

Infrared Identification of Carboxylic Acids Formed in Polymer Photooxidation

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SYNOPSIS

Several low molecular weight carboxylic acids with different substitutions were introduced into various polymer matrices: polypropylene, polystyrene, poly(butylene terephthalate), MDI-based polyurethane, and poly(vinyl chloride). These acids were then submitted to chemical treatments by sulfur tetrafluoride and ammonia. Derivatization reactions by SF₄ and NH₃ gave, respectively, acyl fluorides and carboxylate ions. The wavenumbers corresponding to the $\bar{\nu}_{C=O}$ maxima of the carboxylic acids, acyl fluorides, and carboxylate ions were determined. For each one of these species, noticeable shifts were recorded that depended on the nature of the substituents as well as on the nature of the polymer matrix. In addition, samples of the chosen polymers were exposed to photoaging. Photooxidation of these polymers is known to involve the formation of carboxylic acids. The photooxidized samples were reacted with SF₄ and NH₃. Their IR characteristics were determined before and after the treatments. Comparison with the results obtained with the molecular acids permitted us to specify the chemical structure of the acids formed by photooxidation and then to determine the oxidation sites on the macromolecular chains of the different polymers.

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INTRODUCTION

The photooxidation of hydrocarbon polymers produces a complex mixture of products.¹ The precise identification of these products is the key point for the elucidation of the mechanisms by which the polymers degrade.

Two main difficulties exist that make complex the experimental identification of the products²:

- First, the chemical changes that result from the oxidation of polymers have to be studied on solid polymer matrix to take into account any perturbation that results from heterogeneities of the solid state.
- Second, because mechanical failure of the photooxidized polymers occurs for very slightly oxidized samples, the reaction has to be limited to a low extent, which is usually less than 1%.

Among the possible analytical techniques that permit one to identify the chemical changes of macromolecular chains in oxidative conditions, infrared spectroscopy is probably the most appropriate. However, this technique suffers from modest sensitivity and the weak concentrations of transformed groups imposed by the low reaction extent can constitute a limitation to its application. Fortunately, the development of FTIR spectrometers has permitted an important gain in terms of sensitivity. IR spectroscopy can now be used in most situations where the detection of low concentrations is required.

In hydrocarbon polymers, by far the most useful groups in following the progress of oxidation are in the region 1690–1750 cm⁻¹ and in the region 3000–3700 cm⁻¹. The first region usually corresponds to a composite absorbance of ketones, esters, and carboxylic acids. The presence of carboxylic acids is indicative of chain scission processes, and the extent to which they are present generally correlates well with physical changes in the polymer.³ Hydroxyl groups, including carboxylic acids, alcohols, and hy-

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droperoxides, are also present, but since they give a broad absorbance due to hydrogen bonding, they are generally less useful as a kinetic measure of degradation.

The different absorption bands of carbonylated groups are generally convoluted. Moreover, even if the different maxima are precisely observed, an ordinary IR analysis is far less than sufficient to attribute these maxima to the corresponding products. In the "carbonyl" region ($1690\text{--}1800\text{ cm}^{-1}$), the absorption maxima corresponding to the $\bar{\nu}_{\text{C=O}}$ bands of the different products can be in the range of a few wavenumber units.⁴ As an example, it is generally agreed that carboxylic acids in the dimer form absorb around 1710 cm^{-1} , and the normally accepted absorption of ketonic compounds is around 1720 cm^{-1} . These values have been obtained from studies carried out in the field of polyolefins, e.g., polyethylene and polypropylene.⁵ However, they cannot be extrapolated to other polymer matrices since noticeable shifts of the $\bar{\nu}_{\text{C=O}}$ maxima can be expected depending on the chemical structures of the acids. Even in the case where the same acid is formed by photooxidation of polymers with different chemical structures, no parallel can be drawn between the values obtained since the positions of the $\bar{\nu}_{\text{C=O}}$ maxima are expected to be influenced by the chemical or physical environment of the matrix.

From a practical point of view, appropriate chemical treatments permit one to discriminate between the different products, depending on their own reactivity toward the reagents.

Reactions with NH_3 to generate carboxylate ions provides evidence of the presence of carboxylic acids.⁶ However, this method is not sufficient to determine the exact chemical structure of the acids, apart from the case of macromolecular chains that have only one possible oxidation site (e.g., extremely linear polyethylene).

A one-step determination of both the organic function and the chemical structure can be done for some products including carboxylic acids, hydroperoxides, and alcohols. Hydroperoxides and alcohols can be converted by NO to give nitrites and nitrates, whereas carboxylic acids react with SF_4 to give acyl fluorides. These two methods have been detailed by Carlsson et al. for polyolefins oxidation.⁷ In the case of NO treatment, the authors have shown that both nitrites and nitrates have different IR absorption maxima depending on their primary, secondary, or tertiary character. This means that it is possible from these reactions to discriminate alcohols from hydroperoxides and, moreover, to specify their respective chemical structure. In the case of

SF_4 treatment, the authors have shown that the nature of the α -substitution of acyl fluorides can lead to important shifts of the $\bar{\nu}_{\text{C=O}}$ maximum. These methods applied to the oxidation of polyethylene and polypropylene have permitted the authors to propose oxidation mechanisms for these polymers.

