, the degradation products observed in the SBR mass spectrum come from the butadiene units. The reactivity of the double bonds in the butadiene units seems to be the main precursor of SBR degradation. This phenomenon may be explained by the oxygen insertion into the carbene-carbene double bond. It may be assumed that C₂H₃O⁺ ions come from these oxidized carbene double bond sites. The formation of CHO⁺ and C₃H₃O⁺ ions may be related to further oxidation steps as reported in the ensuing section.

Kinetic study of butadiene units oxidation:- loss of unsaturation

Measurements in the unsaturation degree evolution may be performed by S-SIMS. The unsaturation degree may be measured when the relative intensity of some hydrocarbon ions is considered.¹⁵ This is generally most obvious in the C₁-C₄ hydrocarbon clusters. A measure of the unsaturation degree can be obtained through the determination of certain intensity ratios (27/29, 39/43, 53/57) for positive ions. These ratios increase with the unsaturation degree of the hydrocarbon polymer surfaces. In our case, we used the 27/29 ratio, which corresponds to CH₂=CH⁺ and CH₃-CH₂⁺ for this study.

The development of S-SIMS intensity was followed as a function of the aging time for SBR1. Two kinds of S-SIMS signals were considered, the *R* = 27/29 ion intensity ratio (CH₂=CH⁺ and CH₃-CH₂⁺) and the C_{*n*}H_{*m*}O⁺ ions at *m/z* 29, 43, and 55. Normalization was done using the total positive ion yield of the sample (see Fig. 3). Different steps may be observed: the appearance of ions, a dynamic phase during which the fragment intensities increased, and the saturation of the signal.

The appearance of oxygenated ions was relevant to the oxygen attack into the polymeric chains. The C₂H₃O⁺ fragment appeared first after only 20 min whereas CHO⁺ and C₃H₃O⁺ fragments required longer aging times. Indeed, 60 h was needed to observe them simultaneously on the mass spectrum. The saturation threshold was reached for all fragments after 200 h of oxidation. It may be considered that it is the necessary time for the oxidation process to affect all the groups, which can be oxidized at the polymer surface. At the same time, a loss of unsaturation in SBR, which was characterized by an important decrease of the 27/29 ratio during the first 100 min, was observed. This may be taken as evidence that the lost carbene double bonds are involved in oxidative polymer degradation.

Moreover, when SBRS with different styrene contents were studied after the same aging treatment, it

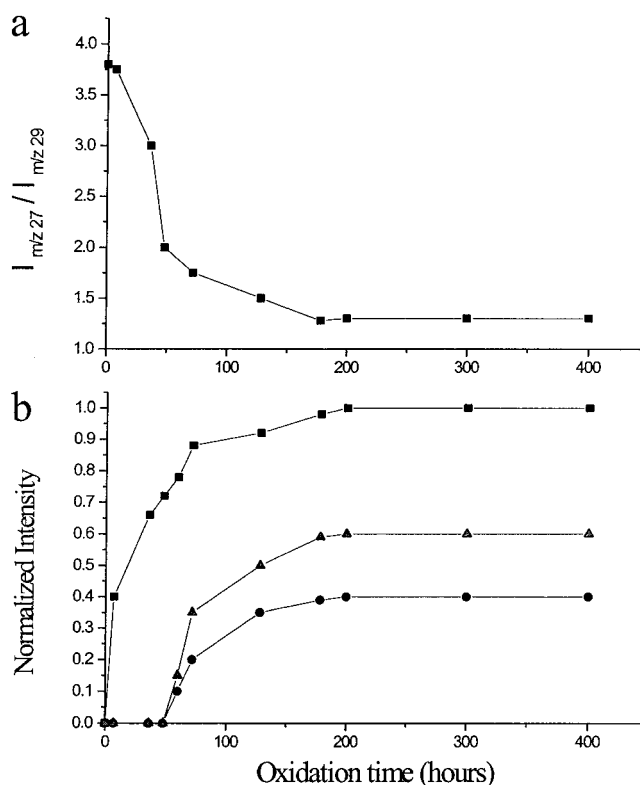


Figure 3 The (a) relative loss of unsaturation and (b) evolution of (●) CHO⁺, (■) C₂H₃O⁺, and (▲) C₃H₃O⁺ fragments as a function of the time for SBR1.

