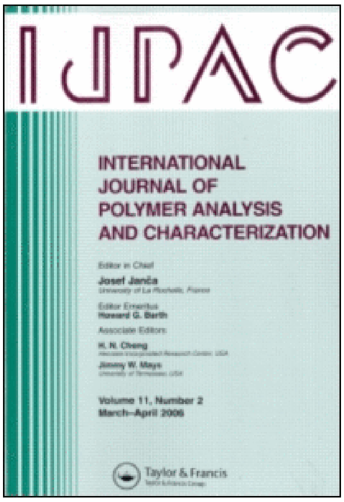

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# Styrene – Isoprene – Styrene Photoperoxidation: FT-IR, Calorimetric and Viscoelastic Study*

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Styrene–isoprene–styrene copolymers are triblock copolymers consisting of a rigid (styrene block), and elastomeric phase. The styrenic phase is known to be resistant to light in comparison with the isoprene phase. A study of the photochemical evolution of a thin film under accelerated conditions has been carried out using conventional spectroscopic methods. Differential scanning calorimetry and chemical titration have been used to assess the content and the stability of the peroxide species. Viscoelastic experiments have shown that at the beginning of the photochemical evolution, chain scission is the main phenomenon while cross-linking begins to appear as photoageing proceeds. This cross-linking leads to insolubility that disappears in the presence of sodium iodide. Thus, the main finding is the formation of interchain peroxide groups (ROOR) in parallel with hydroperoxide formation (ROOH).

*Keywords*: FT-IR; DSC; Viscoelasticity; Peroxide; Photooxidation

## INTRODUCTION

Styrene–isoprene–styrene (SIS) copolymers are triblock copolymers consisting of a rigid phase (styrene block) with an elastomeric one. The mechanism of photodegradation of the corresponding homopolymers has been established in our laboratory by Mailhot and Gardette[1] for

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the styrenic phase and by Adam[2] and Piton[3] for the elastomeric phase. The chemical evolution of SIS copolymer under photoaccelerated conditions has been studied previously[4] and demonstrates improved stability of the styrenic phase in comparison with the elastomeric one. Moreover, it has been shown that the first step is the formation of peroxide species on the polymer backbone. These groups are the key products for understanding the mechanism as well as for gaining a better insight into the correlation of chemical modifications and their consequences on physical properties. Differential scanning calorimetry and chemical titration were used to assess the content and the stability of the peroxide species. Viscoelastic experiments[5-7] were carried out to quantify the molecular changes (chain scissions, cross-linking, *etc.*).

The aim of this study is to characterize the formation of peroxides to be able to correlate chemical with physical properties.

## EXPERIMENTAL

The material investigated was a styrene–isoprene–styrene copolymer provided by National Starch and Chemical S. A. (Villefranche sur Saône, France). This sample is composed of 29 wt% polystyrene and 71 wt% polyisoprene.

In order to obtain a thin polymer film, the sample was pressed between Teflon sheets at 180°C and 200 bar for one min. Free film of SIS was fixed in metal frames for irradiation in an irradiation device (SEPAP 12.24).[8] This apparatus uses four 400 W medium pressure mercury lamps (Mazda MA-400) constructed with borosilicate glass envelopes which filter all wavelengths below 300 nm. Irradiation was performed at 60°C under 'dry' conditions (*i.e.*, ambient relative humidity). All samples were mounted on a centrally rotating carousel to ensure homogeneous irradiation. The sample-to-lamp distance was 20 cm.[8]

To identify unstable products under photolytic and thermolysis conditions, photolysis and thermolysis treatments were performed on the photooxidized sample. The polymer samples fixed on the metallic frames were introduced into Pyrex reactors and flame sealed under vacuum from a mercury-diffusion vacuum line. The reactors were then exposed in the SEPAP unit or in a ventilated oven at 60°C.

## FTIR Analysis

After various exposure times, samples were analyzed spectrophotometrically with an FT-IR spectrophotometer. The film thickness (50 μm) was controlled and determined by IR (absorbance at $1600\,\mathrm{cm}^{-1}$). Infrared analysis was performed with a Nicolet 5-SX FT-IR spectrometer with a nominal resolution of $4\,\mathrm{cm}^{-1}$ and 128 scan summation.