Derivatization methods can now be used to propose an accurate way for the identification of most of the useful products formed by oxidation of hydrocarbon polymers. The basic principle of those methods is to compare the IR spectrum of a treated polymer to those of model compounds (polymers or low molecular weight compounds).

Recent studies carried out at our laboratory have shown that the spectral features of the model compounds were obviously depending on their chemical structure but were also depending on the polymer matrix.⁸ Shifts of several wavenumber units can be observed for the same molecular compound introduced into different matrices, which can make the comparison quite confusing. Limited data are available in the literature concerning the IR characteristics of the model compounds. This means that the use of derivatization methods requires a parallel investigation of some well-chosen products that can constitute proper models for the involved reactions.

In this article, we report on the identification of carboxylic acids formed by photooxidation of polymers. First, we describe the main features of the $\text{C}=\text{O}$ stretching vibrations of some low molecular weight carboxylic acids pure or introduced into various polymers and then treated by SF_4 and NH_3 . On the basis of these results, this procedure is extended to investigations of polymer matrices in photooxidation conditions.

EXPERIMENTAL

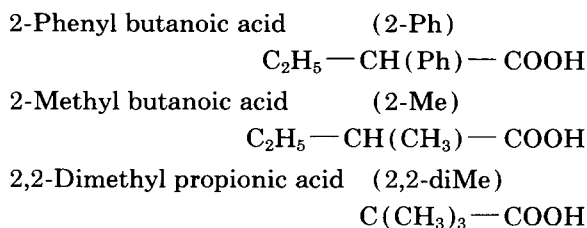
Materials

Different model compounds of molecular carboxylic acids with different structures were used for this study. Four linear carboxylic acids were investigated:

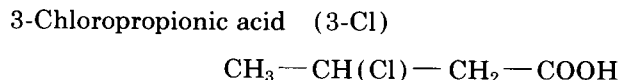
Acetic acid	(C_2)	$\text{CH}_3\text{—COOH}$
Propionic acid	(C_3)	$\text{C}_2\text{H}_5\text{—COOH}$
Hexanoic acid	(C_6)	$\text{C}_5\text{H}_{11}\text{—COOH}$
Decanoic acid	(C_{10})	$\text{C}_9\text{H}_{19}\text{—COOH}$

Two α -monosubstituted carboxylic acids and one α -disubstituted carboxylic acid were studied in order

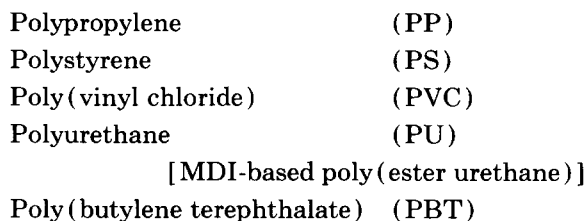
to evaluate the influence of the α -substitution and the influence of the nature of the substitute group:



As concerns the photooxidation of poly(vinyl chloride) (PVC), it was interesting to study the behavior of the following chlorinated acid:



The polymer matrices used for this study were the following:



They were studied in the form of films with a thickness around 100 microns.

Infrared Analysis

Fourier transform IR (FTIR) spectra were recorded with a Nicolet 20SX spectrometer equipped with a TGS detector. Spectra were obtained using 20 scans summation at a nominal resolution of 2 cm^{-1} .

As pure acids were either solid or liquid, they were analyzed in the following different ways: The initial spectra of solid pure acids were recorded by inclusion in a KBr pellet. For liquid acids, the initial spectra were recorded between two KBr windows. When their viscosity was too high to use a cell, they were cast on a KBr plate, then analyzed.

Inclusion of Molecular Acids in Polymer Matrix

The acids were introduced by permeation into polymer films. The film of the polymer (thickness about 100 microns) was immersed in a swelling solvent, depending on the nature of the polymer under investigation, then the acid was added to the solvent.

After 12 h, the film was dried at room temperature. When no swelling solvent exists or when the polymer is soluble in every solvent, the acid was directly put on the polymer film. This was possible only if the pure acid is a liquid. The analysis is limited to liquid acids in the case of polystyrene.

Chemical Treatments

Either the solid acids included in a KBr pellet or the acids introduced in a polymer film were exposed to reactive gas at room temperature in a simple flow system that could be sealed off to allow the reaction to proceed. The gases used were SF_4 and NH_3 (supplied, respectively, by Fluka and UCAR). SF_4 treatment was carried out in an all-Teflon system because SF_4 attacks glass. Reaction time was 1 h. IR spectra were recorded before and after the derivatization reactions.

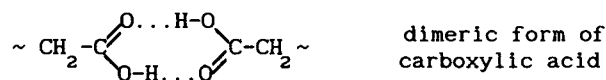
Irradiation of Polymer Films

Irradiation of polymer films at long wavelengths ($\lambda > 300\text{ nm}$) were carried out in a SEPAP 12/24. This unit has been described in several previous articles (see, e.g., Ref. 9). For irradiations in the absence of O_2 , polymer samples were introduced into a Pyrex tube and sealed under vacuum (10^{-6} Torr) using a mercury diffusion vacuum line.

