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Oxidation of polyterpenes: a comparison of poly α, and poly β, pinenes behaviours
Part I – photo-oxidation

M.L. Binet, S. Commereuc*, J.C. Chalchat, J. Lacoste

Laboratoire de Photochimie Moléculaire et Macromoléculaire (UMR CNRS 6505), Université Blaise Pascal et ENS Chimie de Clermont-Ferrand, , F-63 177 Aubiere Cedex, France

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Abstract

The photo-oxidation of polypinenes has been investigated through irradiation at $\lambda > 300$ nm at 35°C. We pay attention to the similarities and differences in behaviour of the two most commonly used polyterpene resins based on α, and β, pinenes. The major photoproducts resulting from oxidation have been identified and quantified using well-known derivatization reactions, specific chemical analysis and physical treatments. From our results, photochemical evolution of poly α, pinene is quite similar to that of poly β, pinene. α, β unsaturated hydroperoxides are assumed to be the main primary photoproducts which undergo photolysis into various α, β unsaturated species. In contrast to dienic polymers, through irradiation, saturation reactions occur in a significant low extent and chain-scissions prevail leading to low molecular weight by-products that can easily diffuse out of the polymer matrix. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Polyterpenes; Photo-oxidation; FTIR spectroscopy; Photoproducts

1. Introduction

Terpenes are widespread chiral natural products. Many of them are produced continuously in great amount in nature. For instance, α- and β-pinenes are readily and abundantly available from pine tree. So, cationic polymerization of pinenes has been extensively studied in order to use them as resins as industrial interest [1–5].

Then terpene resins are low molecular weight hydrocarbon polymers used by adhesive manufacturers to impart tack to both solvent-based and hot-melt adhesive systems, to provide high gloss, good moisture/vapour transmission resistance and good flexibility for wax coating, and to impart viscosity control and density increase to investment casting waxes [5–10].

The most commonly used resins are those based on α, or β, pinene. Selected resins are excellent tackifiers of numerous elastomers as natural rubber, polyisoprene, styrene-butadiene rubber… [6]. But, ageing stability of an adhesive, consisting of elastomeric polymers and oligomeric terpene resins, depends to some extent on the stability of the tackifying resin. Therefore, we decided to investigate the oxidative-ageing of these two polypinenes.

Polypinenes units contain unsaturated double bond and their chemical structures could be considered similar to that of dienic polymers, as polybutadiene, polyisoprene, polynorbornene…, which are known to be very sensitive to oxidative degradation. Many papers have been devoted to the study of the chemical evolution of dienic elastomers submitted to various kinds of oxidations [9–20]. Derivatization reactions, specific chemical analysis and physical treatments allow to identify most of the major products resulting from oxidation. We report on the use of these analytical techniques applied to polypinenes oxidation. The first paper is devoted to the photo-ageing while further study involving thermal ageing will be presented in a subsequent paper. Our attention was focused on the similarities and differences in behaviour of poly α, and poly β, pinenes during oxidative ageing with the aim of comparing with the behaviour of dienic polymers.

2. Experimental

2.1. Materials

Commercial polyterpenes resins were kindly supplied by Derives Resiniques & Terpeniques (DRT, Dax- France) as

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*Corresponding author. E-mail: commereuc@cicsun.univ-bpclermont.fr

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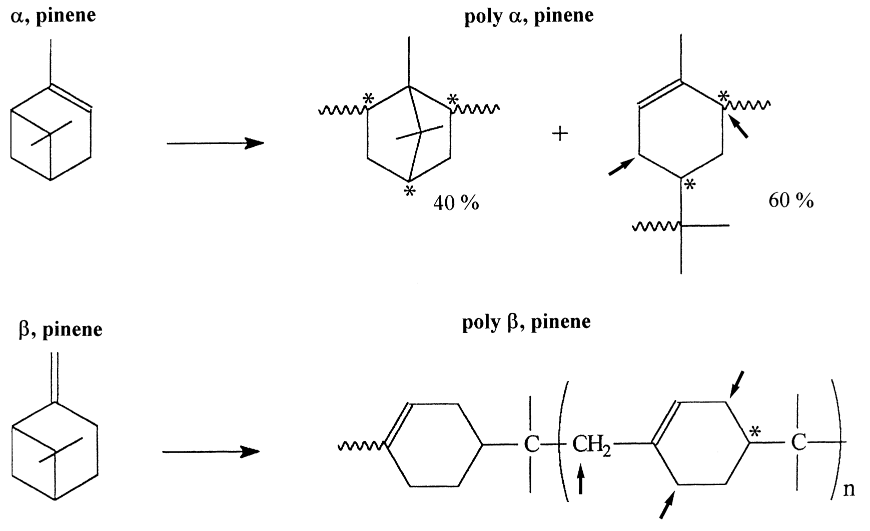


Scheme 1. Chemical structures of polypinenes. Quaternary carbons are marked by (*).

Dercolite® A for the poly α, pinene sample and Dercolite® S for the poly β, pinene.

The chemical structures of both polypinenes used in this study are summarized in Scheme 1 based on ^1H NMR determination [1–3]. These compounds are low-molecular-weight oligomers and their molecular characteristics are shown in Table 1.