## Peroxide Titration

### *Chemical Titration*

Total peroxides were estimated by iodometric titration[9, 10] based on the reduction of hydroperoxides by sodium iodide in excess in acidic medium according to the reaction

$$\mathrm{ROOH} + 2\mathrm{I}^- + 2\mathrm{H}^+ \rightarrow \mathrm{ROH} + \mathrm{I}_2 + \mathrm{H_2O}$$
$$\mathrm{I}_2 + \mathrm{I}^- \rightarrow \mathrm{I}_3^-$$

The concentration of the triiodide formed subsequently was measured by UV spectophotometry at 362 nm using the commonly accepted extinction coefficient of $2.5\ 10^4\,\mathrm{mol}^{-1} \cdot \mathrm{l} \cdot \mathrm{cm}^{-1}$.

### *Thermal Analysis*

The thermal instrument used was a DSC 2920 TA Instrument. The calorimeter was calibrated with indium standard at a heating rate of $20°\mathrm{C} \cdot \mathrm{min}^{-1}$. The TA Instruments Graphware software was used to measure the heat flow. The concentration in peroxide was assessed by dividing the energy of decomposition by 450 kJ, heat of decomposition of one mole of peroxide.[11] Moreover, by this technique we also assessed the thermal stability of the photoperoxided samples.

## Rheological Experiments

The changes in dynamic storage $G'$ (stress/strain in-phase component) and loss $G''$ moduli (stress/strain out of phase component) of photooxidized samples were followed in oscillatory shear mode using a rotational controlled stress rheometer (StressTech/Rheologica) equipped with a parallel plate geometry. The plate diameter was 20 mm and the gap between the plates was about 1 mm. In all cases, the values of the stress amplitude were checked to ensure that all measurements were conducted within the linear viscoelastic region. At different times during the UV exposure, a frequency sweep extending from 0.01 to 30 Hz was performed. All experiments were carried out at 105°C, because it is known that peroxides are quite thermally stable at this temperature.[11] The stability of oxidized samples at 105°C with respect to the measurement duration has obviously been verified.

## RESULTS

### Mechanism of Photodegradation: IR Evolutions Under Photooxidation

Irradiation of SIS leads to noticeable changes of the IR spectra of exposed films in the C═O, OH and C—O vibration domains. Subtraction of the initial spectrum from the spectra recorded after different irradiation times allows the observation of several maxima or shoulders (Fig. 1).

The hydroxyl region (Fig. 1c) reveals a broad absorption band between 3600 to 3100 $\mathrm{cm^{-1}}$ with a maximum shifting from 3430 to 3440 $\mathrm{cm^{-1}}$ as photooxidation proceeds. In the carbonyl region (Fig. 1b), at weak conversion degree, photooxidation leads to the formation of two bands centered at 1722 and 1693 $\mathrm{cm^{-1}}$. As photooxidation proceeds, the intensity of the absorption band at 1722 $\mathrm{cm^{-1}}$ increases and the band shifts to 1717 $\mathrm{cm^{-1}}$. A shoulder appears at about 1772 $\mathrm{cm^{-1}}$ and a broad absorption band is observed between 1690 and 1600 $\mathrm{cm^{-1}}$. Subtraction between the successive IR spectra show that the general inflation of the spectrum between 1690 and 1600 $\mathrm{cm^{-1}}$ results from two phenomena: the formation of photoproducts absorbing at 1675 $\mathrm{cm^{-1}}$ and the consumption of intrinsic groups absorbing at 1663 and 1645 $\mathrm{cm^{-1}}$.

In the region of C—H stretching vibrations, subtracted spectra show a decrease of the C—H stretching vibrations characteristic of unsaturated species at 3068 $\mathrm{cm^{-1}}$ and 3034 $\mathrm{cm^{-1}}$. In the region of C—H deformation vibrations (Fig. 1a), photooxidation leads to a general inflation of the spectrum between 1500 and 700 $\mathrm{cm^{-1}}$. Subtraction of