RESULTS AND DISCUSSION

Pure Acids and Acids Introduced in Different Matrix

Results are listed in Table I. Carboxylic acids exhibit two bands in the carbonyl stretching region ($1900\text{--}1500\text{ cm}^{-1}$) corresponding to the monomer band ($1717\text{--}1758\text{ cm}^{-1}$) and to the dimer band ($1688\text{--}1717\text{ cm}^{-1}$), which revealed H-bonding between two molecules of acids:



In most cases, about 30 cm^{-1} separate the two absorption maxima. The relative intensities of the monomer and dimer bands depend on the concentration of the molecular carboxylic acid in the solvent (which is the polymer matrix in this case). When the acid concentration is above a limiting value, the monomer band is no longer observed, ev-

Table I IR Absorptions of Pure Acids and of Acids Introduced into a Polymer Matrix

Acid	Wave Number (cm ⁻¹)					
	Pure	PP	PS	PVC	PU	PBT
Acetic	1716 1758	1717 1732	1712	1711 1755	1726 1755	—
Propionic	1717	1717	1714 1745	1713 1746	1716 1741	1717
Hexanoic	1711	1712	1709	1706	—	—
Decanoic	—	1712	1708	—	—	—
2-Ph	1694	1710	1706	1706 1745	—	—
2-Me	1708	1710	—	1703 1739	—	—
2,2-diMe	1703	1704	—	1699	—	—
Benzoic	1688	1698 1732	—	1691 1730	1689 1720	1696 1737
3-Cl	—	—	—	1717 1750	—	—

ery acidic function being associated. Concerning the inclusion of a molecular carboxylic acid in a polymer film, there is a noticeable influence of the nature of

the polymer on the position of those bands (see Table I).

Sulfur Tetrafluoride Reactions

It is known that many aldehydes and ketones, in particular conditions, react with SF₄ and are converted to *gem*-difluoro compounds.¹⁰ Esters also react to give trifluorides under vigorous conditions that are far from our experimental conditions.¹⁰ These data concern pure compounds or compounds in solution. When introduced in polymers, low molecular weight ketones and esters are not observed to react under our experimental conditions (room temperature).

In the literature, it is given that carboxylic acids also react with SF₄ to give 1,1,1-trifluorides.¹⁰ The primary product of this reaction is an acyl fluoride that can be isolated:



In polymer matrix, the acyl fluoride appears to be fairly stable. The derivatization reaction by SF₄ has, indeed, been used to measure quantitatively the carboxylic acid groups formed during the photooxidation of polyolefins.⁷ The acyl fluorides formed by

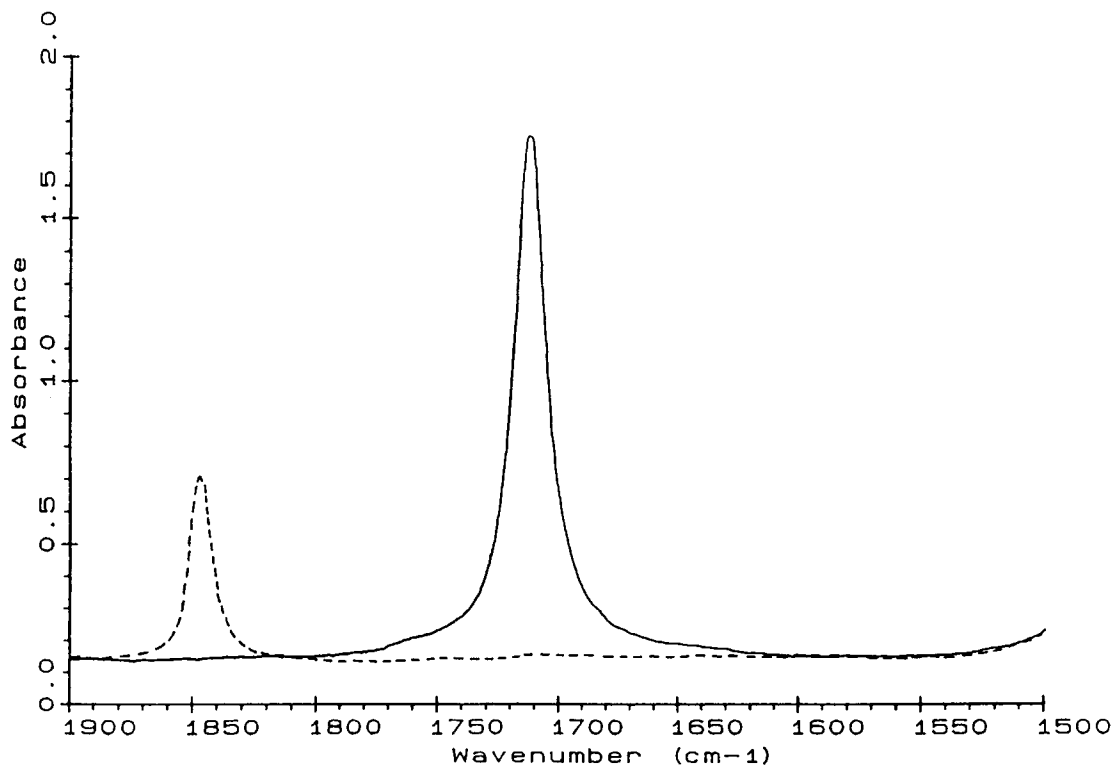


Figure 1 Decanoic acid included in the polypropylene matrix (—) before and (--) after SF₄ treatment.

reaction of carboxylic acid groups with SF₄ are characterized by a C=O absorption above 1800 cm⁻¹ (Fig. 1). The SF₄ reaction has also been shown to give a total disappearance of OH absorptions.

