

Photooxidation mechanism of styrene–isoprene copolymer: evolution of the profile of oxidation according to the composition

L. Gonon*, J.-L. Gardette

Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS 6505, Université Blaise Pascal (Clermont-Ferrand), F-63177 Aubière Cedex, France

Received 11 November 1998; received in revised form 7 May 1999; accepted 13 May 1999

Abstract

The photooxidation of styrene–isoprene copolymers is investigated on the basis of infrared analysis of irradiated films. The results show that the polystyrene segments are stable under irradiation and degradation results only from the photooxidation of the polyisoprene segments. Oxidation of polyisoprene results in chain scissions and generates various carbonylated photoproducts. A three-dimensional structure is formed by cross-linking reactions resulting from additions on the double bonds and formation of ether linkage. In order to determine the influence of the polyisoprene content on the mechanism and the kinetics of oxidation, different compositions have been tested. The extent of degradation is found to be proportional to the polyisoprene content but the rate of photooxidation is constant whatever the composition. The distributions of the oxidation products within the polymer are similar whatever the composition. This behavior can be attributed to the incompatibility between the polyisoprene and the polystyrene segments, which leads to a phase demixion and the formation of nodules. Each nodule can be considered as an independent photochemical reactor. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Photooxidation; Polyisoprene; FTIR

1. Introduction

The photochemical degradation of dienic polymers has been largely described in the literature [1–7]. If intensive works have been carried out on the photooxidation of polybutadiene or its copolymers [3–5], only a few papers deal with the photooxidation of polyisoprene. Rodrigues and De Paoli [8] concentrated on the analysis of the non-volatile photoproducts formed during photooxidation. The presence of hydroperoxides, alcohols, ketones, aldehydes, epoxides and carboxylic acids was detected by IR, ^1H and ^{13}C NMR spectroscopies. Viscosimetric measurements showed that chain-scission predominates over cross-linking. Adam et al. [2] studied the photooxidation of polyisoprene under irradiation at long wavelengths ($\lambda \geq 300$ nm), with various relative concentrations of 1–4, 3–4 and 1–2 double bonds. The comparison of the photochemical behavior of these polymers with that of polybutadiene allowed the authors to propose a scheme accounting for the main routes of the photooxidation. The following conclusions were given:

- The photooxidative degradation of polyisoprene generates alcohols, ketones, epoxides and carboxylic acids.

- A decrease in double bonds concentration occurs as the photooxidation progresses.
- A decrease of the average molecular weight of the material occurs in the first stage of irradiation, then an increase is observed for higher times of irradiation. In the earliest stages of photooxidation, chain-scissions prevail while for longer times of irradiation cross-linking reactions are predominant.
- An inhibition of the photooxidation resulting from a reduction of oxygen permeability due to cross-linking reactions that occurs after only a few hours of irradiation.

The present paper reports results on the photooxidation of styrene–isoprene copolymers with various compositions. Particular attention is given to the influence of the polyisoprene content on the kinetic aspects and the distribution of the oxidation photoproducts within the polymeric sample. This study is divided into two parts:

- The first part deals with the mechanistic aspects of the photooxidation. The recent advances on the knowledge of the mechanism of degradation of polybutadiene [6] permits reinvestigating the oxidation of polyisoprene. Thin films are irradiated in order to limit the effects of oxygen diffusion.
- In the second part, the kinetic aspects of the

* Corresponding author.

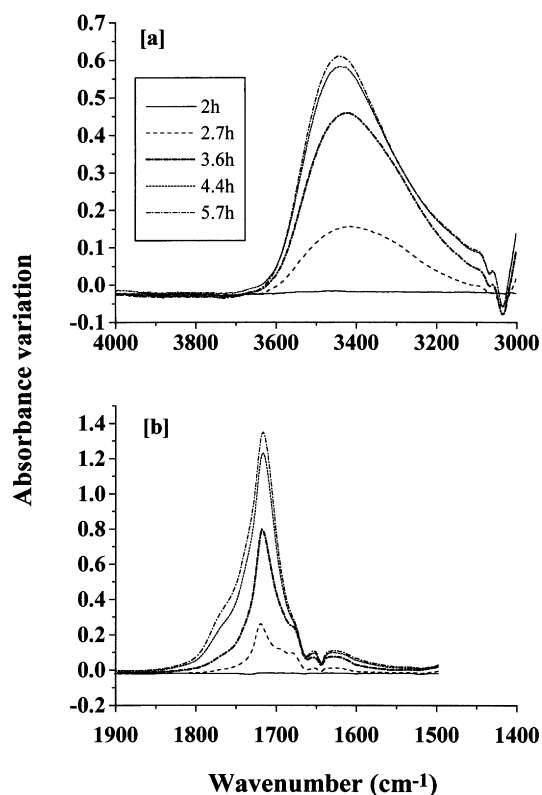


Fig. 1. Changes of the IR spectra of SIS-1 film photooxidized for 7 h at $\lambda \geq 300$ nm, 60°C : spectra from which the virgin spectrum has been subtracted (a) in the hydroxyl region and (b) in the carbonyl region.

photooxidative degradation are analyzed according to the polyisoprene content. Depending on the polyisoprene content, different distributions of the oxidation products are expected. The oxidation profiles are determined using micro FTIR spectroscopic analysis of the one-dimensional gradient. In order to limit the analysis at the surface (between 1 and $10\ \mu\text{m}$), photoacoustic analysis are also performed. The methodology has been previously reported [9].

2. Experimental

The materials investigated were styrene–isoprene copolymers. The samples were kindly donated by National Starch & Chemical S.A. (Villefranche sur Saône, France). Three compositions were tested with different ratios of polyisoprene and polystyrene contents determined by NMR. Sample 1 (SIS-1) is a copolymer containing 15% by weight of polystyrene and 85% of polyisoprene. Sample 2 (SIS-2) has a content in polyisoprene of 71% (by weight) and sample 3 (SIS-3) a content of 56%. The average molecular weight of these copolymers was 100 000 equivalent polystyrene units.

Thin films of polymer (thickness = $50\ \mu\text{m}$) were prepared by the following procedure. After dissolution of the polymer in chloroform, the mixture was spread on a Teflon substrate and free film of SIS was obtained by

solvent evaporation. The complete evaporation of chloroform was controlled by IR spectrometry using the C–Cl vibration at $760\ \text{cm}^{-1}$. The film thickness was controlled and determined by IR (absorbance at $1600\ \text{cm}^{-1}$).