2.2. Sample preparation

Each polymer was precipitated twice from chloroform solution into methanol to remove possible additives. Films were cast onto Kbr plates from solution in chloroform and then dried under vacuum at 30°C overnight. Coating films thicknesses are around 30 μm.

2.3. Photo-oxidation procedure

Cast films were fixed on aluminium holders and then irradiated in a polychromatic set up. A medium pressure mercury source filtered by a borosilicate bulb (Mazda type MA 400) supplies radiation of wavelengths longer than 300 nm. This source is located along the focal axis of a cylinder with elliptical base. Samples turned around the other focal axis. The inside of the chamber is made of highly reflectant aluminium. Temperature of samples is controlled by a thermocouple connected with a temperature regulator device which controls a fan. All experiments were performed at 35°C. Films were analyzed after various exposure times.

Table 1
Molecular characteristics of polypinenes

	M_n	M_w	M_w/M_n
Poly α, pinene	708	1251	1.8
Poly β, pinene	1237	2913	2.3

2.4. Physical treatments

Pre-photo-oxidized films for 6 h at 35°C ($\lambda > 300$ nm) were submitted to photolysis and thermolysis experiments in order to evaluate the photostability of photoproducts and identify the decomposition products of hydroperoxides.

2.5. Analysis

Chemical changes were detected by FTIR spectroscopy (Nicolet Impact 400, Omnic software). Raman spectroscopy (FT Raman Nicolet 910 equipped with laser $NdYVO_4$ and supplying an exciting wavelength at 1064 nm, Omnic software) gives additional information concerning the evolution of the chemical structure through photo-oxidation.

Well-known derivatization reactions with NH_3 and SF_4 allowed us to identify many of the major groups resulting from photo-oxidation [21–23]. Photooxidized films were exposed to reactive gas at room temperature for 4 h in a teflon flask equipped with Tygon inlet and outlet tubing [24]. Gazes used were SF_4 and NH_3, respectively supplied by Fluka and Alphagaz. Carboxylic acids are known to react with SF_4 to give acyl fluorides characterized by a distinctive IR absorption in the range 1810–1845 cm^{-1}, while alcohols and hydroperoxides are converted into alkyl fluorides absorbing at ca. 1100 cm^{-1}. Moreover, acid and ester groups are known to react with NH_3 to give, respectively, ammonium carboxylates and amides.

Total peroxides were estimated by iodometric titration [25,26] based on the reduction of hydroperoxides by sodium iodide in excess in acidic medium according to the reaction:

$$ROOH + 2\,I^- + 2\,H^+ \rightarrow ROH + I_2 + H_2O$$

$$I_2 + I^- \rightarrow I_3^-$$

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

The molecular weight averages of polyterpenes were measured by size exclusion chromatography (SEC) in tetrahydrofuran at room temperature on a Waters-510 chromatograph equipped with refractometric detector (Waters R410-64) and polystyrene gel column. Average molecular weights and molecular weight distribution parameter (M_w/M_n) were calculated from SEC eluograms on the basis of a polystyrene calibration.

3. Results

3.1. Kinetic aspects of photo-oxidation

Photo-oxidation of polypinene films results in significant changes in their IR absorption spectra. Two domains of the spectra should be particularly examined (shown in Fig. 1 for poly β, pinene).

3.1.1. Region of hydroxyl stretching vibrations (3600–3200 cm^{-1})

A broad absorption band centered at 3400 cm^{-1} appears in the earliest stage of photo-oxidation. After about only