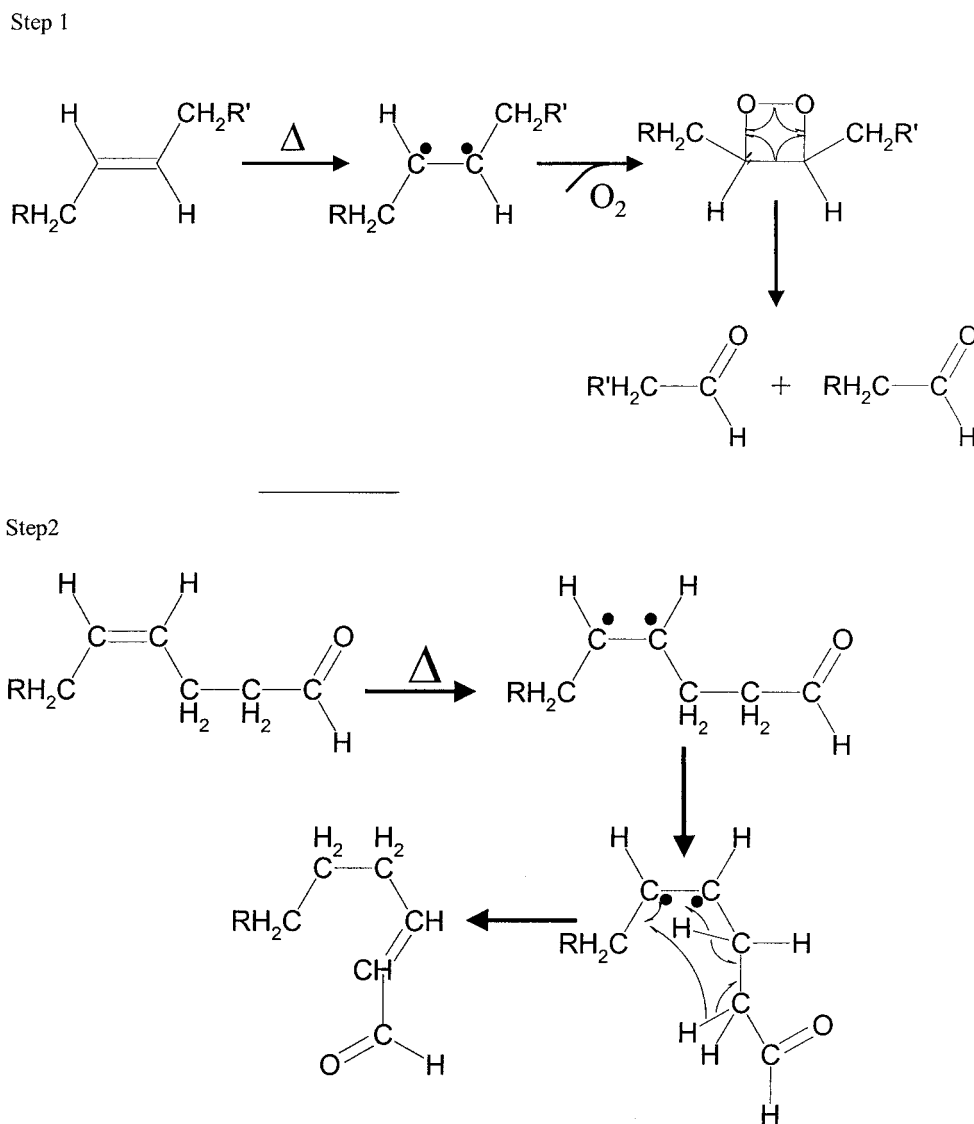


Figure 4 The mechanism of the 1,4 butadiene units' thermooxidative degradation of SBR.

appeared that an increase of butadiene amounts led first to an increase of loss of unsaturation and second to an increase of CHO^+ and $\text{C}_3\text{H}_3\text{O}^+$ ions. Consequently, it may be assumed that the first oxidation step involves the insertion of oxygen in the carbone double bonds of the butadiene unit. The m/z 29 and 55 ions seemed to be relevant to a second step in the oxidation process. The oxidation of the carbone double bonds of the butadiene unit may be expected to easily allow the formation of CHO^+ and $\text{C}_3\text{H}_3\text{O}^+$ ions after ion bombardment. Consequently, the two steps described in Figure 4 may be considered.