The SIS film was fixed on metal frames for irradiation in a SEPAP 12.24 [10] unit at a temperature of 60°C and analyzed spectrophotometrically after various exposure times. Infrared analysis were performed with a Nicolet 5-SX FTIR spectrometer with a nominal resolution of $4\ \text{cm}^{-1}$ and 128 scans summation.

In order to identify the photoproducts resulting from the photooxidation, physical and chemical treatments were carried out:

- Photolysis and themolysis treatments were performed to determine the photo- and thermo-stabilities of the photo-products. The polymer samples fixed on the metallic frames were introduced into Pyrex reactors and the tubes were flame-sealed under vacuum (resulting from a mercury-diffusion vacuum line). The reactors were then exposed in the SEPAP unit or in a ventilated oven at 60°C .
- Chemical treatments allow the identification of carboxylic groups like acids and esters. Irradiated films were exposed to NH_3 and HCl [6] gases at room temperature in a Teflon reactor. The treatments by SF_4 were unsuccessful because the SIS sample reacted with SF_4 before irradiation.

Depth profiling was performed on thick sample (thickness of 3 mm) with a Nicolet 800 spectrometer coupled to a Nicplan microscope (nominal resolution $4\ \text{cm}^{-1}$, 128 scans summation) following a procedure described earlier [11]. We have shown elsewhere [9] that the microtoming operating could provoke the elimination of the first layers, the molecular cohesion of oxidized SIS samples being very poor at the surface. Complementary analyses were then performed with photoacoustic detection to determine the surface oxidation. This methodology has been already presented in the literature [9,12,13]. The photoacoustic FTIR spectra were recorded using a Nicolet 860 SS-FTIR spectrometer in a rapid-scanning mode with a METC Model 300 photoacoustic accessory following the experimental procedure reported previously [9].

3. Results and discussion

3.1. Part I: mechanism of photodegradation of SIS-1

3.1.1. IR evolutions under photooxidation

Irradiation of SIS films under polychromatic light obtained from filtered medium-pressure mercury lamps ($\lambda > 300$ nm, $T = 60^\circ\text{C}$) in the presence of air leads to noticeable changes of the IR spectra of exposed films (Fig. 1). A broad increase of absorbance is observed in the C=O, OH and C–O vibration domains. Subtraction of the

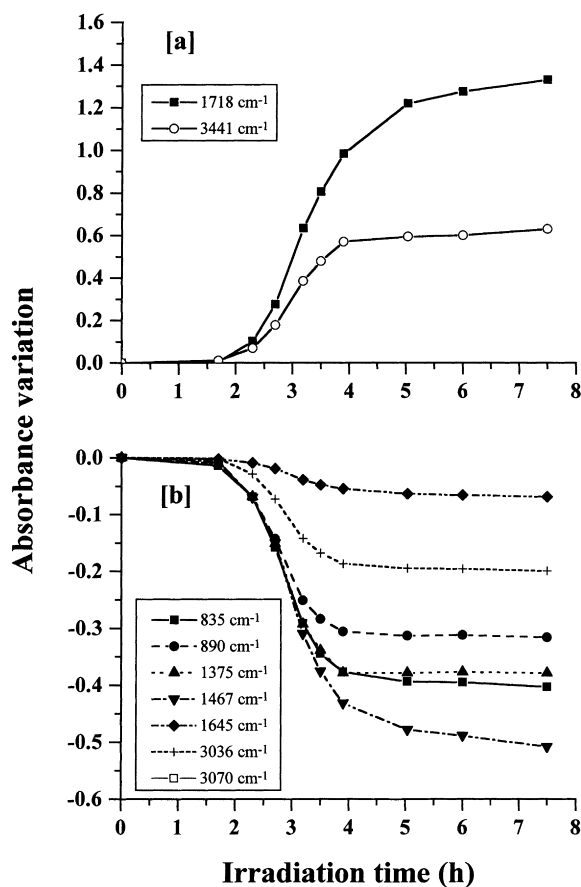


Fig. 2. Kinetic evolution of the IR absorption of the vibrations corresponding to the photoproducts generated by the photooxidation or the consumption of unsaturations under irradiation (SIS-1): (a): (■) 1718, (○) 3441 cm^{-1} ; (b): (■) 835, (●) 890, (▲) 1375, (▼) 1467, (◆) 1465, (+) 3036, (□) 3070 cm^{-1} .

initial spectrum from the spectra recorded after different irradiation times allows the observation of several maxima or shoulders (Fig. 1). The modifications of the spectra throughout irradiation are emphasized when plotting the subtraction between two successive IR spectra.

The hydroxyl region (Fig. 1(a)) reveals a broad absorption band between 3600 and 3100 cm^{-1} with a maximum shifting from 3430 to 3440 cm^{-1} as photooxidation proceeds. In the carbonyl region, at weak conversion degree (Fig. 1(b)), photooxidation leads to the formation of two bands centered at 1722 and 1693 cm^{-1} . As photooxidation proceeds, the intensity of the absorption band at 1722 cm^{-1} increases and the band shifts to 1717 cm^{-1} . A shoulder appears at about 1772 cm^{-1} and a broad absorption band is observed between 1690 and 1600 cm^{-1} . Subtractions between the successive IR spectra shows that the general inflation of the spectrum between 1690 and 1600 cm^{-1} results from two phenomena:

- the formation of photoproducts absorbing at 1675 cm^{-1} ;
- the consumption of intrinsic groups absorbing at 1663 and 1645 cm^{-1} .

In the region of C–H stretching vibrations (Fig. 1(a)), the absorption bands corresponding to the saturated groups prevent from observing any change that would occur during irradiation. The subtracted spectra show the decrease of the C–H stretching vibrations characteristic of unsaturated species at 3068 and 3034 cm^{-1} .

In the region of C–H deformation vibrations (not represented there), photooxidation leads to a general inflation of the spectrum between 1500 and 700 cm^{-1} . Subtraction of the initial spectrum from the spectra recorded after irradiation show a significant decrease of the intensities of several bands at 1446, 1375, 889 and 835 cm^{-1} . New IR absorption bands at 1163, 1112 and 1062 cm^{-1} appear during photooxidation.

The kinetic curves of SIS-1 photooxidation are given in Fig. 2. An induction period of around 2 h is observed. The concentration of the oxidation products reaches a maximum after 4–5 h of exposition.

