Photoinitiated Oxidation of Heterophasic Ethylene–Propylene Copolymers. I. Comparison of Oxidation Products*

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SYNOPSIS

Detailed photoproducts from photoirradiation of heterophasic ethylene–propylene copolymers and their fractions have been compared by infrared spectroscopy combined with chemical derivatization. The oxidized films were treated with gaseous NH_3, SF_4, and NO for the rapid identification and resolution of the various carbonyl species, alcohols, and hydroperoxides. The photoproduct formation depends upon the composition of the sample. The heterogeneities in thin films were also determined by micro FTIR spectroscopy. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Many studies on the photodegradation of polyethylene and polypropylene by ultraviolet and visible light have received extensive attention during the past decade.[1-4] To improve all aspects of the stability of polymers, a fundamental understanding of the degradation process involved is essential. The photooxidative degradation has attracted considerable interest for practical as well as for fundamental reasons.

Copolymers of ethylene with propylene have assumed increasing significance in recent years. Depending on the method of synthesis and the amount of ethylene incorporated, these copolymers can have useful properties from stiff thermoplastics to soft elastomers. Literature predominantly reports the effect of thermal/photooxidative degradation of ethylene–propylene (E–P) copolymers on its mechanical properties.[5] Although photooxidative degradation of amorphous (elastomeric) E–P copolymers has been the subject of a few studies,[6-8] little attention has been paid to heterophasic thermoplastic E–P copolymers. The precise identification and resolution of oxidation products is essential for complete understanding and control of destructive reactions. The conventional infrared method is only partially useful in the resolution of the mixture of carbonyl species formed. Therefore, derivatization reactions have been frequently employed to extend the sensitivity and resolution of IR spectroscopy.[9] Oxidation of all polyolefins share a common feature involving attack of free radicals on the polymer chain followed by reaction of the alkyl radicals with oxygen-giving products such as hydroperoxides, alcohols, acids, ketones, and esters.[10]

The present investigation concerns photooxidative degradation in the solid phase of heterophasic E–P copolymers and their fractions with different ethylene mole ratios and comparison of results with polyethylene and polypropylene homopolymers. We herein report the use of derivatization techniques using NH_3, SF_4, and NO for a systematic comparison of products of photooxidative degradation with the aim of identification of the actual oxidation site in heterophasic polypropylene.

EXPERIMENTAL

Materials

Commercial samples of isotactic polypropylene (i-PP, Koylene S 3030, from Indian Petrochemicals

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Table I Ethylene Content in the E–P Copolymer by FTIR

Sample Name	Sample Code	Ethylene Content (mol %)
i-PP	I	—
EPQ 30R	II	15.1
EPQ 30R (fraction A)	II_A	7.7
EPQ 30R (fraction B)	II_B	40.9
EPF 30R	III	12.0
EPF 30R (fraction A)	III_A	6.2
EPF 30R (fraction B)	III_B	55.7
E–P copolymer	IV	62.0
LLDPE	V	—

Corp., Baroda, India), linear low-density polyethylene (LLDPE, from DuPont, Canada), E–P copolymer (Vistalon, from Essochem, Europe), and copolymers EPQ 30R and EPF 30R (from Himont Italia) were used in this study. The composition of E–P copolymers is given in Table I.

Procedure

The methods of purification, fractionation, and sample preparation ($\sim$ 100 μm-thick films) are given elsewhere.[11] Photooxidation was performed in a SEPAP 12/24 chamber at 60°C. This unit has a
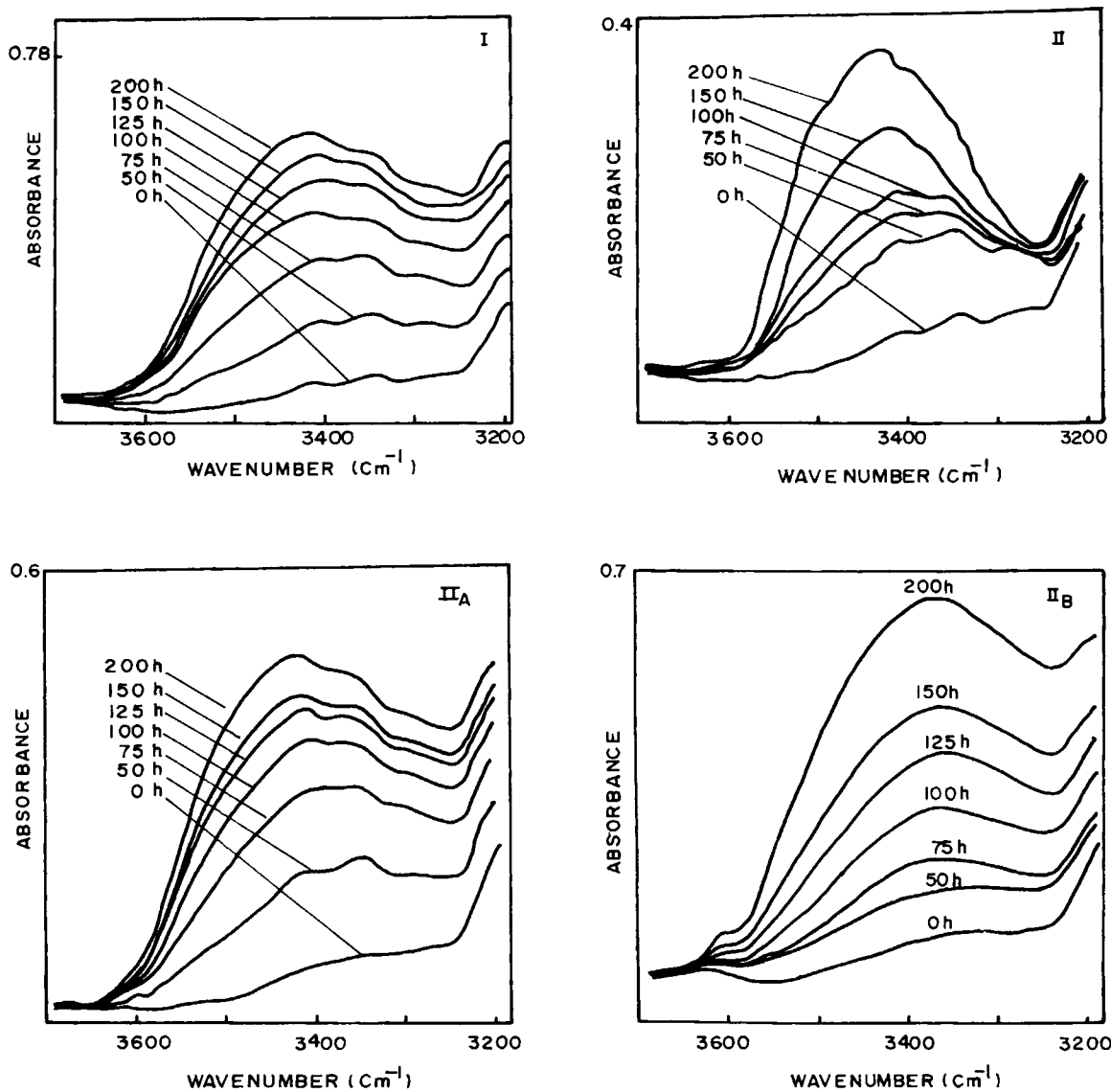
Figure 1 FTIR spectral changes in the hydroxyl region, for various hours, of polychromatic irradiated PE, i-PP, and E–P copolymer samples.