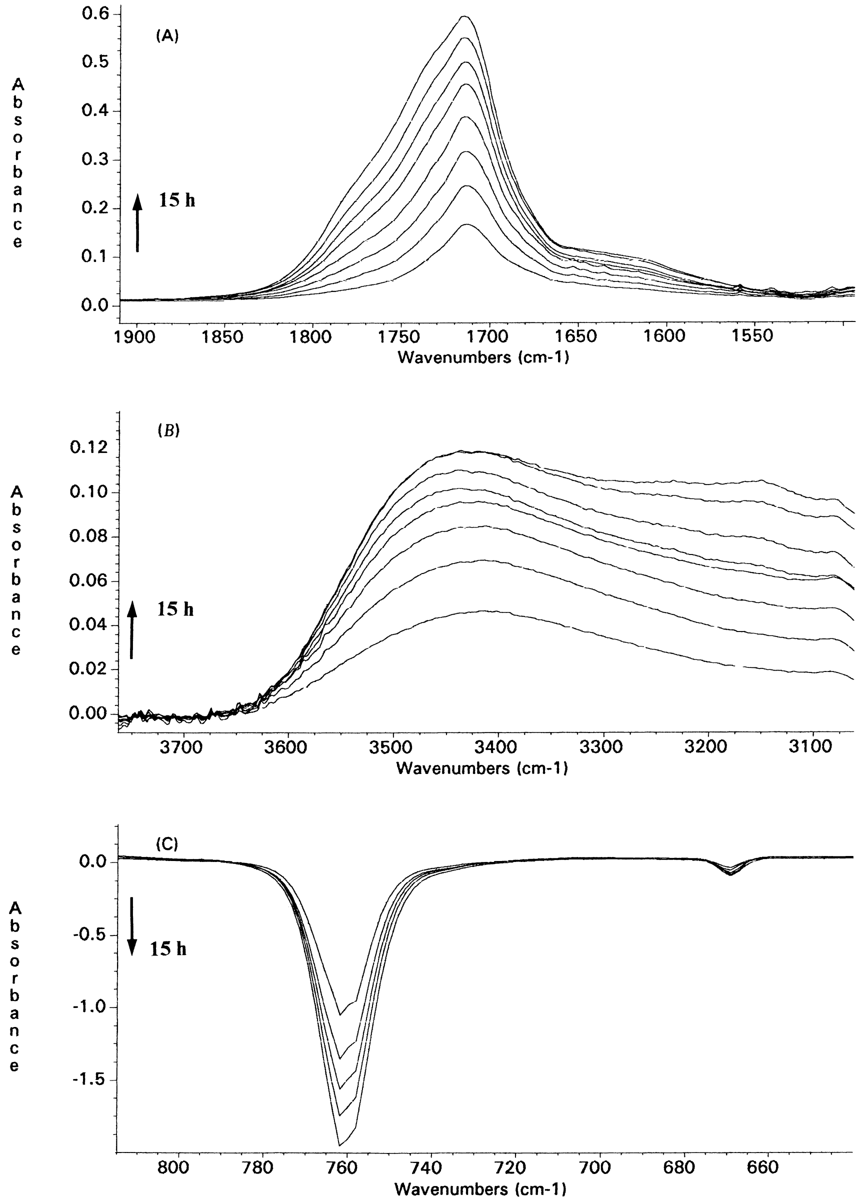


Fig. 1. FTIR changes upon photo-oxidation at $\lambda > 300$ nm at 35°C of poly β, pinene films (27 μm). Each spectrum was obtained by substracting that of a non-oxidized from that of the oxidized sample: (A) carbonyl vibration region; (B) hydroxyl vibration region; (C) deformation vibration region.

5 h of UV exposure, this absorption band stops to increase.

3.1.2. Region of carbonyl stretching vibrations (1840–1600 cm^{-1})

At the very beginning of the irradiation, two absorption bands are detected at 1670 and 1715 cm^{-1} with a shoulder at 1775 cm^{-1}. But, as the photo-oxidation proceeds, an overlapping is rapidly observed. Then, a drastic increase of absorbance over a broad range (1840–1600 cm^{-1}) centered at 1715 cm^{-1} is revealed without any other significant maximum.

The shapes of the broad carbonyl and hydroxyl absorption bands are quite identical for the two studied polypinenes (not shown), and we assume that spectral evolutions are quite similar both in case of poly α, and poly β, pinenes.

Fig. 2 plots both kinetic curves of the formation of carbonylated and hydroxylated photoproducts for each kind of polypinene samples. First, poly α and poly β pinenes exhibit quite similar high oxidation rates. Then, both carbonyl and hydroxyl species tend to a stationary level and an invariant state is reached, as it was previously reported for dienic elastomers [14,15,17,18].

3.1.3. Region of deformation vibrations (1400–600 cm^{-1})

IR absorption increases drastically between 1000 and 1400 cm^{-1} with some significant maxima (not shown). As the photo-oxidation proceeds, a drastic decay of the strong absorption band at 764 cm^{-1} and of the weak one at 669 cm^{-1} is observed (see Fig. 1(C)).

Fig. 3 collects both FTIR and FT Raman spectra of poly β, pinene photooxidized for 6 h compared to those of the initial sample. IR and Raman spectroscopies are complementary. The molecular vibrational frequencies detected by both techniques are nearly the same, but the vibrational band intensities quite differ because of the different excitation mechanisms and, therefore, different selection rules. So, the deformation vibrations of C–H linked to unsaturations exhibit prominent IR absorption located in the 680–980 cm^{-1} region, while they are fairly weak in Raman. Thus, according to the comparison of IR and Raman spectra of initial polypinenes, we assigned the 764 cm^{-1} band to the unsaturations. Then, IR spectra evolution clearly reveals a consumption of double bonds through photo-oxidation (see Fig. 1(C) and Fig. 3(A)).

Moreover, the C=C stretching band at 1664 cm^{-1} is much distinctive in the Raman spectrum because of its highly polarized character. While, the C=O stretch band at 1710 cm^{-1}, by contrast, is quite inactive in Raman. So, carbonylated photoproducts absorbance does not overlap this one characteristic of unsaturated sites. Consequently, the drastic decay of the Raman absorption band at 1664 cm^{-1} as the photo-oxidation proceeds is undoubtedly attributed to saturation reactions.

Elsewhere, the absorption at 669 cm^{-1} could be reasonably ascribed to the symmetrical C–C stretching mode of the quaternary carbon of the β, pinene unit ($C{-}C(CH_3)_2$). Indeed, this band is polarized, and very often it is the most intense Raman band below 1000 cm^{-1}. This assignment is supported by the sharp additional band seen at 1217 cm^{-1} in the IR spectrum [27]. Thus, Raman spectra evolution obviously indicates the disappearance of the quaternary carbon upon UV exposure.