3.1.2. IR evolutions resulting from physical and chemical treatments of photooxidized samples

Photolysis and thermolysis treatments were carried out on a sample photooxidized for 140 min at $\lambda > 300 \text{ nm}$, 60°C. The purpose of these experiments was to identify the unstable products under photolytic and thermolytic conditions and to propose a mechanism accounting for the decomposition of these products (Fig. 3(1) and (2)).

In the hydroxyl range (Fig. 3(1a) and (2a)), a decrease of the broad band between 3200 and 3600 cm^{-1} can be observed, with a concomitant shift of the maximum from 3410 to 3460 cm^{-1} . The subtracted spectra reveal that their shift results from the decrease of an absorption band centered at 3330 cm^{-1} .

In the carbonyl range (Fig. 3(1b) and (2b)), the consequences of photolysis appear more complex. At weak conversion degree (between 1 and 5 h of photolysis), photolysis leads to the formation of an absorption band at 1780 cm^{-1} , an increase and a widening of the IR absorption band at 1720 cm^{-1} and a general deflation of the spectra between 1700 and 1600 cm^{-1} (Fig. 3(1b)). As photolysis proceeds (Fig. 3(2b)), a decrease of the absorption band at 1720 cm^{-1} is detected. The differences between the successive spectra show that the diminution of the IR absorption results from the disappearance of the unsaturated products at 1690, 1677 with a shoulder at 1665 and 1645 cm^{-1} and also a disappearance of the carboxylic product absorbing at 1718 cm^{-1} leading to a decrease of the IR absorption at 1720 cm^{-1} . As these two bands are convoluted, the frequency of the absorption maximum found by subtraction cannot be considered as the absorption maximum of the band that decreases.

In the range of the C–H deformation vibrations, the modifications of the spectra are similar to those observed during photooxidation. The subtracted spectra reveal an increase of the IR absorption band at 1160 cm^{-1} and a decrease of the broad absorption band at 1100 cm^{-1} . A

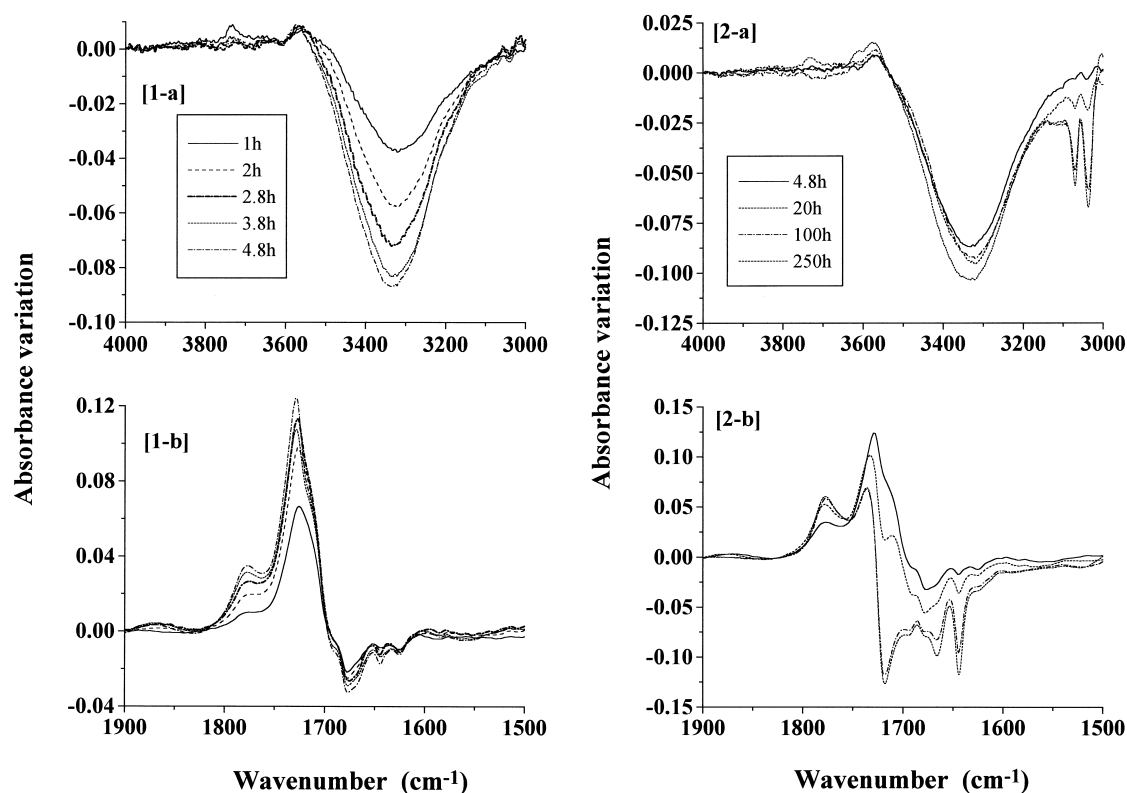


Fig. 3. Changes of the IR spectra of SIS-1 film photooxidized for 140 min at $\lambda \geq 300$ nm, 60°C then photolyzed at $\lambda \geq 300$ nm, 60°C . Only subtracted spectra between the photooxidized film and the film photolyzed are represented (SIS-1): (1) for short irradiation times and (2) for long irradiation times (a) in the hydroxyl region and (b) in the carbonyl region.

decrease of the band characteristic of the unsaturated groups at 1441, 1375, 889 and 835 cm^{-1} is also observed.

The kinetic curves corresponding to the photolysis experiments are reported in Fig. 4. The following comments have to be made:

- The intensity of the absorption band at 1780 cm^{-1} increases rapidly in the first hours of irradiation and reaches a constant value after 100 h of photolysis.
- The concentration of the carboxylic products corresponding to the absorption band at 1717 cm^{-1} increases in the first hours of irradiation and then decreases to reach a constant value.
- A decrease of the IR absorption bands at 835, 889, 1375, 1441, 1645 and 1665 cm^{-1} occurs.
- The IR absorption bands at 1678, 1690 and 3330 cm^{-1} decrease rapidly and reach a constant value.

Throughout the thermolysis experiments (Fig. 5) the absorbances at 1780, 1720, 1690 and 1680 cm^{-1} increase whereas a decrease of the IR absorption at 3329 cm^{-1} is observed. The decrease of the absorption bands at 1665, 1645, 1375 and 1441 cm^{-1} noted after photolysis is not observed in thermolysis.

These experiments show the thermal and photochemical stability of the products corresponding to the bands at 1780 and 1720 cm^{-1} and the photochemical instability of the species absorbing at about 1717, 1693 and 1680 cm^{-1} .