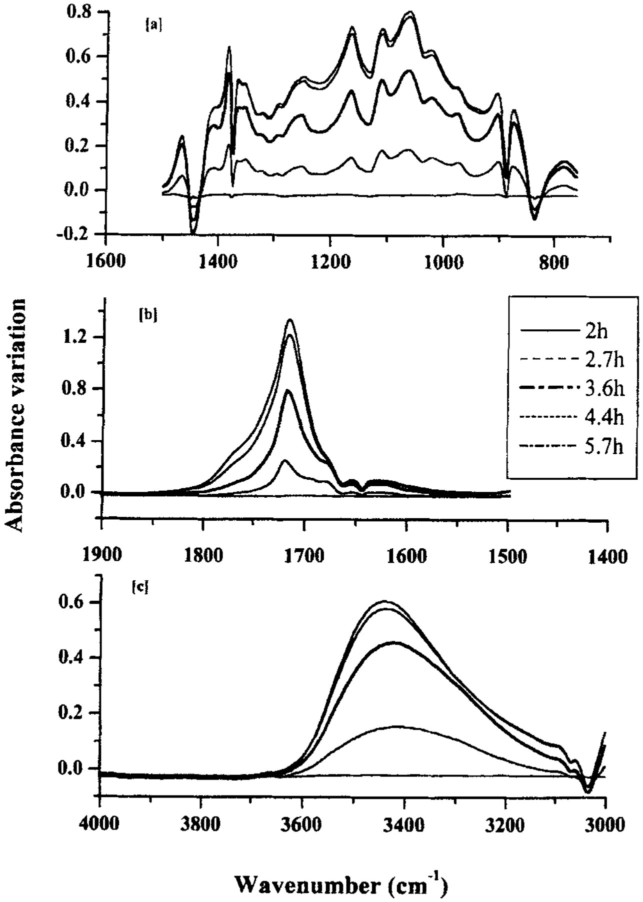


FIGURE 1 Changes of the IR spectra of SIS film photooxidized for different irradiation times: spectra from which the virgin spectrum has been subtracted; a: 1600–700 cm$^{-1}$, b: 1900–1500 cm$^{-1}$, c: 4000–3000 cm$^{-1}$.

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$^{-1}$ and the formation of new IR absorption bands at 1163, 1112 and 1062 cm$^{-1}$.

The kinetic curve of SIS photooxidation is given in Figure 2. After an induction period of about 2 h, the concentration of the oxidized products characteristic of the photodegradation increases rapidly to a maximum after about 4 h of exposure.

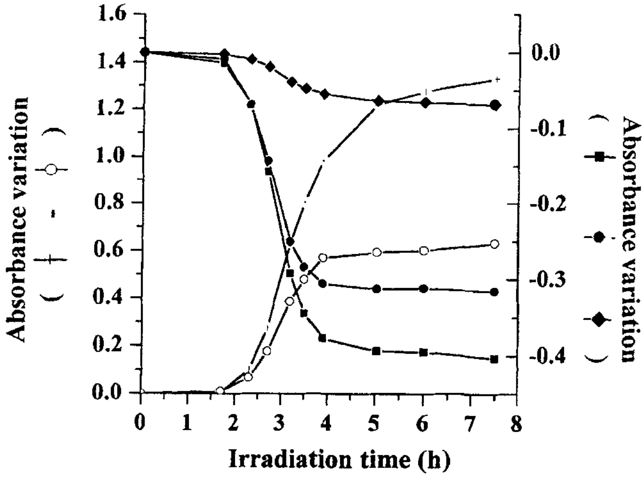


FIGURE 2 IR absorption of vibrations corresponding to the photoproducts generated by the photooxidation or the consumption of unsaturation under irradiation: + 1718 cm$^{-1}$, o 3441 cm$^{-1}$; ■835 cm$^{-1}$, ● 890 cm$^{-1}$, ◆ 1645 cm$^{-1}$.

The FT-IR analysis performed on the sample after physical treatment (photolysis and thermolysis) give the following information (the recorded spectra are not represented here):

- In the hydroxyl range, the broad absorption band centered at 3430 cm$^{-1}$ results from the convolution of two absorption bands: an absorption at 3330 cm$^{-1}$, which decreases under these physical treatments, and an absorption at 3460 cm$^{-1}$, which is not modified during these treatments.
- In the carbonyl range, 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 cm$^{-1}$ and their associated bands (1665 and 1645 cm$^{-1}$) under photolytic treatment, whereas the formation of these absorbing products is favored during thermolysis treatment.
  - the photolytic decomposition of the carboxylic product absorbing at 1718 cm$^{-1}$ leading to a decrease of the IR absorption at 1720 cm$^{-1}$. An inverse evolution is observed during thermolysis treatment.

- 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 band characteristic of the unsaturated groups at 1441, 1375, 889 and 835 cm$^{-1}$. No modifications are detected during thermolysis treatment.

