

# Structural and Photooxidation Studies of Poly(styrene oxide) Prepared with Maghnite-H<sup>+</sup> as Cationic Catalyst

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Received 28 March 2007; accepted 2 July 2008

DOI 10.1002/app.28912

Published online 8 September 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The nature of irregularities and end-groups in poly(styrene oxide) samples prepared using Maghnite-H<sup>+</sup> as a cationic catalyst were studied by <sup>1</sup>H- and <sup>13</sup>C-NMR at 200 MHz. Head-to-head (H-H) and tail-to-tail (T-T) irregularities are detected in all the samples studied. Secondary hydroxyl terminal groups are identified in polymers prepared with Maghnite-H<sup>+</sup>. Poly(styrene oxide) was found to undergo chain scission by aging at 25°C. It was confirmed that oxidation of this type of polymers results from the important sensitivity of the polyether soft segment to oxidative degradation. For this reason, the scis-

sions due to the oxidation of the material lead to notable quantities of low molecular weight photoproducts. Among the various structures produced by the oxidative degradation process, benzoate and secondary hydroxyl groups are identified by MALDI-TOF-MS. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3195–3202, 2008

**Key words:** montmorillonite; Maghnite; ecocatalyst; epoxies; styrene oxide; ring opening polymerization; photodegradation; MALDI-TOF-MS

## INTRODUCTION

The behavior of polyethers on exposure to UV irradiation has been studied in detail and the mechanism accounting for the photooxidation of these polymers can be considered as fairly well understood.<sup>1,2</sup> Polyethers have been shown to have significant sensitivity toward photooxidation. Polyethers reach very high levels of oxidation within only several tens of hours of exposure to artificial photoageing in medium accelerated conditions. The photosensitivity of polyethers results from the oxidizability of carbon atoms in  $\alpha$ -position to the oxygen atoms.

Few publications have been devoted to the study of poly(styrene oxide) (PSTO) microstructure by NMR.<sup>3,4</sup> <sup>13</sup>C-NMR investigations were essentially undertaken to demonstrate the regular head-to-tail structure of polymers<sup>5</sup> in connection with the mode of ring opening. In these studies, additional peaks observed between methine and methylene carbon resonances were usually neglected,<sup>3–5</sup> though they

might possibly be due to the presence of irregular enchainments. Recently, the tacticity of PSTO prepared with a ZnEt<sub>2</sub>/H<sub>2</sub>O initiator was investigated by <sup>1</sup>H-NMR on a deuterated polymer.<sup>6</sup> There is, to date, no information on the MALDI-TOF-MS studies of PSTO photodegradation.

In this article, which is the first of a series dealing with the photooxidation of polymer based on poly(ethers), we report on the identification of the oxidation photoproducts by <sup>1</sup>H- and <sup>13</sup>C-NMR, FTIR, and MALDI-TOF-MS analysis of the PSTO, prepared with an acid exchanged montmorillonite called Maghnite-H<sup>+</sup> (Mag-H<sup>+</sup>) as the cationic catalyst,<sup>7,8</sup> exposed to ordinary laboratory light at ambient temperature.

## EXPERIMENTAL

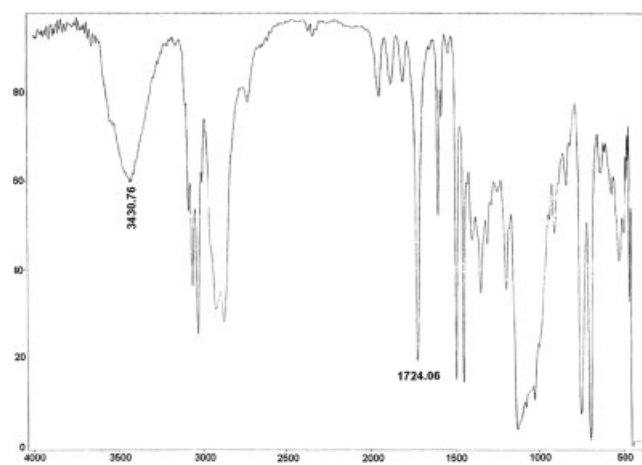
### Materials

Styrene oxide (SO; Aldrich) was dried over calcium hydride and distilled under reduced pressure before use. Toluene, dioxane, chloroform, *n*-hexane, and petroleum ether were purified following standard techniques and used after distillation over their respective drying agents.

The Montmorillonite clay (Maghnite), which has been used as catalyst, is supplied by ENOF Maghnia (Western of Algeria). The Mag-H<sup>+</sup> was prepared

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Contract grant sponsor: Algerian National Agency for Development and Research.