UV source supplying radiation longer than 300 nm. The samples are rotated at a constant speed and distance from the source.

The oxidative photoproducts were identified with good resolution by Fourier transform infrared (FTIR) spectroscopy (Nicolet 5 SX spectrometer). Oxidized polyolefins are unstable at room temperature and can continue to slowly oxidize during dark storage.[9] To minimize this effect, all oxidized samples were either analyzed immediately or stored at $-20°C$ until analysis was performed. The oxidized films were exposed to each reactive gas at room temperature in a simple flow system that could be sealed

off by valves to allow the reaction to proceed. The gases used included NH_3, SF_4, and NO. The NO reaction was performed with films at $-20°C$. To prevent NO_2 formation from the $NO-O_2$ reaction, films were swept with nitrogen for about 5 min prior to NO introduction. Since SF_4 attacks glass, this reaction was carried out in a Teflon bottle. From changes in FTIR, it was inferred that reactions were virtually completed in 3 h for NH_3, 24 h for SF_4, and 72 h for NO. To eliminate the interference ripples, which are often found in the IR spectra and complicate the accurate measurement of IR absorbances, some films were tilted at the Brewster angle
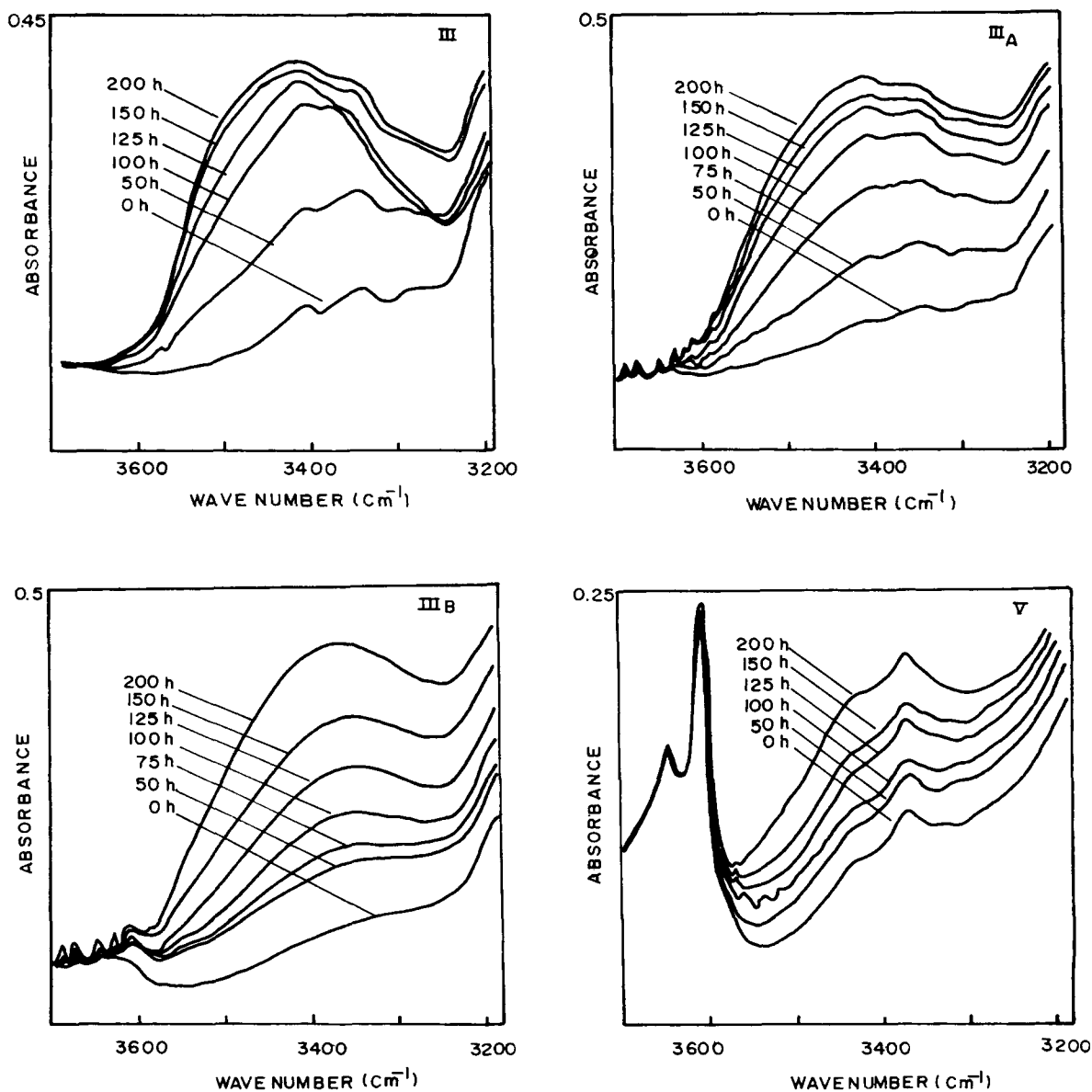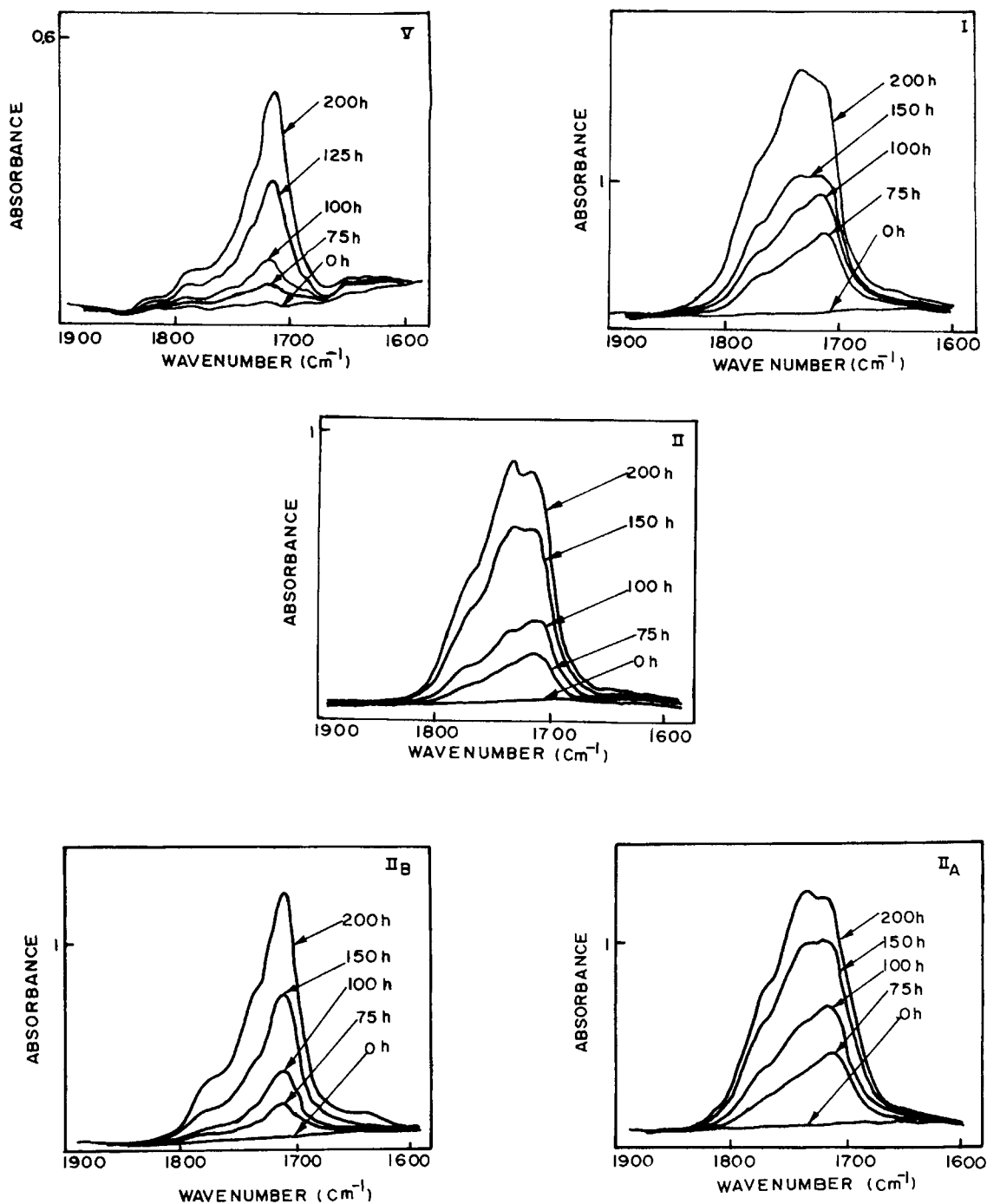