Table II gives the absorption maximum of the C=O bands for the carboxylic acids listed above when introduced in various polymer matrices and treated by SF₄.

Linear Carboxylic Acids

The results obtained with linear carboxylic acids indicate that the absorption maxima are dependent on the polymer matrix. As an example, up to 9 cm⁻¹ separate the C₆ acyl fluoride in poly(vinyl chloride) and in the polypropylene matrix. Concerning the effect of the chain length of the acids, two different situations appear: In the case of polypropylene and poly(butylene terephthalate) matrices, the chain length has no effect on the frequency of the absorption maxima. In poly(vinyl chloride) and polyurethane matrix, the longer the chain, the lower the wavenumber.

α -Substituted Carboxylic Acids

When the substitution degree increases, the maximum in absorption of the fluoride derivative is shifted to shorter wavenumbers: The more substituted the acid, the lower the wavenumber. No difference was observed between the absorption of a phenyl and a methyl substituent in the α position of the carboxylic acid group.

Benzoic Acid

The absorption maximum of the $\bar{\nu}_{C=O}$ band of the fluoride derivatives from benzoic acid in the different polymer matrix are also reported in Table II. A shift of about 30 cm⁻¹ is observed between the fluoride derivative of an aliphatic acid and the fluoride derivative of an aromatic acid. The derivatization by SF₄ is then quite accurate in identifying an aromatic acid.

Conclusion

There is important influence of the nature of the polymer matrix, of the substitutive degree of the C in α of the carboxylic acid, and of the nature (aromatic or aliphatic) of the acid considered on the $\bar{\nu}_{C=O}$ absorption band of the acyl fluoride. Based on these results, SF₄ can be a very good reagent to detect as well as to identify the structure of the carboxylic acids.

Table II IR Absorptions of the Acyl Fluoride After SF₄ Treatment on the Carboxylic Acids Pure or Introduced into a Polymer Matrix

Acid	Polymer (cm ⁻¹)					
	Pure	PP	PS	PVC	PU	PBT
Acetic	—	1848	—	1844	1844	—
Propionic	—	1849	1844	1841	1842	1841
Hexanoic	—	1847	1841	1838	1841	1841
Decanoic	—	1847	—	—	—	1841
2-Me	—	1841	1838	1837	—	1841
2-Ph	1837	1840	1837	1835	1837	—
2,2-diMe	—	1836	—	1828	1833	—
Benzoic	—	1818	1813	1811	1815	1815
3-Cl	—	—	—	1845	—	—

Ammonia Reactions

Carboxylic acids react with NH₃ to give the corresponding carboxylate. Carboxylate ions present an asymmetric carbonyl stretching vibration, which appears generally between 1550 and 1610 cm⁻¹, and a symmetric carbonyl stretching vibration with an absorbance between 1300 and 1400 cm⁻¹. It is usually more useful to follow the asymmetric $\bar{\nu}_{(CO_2)}$ because this region of the IR spectra is less obstructed by other vibrations than is the region between 1300 and 1400 cm⁻¹ (Fig. 2).

The results of the treatments by ammonia carried out on carboxylic acids included in a polymer matrix are given in Table III. The nature of the polymer has nearly no influence on the position of the carboxylate absorption. Our results also show that for linear carboxylic acids (C₂ to C₆), the longer chain length, the lower the wavenumber of $\bar{\nu}_{(CO_2)asym}$. For the substituted acids, it is observed that the $\bar{\nu}_{(CO_2)asym}$ absorption is shifted to longer wavenumbers when the substitution degree increases.

NH₃ treatment carried out on benzoic acid develops a maximum between 1537 and 1553 cm⁻¹. We were expecting specific behavior for benzoic acid but the results obtained were similar to those obtained with α -substituted acids.

Conclusion

NH₃ treatment is very useful in order to detect the presence of carboxylic acids. However, this treatment does not permit one to determine the chemical structure of the acids. Comparison of the results obtained by both the methods show that treatments by SF₄ offer better accuracy for the determination of the chemical structure of the acids.

Table III IR Absorptions of the Carboxylate Ions After NH₃ Treatment of the Acids Pure or Introduced into a Polymer Matrix

Acid	Wave Number (cm ⁻¹)				
	Pure	PP	PVC	PU	PBT
Acetic	—	1558	1559	—	—
Propionic	—	1554	1554	—	1559
Hexanoic	—	1549	1547	—	—
2-Me	—	1541	1540	—	—
2-Ph	1532	1535	1533	1532	—
2,2-diMe	—	1529	1531	1525	—
Benzoic	1538	1537	1537	1553	1543
3-Cl	—	—	1565	—	—

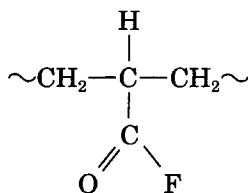
Application to the Photooxidized Polymers

Photooxidized polymers were submitted to both NH₃ and SF₄ treatments and analyzed by FTIR spectroscopy. Results obtained were compared to those obtained with molecular models. Results are listed in Table IV.