NH_3 treatment carried out on photooxidized samples (after 140 min of irradiation) provokes the disappearance of a large absorption band between 1760 and 1700 cm^{-1} centered at 1720 cm^{-1} with a shoulder at about 1695 cm^{-1} . The formation of a new absorption band at 1570 cm^{-1} is detected. Furthermore after reaction with HCl vapors, the absorption band at 1570 cm^{-1} decreases whereas the carbonyl absorptions at 1717 and 1693 cm^{-1} are restored.

3.1.3. Photooxidation mechanism

The photolysis experiments show that the absorption band between 3600 and 3100 cm^{-1} results from the convolution of two absorption bands with maxima at 3440 and 3325 cm^{-1} corresponding, respectively, to alcohols and associated hydroperoxides. This result is in good agreement with the work carried out by Adam et al. [2] that had shown that the photooxidation of polyisoprene led to a high concentration of hydroperoxides.

The maximum at 1722 cm^{-1} has been formerly [2] assigned to methyl ketone on the basis of the disappearance of the band in conditions of photolysis or thermolysis. The photolysis experiment carried out in the present study indicates, however, that only part of this photoproduct decomposes. This result is confirmed by the NH_3 treatment. This indicates that the absorption at 1722 cm^{-1} could be the convolution of two bands corresponding to a methyl ketone

as proposed by Adam et al. [2] and to an α,β -unsaturated ester. The photolytic decomposition of ketone results from Norrish I reaction.

Formation of carboxylated products absorbing at 1772 cm^{-1} is detected and can be attributed to lactone or the monomer form of carboxylic acids [6]. It is important to point out that Norrish II reaction cannot occur because of the substitution of the carbon atom in the γ -position from the carbonyl group. The decomposition of hydroperoxides to alcohol has to be considered as a minor process since no increase of the absorption band at 3440 cm^{-1} is detected. A concerted mechanism of decomposition of the hydroperoxides should be postulated as responsible for the formation of ester groups. According to literature data [14], the IR absorption band at 1163 cm^{-1} can be assigned to the stretching vibration of the C–O group of the α,β -unsaturated ester groups.

The maxima at 1693 and 1680 cm^{-1} are associated to α,β -unsaturated carbonyl functions, on the basis of their thermal stability and their photolytic decomposition. The maximum at 1690 cm^{-1} had been previously assigned to α,β -unsaturated ketone [2,4], from the unreactivity with NH_3 and the photolytic decomposition. A closer inspection of the IR absorption after NH_3 treatment shows that product reacts with NH_3 . This reaction appears to be reversible after an HCl treatment. The photooxidation mechanism of degradation of polybutadiene proposed by Rivaton [6] shows that this IR absorption cannot be attributed to an α,β -unsaturated ketone but indicates the formation of an α,β -unsaturated acid whereas the 1680 cm^{-1} absorption has to be attributed to an α,β -unsaturated ketone. This last product is too photo-unstable to be detected.

The significant decrease of the bands assigned to the microstructure (1,4 unsaturations at 835 cm^{-1} and 3,4 unsaturations at 889 cm^{-1}) has been previously reported to occur throughout photooxidation at $\lambda > 300\text{ nm}$. These variations must be related to:

- the decrease of the absorption bands at 1645 and 1663 cm^{-1} assigned to the C=C vibration of 3,4 and 1,4 double bonds;
- the decrease of the absorption bands at 3068 and 3034 cm^{-1} assigned to C–H stretching vibration of 3,4 and 1,4 double bonds;
- the decrease of the absorption bands at 1441 and 1375 cm^{-1} assigned, respectively, to the CH_2 *cis*-deformation of the 3,4 unsaturation and to the C–H rock vibration of the 1,4 unsaturation.

As an example, the correlation between the IR absorbances at 3034 and 835 cm^{-1} characteristic of the 1,4 unsaturations is shown in Fig. 6.

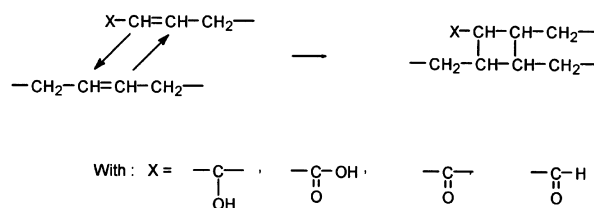
It is worthy to note that the absorption band characteristic of the 1,2 unsaturations at 910 cm^{-1} is not easily observed on the initial spectrum. However as photooxidation proceeds, the consumption of the unsaturations leads to a decrease of the IR absorption at 889 cm^{-1} which simplifies

the spectrum, and permits observing the absorption band at 910 cm^{-1} on the spectra of difference.

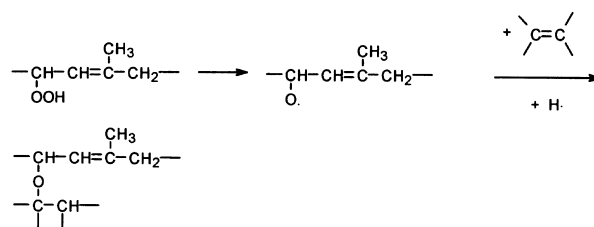
The kinetic curves reported in Fig. 2 indicate that after 8 h of irradiation, the concentration in carbonyl groups reaches a limit value, as well as the intensity of the unsaturation bands. It is important to point out that about 70% of the initial unsaturations react within only 4 h of irradiation (Fig. 7) and that the disappearance of unsaturations is simultaneous to the formation of carboxylic species.

This behavior has been explained by Adam et al. [2] as resulting from oxidative cross-linking reactions which would result in a decrease of the oxygen permeability of the material. The solubility of the polymer in chloroform diminishes as the photooxidation proceeds and after 8 h of irradiation, the material becomes insoluble in CHCl_3 , demonstrating the formation of a tridimensional structure. The same evolution can be observed during the photolysis of a prephotooxidized sample. Rivaton and coworkers [6] have postulated that this cross-linking reaction would result from:

- the loss of unsaturation of α,β -unsaturated oxidized products through cross-linking:



- the formation of ether linkage through photooxidation:



It is important to note that no trace of the photoproducts that could be attributed to the photooxidation of polystyrene segment is detected. This indicates that the photodegradation of the polyisoprene segments does not induce the photodegradation of the polystyrene segments on this time-scale. Thus, the mechanism of degradation can be proposed as in Schemes 1–3.

