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Polyolefin Oxidation: Quantification of Alcohol and Hydroperoxide Products by Nitric Oxide Reactions*

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ABSTRACT

A new procedure has been developed for the identification and quantification of key products from the oxidation of solid polyolefins, based on reactions with gaseous nitric oxide. Alcohol and hydroperoxide groups are converted to nitrites and nitrates, respectively, and can be detected with high sensitivity by infrared spectroscopy. Furthermore, the nitrate and nitrite absorptions are influenced by the primary, secondary or tertiary nature of the alkyl substituents so that it is possible to identify differing sites of attack in branched polyolefins. Preliminary results from the application of nitric oxide reactions to the analysis of polyethylene and polypropylene oxidized by γ -irradiation are used to illustrate the potential of the technique and a comparison made with other current methods.

INTRODUCTION

The oxidation of polyolefins is an important cause of the premature failure of articles made from these low cost polymers. The oxidation processes may be triggered by heat, light, mechanical action or high energy radiation. A detailed understanding of these oxidation reactions is important both in the development of stabilizers to protect against such oxidative degradation and

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in the use of selective degradation of polyolefins for specific applications. However, the oxidation of solid polymers is appreciably more complex than expected from the well established oxidation mechanisms for liquid hydrocarbons. This complexity stems from restricted mobility effects on the rates and mechanisms of the reactions and from the formation of domains of high local oxidation, surrounded by essentially non-oxidized resin. Nevertheless, significant advances in the identification of polymer oxidation products have been made by infrared (IR) studies^{1,2} and nuclear magnetic resonance (nmr) studies.^{3,4} In some cases, work has been concentrated on the identification of the complex mix of carbonyl species resulting from initial and subsequent free-radical reactions. Identification of the —OH species (alcohols and hydroperoxides) is much less well developed, and in several studies based solely on their combined IR absorption at $\sim 3400\text{ cm}^{-1}$, or on total peroxide determination (hydroperoxide + peracids + some dialkyl peroxides) by iodometry, or on liquid phase nmr after protracted solution times. Hydroperoxides are the dominant, initial product from polyolefin oxidation and their formation and decomposition largely dictate the course of oxidation.

As in liquid hydrocarbons, any tert—C—H sites in polyolefins are assumed to be much more reactive than secondary sites, which, in turn, are more reactive than primary.⁵ Attack may occur nevertheless at any of the three types of sites and result in —OOH or (eventually) —OH groups in all three locations. As part of a comprehensive study of polymer oxidation products we have now developed an analytical procedure which allows the separate quantification not only of alcohol and hydroperoxide groups, but also primary, secondary and tertiary species of each type. This procedure depends upon the reaction of oxidized sites with nitric oxide (NO), a small gas molecule which can presumably reach all sites in the solid polymer, previously accessible to O₂.

EXPERIMENTAL

Polyolefins studied included isotactic polypropylene (iPP, 30 μm film, Profax resin), films cast from a completely atactic PP [aPP, made by the hydrogenation of anionically polymerized poly(2-methylbutadiene)], a linear low density polyethylene (LLDPE, 100 μm film, DuPont Sclair resin) and a high density polyethylene (HDPE 25 μm film, Union Carbide resin). All commercial films were unoriented and were acetone extracted for 48 h to remove processing stabilizers. Films were oxidized in air by heat (forced air circulating oven at 100°C), light (2500 W xenon arc WeatherOmeter) and by γ -irradiation (AECL 220 Gammacell, 1.0 Mrad h⁻¹ dose rate).

For comparison purposes some model alkanes were oxidized by γ -irradiation. These alkanes included hexadecane (Aldrich) 1,3,5-trimethylcyclohexane, 2,4,6-trimethylheptane (both from ICN Biomedicals) and 2,6,10,14-tetramethylpentadecane (Eastman).

Oxidized films and liquids were characterized by Fourier Transform Infrared (FTIR) spectroscopy (Perkin-Elmer 1500) and iodometry.⁶ For film samples, IR interference ripple problems were minimized by Harrick's method.⁷ Oxidized polyolefins are unstable and can continue to oxidize thermally during storage at room temperature.⁸ To minimize this post-oxidation, oxidized samples were analyzed immediately, or stored at -15°C until analysis was possible. Peroxyl radicals and their reactions with NO were studied by electron spin resonance (esr) using a Varian E4 spectrometer at various temperatures.

Oxidized films and liquids and model compounds were exposed to NO in a simple all-glass flow system, designed so that O_2 could be completely removed by sweeping with a N_2 stream for ~ 5 min prior to NO (Matheson) admission. NO was passed for 1–2 min before isolating the samples in the NO atmosphere for various times. The NO was finally swept from the system with N_2 for 5 min.