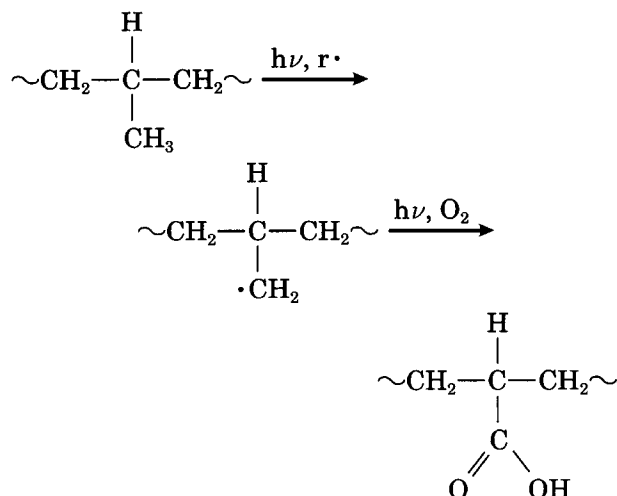
Polypropylene

NH₃ treatment carried out on a photooxidized sample of polypropylene develops a new absorption band whose maximum is at 1557 cm⁻¹. The increase of this band is correlated to the decrease of the maximum at 1713 cm⁻¹. Those results permit identification of a carboxylic acid that absorbs at 1713 cm⁻¹ and its carboxylate ion at 1557 cm⁻¹.

SF₄ treatment carried out on photooxidized polypropylene induced the formation of an absorption band with a maximum at 1841 cm⁻¹ and the decrease of the maximum at 1713 cm⁻¹. The maximum at 1841 cm⁻¹ had been observed previously in γ -irradiation conditions and was initially attributed to an acyl fluoride with this structure⁷:

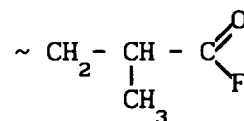


The carboxylic acid leading to this acyl fluoride was postulated to be formed by oxidation of the methyl side group following the reaction

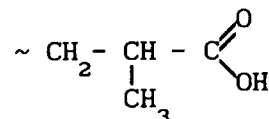


However, this reaction is highly questionable since the tertiary or even secondary carbons are far more oxidizable.

Indeed, comparison to the model compounds shows that the maximum at 1841 cm⁻¹ may be attributed to a methyl α -substituted acyl fluoride:



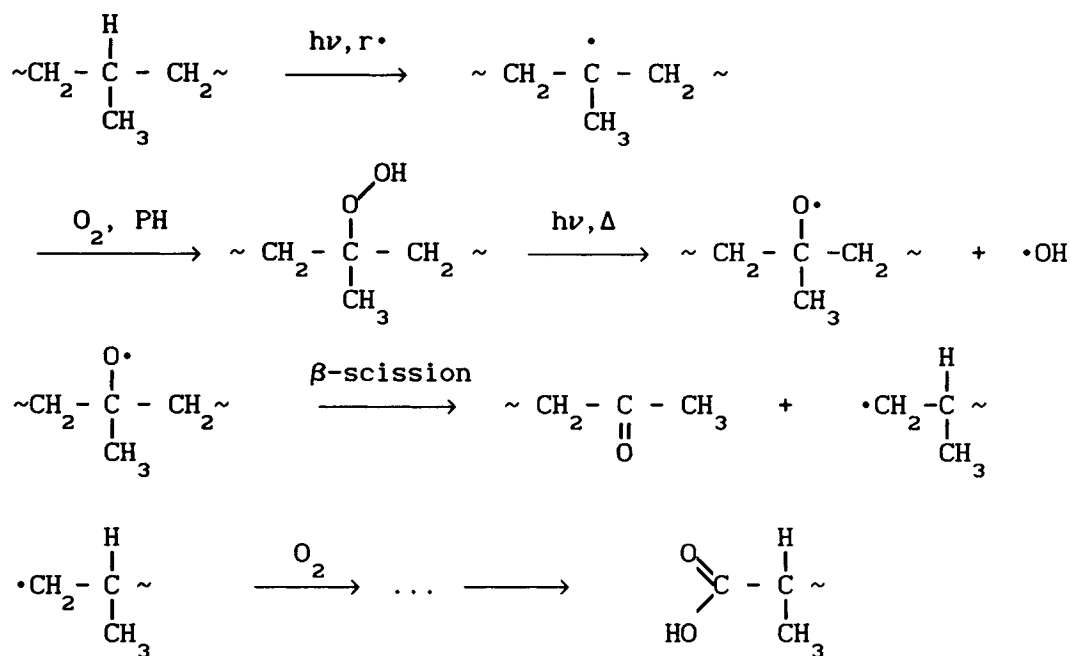
This compound is derived from the carboxylic acid



The formation of this acid involves the following reactions:

Table IV $\bar{\nu}_{\text{C=O}}$ in Photooxidized Polymers Before and After Chemical Treatments