## Peroxide Titration

The evolution of the concentration of peroxides through photooxidation is reported in Figure 3. These results indicate a high concentration of peroxide structures as reported earlier.[2]

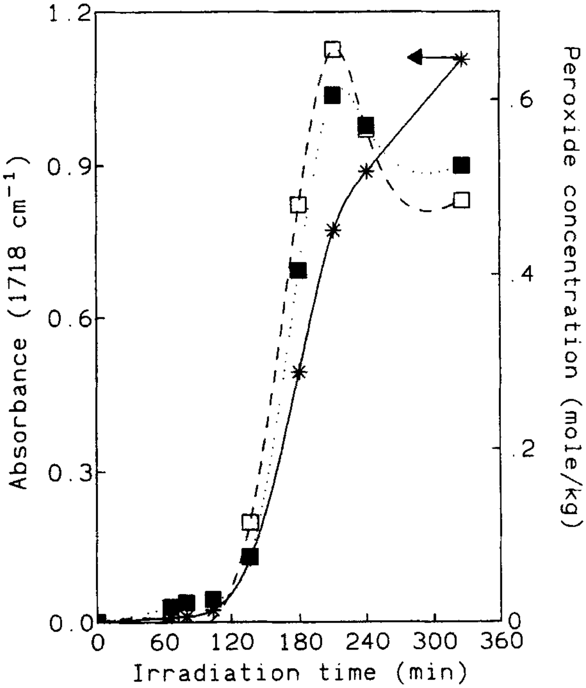


FIGURE 3 Variation of peroxide concentration (■ by iodide titration and □ by DSC titration) and carbonyl absorbance (*) through photooxidation.

## Dynamic Viscoelastic Properties Through Photooxidation

The evolution of the storage $G'$ and loss moduli $G''$, characteristic for respectively the elastic and the viscous responses of the material, through photooxidation is illustrated in Figures 4 and 5. In a first step, both moduli diminish with respect to the irradiation time ($t \leq 200$ min). In a second step, increasing the irradiation time leads

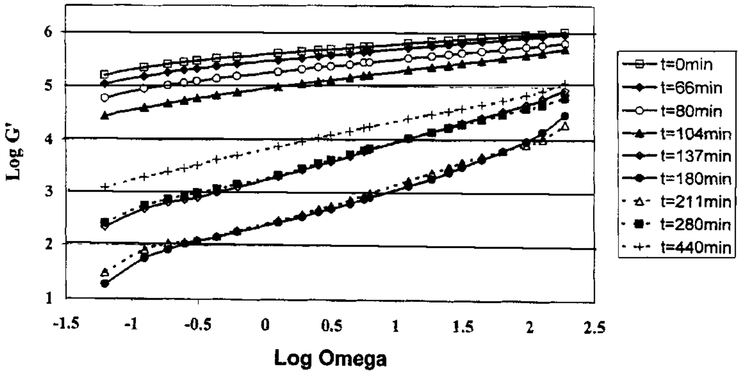


FIGURE 4 Variation of the dynamic storage modulus *versus* frequency through photooxidation at a temperature of 105°C.

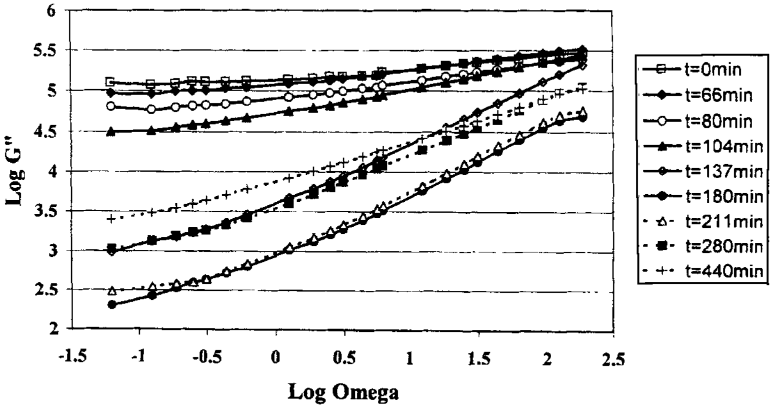
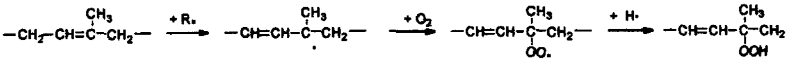


FIGURE 5 Variation of the dynamic loss modulus *versus* frequency through photooxidation at a temperature of 105°C.

to an increase of both moduli, indicating chain recombination or cross-linking process. Moreover, during the induction period (as determined from IR carbonyl absorbance), loss and storage moduli values are divided by a factor of 10 revealing the very high sensitivity of rheological measurements. Then, if the rheological experiments are carried out at high temperatures ($T > 180°C$) both moduli sharply decrease, indicating that chain scissions occur at high temperature whatever the irradiation time.