**Figure 1** FTIR spectrum of a PSTO film before irradiation.

by using a method similar to that described by Yahiaoui et al.<sup>9</sup>

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in CDCl<sub>3</sub>. Tetramethylsilane was used as the internal standard in these cases. IR spectra were recorded with an ATI Matson FTIR N°9501165 spectrometer. Average molecular weights and molecular weight distributions of the different polymers were measured using gel permeation chromatography (GPC) on a system equipped with a Spectra SYSTEM AS1000 auto sampler. The MALDI-TOF-MS were recorded on a Bruker Biflex III equipped with a nitrogen laser ( $\lambda = 337$  nm). All mass spectra were recorded in the linear mode with an acceleration voltage of 19 kV. The irradiation targets were prepared from THF or CH<sub>2</sub>Cl<sub>2</sub> solutions with dithranol as matrix and NaI as dopant.

### Experimental procedure

Polymerizations were performed in chloroform at 20°C. The procedure was identical in both cases, involving addition of catalyst to the stirred solution containing STO in chloroform. Prior to use, Mag-H<sup>+</sup> was dried at 120°C overnight and then transferred to a vacuum desiccator, containing P<sub>2</sub>O<sub>5</sub>, to cool to room temperature overnight. An example reaction is detailed here. After charging the reaction vessel with STO solution in chloroform (2M), the catalyst (1% w/w to monomer) was added. At the end of the reaction, the resulting mixture was filtered to remove the clay and then dried under vacuum to yield the polymer. The later was dried in a vacuum oven prior to characterization by GPC, IR, <sup>1</sup>H-, <sup>13</sup>C-NMR, and MALDI-TOF-MS analysis (yield for this example was 71%).

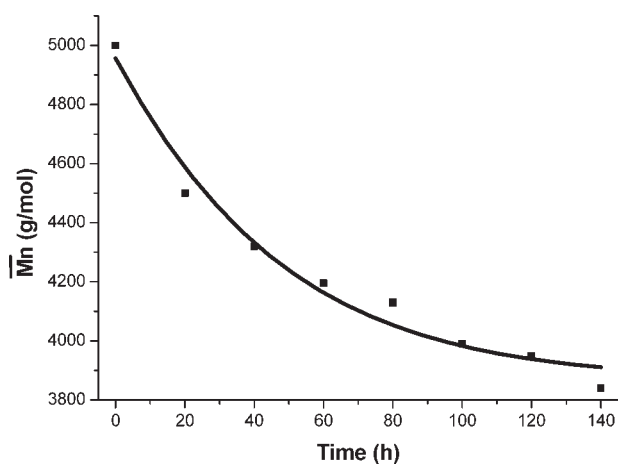
## RESULTS AND DISCUSSION

The PSTO obtained from the preparation was a light yellow gum-like material. When it was stored under ordinary laboratory light at ambient temperature, a red discoloration developed after a few days.

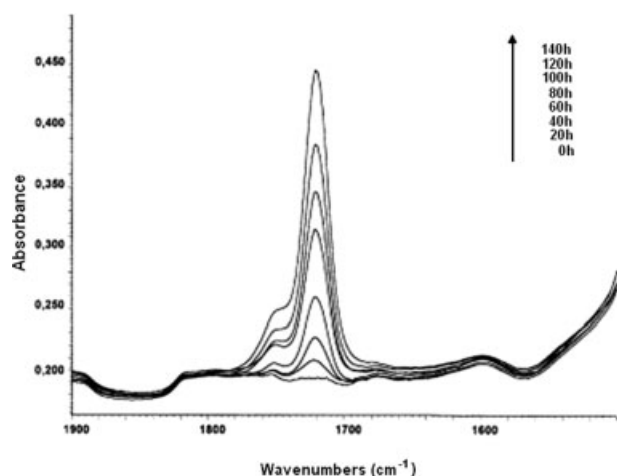
The characteristics of the samples (before irradiation) examined are presented in Figure 1. They all show strong characteristics absorption bands of benzene ring (1607, 1587, 1493 cm<sup>-1</sup>), -C-O- group (1150 cm<sup>-1</sup>), and of C-H in benzene (700 cm<sup>-1</sup>), which are similar to PSO obtained with other catalysts.<sup>10</sup> All the polymers were prepared cationically using Mag-H<sup>+</sup> as catalyst.

### Analysis by gel permeation chromatography

Exposed to ordinary laboratory light at ambient temperature and after the second day of irradiation, all examined polymers had low molecular weights resulting from the oxidative (under ordinary laboratory light) degradation of high molecular weight polymers. Figure 2 shows the variations of the molar weights of PSTO during irradiation at 25°C, and the changes caused by irradiation of the PSTO are characterized by a shift of the molar weight distribution curves toward lower molar weights. The average molar weight decreases by about 18% after 80 h of irradiation and 23% after 140 h. This decrease in the average molar weight can be attributed to the chain scissions resulting from the photooxidation of PSTO. This indicates that a dramatic degradation process takes place during the oxidation of the polymer. This decrease in molar weight is correlated to the chain scissions due to the formation of formate and benzoate end groups.