Chemical Treatment	Wave Number (cm ⁻¹)					
	PP	PS	PVC	PU	PBT	
$\bar{\nu}_{\text{C=O}}$						
	Photooxidized	1713	1698 1710 1732 1753	1718	1696 1733	
	NH ₃	1557	1553	1575	1550	1549
	SF ₄	1841	1813 1841	1845	1802 1842	1815



These reactions require an initial oxidation of the tertiary carbon, which is more likely to occur than the oxidation of the primary carbon of the methyl group. This mechanism is in good accordance with recent findings.¹¹

Polyurethane Based on MDI

SF₄ treatment carried out on a photooxidized film of MDI-based polyurethane leads to the formation

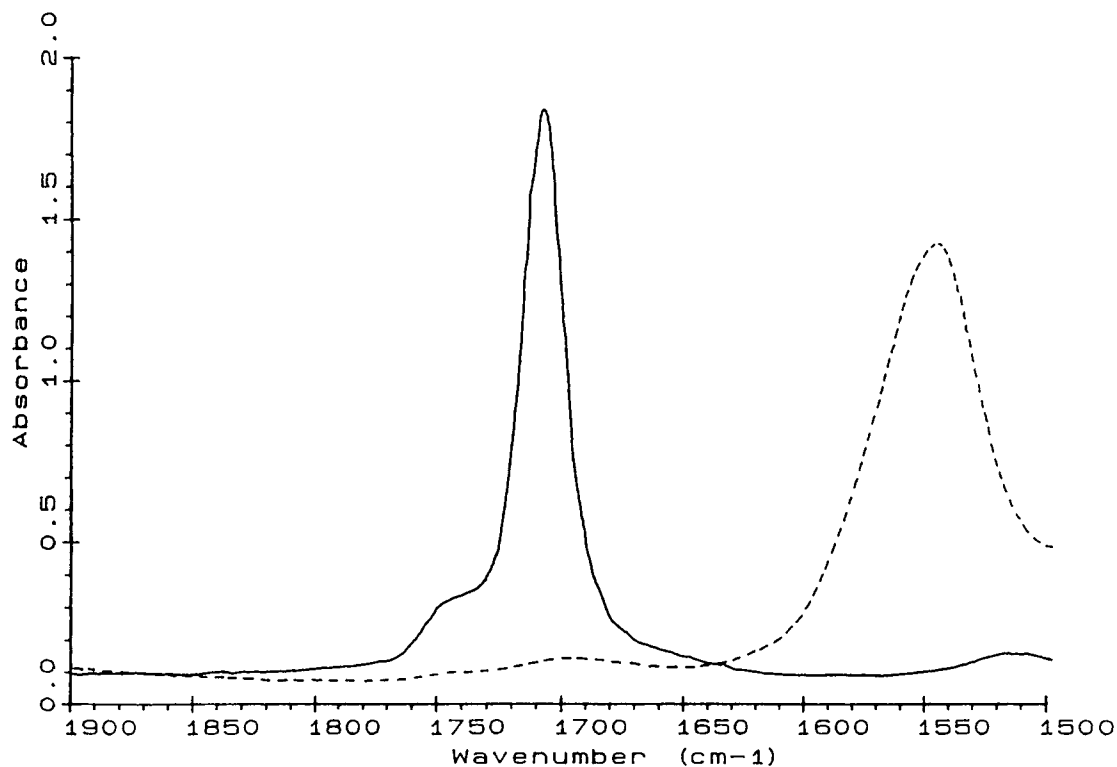
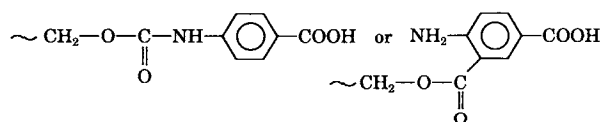


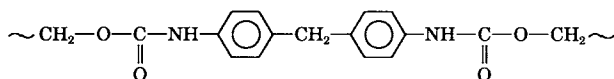
Figure 2 Hexanoic acid included in PVC matrix (—) before and (---) after NH₃ treatment.

of two new absorption bands at 1842 and 1802 cm^{-1} . Judging from the results obtained with the molecular model compounds, those new absorptions correspond to two different acyl fluorides:

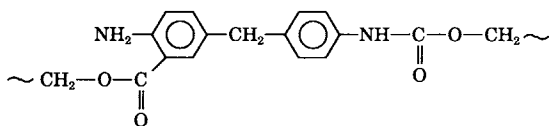
- The maximum observed at 1842 cm^{-1} can be attributed to the acyl fluoride corresponding to a linear carboxylic acid $\sim \text{CH}_2 - \text{COOH}$.
- The maximum at 1802 cm^{-1} is attributed to the derivative of an aromatic carboxylic acid with the following structure:



These acids are obtained by the photoinduced oxidation of the methylene between the two aromatic rings of the MDI moities:



or of their photo-Fries derivative¹²:



Polystyrene

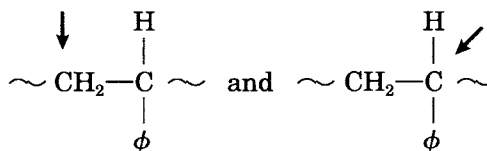
SF_4 treatment on photooxidized polystyrene samples leads to the decrease of several absorption maxima at 1698, 1710, 1732, and 1753 cm^{-1} . New absorption bands are observed at 1813 and 1841 cm^{-1} .