## DISCUSSION AND CONCLUSION

The FT-IR analysis performed on the material during the photooxidation give important information needed to elucidate the mechanism of photodegradation. The absorption detected in the hydroxyl region reveals a high concentration of hydroxyl structures. The physical treatment performed on the photooxidized material reveals that this absorption results in the convolution of two absorption bands: 3325 and 3440 cm$^{-1}$. The photolytic and thermolytic unstability of the photoproduct absorbing at 3325 cm$^{-1}$ is characteristic of peroxide structures. These peroxides result from the oxidation of radical species issued from chromophoric impurities. The mechanism of formation of these structures is the following:

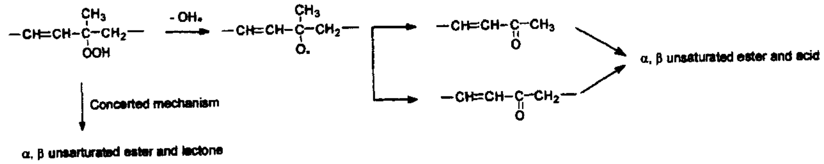


$$-CH_2-CH=\overset{CH_3}{\overset{|}{C}}-CH_2- \xrightarrow{+R\cdot} -CH=CH-\underset{\cdot}{\overset{CH_3}{\overset{|}{C}}}-CH_2- \xrightarrow{+O_2} -CH=CH-\underset{OO\cdot}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2- \xrightarrow{+H\cdot} -CH=CH-\underset{OOH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-$$

As the photodecomposition of these hydroperoxides does not modify the absorbance at 3440 cm$^{-1}$, their decomposition to alcohol has to be considered as a minor process. A concerted mechanism of decomposition of hydroperoxides has been postulated[4] as responsible for the formation of $\alpha$, $\beta$-unsaturated ester groups characterized by the IR absorption at 1720 and 1163 cm$^{-1}$ and lactone at 1772 cm$^{-1}$.

This result is in good agreement with the iodometric and DSC analysis performed on the photooxidized material which demonstrate that the photooxidation of polyisoprene leads to a high concentration of hydroperoxides.

The photolytic treatment indicates that the absorption at 1718 cm$^{-1}$ is the convolution of two bands: 1722 cm$^{-1}$ corresponding to a methyl ketone and 1717 cm$^{-1}$ to an $\alpha$, $\beta$ unsaturated ester. On the basis of litterature data[3,4] the maxima at 1693 and 1680 cm$^{-1}$ must be associated with $\alpha$, $\beta$-unsaturated acid and with $\alpha$, $\beta$-unsaturated ketones. The mechanism of formation of these species is the following:



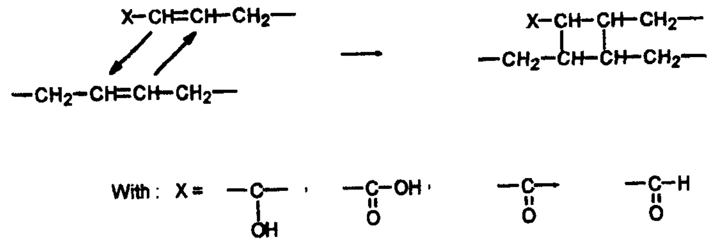
IR analysis performed on the photooxidized samples indicate a significant decrease of the bands assigned to the microstructure (1,4 unsaturation at 835 cm$^{-1}$ and 3,4 unsaturation at 890 cm$^{-1}$). These variations must be related to

- 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 cm$^{-1}$ 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.