3.2. Identification of the carbonylated photoproducts by derivatization reactions

3.2.1. NH_3 treatment

Reactions of photo-oxidized poly α and poly β pinene films for 6 h with ammonia results in a broad ammonium

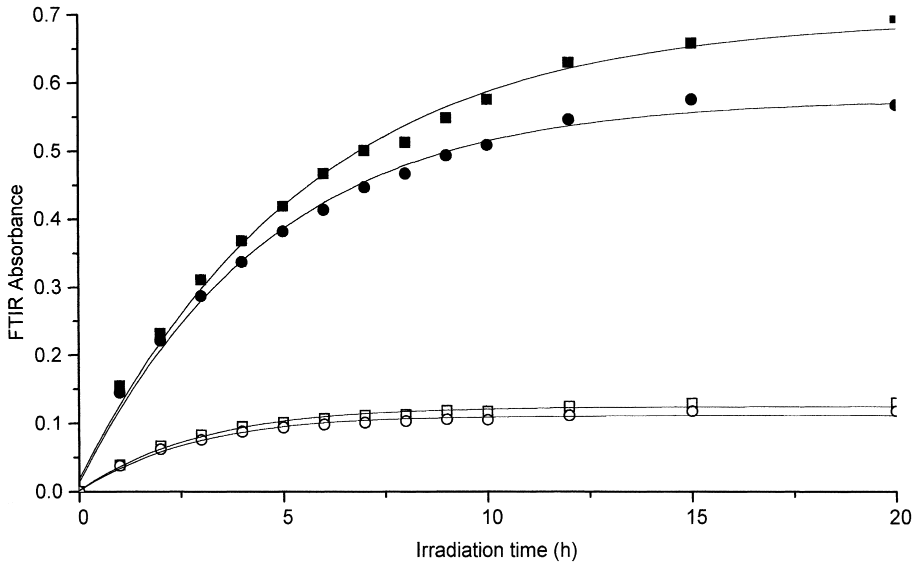


Fig. 2. Kinetic curves of photo-products from oxidation of (□, ■) poly α, pinene and (○, ●) poly β, pinene. Films thickness 26 μm; open symbols: hydroxyl absorbance at 3400 cm^{-1} and solid symbols: carbonyl absorbance at 1715 cm^{-1}.

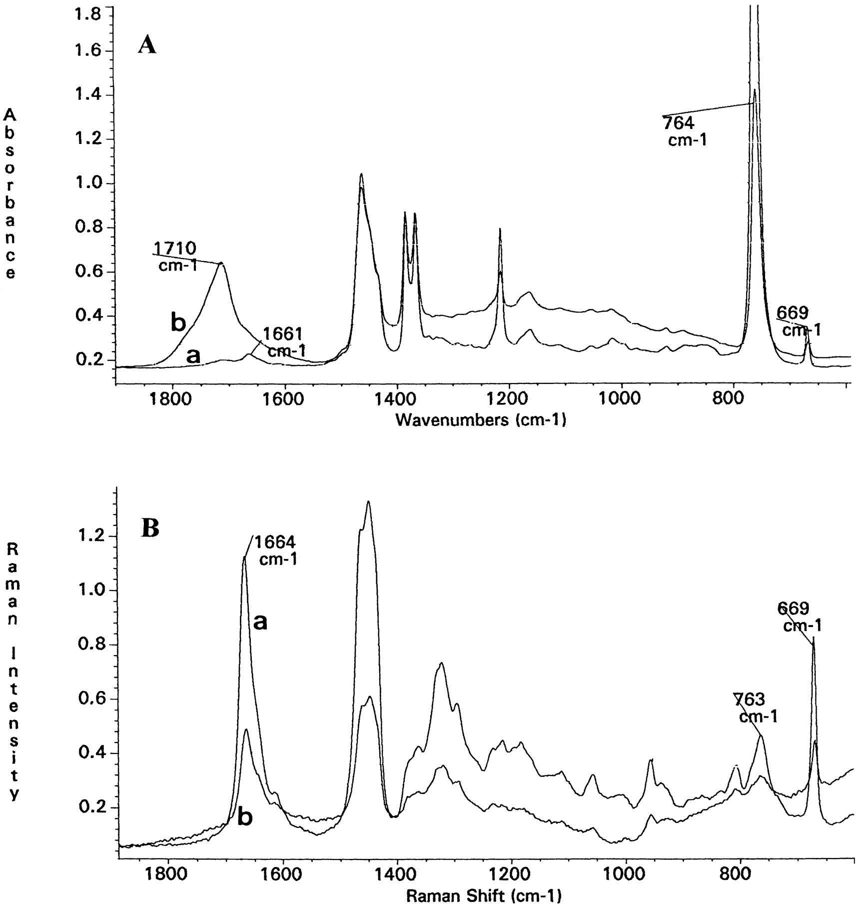


Fig. 3. Evolution of the FTIR (A) and FT-Raman (B) spectra upon photo-oxidation at $\lambda > 300$ nm at 35°C of poly β, pinene films (30 μm); (a) $t = 0$ h, (b) $t = 6$ h.

carboxylate absorption band at 1560 cm^{-1} from reaction with carboxylic acid groups and a weaker one at 1661 cm^{-1} assigned to amide groups from reaction with ester (see Fig. 4).