Figure 1   (*Continued from the previous page*)

Figure 2 FTIR spectral changes in the carbonyl region, for various hours, of polychromatic irradiated PE, i-PP, and E–P copolymer samples.

and a gold wire grid polarizer was placed in the sample beam.[12]

The heterogeneity in photooxidized films was characterized by microspectrophotometric measurements.[13] Measurements were performed on a Nicolet 800 equipped with a Nicplan microscope

(liquid nitrogen-cooled MCT detector, 128 summations). The oxidized films (50 h) were sliced with a Reichert and Jung microtome (2050 Supercut). Slices with a thickness of ca. 20 μm were obtained, and then at the maximum, hydroxyl and carbonyl regions were examined through an FTIR microscope.
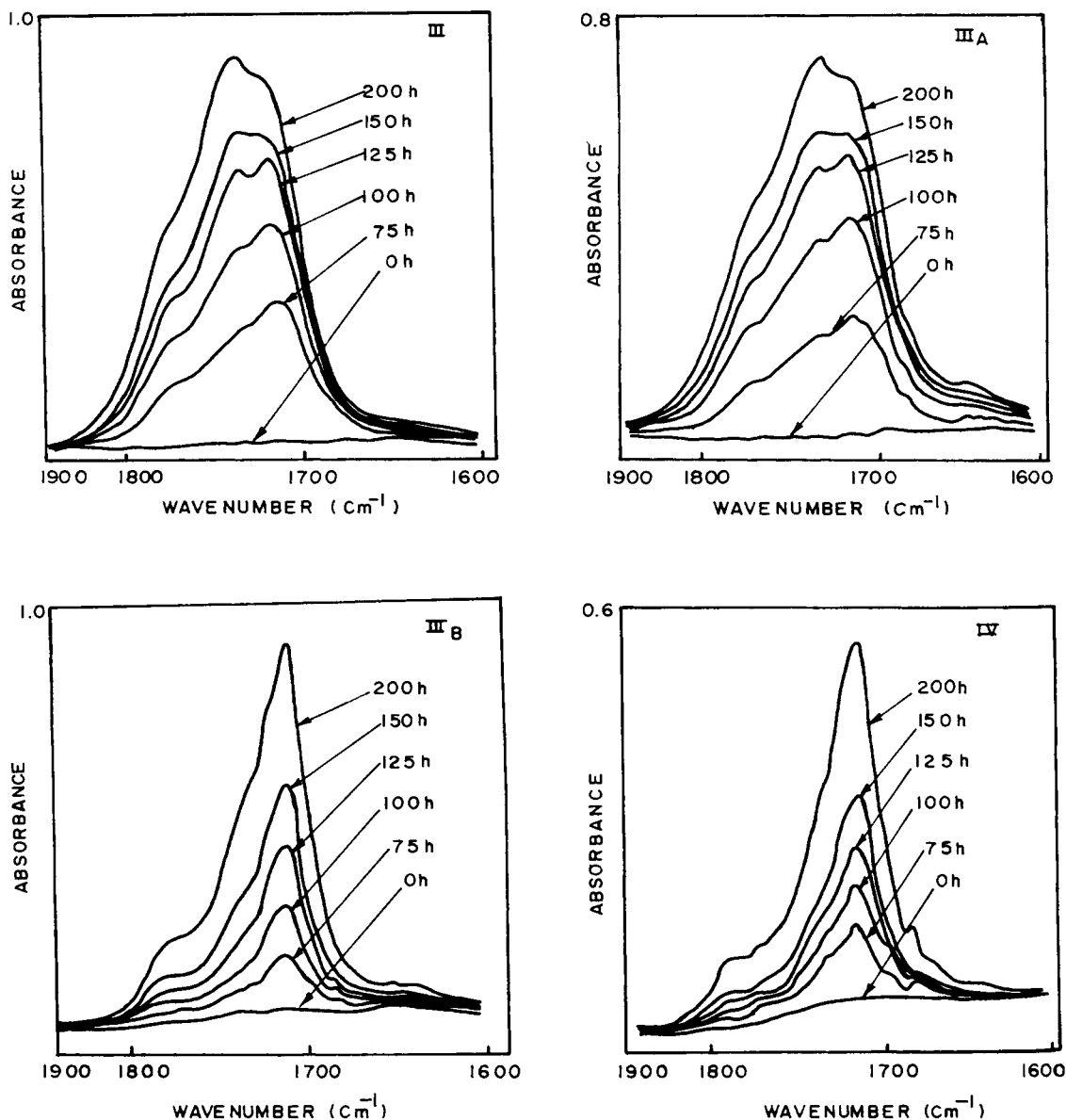
Figure 2   (*Continued from the previous page*)

RESULTS AND DISCUSSION

Changes in Hydroxyl and Carbonyl Regions

Exposure of E-P copolymer films and their fractions (samples: i-PP, EPQ 30R, EPQ 30R-A, EPQ 30R-B, EPF 30R, EPF 30R-A, EPF 30R-B, E-P copolymer, and