3.2. Part II: kinetic and profile of degradation

The modifications of the IR spectra recorded for the two other materials (SIS-2 and SIS-3) are similar to those recorded for the copolymer SIS-1 (Fig. 1). The subtractions between the successive spectra reveal the formation of carboxylic species absorbing at 1772 , 1740 , 1722 , 1717 , 1690 and 1675 cm^{-1} . On this basis, it can be concluded

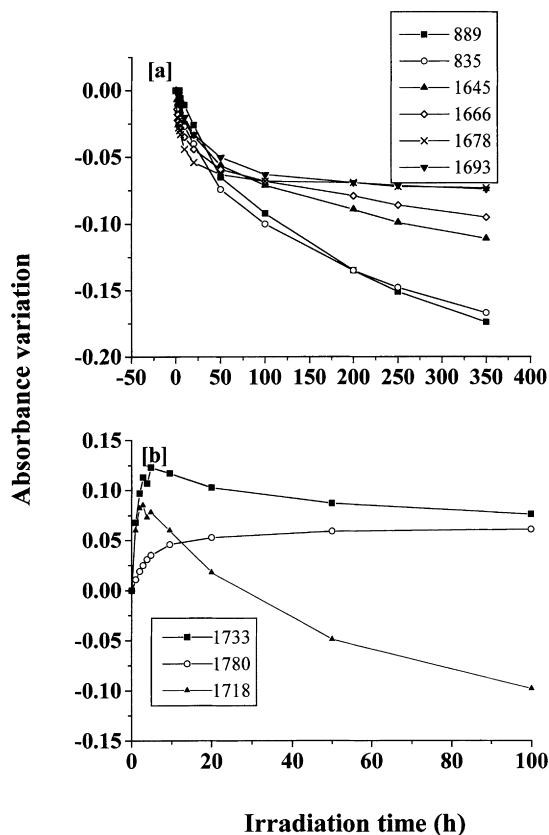


Fig. 4. Kinetic evolutions of the photoproducts generated by photooxidation or the consumption of the unsaturations during the photolysis experiments (SIS-1): (a) (■) 889, (○) 835; (▲) 1645, (◇) 1666; (×) 1678, (▼) 1693 cm^{-1} ; (b): (■) 1733, (○) 1780, (▲) 1718 cm^{-1} .

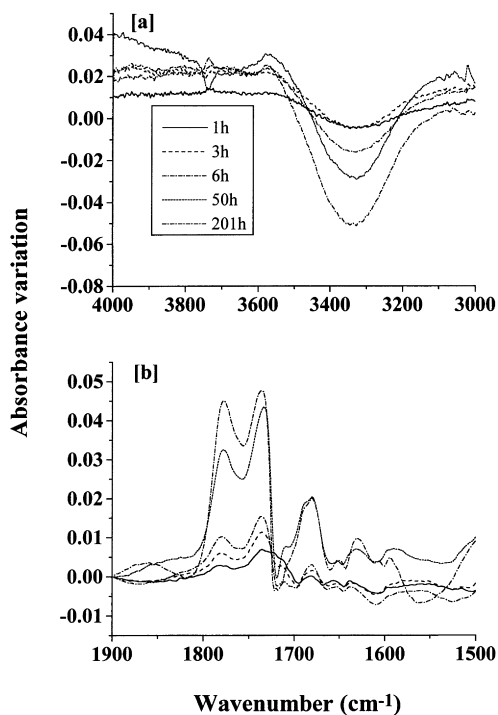


Fig. 5. Changes of the IR spectra of SIS-1 film photooxidized for 140 min at $\lambda \geq 300$ nm, 60°C then thermolyzed at 60°C : subtracted spectra between the photooxidized film and the film thermolysis for various durations (a) in the hydroxyl region and (b) in the carbonyl region.

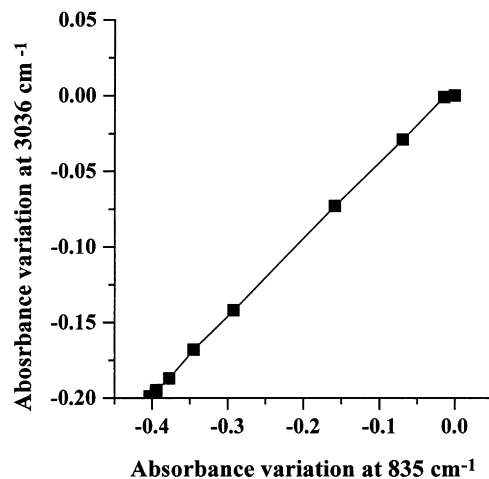


Fig. 6. Relationship between the IR absorbances at 1375 and 835 cm^{-1} .

that the mechanism of the photooxidative degradation of these copolymers (SIS-1, SIS-2, SIS-3) are not depending on the polyisoprene content.

The presence of polystyrene could however modify the extent of degradation by limiting the oxidative cross-linking process. As the analyses show that the polystyrene segments are not photooxidized on this timescale, the kinetics of degradation will have to be compared for the same level of polyisoprene. The results have then to be corrected on the basis of the theoretical composition in polyisoprene segments. The factors applied are reported in Table 1. The corresponding kinetic curves of oxidation of the various samples are reported in Fig. 8.

These results confirm that the evolutions of these materials are similar whatever the composition of the copolymers. The extent of degradation is not dependent on the content of polyisoprene. One could then postulate that the profile of oxidation through the sample thickness should be similar. The determination of the distribution profiles were performed by microspectrophotometry and photoacoustic