**Figure 2** Effect of the irradiation time on the molecular weight of polymers.

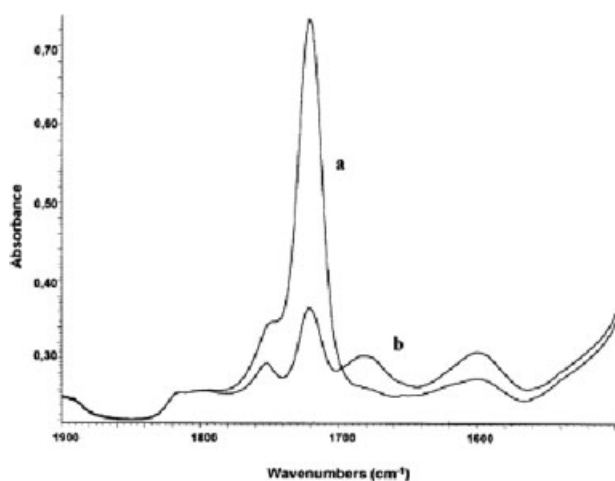


**Figure 3** FTIR spectra of PSTO films photooxidized at 25°C in domain 1900–1500  $\text{cm}^{-1}$ .

### Analysis by infrared spectroscopy

Irradiation of PSTO films leads to the appearance of new absorption bands in the carbonyl vibration region (1900–1700  $\text{cm}^{-1}$ ). Figure 3 shows the changes in the carbonyl region of spectra obtained from PSTO for several irradiation times ranging from 0 to 140 h. Monitoring each spectrum necessitated that a sample was prepared, following the procedure described in the experimental part. In the carbonyl region, two absorption bands develop at 1750 and 1724  $\text{cm}^{-1}$ , and at 1590  $\text{cm}^{-1}$ . The two absorption bands at 1750 and 1724  $\text{cm}^{-1}$  have already been observed in the case of irradiation of PEO in solid state.<sup>11</sup>

Acid and ester groups are known to react with  $\text{NH}_3$  to give, respectively, ammonium carboxylates



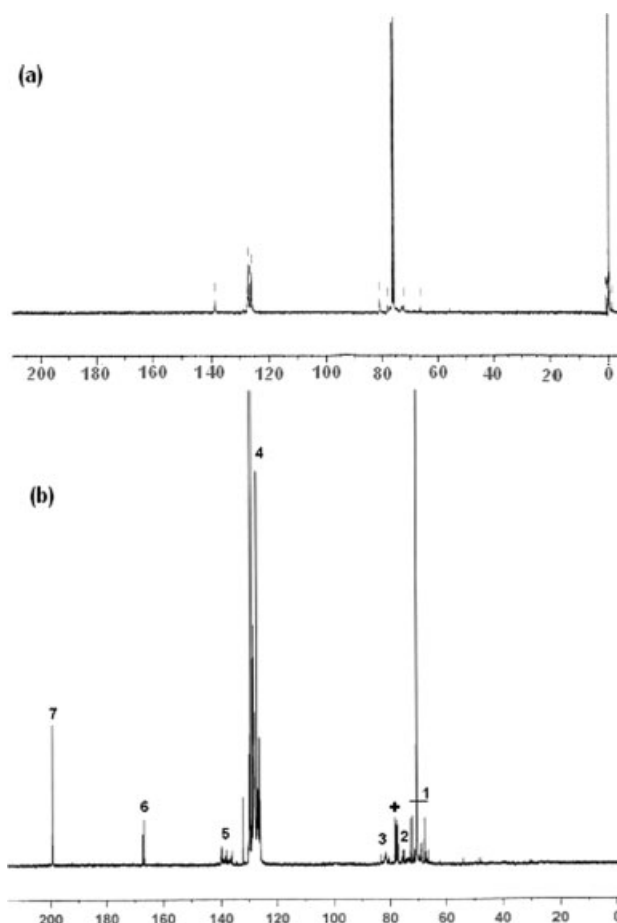
**Figure 4**  $\text{NH}_3$  treatment of a PSTO film photooxidized for 140 h exposed to ordinary laboratory light at ambient temperature. Direct spectra (top) and subtracted spectrum between the irradiated and the treated film (a) before treatment and (b) after treatment.

and amides.<sup>12</sup> The ammonium carboxylates are characterized by an IR absorption band in the range 1560–1580  $\text{cm}^{-1}$  and amides by an IR absorption band in the range 1660–1680  $\text{cm}^{-1}$ .<sup>13</sup> In the carbonyl vibration region (Fig. 4), one observes a decrease of the main oxidation band at 1725  $\text{cm}^{-1}$  correlated with an increase of band at 1680  $\text{cm}^{-1}$ .  $\text{NH}_3$  reacts with formate end groups to give formamide, and the corresponding absorption band is observed at 1680  $\text{cm}^{-1}$ .