The differential spectrum (oxidized polypinene after NH_3 minus before NH_3 treatment) seen in Fig. 4 for poly β, pinene shows a broad negative band centered at 1717 cm^{-1} which may be ascribed as the convolution of two carbonylated photoproducts: carboxylic acid and ester. A weak negative shoulder is also detected at 1772 cm^{-1} which has been previously assigned to various species as anhydride, lactone or perester, reacting with NH_3.

In addition, the residual absorbance centered at 1710 cm^{-1} does not allow a satisfactory interpretation. After NH_3 treatment, no dominant maximum in the range 1800–1680 cm^{-1} is revealed, just a decrease of the initial broad absorption band is observed. Thus, we assume that the concentration of unreactant products (aldehydes, ketones) is fairly significant and, the residual absorbance results from the convolution of various reactant as unreactant carbonyl species.

3.2.2. SF_4 treatment

SF_4 treatment of the same samples results in two sharp acid fluoride absorptions from reaction with carboxylic acid groups. As reported before [21], the absorption of acid fluorides is dependent on the nature of the α carbon. Absorptions at 1840 and 1815 cm^{-1} were ascribed to >CH–C(O)F and ∼CH=CH–C(O)F, respectively.

Then, the differential spectrum (oxidized polypinene after SF_4 minus before SF_4 treatment, see Fig. 5 for poly α, pinene) consistently shows two negative absorption bands at 1700 cm^{-1} (saturated carboxylic acid) and at 1675 cm^{-1} (unsaturated carboxylic acid). Moreover, a weak negative shoulder is detected at 1753 cm^{-1} which could be assigned to α, β unsaturated anhydride. Thus, the weak negative shoulder detected at 1772 cm^{-1} after NH_3 treatment could be interpreted as the convolution of absorptions of three potential photo-products: anhydride (expected to be reactive toward both SF_4 and NH_3) and lactone and perester (reacting with NH_3 but unreactive toward SF_4).

Conversely to dienic polymers, as polybutadiene [17] or polyoctenamer [18], a readily high content of α, β unsaturated carboxylic acid groups is recorded in oxidized polypinenes.

Furthermore, the removal of carboxylic acid absorption from 1800 to 1700 cm^{-1} by conversion to acid fluorides does not simplify the carbonyl region. It could be reasonably attributed to the incompleteness of the SF_4 reaction. A residual absorbance in the hydroxyl region after the gaseous