Surface chemical modifications characterized by LA-FTICRMS

The positive LA-FTICR mass spectrum of SBR1 obtained at a $1.5 \times 10^7 \text{ W cm}^{-2}$ laser power density using the 193-nm wavelength after a 72-h aging treatment

did not denote significant differences with the standard fingerprint. However, some oxygen containing fragments as observed in the SIMS measurements appeared at m/z 29, 43, 55, 69, and 81 (see Fig. 5) and were unambiguously assigned to HCO^+ , CH_3CO^+ , $\text{C}_2\text{H}_3\text{CO}^+$, $\text{C}_3\text{H}_5\text{CO}^+$, and $\text{C}_4\text{H}_5\text{CO}^+$ ions, respectively (Table III).

According to the high mass resolution and mass accuracy attained by FTMS, ions at m/z 69 and 81 were specifically detected by LA-FTICRMS. They may come from different methods. On the one hand, it may be assumed that they come from deeper layers of the polymer. The LA involved a greater volume than ion bombardment. In this way, the microvolume involved in the ablation process may lead to the detection of these larger species. On the other hand, the low power density may be considered to favor the formation of larger species and to reduce fragmentation after ion

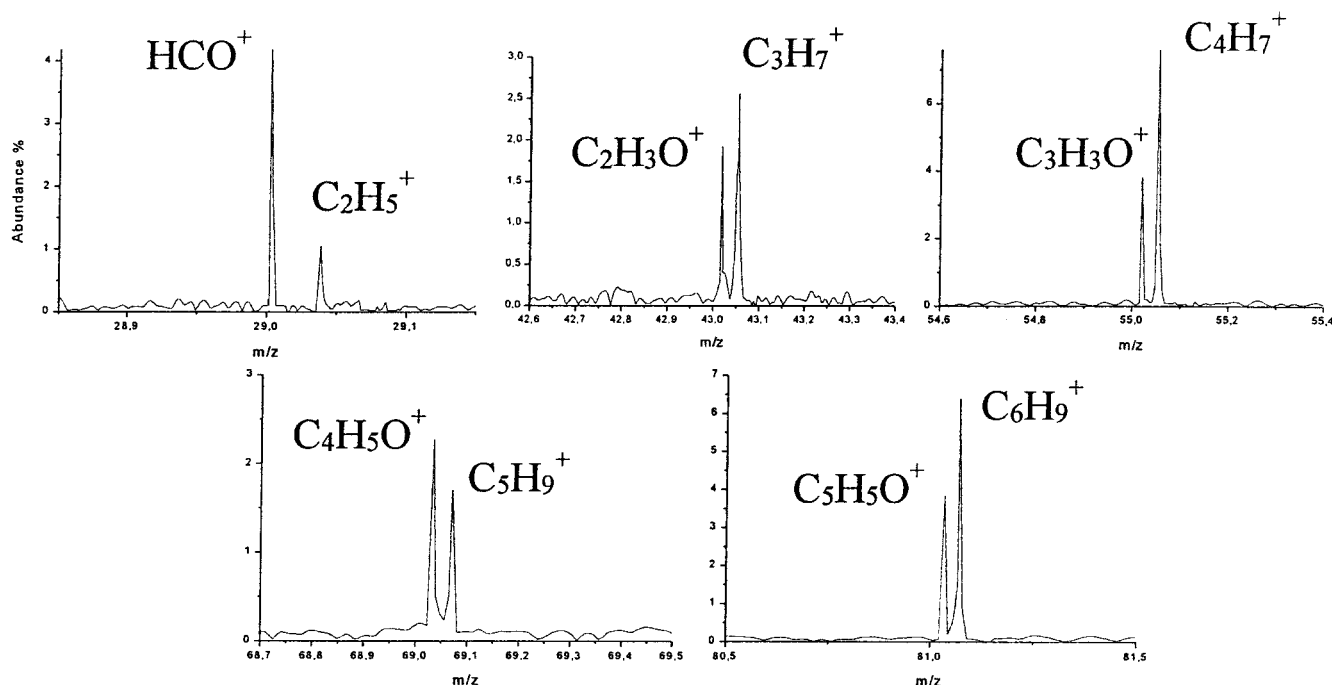


Figure 5 The positive LA-FTICRMS spectrum of SBR1 after a 72-h aging treatment at a wavelength of 193 nm with a laser power density of $1.5 \times 10^7 \text{ W cm}^{-2}$.