Quantitative results cannot be obtained by measuring the diminution of absorbance of the  $\nu(\text{C}-\text{O}-\text{C})$  band at 1150  $\text{cm}^{-1}$  as this ether band is too intense even for thin films.

### $^{13}\text{C}$ -NMR analysis

In the  $^{13}\text{C}$ -NMR spectrum [Fig. 5(b)], signal 1 is assigned to methylene carbons, whereas signals 2 and 3 are assigned to methane carbons. These signals can be reasonably attributed to irregular enchainments of head-to-head (H-H) and tail-to-tail (T-T) types resulting from some cleavage of the  $\text{O}-\text{CH}$  linkage ( $\alpha$ -scission) instead of the  $\text{O}-\text{CH}_2$  bond ( $\beta$ -scission) in the oxirane ring.



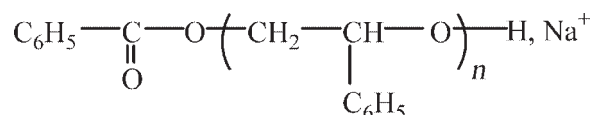
**Figure 5**  $^{13}\text{C}$ -NMR Spectra of PSTO: (a) nondegraded and (b) degraded (+)  $\text{CDCl}_3$ .

Comparing spectra of nondegraded and degraded PSTO [Fig. 5(a,b)] allows one to identify the resonances corresponding to particular structures resulting from the oxidative degradation of the polymer by aging.

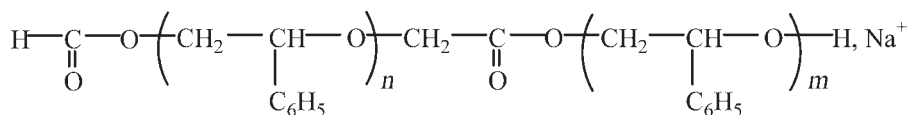
Two weak resonances at 166.5 and 200 ppm are observed in the carbonyl region of the degraded polymer spectrum [Fig. 5(b)]. Both may be assigned to carbonyl carbon resonances in ester groups. The key step in autoxidation or photoautoxidation of polyethers is the formation of hydroperoxides (A).

### MALDI-TOF-MS analysis

To further investigate the resulting polymer, MALDI-TOF-MS (Fig. 6) was performed on the PSO synthesized by Mag-H<sup>+</sup>. To improve the ionization/desorption process, the polymer was mixed with both dithranol and NaI before spotting. Three series of peaks are observed as shown in Figure 6. As expected, the signals for each series are separated by 120 *m/z*. The first series with formula:



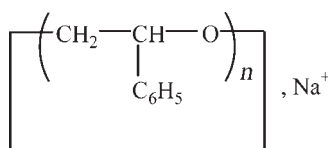
corresponds to polymers terminated with a benzoate group at one end of the polymer chain and a hydroxyl group at the other end; with Na<sup>+</sup> as the counter ion. The molar masses involved are repeat unit, -CH<sub>2</sub>-CH(Ph)-O-, 120 g/mol, counter ion



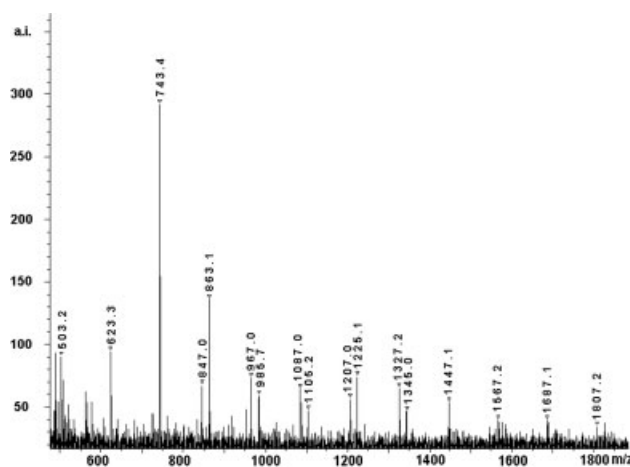
After subtracting the end group, -H, 1 g/mol, HCO-, 45 g/mol, -CH<sub>2</sub>-C(O)O-, 58 g/mol, and the counter ions molecular weight (Na<sup>+</sup>) from one of each of the signals, and dividing the resulting number by the repeat unit mass, an integral number for the degree of polymerization is obtained:

(1567.2 g/mol - 1 g/mol - 45 g/mol - 58 g/mol - 23 g/mol)/120 g/mol = 12.