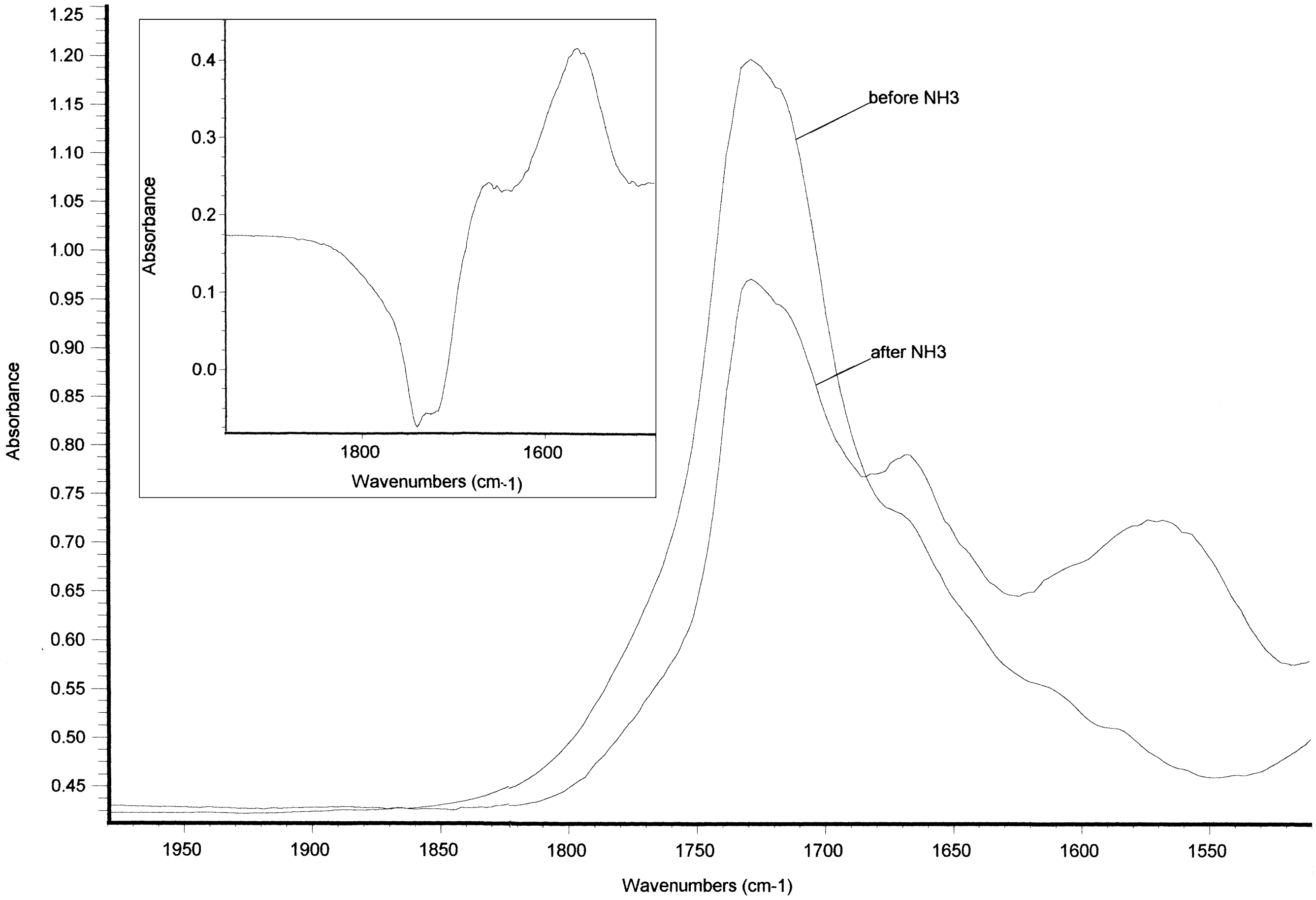


Fig. 4. FTIR changes after derivatization reaction. FTIR spectra of photo-oxidized poly β, pinene films for 6 h at $\lambda > 300$ nm at 35°C before and after NH_3 treatment for 4 h. The inset shows the substracted spectrum (after minus before NH_3 treatment).

treatment acts as a proof (ROOH and ROH both react with SF_4 too).

3.2.3. Physical treatments

Fig. 6 collects the evolution of IR spectra of poly β, pinene film photooxidized for 6 h and then photolyzed for 5 and 35 h. A small increase of absorbance is noticed at the very beginning of the photolysis. But, as the photolysis proceeds, a decrease of the broad absorbance band is observed. Two shoulders at 1740 and 1775 cm^{-1} are also detected after photolysis. So, we can assume that the concentration of very photo-unstable photoproducts (as aldehydes, ketones) is readily significant.

In addition, thermolysis carried out in dark at 60°C during 2 h leads to a drastic decrease of the overall carbonyl absorption indicating a loss of some molecular compounds.

In conclusion, most of the photoproducts formed upon photo-oxidation of polypinenes are low molecular weight compounds or their photolysis leads to molecular products that can diffuse easily out of the polymer matrix.

3.3. Hydroxylated photoproducts

Hydroperoxides are detected both by photolysis experiment and by chemical titration.

Photolyzed pre-oxidized films for 6 h show a significant decrease and a shift to 3440 cm^{-1} of the broad band centered at 3400 cm^{-1}. This indicates that the conversion of hydroperoxides into alcohol is a minor process since ROH formation cannot counterbalance ROOH consumption despite quite similar extinction coefficient ($\varepsilon_{OH} \sim \varepsilon_{OOH}$). After vacuum treatment, the residual absorption at 3440 cm^{-1} can be assigned to the convolution of hydroxyl absorption of alcohol and acid groups.

Hydroperoxides titration was carried out on photooxidized poly α, and poly β, pinenes. Significantly higher ROOH contents are obtained for poly α, pinene comparatively with poly β, pinene (see Table 2).

4. Discussion

We lay emphasis on the quite similar photooxidative-ageing of the two selected polypinenes. No difference is detected between the behaviour of poly α, pinene and poly β, pinene through photo-oxidation at $\lambda > 300$ nm at 35°C.

On the basis of NMR analysis, the end-groups of oligomeric α, and β, polypinenes are identified as aromatic ring. This result is quite consistent with the literature data which