For comparison with the IR spectra of NO-treated films, model nitrates and nitrites were examined. These included *n*-butyl and *n*-propyl nitrite (Aldrich), and nitrites from alcohol–NO reactions, together with nitrates from $\text{HNO}_3/\text{H}_2\text{SO}_4$ reaction with alcohols or NO reactions with hydroperoxides.^{9,10} Reagents used included tert-butyl hydroperoxide, tert-butanol, di-tert-butyl peroxide, isopropanol, 3-methylpentan-3-ol, undecan-1-ol (Aldrich), nonan-4-ol, 2,6,8-trimethylnonan-4-ol (Baker) and 1,1,3,3-tetramethyl-1-butyl hydroperoxide (Lucidol). In addition, NO reactions with films of model polymers containing known functional groups were examined by FTIR. These included poly(methyl methacrylate)(PMMA), a propylene/acrylic acid copolymer (Polysciences), an ethylene/carbon monoxide copolymer, Phenoxy (Union Carbide polymer from 2-hydroxypropylether and bisphenol A) and polyvinyl alcohol (Polysciences). Some oxidized films were NO exposed after iodometry which had converted $-\text{OOH}$ to $-\text{OH}$ groups, but also caused some extraction of oxidized species.

RESULTS

Although we have examined polyolefin films which were oxidized by exposure to ultraviolet or γ -irradiation and by heat, detailed data for only the γ -exposed LLDPE and isotactic PP (iPP) samples are shown here.

Fig. 1. Reactions of oxidized LLDPE. 20 Mrad γ -initiated oxidation. FTIR spectra generated by subtraction of the spectrum of the non-oxidized film. $\cdots$, as oxidized; $---$, oxidized then NO treated; $—$, oxidized then NO₂ treated.

LLDPE and HDPE displayed quantitatively the same γ -oxidation behaviour. Furthermore, both iPP and aPP showed qualitatively similar changes. The FTIR spectra of LLDPE and iPP oxidation products are shown in Figs 1 and 2. Chemical changes in film samples were clearly shown by spectral subtraction; that is, by subtracting as precisely as possible the stored spectrum of the original (non-oxidized) polymer film from that of the oxidized or treated film, using the dedicated FTIR computer. These spectra show the formation of the well established oxidation products: alcohols and/or hydroperoxide groups at $\sim 3400\text{ cm}^{-1}$, carboxyl species at $\sim 1715\text{ cm}^{-1}$

and (less visible) other —C—O—? species (alcohols, ethers, peroxides, etc.) at

$\sim 1170\text{ cm}^{-1}$.^{1,6} Total hydroperoxide yields were measured by iodometry and approximate total alcohol and hydroperoxide levels calculated from the 3400 cm^{-1} absorbance (IR extinction assumed $90\text{ litre mol}^{-1}\text{ cm}^{-1}$ for both types of hydrogen bonded —OH groups).

Exposure of the oxidized films to O₂-free NO produces the spectral changes shown in Figs 1 and 2. Several new bands are clearly visible and the 3400 cm^{-1} (—OH) absorption has disappeared. The NO reaction times required for complete reaction (constant intensity of new bands and complete 3400 cm^{-1} loss) varied quite widely. For γ -ray oxidized films, reaction was

Fig. 2. Reactions of oxidized iPP. 10 Mrad γ -initiated oxidation. FTIR spectra generated as in Fig. 1.

complete within ~ 16 h for thin films ($25\text{--}50\text{ }\mu\text{m}$) and about 30 h for thicker films (up to $150\text{ }\mu\text{m}$). Photo-oxidized PP and PE films required surprisingly long reaction times of up to 150 h for highly oxidized $150\text{ }\mu\text{m}$ films. The IR regions centered at $\sim 1635\text{ cm}^{-1}$ and $\sim 1290\text{ cm}^{-1}$ contain many bands useful for product identification. These regions are shown in greater detail in Figs 3 and 4.

Hydroperoxide and alcohol groups are reported to react with NO to produce organo-nitrates and nitrites.^{9,11} For comparison with the film products, the IR spectra of a series of model nitrates and nitrites were recorded. Major bands and their calculated extinction coefficients are listed in Table 1. Where available, absorption maxima agreed with literature values to within $3\text{--}4\text{ cm}^{-1}$.^{9,12} NO exposure of thin films of phenoxy and poly(vinyl alcohol) produced IR absorptions close to those found for the model secondary nitrites. The new absorptions in the NO exposed polyolefins are also listed in Table 1 for ease of comparison with the model compounds.

Some liquid alkanes were γ -irradiated after O_2 -saturation and then NO exposed. Hexadecane gave IR changes very similar to those observed with

TABLE 1
IR Data for Model Nitrates and Nitrites

Group	Model compound ^a	Absorbance maximum (cm ⁻¹) [Extinction coefficient, litre mole ⁻¹ cm ⁻¹]		
$\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{ONO}_2 \\ \\ \text{H} \end{array}$	CH ₃ (CH ₂) ₁₀ ONO ₂	1 642 [2 200]	1 279 [1 210]	860 [421]
$\begin{array}{c} \\ -\text{C}-\text{ONO}_2 \\ \\ \text{H} \end{array}$	2,6,8-(CH ₃) ₃ -4-nonyl nitrate	1 633 [1 933]	1 277 [660]	867 [544]
$\begin{array}{c} \\ -\text{C}-\text{ONO}_2 \\ \end{array}$	tert.-butyl nitrate	1 630 [422]	1 300 [260]	860 [140]
	1,1,3,3-tetramethyl-1-butyl nitrate	1 628 [420]	1 292 [408]	865 [140]
$\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{ONO} \\ \\ \text{H} \end{array}$	CH ₃ (CH ₂) ₃ ONO	1 657 [470]		780 [245]