The last series is consistent with macrocyclic PSO oligomers with formula:



The molar masses involved are repeat unit, -CH<sub>2</sub>-CH(Ph)-O- at 120 g/mol, and counter Na<sup>+</sup>



**Figure 6** MALDI-TOF-MS spectrum of degraded poly(styrene oxide).

Na<sup>+</sup>, 23 g/mol, end group, -H, 1.01 g/mol, and benzoate group, Ph-C(O)O-, 121 g/mol. Subtracting the benzoate group and -H end groups and the counter ion masses from each of the signals and dividing the result by the repeat unit mass, an integral number for the degree of polymerization was obtained, e.g.:

(1105.2 g/mol - 121 g/mol - 1 g/mol - 23 g/mol)/120 g/mol = 8.

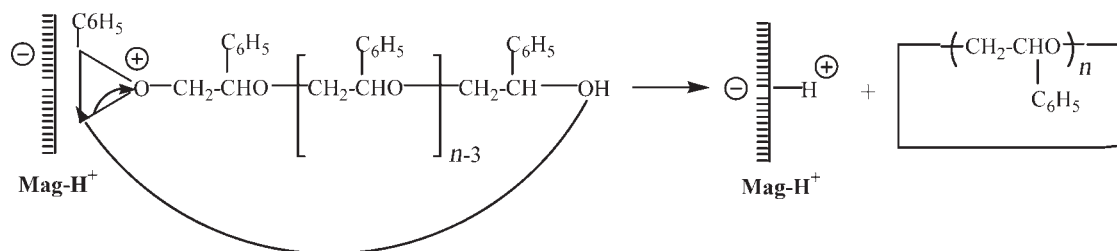
The second series is assigned to polymers terminated with a formate group at one end, a hydroxyl group at the other end and an acetate group in the middle of the polymer chain [Na<sup>+</sup>, (Na<sup>+</sup> as the counter ion)]. This can be described by formula:

ion at 23 g/mol. Subtracting the counter ion masses from each of the signals and dividing the result by the repeat unit mass, an integral number for the degree of polymerization (macrocyclic size) was obtained, e.g.:

(743.3 g/mol - 23 g/mol)/120 g/mol = 6.

The macrocyclic formation may be caused by a slow depolymerization reaction and the propagation, which takes place through nucleophilic attack of the monomer onto an end-standing cyclic oxonium ion. Nevertheless, a specific character of epoxies lies in its lower nucleophilicity as compared with that of open-chain ether functions. This results in intermolecular chain transfer to polymer (reshuffling reaction), as well as intramolecular chain transfer (back-biting and end-biting) at the