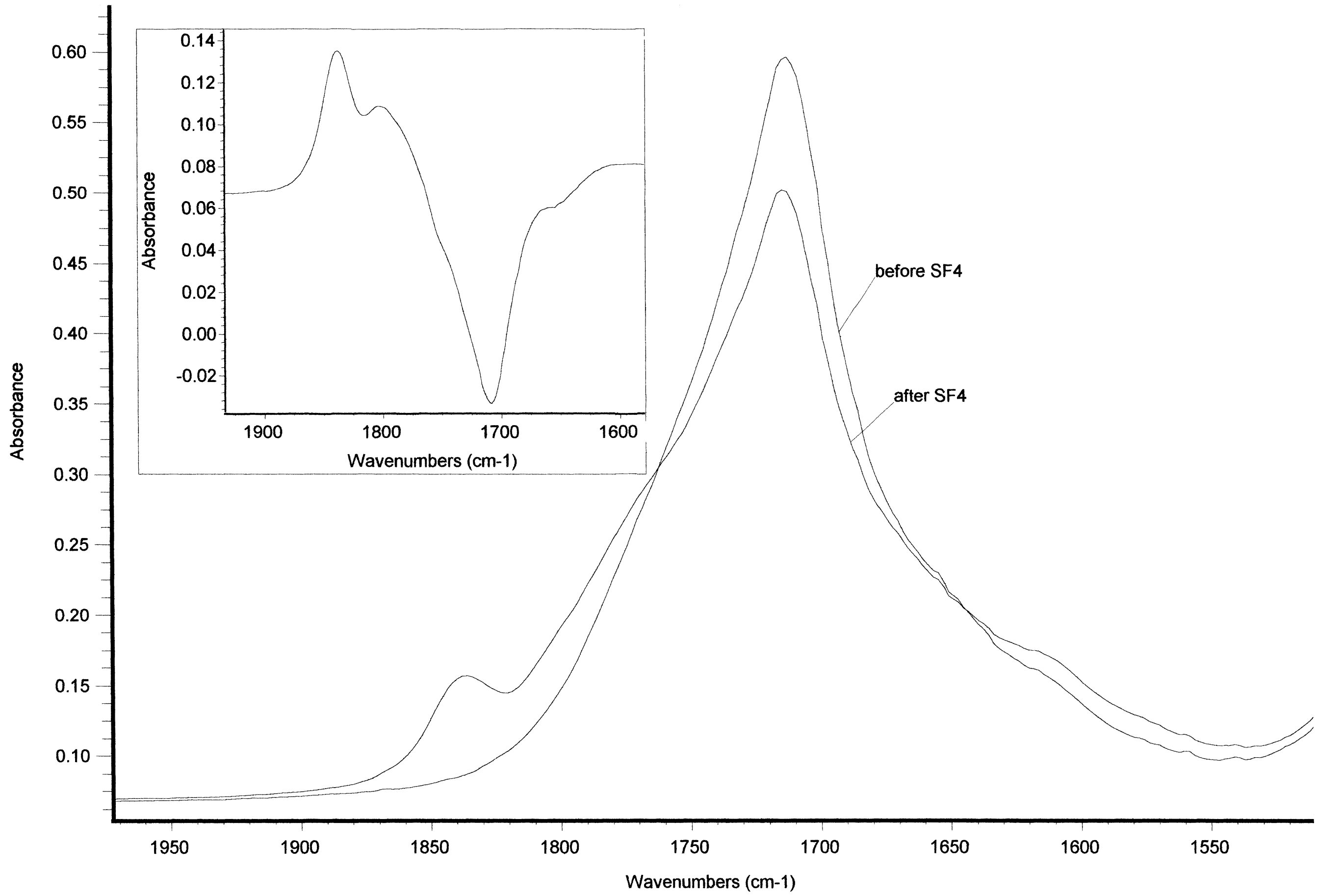


Fig. 5. FTIR changes after derivatization reaction. (A) FTIR spectra of photo-oxidized poly α, pinene films for 6 h at λ > 300 nm at 35°C before and after SF_4 treatment for 4 h. The inset shows the substracted spectrum (after minus before SF_4 treatment).

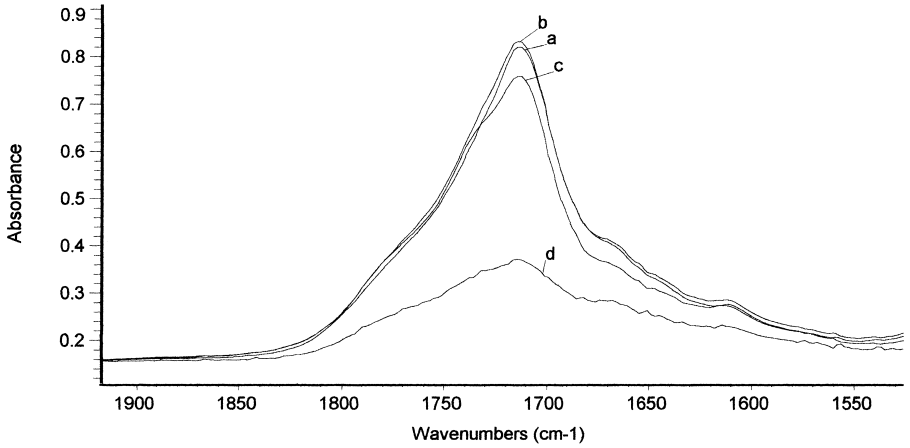


Fig. 6. FTIR changes through physical treatments of pre-photo-oxidized poly β, pinene (30 μm): pre-photo oxidized film for 6 h (a), then photolyzed at λ > 300 nm at 35°C for 5 h (b) and 35 h (c), or then thermolized at 60°C for 24 h (d).

relate that the termination step is a chain transfer to aromatic solvent during commercial manufacture of polypinenes [1–5]. Consequently, we can consider that the unsaturated repeating units are much more sensitive to photo-oxidative degradation at λ > 300 nm than the aromatic end-groups.

As proposed for dienic polymers [9–20], we can assume that the mechanism of polypinenes photo-oxidation involves a primary radical attack on labile hydrogen in the α position to double-bond. Subsequent oxygen addition followed by hydrogen abstraction results in the formation of α, β-unsaturated hydroperoxides. As regard to the chemical structure of the poly β, pinene unit, three different allyl radicals (marked by arrow in Scheme 1) could be formed by this abstraction mechanism involving the formation of second-

Table 2
Hydroperoxide content in photo-oxidized polypinenes by iodometric titration

Irradiation time (h)	Poly α, pinene	Poly β, pinene
6	36 mmol/kg	31 mmol/kg
20	91 mmol/kg	51 mmol/kg

ary hydroperoxides (*sec*-ROOH). On the other hand, two kinds of α, β-unsaturated hydroperoxides (*sec*- and *tert*-ROOH, marked by arrow on Scheme 1) could be expected in the case of poly α, pinene. As reported before [28,29], primary peroxy radicals and their resultant primary hydroperoxides are considered to be insignificant.

Furthermore, an alternative route could be postulated on the basis of a radical attack on the labile hydrogen beared by a tertiary carbon. Then, five different *tert*-ROOH could be generated in case of poly α, pinene (marked by asterisk in Scheme 1) while the poly β, pinene unit has just one tertiary carbon.