Comparison of these evolutions with the results given above leads to the following assignments:

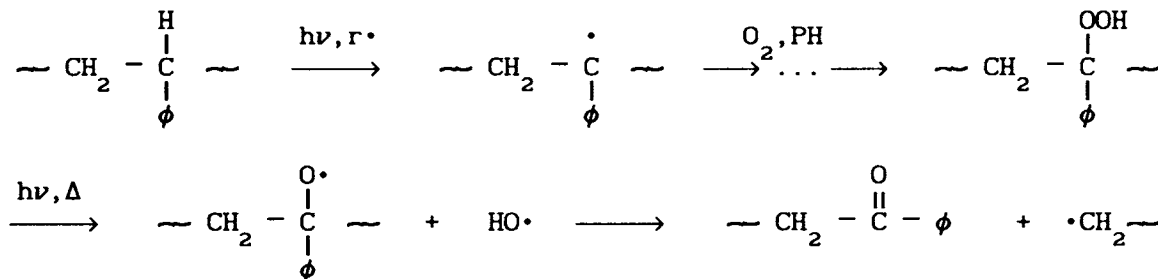
- The absorption maxima at 1698 and 1732 cm^{-1} are, respectively, attributed to the dimer and the monomer forms of benzoic acid. Benzoic acid reacts with SF_4 to give the absorption maximum at 1813 cm^{-1} .
- The absorption maxima at 1710 and 1753 cm^{-1} are, respectively, attributed to the dimer and the monomer forms of a carboxylic acid $\sim \text{CH}_2 - \text{COOH}$. The acyl fluoride $\sim \text{CH}_2 - \text{COOF}$ obtained by reaction with SF_4 presents a maximum at 1841 cm^{-1} .

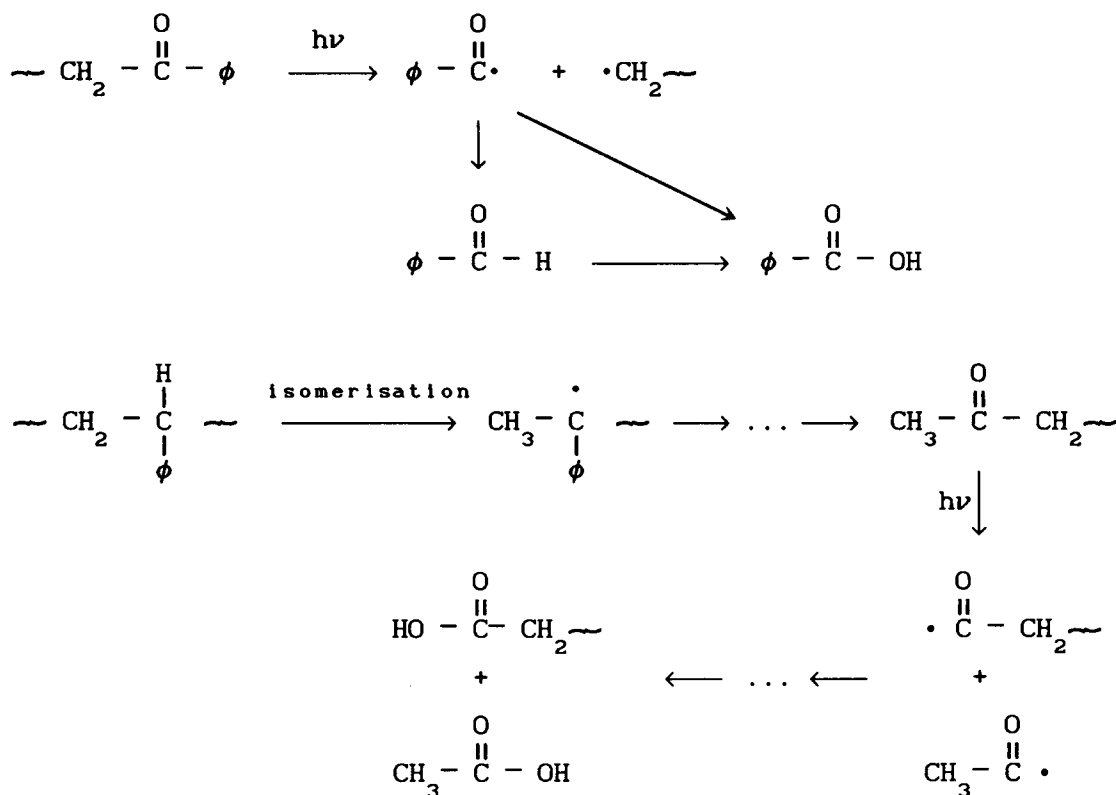
Reaction of photooxidized polystyrene film with ammonia leads to the decrease of the carbonyl bands between 1680 and 1800 cm^{-1} and to an increase of absorbance between 1680 and 1500 cm^{-1} . The subtraction of spectra before and after NH_3 treatment shows that the decrease of the carbonyl band corresponds to the decrease of the maxima at 1698, 1710, 1732, and 1753 cm^{-1} . The increase of absorbance between 1680 and 1500 cm^{-1} reveals a maximum at 1553 cm^{-1} . The absorbance maximum at 1553 cm^{-1} corresponds to a convolution of the bands of the carboxylate ions derived from a carboxylic acid group $\sim \text{CH}_2 - \text{COOH}$ and from benzoic acid.