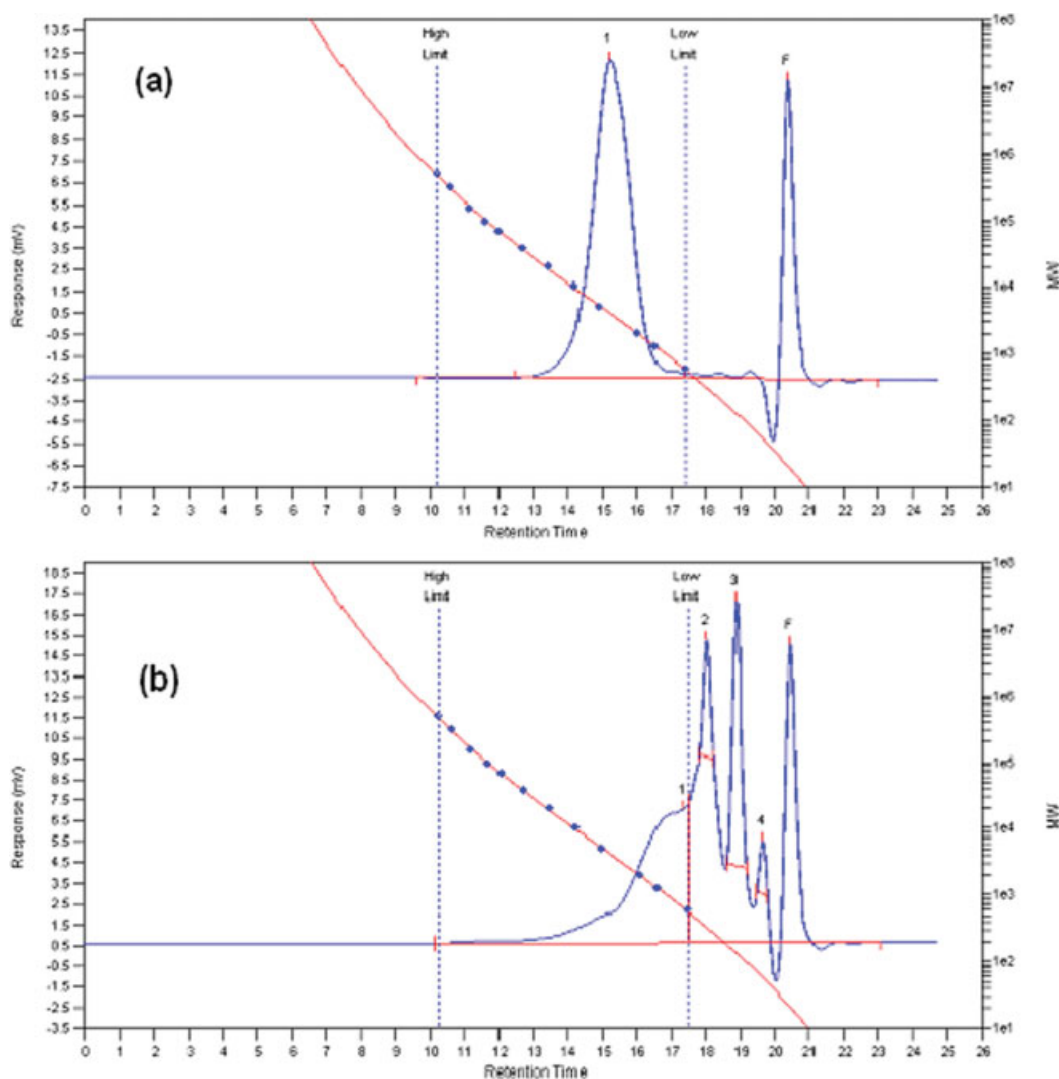


origin of macrocytic formation (Scheme 1), consequently resulting in a decrease in the molecular weight.<sup>14,15</sup> This is confirmed by the GPC curve [Fig. 7(b)] where one can see several peaks (peaks 2, 3, and 4) at high elution volumes indicating the presence of macrocycles.<sup>16</sup>

The assignments for all peaks of the three series are summarized in the Table I.

### Degradation mechanism

PSTO is very sensitive to photooxidation. The degradation can be initiated by chromophoric impurities



**Figure 7** GPC chromatograms of poly(styrene oxide) obtained by  $\text{Mag-H}^+$  catalytic system: (a) nondegraded polymer and (b) degraded polymer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

TABLE I  
Degraded Polymer Maldi-Tof-MS Assignments of Peaks

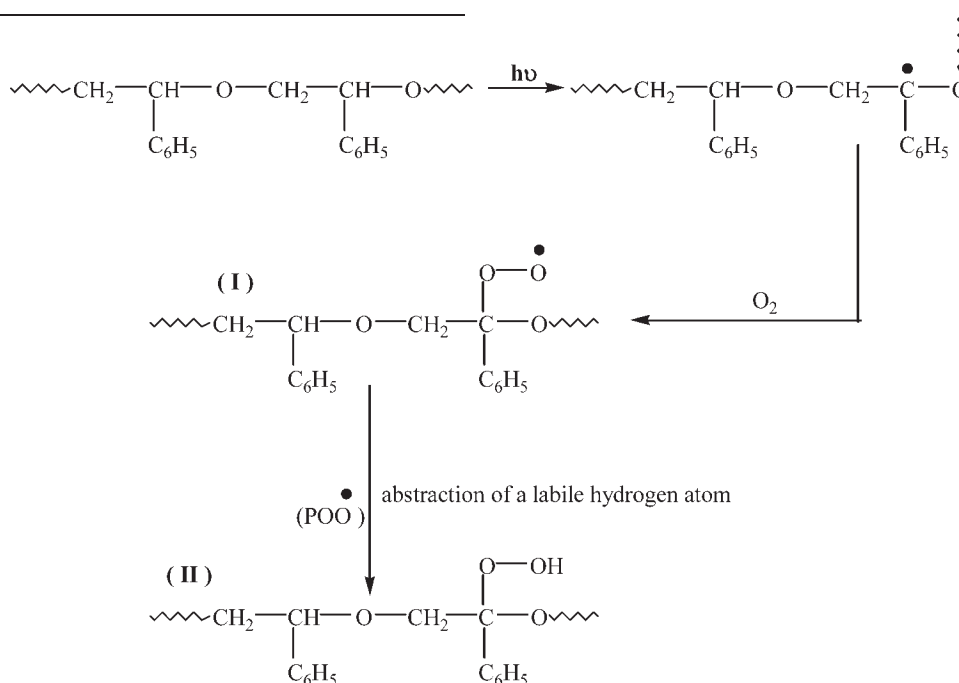
First series	985.7 g/mol = 7 (120) + 1 + 121 + 23
	1105.2 g/mol = 8 (120) + 1 + 121 + 23
	1225.1 g/mol = 9 (120) + 1 + 121 + 23
	1345.0 g/mol = 10 (120) + 1 + 121 + 23
Second series	847.0 g/mol = 6 (120) + 1 + 45 + 58 + 23 ( $n + m = 6$ )
	967.1 g/mol = 7 (120) + 1 + 45 + 58 + 23 ( $n + m = 7$ )
	1087.0 g/mol = 8 (120) + 1 + 45 + 58 + 23 ( $n + m = 8$ )
	1207.0 g/mol = 9 (120) + 1 + 45 + 58 + 23 ( $n + m = 9$ )
	1327.2 g/mol = 10 (120) + 1 + 45 + 58 + 23 ( $n + m = 10$ )
	1447.1 g/mol = 11 (120) + 1 + 45 + 58 + 23 ( $n + m = 11$ )
	1567.2 g/mol = 12 (120) + 1 + 45 + 58 + 23 ( $n + m = 12$ )
1687.1 g/mol = 13 (120) + 1 + 45 + 58 + 23 ( $n + m = 13$ )	
Third series	1807.2 g/mol = 14 (120) + 1 + 45 + 58 + 23 ( $n + m = 14$ )
	503.2 g/mol = 4 (120) + 23
	623.3 g/mol = 5 (120) + 23
	743.4 g/mol = 6 (120) + 23
	863.1 g/mol = 7 (120) + 23