So, the main difference between poly β, pinene and poly α, pinene consists in the ability of the latter to give tertiary hydroperoxides, and especially, an allylic *tert*-ROOH. Then, the higher ROOH content in photooxidized poly α, pinene films is consistent with possible tertiary structures of ROOH (saturated or α, β-unsaturated) which are reported to be more stable than secondary structure, implying an accumulation of these species in the matrix [14,15,29].

Although tertiary species are probably quite stable at 35°C, they are very photounstable and Guillet measured high values of quantum yields for decomposition of *cis*-poly(isoprene hydroperoxide) (*tert*-ROOH) [30], suggesting that the kinetic of homolysis is readily independent of the chemical structure of hydroperoxides. So, based on kinetic evidence (poly β, and poly α, pinenes reveal a quite similar oxidation rate, Fig. 2), we can assume that the structure of the main primary photoproducts (ROOH) does not affect the rate of photo-oxidation of polypinenes.

The homolysis of α, β-unsaturated hydroperoxides leads to the formation of α, β-unsaturated carbonylated and hydroxylated photo-products. These species undergo saturation reactions as the photo-oxidation proceeds. But, saturation reactions occur to a lower extent than in case of other dienic polymers as polybutadiene [14,15,17] or polyoctenamer [18]. Somewhat, as shown by the almost total consumption of double-bonds upon irradiation, saturation reactions consist in an essential stage under our oxidation conditions and they can explain that oxidation process stops after 20 h of UV exposure (Fig. 2).

Upon photo-oxidation, a competition between cross-linking and chain-scission is reported for dienic elastomers [12–17]. Almost total disappearance of the quaternary carbon absorbing at 669 cm^{-1} through photo-oxidation suggests that chain-scissions prevail in case of photo-ageing of polypinenes. In addition, the formation of low molecular weight photoproducts is consistent with the scission of the main chain.

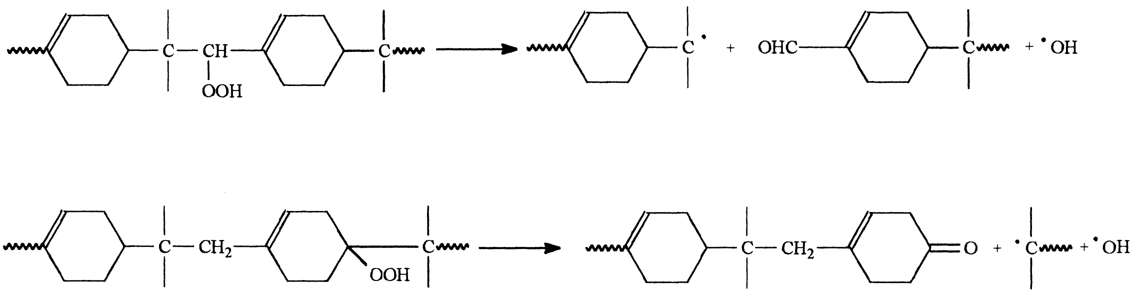
It is important to note the complexity of the chemical structure of polypinenes. So, it is difficult to propose a well-defined scheme to explain the photo-oxidation mechanism of polypinenes. In theory, numerous different hydroperoxides could be generated from primary radical attack (secondary or tertiary, allylic or saturated ROOH).

Somewhat, β-scission of hydroperoxides, largely discussed in the literature [14–16,19,29,31], readily explains the disappearance of the quaternary carbon upon photo-oxidation of polypinenes. So, the β-scission of *sec*-hydroperoxides is reported to lead to aldehydes [17,31] which are very photo-unstable by-products, and then, not detected by FTIR. Moreover, *tert*-hydroperoxides can be converted into end chain ketonic groups by β-scission. Additional Norrish reactions of ketones imply the formation of acidic species, quite clear through photo-oxidation of polypinenes. Two of the possible β-scission reactions are exemplified in Scheme 2 in case of poly β, pinene.

It is worthwhile to note that these proposals are in good agreement with the observed results from NH_3 treatment of photo-oxidized polypinenes and photolysis experiments. Indeed, they suggest that the concentration of very photo-unstable by-products (as aldehydes, ketones) are readily significant. So, it can be said that acidic species are the final photoproducts which accumulate in the polymer.

5. Conclusion

This first paper is focused on the photo-oxidation of polypinenes. We assert that no difference could be detected



Scheme 2. Possible β-scission reactions in case of poly β, pinene.

between the behaviour of poly β, pinene and poly α, pinene through photo-oxidation at long wavelengths ($\lambda > 300$ nm) at 35°C. Moreover, a systematic examination of the chemical evolution of polypinenes upon irradiation shows that, in general, the observed processes are similar to those described for the photo-oxidation of other dienic polymers. The main difference consists in the unusual high content of low molecular weight photoproducts that can easily diffuse out of the polymer matrix. The low average molecular weights of initial polymers are probably the reason why β-scissions rapidly lead to molecular compounds. So, identification of products resulting from photolysis of hydroperoxides is slightly complicated.

A second paper will be devoted to the study of the thermo-oxidation of these two terpene resins with the aim of systematically comparing with photo-ageing results.

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