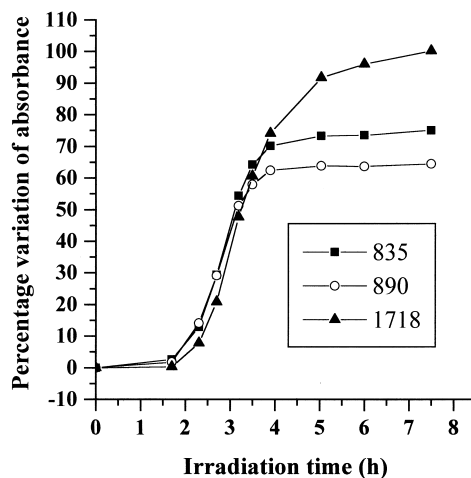
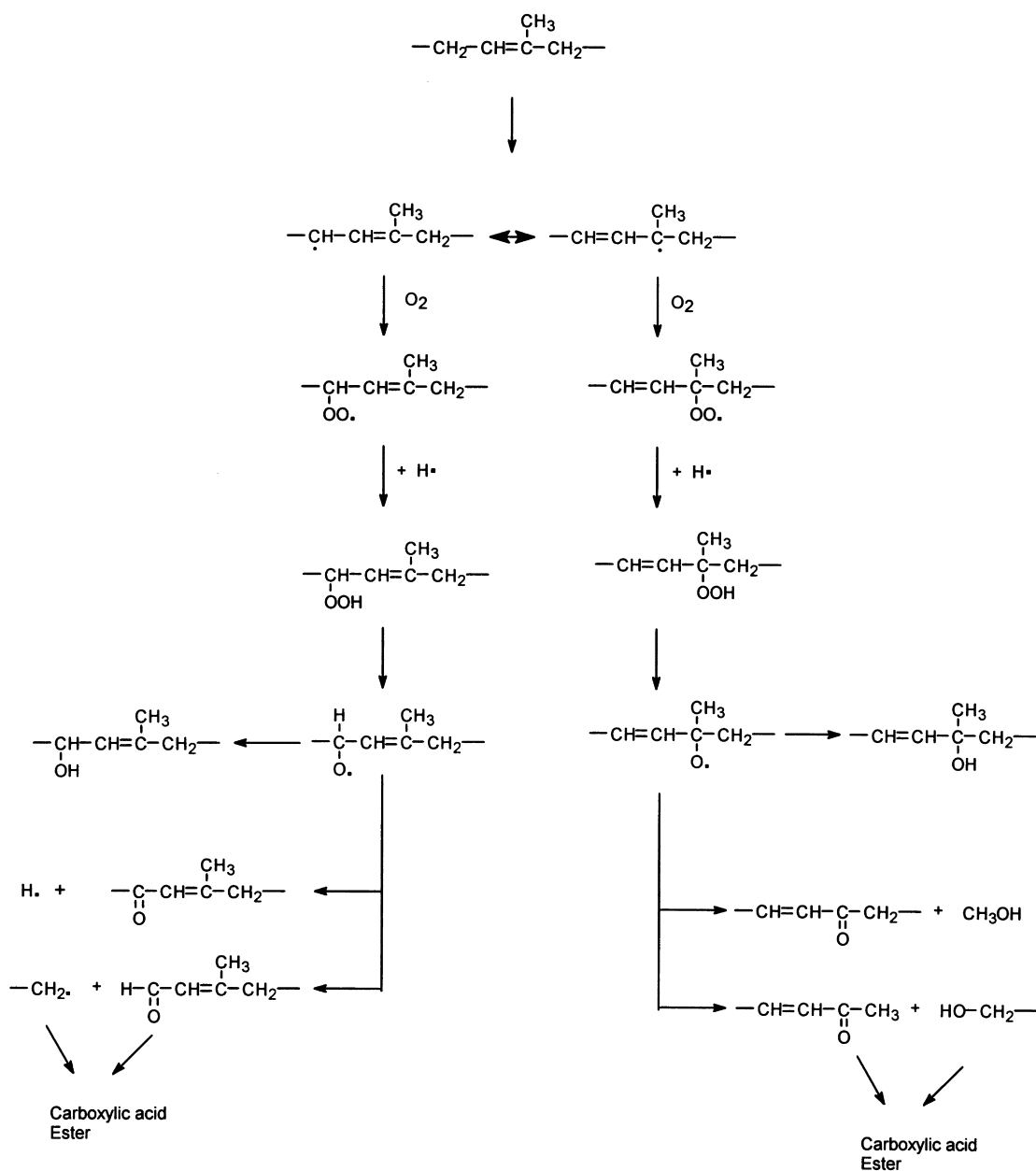


Fig. 7. Kinetic of formation of the carboxylic products absorbing at (▲) 1717 cm^{-1} and the consumption of the double bands at (■) 835 and (○) 890 cm^{-1} during the photooxidation (SIS-1 sample).



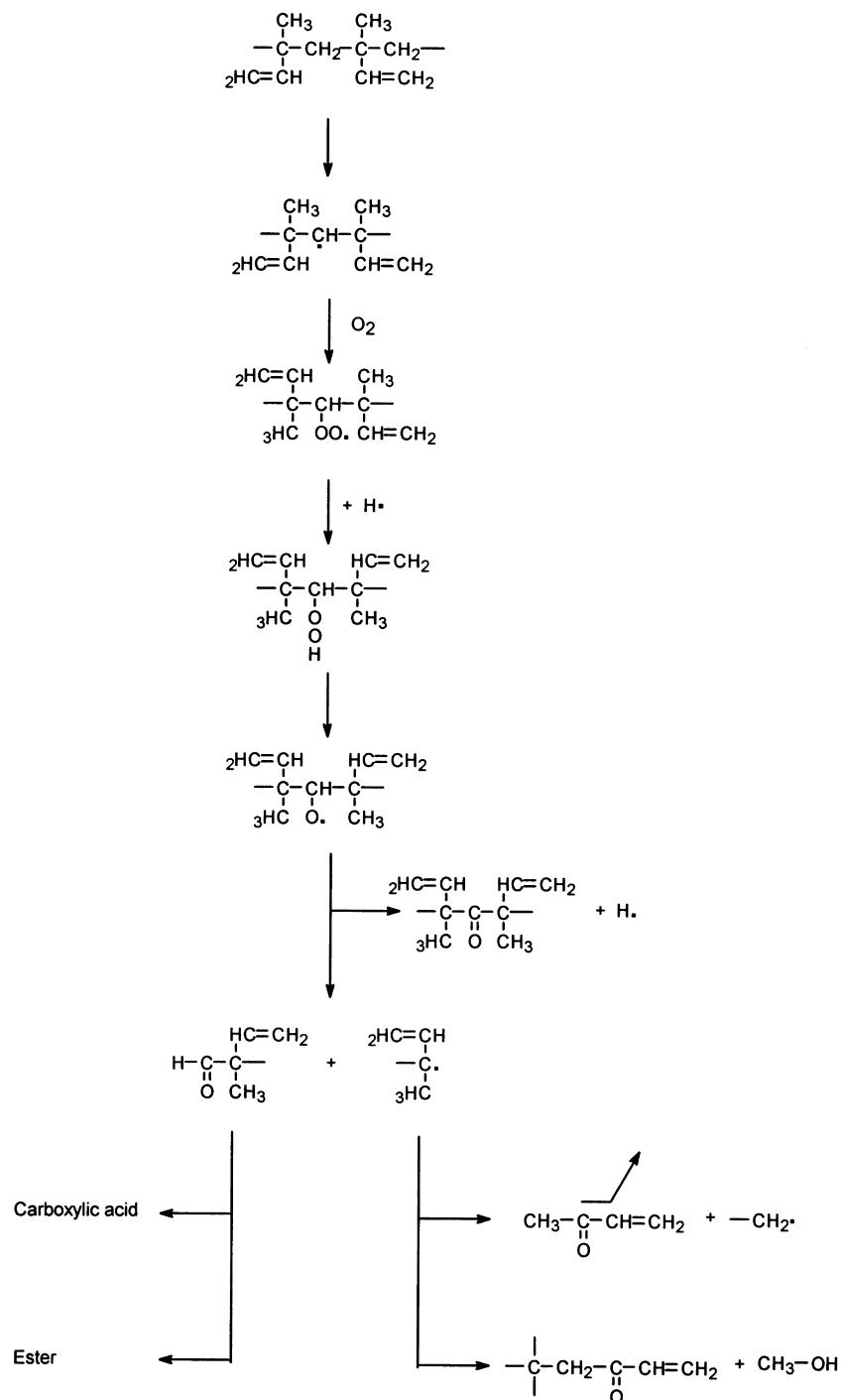
Scheme 1. Mechanism of photooxidation of 1-4 segments.