emission. However, carbon addition on $C_nH_mO^+$ at m/z 29, 43, and 55 during ion molecule reactions cannot be excluded. Indeed, the mass difference between m/z 69 and 81 corresponds to $\Delta m = 12$ (carbon addition). Finally, chemical modifications induced by the degradation of the polymeric chains were easily detected by MS, whatever the technique used. The evidence of $C_nH_mO^+$ ions results from the butadiene unit degradation at the sample surface. Consequently, it may be assumed that the first step of the surface thermooxidative process of SBR copolymers is the degradation of butadiene units involving a two-step process. The results obtained by MS were finally in agreement with the results already obtained by other techniques like IR, and NMR spectroscopy techniques or differential scanning calorimetry and thermogravimetric analysis.¹⁶ Unlike these classical techniques, MS provides a means for a direct determination of degradation products. Moreover, the MS difference spectrum yielded structural information on reaction

products that were due to small spectral changes. The identification and evolution of ions on mass spectra with the aging treatment time gave relevant information on the degradation processes involved.

Influence of copolymer repeat unit sequence

The influence of the copolymer repeat unit sequence on the kinetics of the thermodegradation process was finally considered. According to the results and conclusions reported in a previous section, different microstructures of SBR copolymers were expected to greatly influenced the oxidative degradation processes. Three different SBR copolymers with 30% styrene were considered: block SBS, branched SBR, and random SBR copolymers.

Figure 6 reports the $C_nH_mO^+$ fragments' intensity according to these three copolymers after 120 h of oxidation. If random conformation results were taken as reference, the branched and blocked copolymer did not have the same sensibility besides the thermal degradation. The main observed differences were the oxidation rate and fragment ion behaviors.

For branched and blocked SBR copolymers, the m/z 43 ion relative intensity dramatically decreased when they were compared to m/z 29 and 55 ion ones. Assuming that the m/z 29 and 55 ions come from the polymers after the secondary degradation process, it clearly appeared that this second step was greatly influenced by the copolymer repeat unit sequence. The presence of a consecutive butadiene unit or

TABLE III
Measurement and Ion Assignment of Oxygenated Ions in LA-FTICRMS Spectrum of SBR1

Ions	Measured	Calculated	δm (ppm)	Resolution
CHO^+	29.0026	29.0027	3.44	10760
$C_2H_3O^+$	43.0186	43.0184	4.65	8970
$C_3H_3O^+$	55.02000	55.0198	3.63	7160
$C_4H_5O^+$	69.0340	69.0339	1.44	5630
$C_5H_5O^+$	81.0337	81.0339	2.46	5010