LLDPE, i.e., I, II, II_A, II_B, III, III_A, III_B, IV, and V, respectively) to polychromatic irradiations ($\lambda > 295$ nm) led to development of IR bands in the hydroxyl and carbonyl regions. A very broad hydroxyl absorption region (3700–3200 cm^{-1}) with a maximum centered at 3400 cm^{-1} during photoir-

radiation appeared (Fig. 1). This band is due to the neighboring intramolecular hydrogen-bonded hydroperoxides and alcohols. Hydrogen-bonded hydroperoxides (3420 cm^{-1}) and associated alcohols (3380 cm^{-1}) were also present. The absorption in the hydroxyl region is more intense in i-PP and fraction A but minimum in fraction B and LLDPE.

The carbonyl region (1850–1550 cm^{-1}) showed several overlapping absorption bands (Fig. 2). This region is broad in thermoplastic E-P copolymers but sharp and narrow in polyethylene and elastomers. The absorption at 1712, 1722, 1740, and 1785 cm^{-1} have been assigned to carboxylic acid, ketone,
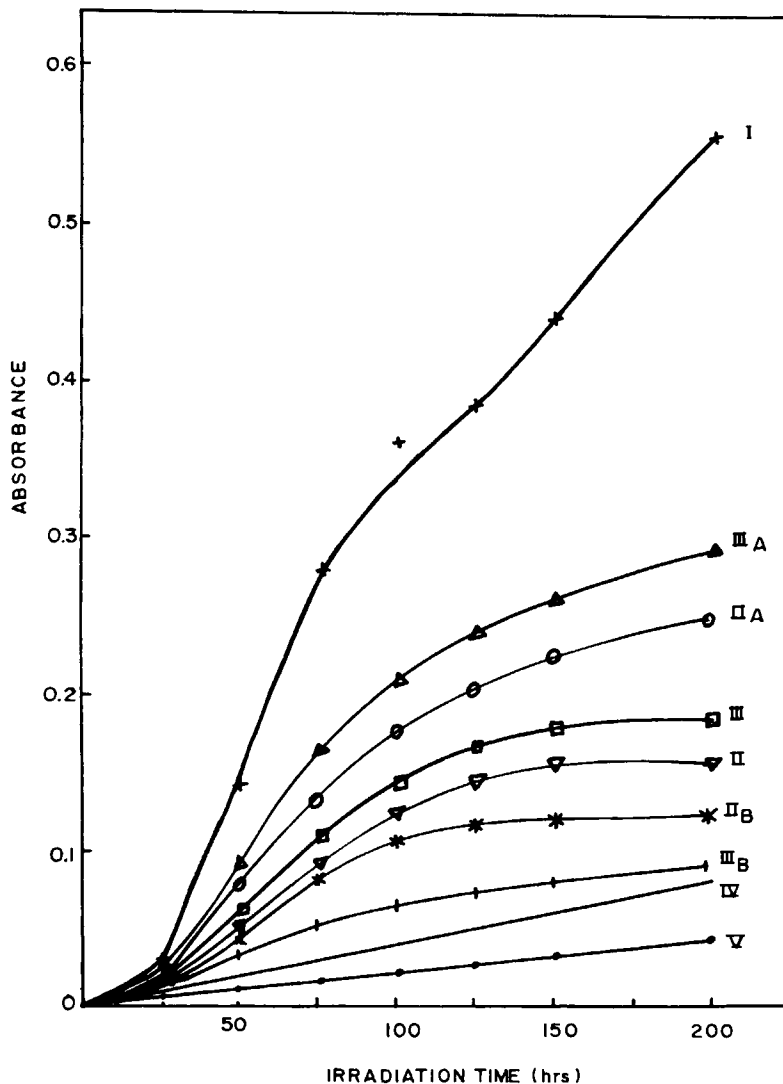
Figure 3 Rate of hydroxyl group formation with time upon polychromatic irradiation.