which absorb UV light and produce radicals which react further with the polymer.<sup>17</sup>

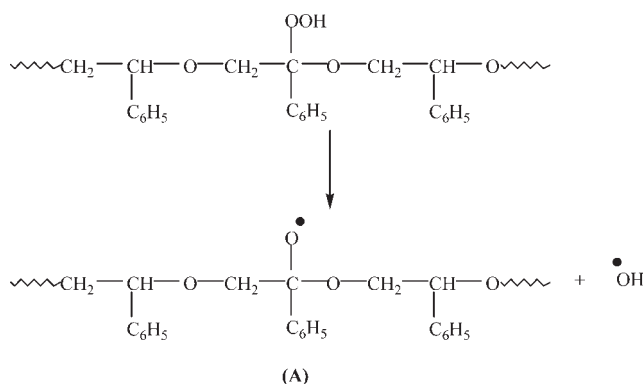
The high photosensitivity of polyethers to UV induced oxidation has been shown to result from the oxidizability of the carbon atoms in the  $\alpha$ -position to the oxygen atoms of ether groups.<sup>18–22</sup> The first step of the oxidative reaction is an hydrogen abstraction on the polymeric backbone by free radicals formed by photonic excitation of chromophoric species. Previous results<sup>18</sup> have shown that the macroradical produced reacts

with oxygen, leading to a peroxy radical that gives a hydroperoxide by abstraction of a labile hydrogen atom.

On the basis of the experimental results presented above, one may propose the following mechanism to explain the photooxidation of PSTO. Initiation of the oxidation results from hydrogen abstraction on the tertiary carbon atom and leads to radicals (I) for PSTO. Oxidation of radicals (I) followed by hydrogen abstraction by the peroxy radicals obtained leads to hydroperoxides (II):

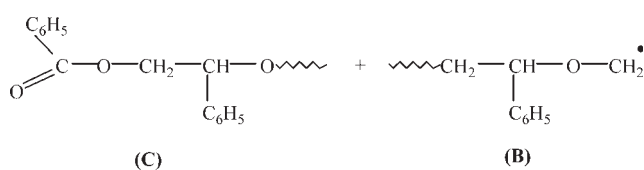


Hydroperoxides are photochemically unstable and by homolysis of the O—O band these products lead to the formation of alkoxy radical **A**:

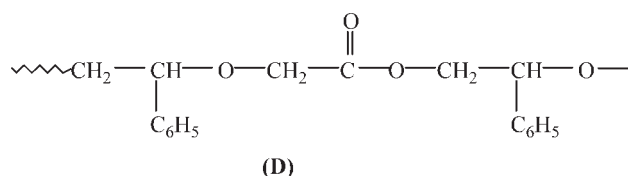


These hydroperoxides are responsible for the important absorption band at  $3400\text{ cm}^{-1}$ . The presence of hydroperoxide function in the degraded polymers was clearly shown by the test in the potassium iodide. A release of iodine is observed when a KI saturated solution in the acetone is added to the solution of the polymer in the same solvent.