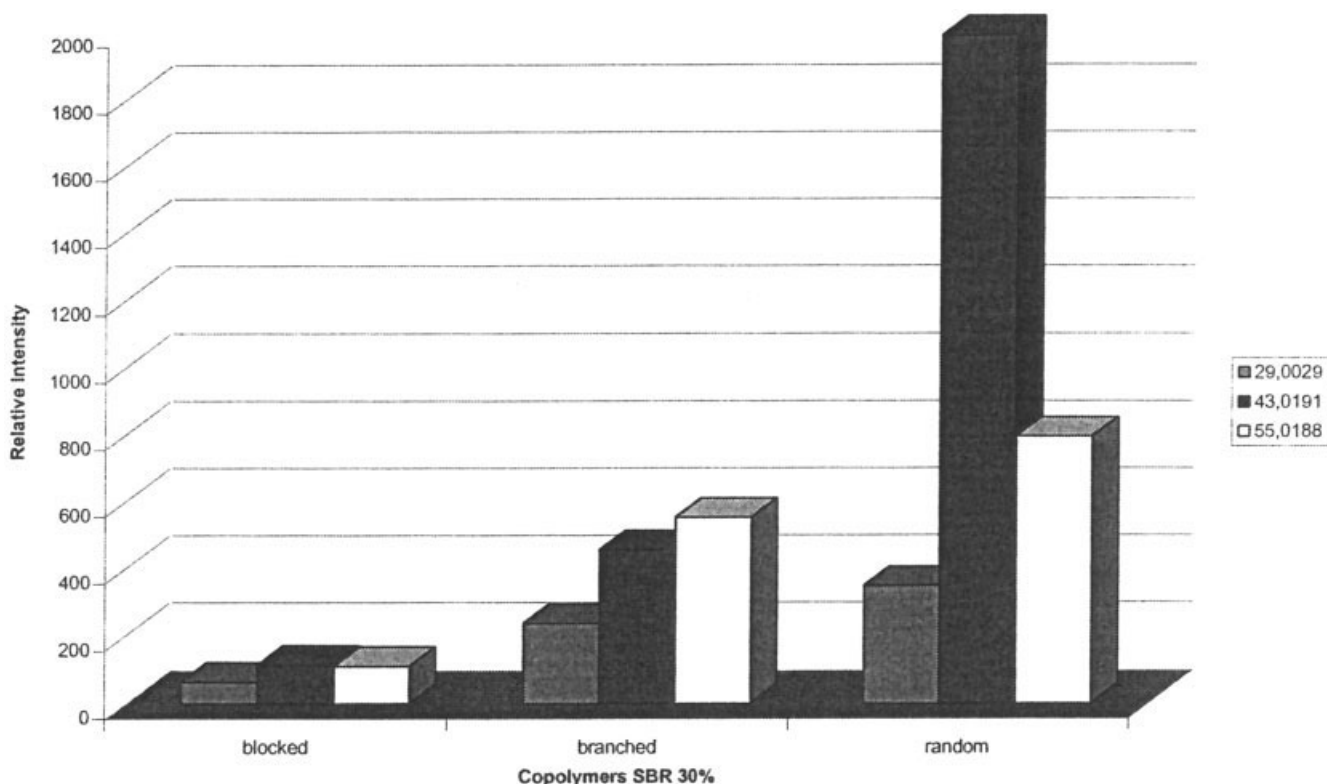


Figure 6 The $C_nH_mO^+$ fragment intensity according to the blocked, branched, and random SBR copolymers (30% styrene) after 120 h of oxidation.

branched carbon seemed to favor the degradation of the SBR copolymer. However, it may also be considered that the branched and blocked copolymer sequence inhibited the first oxidation step. For random copolymers, the oxygen molecules attack on double bonds occurred more rapidly and more efficiently than it did for branched and blocked ones. In random copolymers, carbon double bonds may be considered more accessible for oxidation insertion than for blocked or branched copolymers. For these latter ones, styrene units and reticulation seem to protect the butadiene double bonds and reduced the diffusion of O_2 at the polymer surface. Finally, a superposition of both effects may be considered to occur. The random copolymer consequently seems to be more sensitive to the first oxidation step whereas the second one is quicker for blocked and branched copolymers. A different sensibility for thermal degradation as a function of the copolymer repeat unit sequence may be established and an order proposed: SBR random < SBR branched < SBR block.

Consequently, the sensibility of the S-SIMS technique allows the differentiation of the different profiles of thermooxidative degradation.

CONCLUSION

When SBR copolymers undergo an aging treatment, several reactions, especially oxidation ones, take place

at the copolymer surface. MS allows the detection of these chemical modifications by the detection of $C_nH_mO^+$ ions in the mass spectra. The simultaneous detection of these ions by S-SIMS and LA-FTICRMS demonstrates the slight oxidation of the surface. The SIMS analyses showed that $C_nH_mO^+$ degradation products come from butadiene units. Consequently, the first step of surface oxidation involves butadiene. The kinetic evolution of SBR compounds shows a dynamic oxidation phase, which involves a two-step process and coincides with loss of unsaturation.

The influence of the copolymer repeat unit on the $C_nH_mO^+$ ion intensities was demonstrated. Thermooxidative degradation is greatly dependent on the conformation changes.

To conclude, ion bombardment and LA coupled with MS have potential use in the study of polymer surface thermal degradation processes.

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