FTIR. As introduced previously [9], the major drawback of the PAS technique is that the signal depends on several parameters which cannot be exactly controlled. In order to overcome this problem, the utilization of a reference absorption band as internal standard must be applied. The investigations on the mechanism have shown the stability of the styrene phase during the irradiation. The IR absorption bands of this phase can then be used as reference for the calibration of the PAS experiments.

The IR absorption at 1600 cm^{-1} characteristic of the aromatic ring was chosen. In order to define the oxidation profile from the surface to the bulk, the same methodology must be applied to the microspectrophotometric analysis. The IR analysis of the photooxidation has shown that the

absorption band at 1717 cm^{-1} is characteristic of the major oxidation photoproducts. The profiles of the oxidation products are then drawn as the ratio 1717/1600 through the sample thickness. As the extent of degradation of the material is directly proportional to the content in polyisoprene, the profiles must be normalized to be comparable. The normalization is realized by dividing the ratio 1717/1600 cm^{-1} by the value found on the outer surface of the sample. The profile determined by these techniques are reported in Fig. 9.

These results demonstrate that the oxidation is not modified by the presence of the polystyrene segments. The same concentration of photoproducts is formed through the sample thickness.



Scheme 2. Mechanism of photooxidation of 1-2 segments.

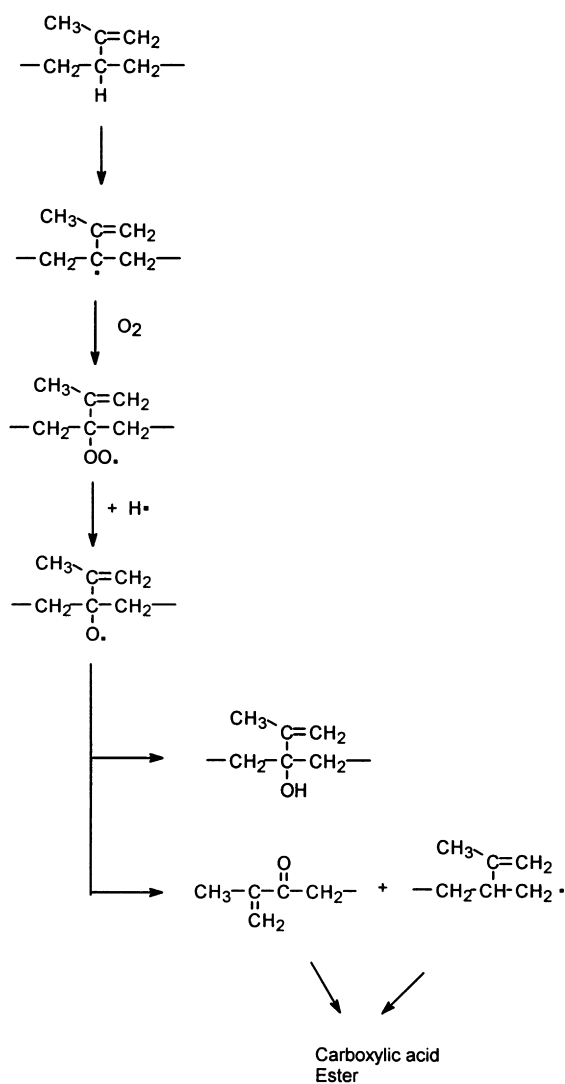
The mechanism of photooxidative degradation proposed is based on the chemical evolution of the polymer under irradiation. An oxidative cross-linking process has been proposed to explain the apparent stability of these materials after 8 h of irradiation whereas the rate of oxidation is very important in the first hours of exposition. This mechanism is based on:

- a decrease of the permeability to oxygen of these materi-

als after only a few hours of irradiation [2,6] resulting from the cross-linking of the material;

- a rapid reaction of unsaturations under irradiation leading to their disappearance;
- the apparent photostability of these materials after 8 h of exposition.

As cross-linking implies the addition of two unsaturations, the introduction of a photostable product should be



Scheme 3. Mechanism of photooxidation of 3-4 segments.

expected to modify the mechanism of degradation. Indeed, the introduction of polystyrene segments should contribute to:

- the formation of an entanglement of the macromolecular chains and as a consequence a physical dilution of the polyisoprene segments;
- a decrease of the molecular mobility of the chain as the glass transition of the polystyrene segments is about 100°C.