The main route of evolution to alkoxy radical **A**, as shown in aliphatic polyethers,<sup>20,23,24</sup> is a  $\beta$ -scission, which leads to the formation of benzoate end groups ( $1725/1150\text{ cm}^{-1}$ ) and to a macroradical **B**:

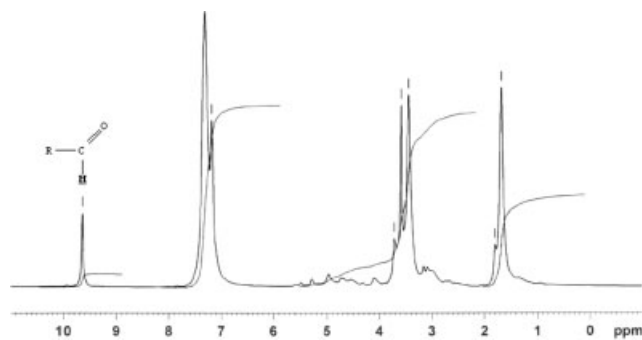


Two types of esters, **C** and **D**, may result from the decomposition of these hydroperoxides<sup>25,26</sup>:



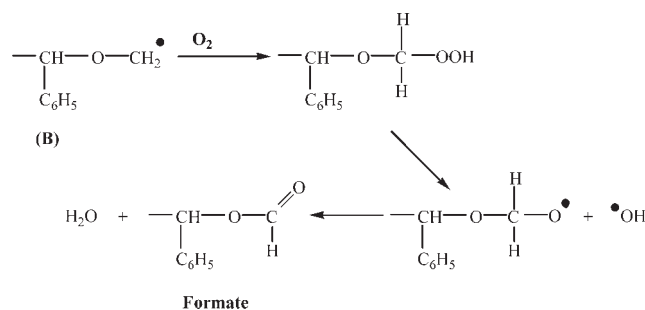
From the comparison with parent compounds deriving from polyoxyethylene,<sup>27</sup> the resonance at 200 ppm is assigned to the carbonyl carbon in structure **D**. The carbonyl carbon resonances in methyl, ethyl, and butyl benzoate are located at 167, 164.9,<sup>28</sup> and 166.4 ppm,<sup>29</sup> respectively, and thus the resonance at 166.5 ppm is assigned to the carbonyl carbon in benzoate terminal group **C**.

A possible route of decomposition of macroradical **B** is an oxidation leading to secondary hydroperoxides. Hydroperoxides can be decomposed to give carboxylic acids either by a direct oxidation<sup>30</sup> or by an oxidation involving the formation of alde-

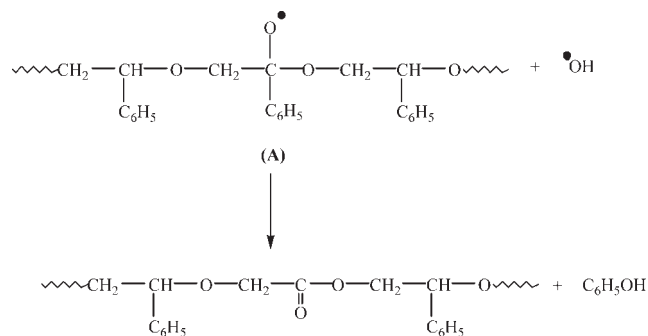


**Figure 8**  $^1\text{H-NMR}$  spectrum of degraded PSTO in  $\text{CDCl}_3$ .

hydes.<sup>17</sup> This is confirmed by the  $^1\text{H-NMR}$  spectrum (Fig. 8) where one can see a peak at  $\delta = 9.6\text{ ppm}$  indicating the presence of an aldehyde proton. This reaction leads also to a primary radical (**B**)  $\cdot\text{CH}_2-\text{O}\sim$  that is readily oxidized to give hydroperoxides  $\text{HOO}-\text{CH}_2-\text{O}\sim$ . Photochemical homolysis of the hydroperoxides leads to a pair of radicals  $\text{HO}\cdot$  and  $\cdot\text{O}-\text{CH}_2-\text{O}\sim$ . A cage reaction between these radicals gives a formate and water:



Cage reaction of the alkoxy radical **a** (with  $\text{HO}\cdot$ ) may occur, leading to ester functions.



## CONCLUSIONS

The photochemical evolution of PSTO is described as involving a succession of reactions which can occur in a concerted manner. This study has shown that PSTO is very sensitive to oxidation, which takes place on the carbon atoms in the  $\alpha$ -position to the oxygen atoms of ether groups. The hydroperoxides formed react photochemically to yield several

products that have been identified. In photooxidation, the route of decomposition of the macroalkoxy radicals is a  $\beta$ -scission, which generates formates.

The nature of irregularities and end-groups in PSTO samples prepared using Mag-H<sup>+</sup> as cationic catalyst were studied by <sup>1</sup>H and <sup>13</sup>C-NMR at 200 MHz. Head-to-head (H-H) and tail-to-tail (T-T) irregularities are detected in all the samples studied. Secondary hydroxyl terminal groups are identified in polymers prepared with Mag-H<sup>+</sup>. PSTO was found to undergo chain scission by aging at 25°C. Among the various structures produced by the oxidative degradation process, benzoate and secondary hydroxyl groups are identified by MALDI-TOF-MS.

The authors thank the Professors J.-C. Soutif and L. Fontaine (Maine University, Le Mans France) for the NMR, GPC, and Maldi-Tof analysis of polymers.

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