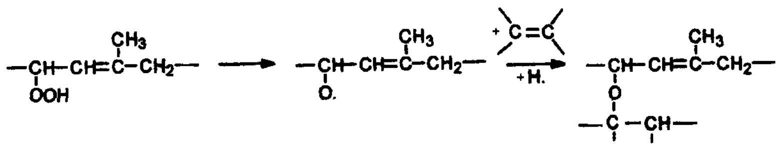
The kinetic curves reported in Figure 2 indicate that this photodegradation begins by the consumption of unsaturation (890 and 835 cm$^{-1}$). After 4 h of exposure, the concentration of residual unsaturations is reduced by a factor of 70%. The carboxylic species issued from the photooxidation appear after the beginning of the process and reach a limit value after 8 h of exposure.

This apparent photostability of the material 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. Piton and Rivaton[3] have postulated that this cross-linking reaction would result from

- the loss of unsaturation of $\alpha$, $\beta$-unsaturated oxidized products through cross-linking

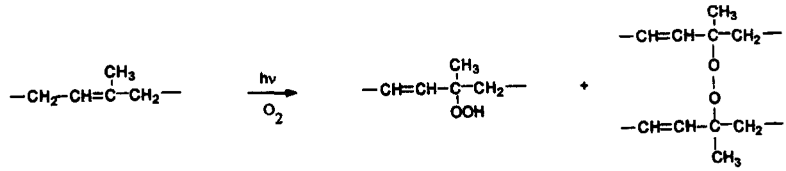


– the formation of ether linkage through photooxidation



This cross-linking process is confirmed by the solubility of the polymer in chloroform, which diminishes as the photooxidation proceeds. After about 3 h of irradiation, the material becomes insoluble in $CHCl_3$. Material is solubilized by addition of a chemical reducer like sodium iodide. The previous postulated processes by Piton and Rivaton[3] cannot be taken into account to explain the formation of a tridimensional structure. Indeed, these two process should lead to the formation of a structure, which cannot be removed by a reducer like NaI.

Sodium iodide, however, is a chemical reducer for peroxide species. IR analysis has shown that the photooxidation leads to the formation of hydroperoxide structures. But, the rheological analysis has pointed out that cross-linking becomes the predominant process when the peroxide concentration becomes significant. Moreover, this cross-linking can be suppressed by increasing the experimental temperature of the rheological measurement. Thus, we assumed the formation of peroxide structures in parallel with hydroperoxide structures accumulation



In conclusion, Figure 6 exemplifies such behavior. The variations of the loss angle tangent ($G''/G'$) exhibit the competition between chain scission and cross-linking. Let us recall that an increase of *tg δ* value characterizes an increase of the macromolecular mobility of the chains. When, the peroxide concentration reaches a certain level and the molecular mobility is sufficiently high (by chain scission), then the probability for recombination of alkoxy radicals becomes very high leading to the formation of peroxide structures.[12] Thus, SIS oxidation leads to the accumulation of hydroperoxide and peroxide structures. At the very beginning of the process, the first one are predominant while an inversion occurs as far as photoxidation proceeds.

This study shows the necessity to use different techniques, such as chemical ones (iodometric titration, infrared) and physical ones (DSC,

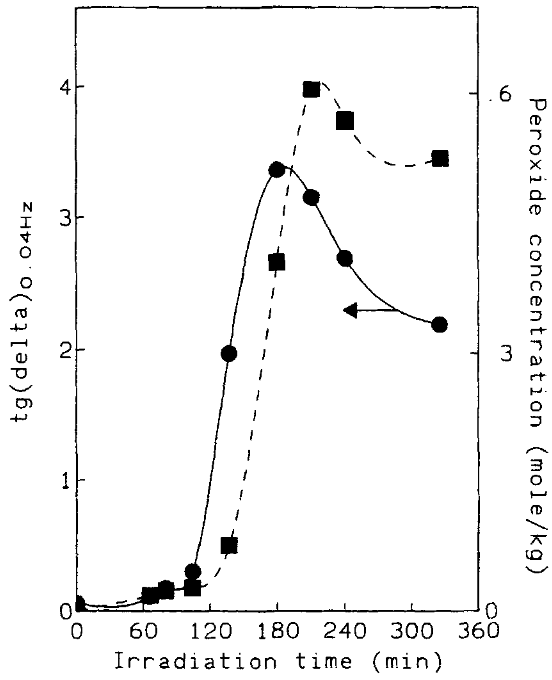


FIGURE 6 Variation of peroxide concentration (■ by iodide titration) and *tg δ* (•) through photooxidation at a temperature of 105°C.

viscoelasticity), to study photochemical mechanisms in macromolecular media.

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