Table 1

Correction factor applied on the kinetic curves to reach a constant concentration in polyisoprene whatever the composition of the sample

Copolymer	Polyisoprene segments (wt%)	Correction factor
SIS-1	85	1
SIS-2	71	1.2
SIS-3	56	1.5

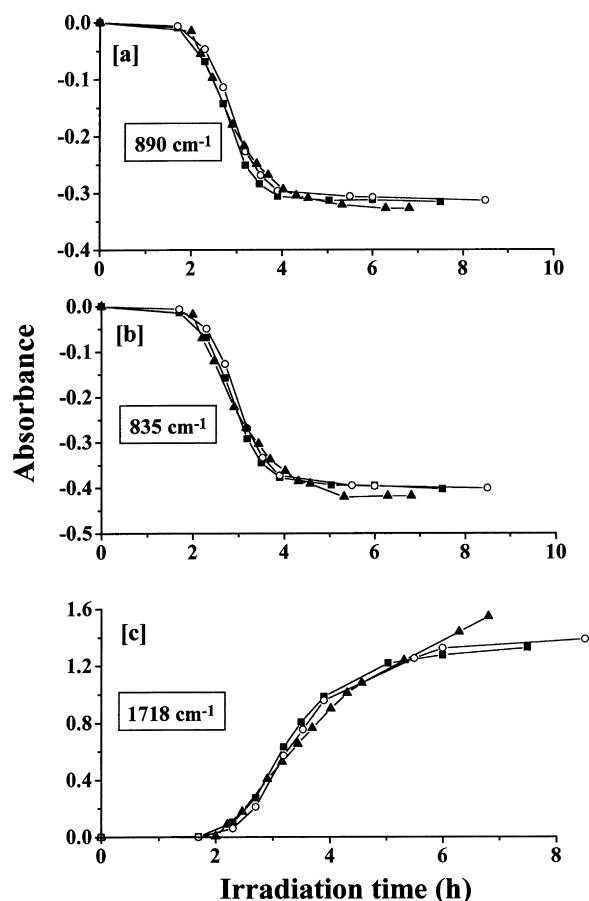


Fig. 8. Variation of the absorbance corresponding to the oxidation photo-products and to the unsaturations under irradiation: (▲) SIS-1, (■) SIS-2, (○) SIS-3 based on a same content of polyisoprene (the corrected factors applied are reported in Table 1). (a) 890, (b) 835, (c) 1718 cm^{-1} .

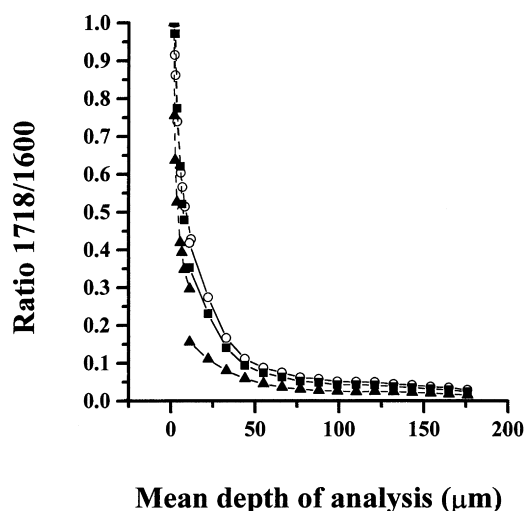


Fig. 9. Depth analysis (oxidation profiles) of photooxidized copolymers based on the ratio 1718 cm^{-1} /1600 cm^{-1} determined by PAS-FTIR spectroscopy (---) and micro-FTIR (—): (▲) copolymer SIS-1, (■) copolymer SIS-2 and (○) copolymer SIS-3.

These two parameters should contribute in reducing the oxidative cross-linking process and then oxidation would not be limited to the outer surfaces of the sample. Our results show that this is however not the case. The literature [15–18] reports that the non-miscibility of polystyrene and polyisoprene leads to a phase separation. Differential scanning analysis performed on these materials shows two glass transitions at about -60 and 75°C (at the mid point). A complete demixion phase has to be excluded considering a sample containing 44% of polystyrene (SIS-1). Nevertheless, according to the glass transitions found, it can be considered that there are two phases, one which contains a high content of polyisoprene (more than 90% from a mixture law) and the other very rich in polystyrene (more than 92%). Each phase can then be considered as an independent photochemical reactor. So, the mechanism of degradation and as a consequence, the extent of oxidation of these materials is independent of their composition.

4. Conclusion

The mechanism of photodegradation established from the physical evolution of styrene–isoprene copolymers indicates that the styrene segments can be considered as photostable under irradiation. The photooxidation of isoprene segments leads to:

- the formation of carbonylated photoproducts identified to ketones and α,β -unsaturated esters absorbing at 1717 cm^{-1} ;
- the consumption of the intrinsic unsaturations;
- the formation of a three-dimensional structure.

The analysis of different mass compositions (polyisoprene/polystyrene ratio) indicates that:

- the kinetic of oxidation of these materials is independent of the polyisoprene content;

- the degree of oxidation is proportional to the polyisoprene content;
- the distribution of the photoproducts through the material thickness is not modified by the variations of the composition.

These results indicate that the polystyrene segments can be considered as an inactive charge in terms of photooxidative degradation of the material. It may be postulated that the absence of interactions between the polyisoprene and the polystyrene segments results from an incompatibility between these polymers leading to a phase demixion. The nodules can be considered as independent photochemical reactors with their own kinetic of degradation.

References

- [1] Shelton JR. *Rubber Chem Tech* 1972;45:359.
- [2] Adam C, Lacoste J, Lemaire J. *Polym Deg Stabil* 1991;32:51.
- [3] Adam C, Lacoste J, Lemaire J. *Polym Deg Stabil* 1989;26:269.
- [4] Adam C, Lacoste J, Lemaire J. *Polym Deg Stabil* 1989;24:185.
- [5] Adam C, Lacoste J, Lemaire J. *Polym Deg Stabil* 1990;29:305.
- [6] Piton M, Rivaton A. *Polym Deg Stabil* 1996;53:343.
- [7] Adam C, Lacoste J, Lemaire J. *Polym Deg Stabil* 1990;27:85.
- [8] Rodrigues JF, De Paoli MA. *Eur Polym J* 1985;21:15.
- [9] Gonon L, Vasseur OJ, Gardette JL. *Appl Spectr* 1999;53:157.
- [10] Lemaire J, Arnaud R, Gardette JL. *Rev Gen Caoutch Plast* 1981;613:87.
- [11] Mailhot B, Gardette JL. *Macromolecules* 1992;25:4127.
- [12] Delprat P, Gardette JL. *Polymer* 1993;34:933.
- [13] Urban MW. *J Coat Tech* 1987;59:29.
- [14] Avram M, Mateescu, GHD. *Spectroscopie Infrarouge: applications en chimie organique*, DUNOD, 1970.
- [15] Khandpur AK, Förster S, Bates FS, Hamley IW, Ryan AJ, Bras W, Almdal K, Mortensen K. *Macromolecules* 1995;28:879.
- [16] Manzur A, Rubio L. *J Macromol Sci Phys* 1997;36:103.
- [17] Jo WH, Nam KH, Cho JC. *J Polym Sci, Polym Phys Ed* 1996;34:2169.
- [18] Hourston DJ, Song M, Hammiche A, Pollock HM, Reading M. *Polym Papers* 1997;38:1.