ester, and γ-lactone, respectively. The carbonyl region increases with increase in irradiation time. The band at 1722 cm^{-1} appeared first, but as the oxidation progressed with irradiation, the ~ 1785 cm^{-1} band[14] became prominent with a simultaneous increase in other bands. Li and Guillet[8] also found a negligible increase at ~ 1785 cm^{-1} during photodegradation of polyethylene, but a significant increase in polypropylene, which is in agreement with our observation. It was confirmed that in the deformation region vinyl groups (at 909 and 995 cm^{-1}) are present during photooxidation of polyethylene and elastomeric fractions, but these groups were not detected in photooxidized i-PP and fraction A. The vinyl group formation was very low in photooxidized

heterophasic PP (EPQ 30R and EPF 30R) since the sample also contains elastomeric fractions.

The rate of formation of hydroperoxidation increases with time of irradiation, but the increase in hydroperoxide group concentration is maximum in I and decreases with increasing ethylene content (Fig. 3). The same behavior was also observed in the amount of carbonyl group formation (Fig. 4). This is because the hydroperoxide/hydroxyl and carbonyl group formation is minimum in LLDPE and maximum in i-PP. The i-PP photooxidation occurs via the formation of unstable alkyl and peroxyl radicals and a photounstable intermediate such as tertiary hydroperoxides.

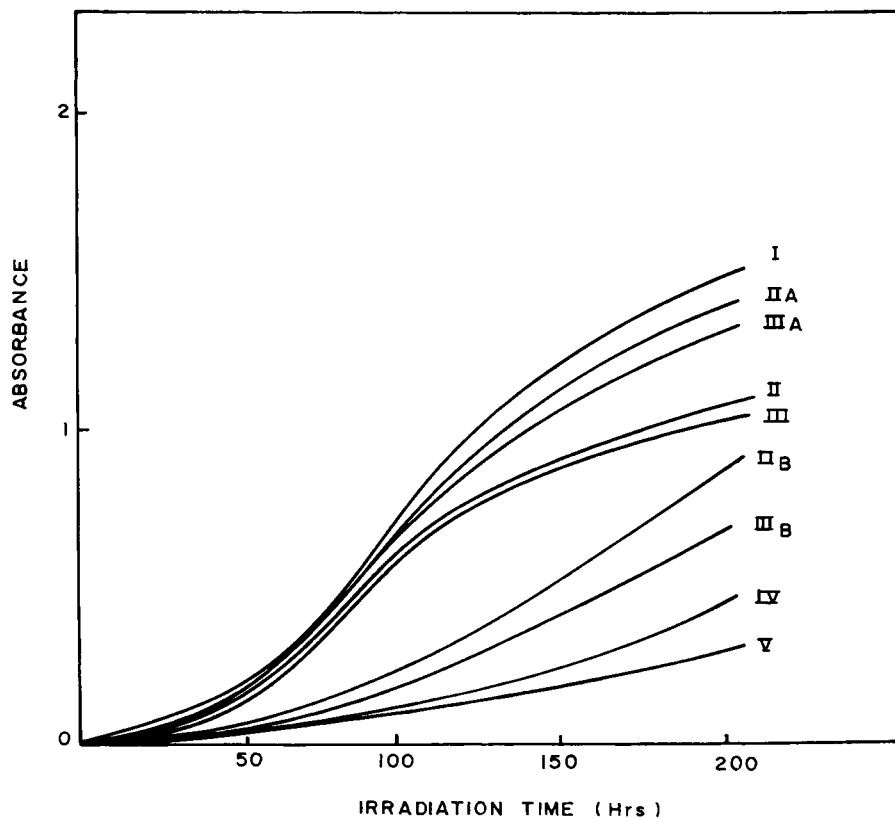It is concluded from these observations that frac-

Figure 4   Rate of carbonyl group formation with time upon polychromatic irradiation.

tion A (II_A and III_A) shows a similar oxidation behavior to that of i-PP, whereas the oxidation behavior of elastomeric fractions (II_B, III_B, and IV containing > 40 mol % ethylene) is similar to that of LLDPE. In spite of the low contents of elastomer, the heterophasic PP (II and III) has an intermediate behavior that shows a greater resemblance to i-PP photodegradation.

Derivatization Reactions

The overlapping carbonyl region was separated and identified by derivatization reactions of polymeric acids. It is clear from Figure 5 that the ammonium carboxylate,[15] obtained after reaction of photooxidized samples with gaseous ammonia, gives absorptions at 1555 cm^{-1}:

$$-R-\underset{\underset{O}{\parallel}}{C}-OH \xrightarrow{NH_3} -R-\underset{\underset{O}{\parallel}}{C}-O^-NH_4^{\oplus}$$
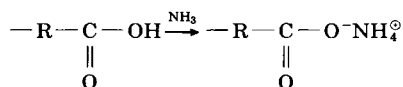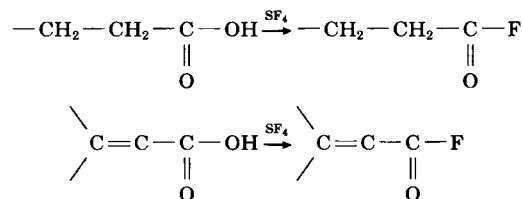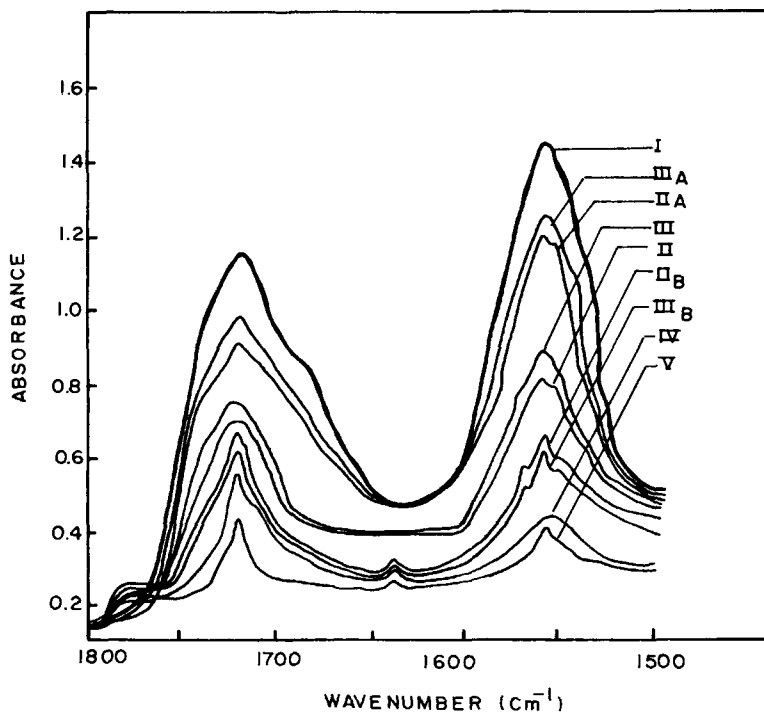
The ammonium salt formation is quantitative, i.e., maximum in I and minimum in photooxidized

V film. However, these absorptions are very broad and the method is inferior to acid measurement by SF$_4$ derivatization. The SF$_4$ exposure causes complete loss of all hydroxyl absorptions and generates acyl fluorides at 1840–1848 cm^{-1}:

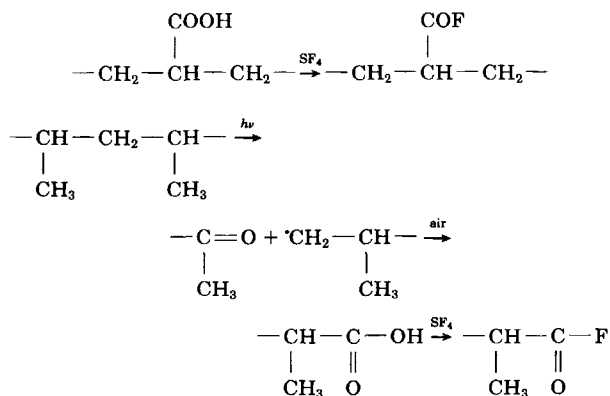$$-R-\underset{\underset{O}{\parallel}}{C}-OH \xrightarrow{SF_4} -R-\underset{\underset{O}{\parallel}}{C}-F$$
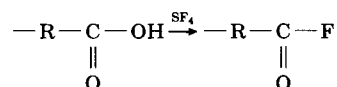
The photooxidized LLDPE and i-PP give rise to distinctly different acyl fuoride absorptions, as is shown in the difference spectra of Figure 6. The absorbance in LLDPE after SF$_4$ treatment lies at 1848 and 1815 cm^{-1}, which are attributed to chain-end acid fluoride and α,β-unsaturated acid fluoride, respectively:

$$-CH_2-CH_2-\underset{\underset{O}{\parallel}}{C}-OH \xrightarrow{SF_4} -CH_2-CH_2-\underset{\underset{O}{\parallel}}{C}-F$$

$$\underset{/}{\overset{\backslash}{C}}=C-\underset{\underset{O}{\parallel}}{C}-OH \xrightarrow{SF_4} \underset{/}{\overset{\backslash}{C}}=C-\underset{\underset{O}{\parallel}}{C}-F$$
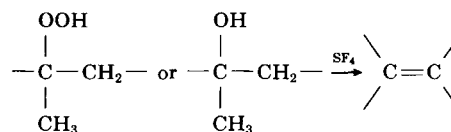
Figure 5 FTIR spectral changes of 200 h photooxidized and ammonia-treated E–P copolymer films.

The weak absorption of α, β-unsaturated acid fluoride is confirmed with a model compound reaction such as acrylic acid and sorbic acid.[16] The absorbance in photooxidized i-PP after SF$_4$ exposure is at 1841 cm^{-1}. In i-PP, carboxylic acid groups can be expected in a low extent from the free-radical oxidation of the methyl groups and to a larger extent from the β-scission of alkoxyl radical:[12,17]
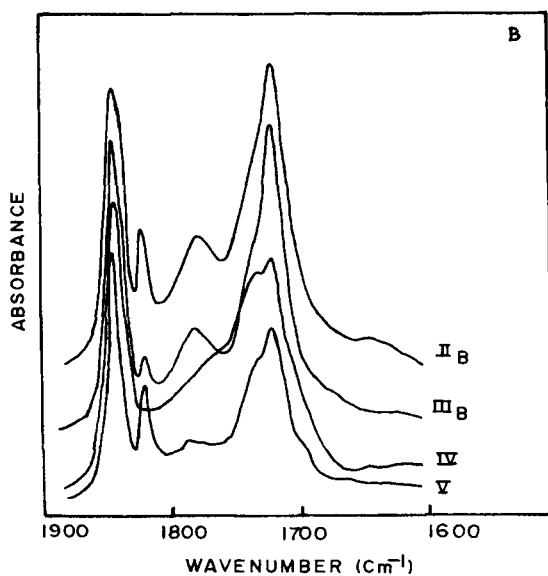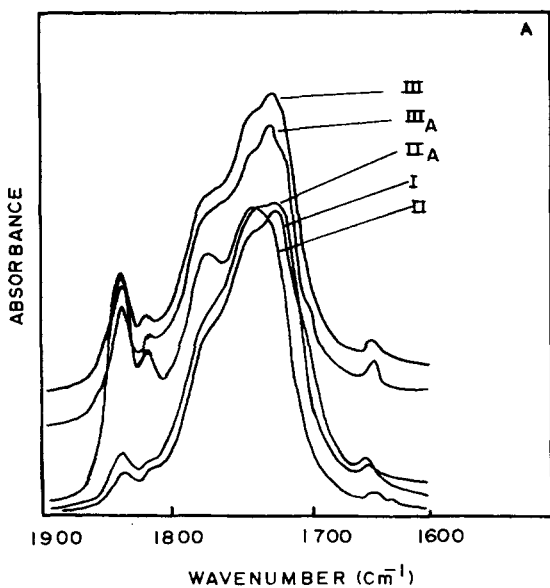
$$\begin{array}{ccc} \text{COOH} & & \text{COF} \\ | & & | \\ -\text{CH}_2-\text{CH}-\text{CH}_2- & \xrightarrow{\text{SF}_4} & -\text{CH}_2-\text{CH}-\text{CH}_2- \end{array}$$