The determination of the structures of acid groups formed by photooxidation of polystyrene has permitted us to discriminate between the two different possible oxidation sites⁸:



Oxidation of the tertiary carbon leads to the formation of benzoic acid and aliphatic acid following the reaction





Poly(butylene terephthalate)

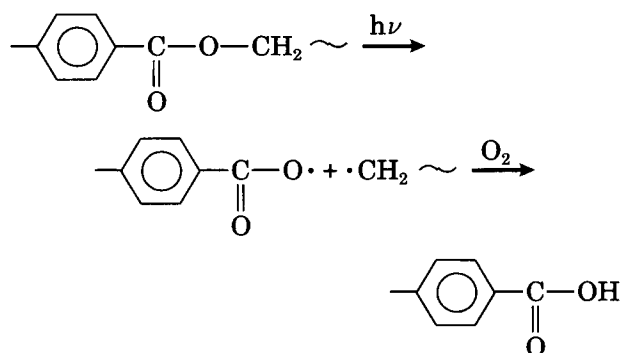
The IR spectrum of a sample photooxidized in the presence of O_2 and treated with gaseous SF_4 shows the disappearance of the carbonyl band at 1697 cm^{-1} and a decrease of the band at 1737 cm^{-1} with parallel development of two carbonyl bands at 1815 cm^{-1} (intense) and at 1841 cm^{-1} (weak).¹³

The two absorption bands that develop in the range $1800\text{--}1500 \text{ cm}^{-1}$ can be attributed to an aromatic acyl fluoride (1815 cm^{-1}) and to an aliphatic acyl fluoride (1841 cm^{-1}) corresponding, respectively, to the conversion of aromatic and aliphatic acids. The IR bands at 1697 and 1737 cm^{-1} that are converted into the band at 1815 cm^{-1} are attributed to the dimer and monomer carbonyl vibration bands of benzoic acid-type end groups (1696 and 1733 cm^{-1}).

The carbonyl stretching vibration of the aliphatic acid is expected to absorb at 1718 cm^{-1} . It cannot be directly observed on IR spectra due to the strong initial absorption of the $\text{C}=\text{O}$ of the poly(butylene terephthalate) matrix. Furthermore, judging from the compared intensities of the bands at 1841 and 1815 cm^{-1} , the concentration of the aliphatic acid is presumed to be fairly low compared to the concentration of the aromatic acid. These results contributed to the proposition of a general mechanism

for the photooxidative pathways of poly(butylene terephthalate).¹³

SF_4 treatment carried out on a sample photolyzed in the absence of O_2 leads to the formation of a band at 1815 cm^{-1} and the decrease of the intensity of the bands at 1697 and 1733 cm^{-1} .¹³ These results gave evidence of the formation of benzoic acid-type end groups by a direct scission of the $\text{O}-\text{C}$ bond and hydrogen abstraction by the so-formed radical¹⁴:

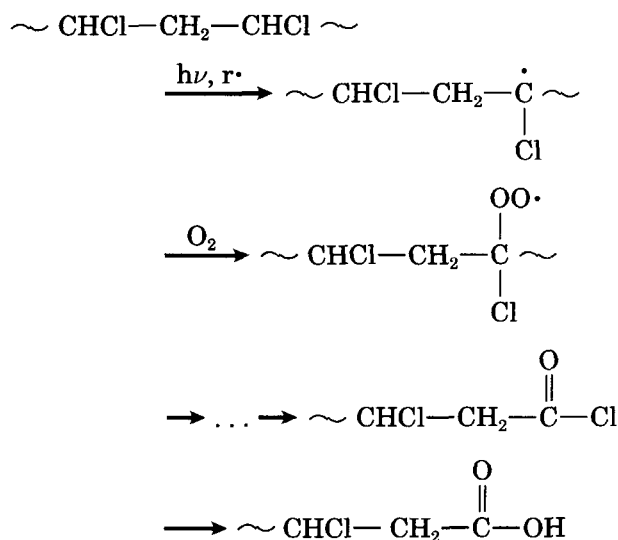


Poly(vinyl chloride)

The photooxidation of PVC produces various photoproducts, some of them being detected by giving

a complex carbonyl band between 1800 and 1600 cm^{-1} . Treatment by SF_4 of a photooxidized sample leads to decreases of the absorption maxima at 1717 and 1750 cm^{-1} . The SF_4 derivatization reaction leads also to the formation of a carbonyl band with a maximum at 1845 cm^{-1} .

Previous investigations have permitted us to attribute the maxima at 1750 and 1717 cm^{-1} , respectively, to the monomer and dimer forms of a β -chlorocarboxylic acid $\sim \text{CHCl}-\text{CH}_2-\text{COOH}$ following the reaction¹⁵



Further investigations involving SF_4 treatments were carried out to corroborate this attribution since it has been reported above that the IR characteristics of the 3-chloropropionic acid in a PVC matrix were

similar to those of the product of acidic nature formed by photooxidation of PVC.

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