$$\begin{array}{cc} -\text{CH}-\text{CH}_2-\text{CH}- & \xrightarrow{h\nu} \\ | \qquad\qquad | & \\ \text{CH}_3 \qquad \text{CH}_3 & \end{array}$$

$$\begin{array}{cc} -\text{C}=\text{O} + {}^{\cdot}\text{CH}_2-\text{CH}- & \xrightarrow{\text{air}} \\ | \qquad\qquad\quad | & \\ \text{CH}_3 \qquad\qquad \text{CH}_3 & \end{array}$$

$$\begin{array}{ccc} -\text{CH}-\text{C}-\text{OH} & \xrightarrow{\text{SF}_4} & -\text{CH}-\text{C}-\text{F} \\ | \quad\ \| & & | \quad\ \| \\ \text{CH}_3\ \ \text{O} & & \text{CH}_3\ \ \text{O} \end{array}$$

The carbonyl region after SF$_4$ treatment reveals the presence of unsaturation at 1640 cm^{-1} ($\rangle$C$=$C$\langle$) due to the dehydration reaction of hydroperoxide/hydroxyl groups:

$$\begin{array}{ccc} \text{OOH} & \text{OH} & \\ | & | & \\ -\text{C}-\text{CH}_2- \ \text{or} & -\text{C}-\text{CH}_2- \xrightarrow{\text{SF}_4} & \diagdown \diagup \\ | & | & \text{C}=\text{C} \\ \text{CH}_3 & \text{CH}_3 & \diagup \diagdown \end{array}$$

This unsaturation is more significant in i-PP and fraction A due to the formation of hydroperoxide and alcohol comparatively in large quantities in those samples. The SF$_4$ derivatization of II$_A$ and III$_A$ shows a behavior similar to that of i-PP oxidation, whereas that of II$_B$, III$_B$, and IV, to that of PE (Fig. 6). The heterophasic polypropylene (II and III) shows intermediate behavior with more resemblance to i-PP. It means that the initial photodegradation occurs on the i-PP phase but that the elastomeric portion also takes part in the degradation. A further simplification of the carbonyl absorption comes from the loss of the —OOH and —OH groups. The ammonium carboxylate absorption at 1555 cm^{-1} seems to be higher than the corresponding acid fluoride band at 1841 cm^{-1} in i-PP and fraction A, probably because some low molecular weight carboxylic acid becomes volatile after SF$_4$ treatment.
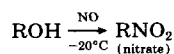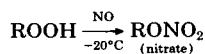
The most informative derivatization reaction of oxidized E–P copolymer samples for product identification is nitric oxide (NO). The NO gas reacts

It is essential to work at $-20°C$ to react peroxy radicals smoothly and to identify and quantify tertiary nitrates accurately that decompose rapidly at room temperature. It has been reported[18,19] that the sharp, intense IR spectra of these organonitrates and nitrites can be used to differentiate between primary, secondary, and tertiary species. Carlsson

Figure 6   FTIR spectral changes upon 200 h photooxidation in SEPAP 12/24, then SF_4 treatment. Spectral subtraction by subtracting the spectrum of the corresponding non-oxidized films: (A) I, II, II_A, III, and III_A; (B) II_B, III_B, IV, and V.
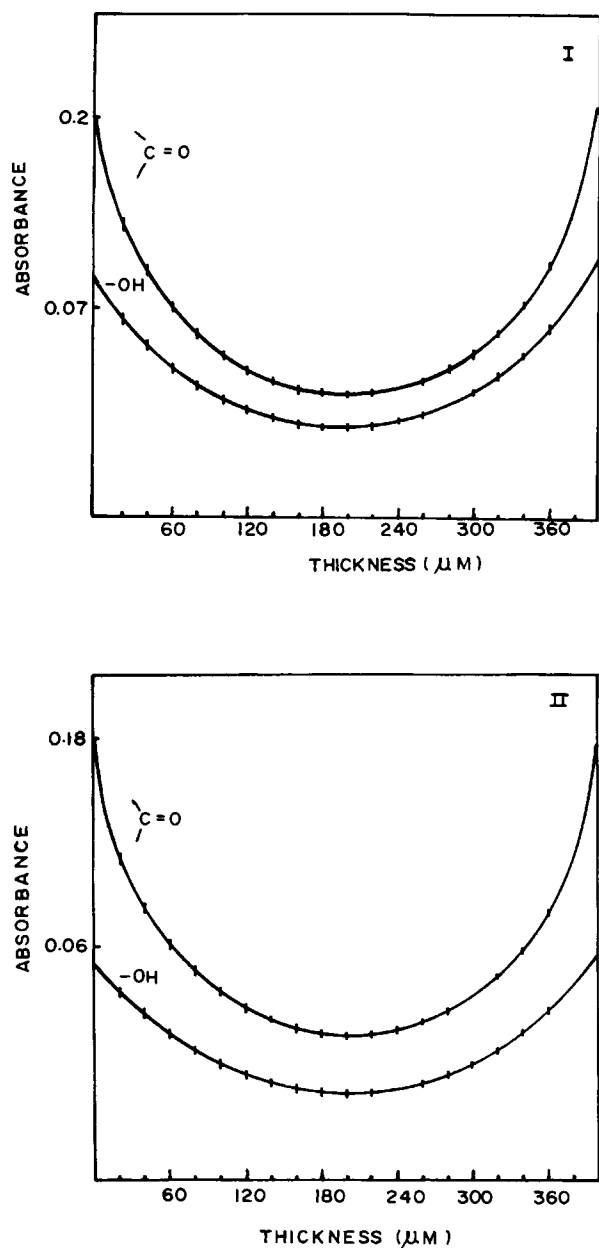
with hydroperoxides and alcohols to give, respectively, nitrates and nitrites:

$$ROOH \xrightarrow[-20°C]{NO} RONO_2 \text{ (nitrate)}$$

$$ROH \xrightarrow[-20°C]{NO} RNO_2 \text{ (nitrate)}$$
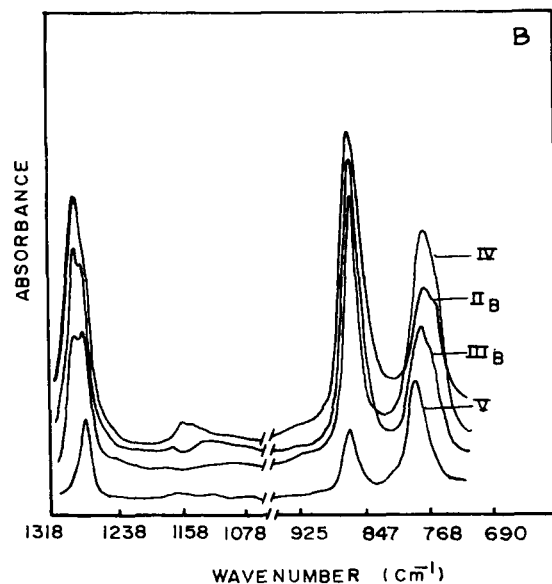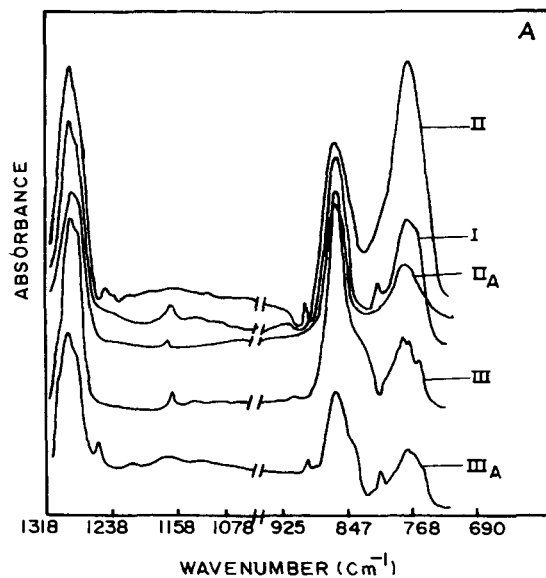
Figure 7   FTIR spectral changes upon 200 h photooxidation in SEPAP 12/24, then NO treatment. Spectral subtraction by subtracting the spectrum of the corresponding oxidized (but not NO-treated) films.

Figure 8 The distribution of carbonyl and hydroxyl groups as a function of the thickness of 50 h photooxidized I and II samples.

et al.[15,20] exploited this IR derivatization technique to identify and quantify hydroperoxide and alcohol products in oxidized polymers. After NO treatment, photooxidized LLDPE shows a symmetric nitrate absorption at 1276 cm^{-1} from secondary hydroperoxide and a small secondary nitrite peak at 778 cm^{-1} from secondary alcohol [Fig. 7(B)]. However, primary alcohol/hydroperoxides were not prominent after photooxidation of LLDPE or i-PP. The NO

treatment of photooxidized i-PP yields a much more complex absorption than that of PE. A secondary nitrate absorption at 1278 cm^{-1} was again found but tertiary nitrate absorptions at 1302 and 1290 cm^{-1} were dominant. Small absorptions of tertiary nitrite (760 cm^{-1}) and secondary nitrite (778 cm^{-1}) were also found. The detection of two types of tertiary nitrate absorption (1302 and 1290 cm^{-1}) show a complex behavior, but the peaks were identified by comparison of NO products from oxidized model alkanes. Carlsson et al.[20] found that the 1290 cm^{-1} absorption results from the NO reaction of —OOH groups along the backbone, whereas the 1302 cm^{-1} band is from the reaction of NO with —OOH groups at the chain end. Figure 7(A) and (B) shows that II$_A$ and III$_A$ give the derivatization like that of i-PP, whereas elastomeric samples (II$_B$, III$_B$, and IV) shows the behavior of PE. The heterophasic polypropylene (II and III) shows intermediate behavior with much more resemblance to i-PP. This is because II and III also contain elastomeric fraction in their matrix.

Profile Concentration Analysis

The photoproduct distribution through the matrix of E–P copolymers and their fractions has been measured in a plane perpendicular to the axis of irradiation by using the micro FTIR technique (Fig. 8). The i-PP and polypropylene-based fractions present a sharp profile in oxidation products. The photooxidation was localized within 60 microns, which implies that oxidation is stopped after 60 microns and the inner matrix becomes impermeable to oxygen. The elastomeric fractions (II$_B$, III$_B$, and IV) do not show any profile in the photoproduct distribution because the permeability to oxygen is quite high and cross-linking reactions, if any, are not sufficient to decrease the oxygen permeability. Figure 8 presents the distribution of the carbonyl and hydroxyl regions as a function of the thickness (370 μm) of I and II films of the area on the irradiated side (20 μm width). The absorbance varies from 0.2 to 0.18 at the edges and from 0.07 to 0.06 at the middle of the I and II samples, respectively, for the carbonyl regions. The sharp profiles observed are consistent with their relative photooxidation.

In conclusion, the photooxidative degradation of heterophasic E–P copolymers is concerned mainly with the polypropylene phase in spite of its crystalline nature. Under these conditions, only a weak oxidation of the elastomeric phase has been observed.

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