$\begin{array}{c} \\ -\text{C}-\text{ONO} \\ \\ \text{H} \end{array}$	2,6,8—(CH ₃) ₃ —4-nonyl nitrite	1 648 [798]			778 [639]
$\begin{array}{c} \\ -\text{C}-\text{ONO} \\ \end{array}$	tert.-butyl nitrite	1 638 (780)			760 [652]
<i>Oxidized polymer + NO^b</i>					
Oxidized LLDPE		1 631 1 645 (wk)	1 276	870	778 (wk)
Oxidized LLDPE after iodometry		1 645 1 657 (wk)			778
Oxidized iPP		1 629	1 302 (sh) 1 290 1 278 (sh)	865	760 (wk) 778 (wk)
Oxidised iPP after iodometry		1 638 1 646 (sh) 1 653			760 778

^a As dilute solutions in hexane.

^b Abbreviations: wk—weak; sh—shoulder.

Fig. 3. NO reaction products from γ -oxidized LLDPE. 20 Mrad γ -initiated radiation. FTIR spectra generated as in Fig. 1. —, Oxidized then NO treated; ····, oxidized then NO treated after iodometry.

LLDPE, whereas 2,4,6-trimethylheptane and 2,6,10,14-tetramethylpentadecane both gave a group of absorptions quite similar to iPP (1293 dominant, weaker 1278 absorption and a shoulder or broadening at $\sim 1300\text{ cm}^{-1}$).

No reaction was detected between NO and model compounds including alkanes, di-*tert*-butyl peroxide, carboxylic acids (including the propylene/acrylic acid copolymer), esters (including PMMA) or ketones (including the ethylene-CO copolymer). Neither nitrous acid nor nitric acid was detected after NO treatment (distinctive strong absorptions at 794, 1266, 1695 cm^{-1} and 920, 1310, 1700 cm^{-1} , respectively).^{13,14}

The reaction of NO with *tert*-butyl hydroperoxide in hexane was examined as a readily available model of *tert*-hydroperoxide reactivity. FTIR showed that rapid reaction (complete loss of —OH absorptions in 1–2 min for 0.3 ml at 25°C) of dilute ($0.2\text{ mole litre}^{-1}$) solutions occurred to give an equimolar yield of the corresponding nitrate and nitrite. Undiluted hydroperoxide ($\sim 0.3\text{ ml}$) reacted much more slowly (15 h at 25°C) and gave a close-to-quantitative yield of nitrate, with only traces of nitrite. The reaction of NO with model alcohols gave quantitative yields of nitrites, but the reaction rate decreased in the sequence tertiary > secondary > primary and also decreased as the alcohol concentration increased.

Fig. 4. No reaction products from γ -oxidized iPP. 10 Mrad γ -initiated oxidation. FTIR spectra generated as in Fig. 1. —, Oxidized then NO treated; ····, oxidized then NO treated after iodometry.

Reactions of NO_2 with oxidized polyolefins were also investigated. However, more complex mixtures of products resulted than those formed with NO, together with large increases in the carbonyl region (Figs 1 and 2). This latter increase may indicate direct attack on the polyolefins, as well as extensive decomposition of the hydroperoxide group, rather than a clean reaction to give nitrates or nitrites, as reported by Pryor *et al.*¹⁵ A complex mix of products was formed even when pure hexane was NO_2 exposed. Consequently, NO_2 reactions are unsuitable as the basis for a useful method of oxidation product identification. The strong absorptions at ~ 1700 , ~ 1305 and 925 cm^{-1} visible after NO_2 exposure of oxidized PP and LLDPE (Figs 1 and 2) are consistent with the formation of nitric acid.²⁶

Because of the possible effect on the NO reaction of residual O_2 dissolved in the oxidized polyolefin films (by rapid formation of NO_2 , for example), some NO treatments were performed under high vacuum. Films were evacuated for ~ 15 h at 10^{-4} mm Hg prior to NO addition. Identical FTIR changes were found for these samples and similar samples treated in the N_2 -purged, flow system. Under vacuum, when the oxidized films were cooled in dry ice shortly after NO admission, pale yellow-green liquid droplets condensed. This was not NO_2 (white solid).

Heat exposure of NO-treated, oxidized polyolefins showed marked differences in product stability. After 24 h at 100°C , the 1290, 1302 and

760 cm^{-1} absorptions in the iPP film had virtually disappeared, whereas the $\sim 1278 \text{ cm}^{-1}$ and 778 peaks in iPP and LLDPE films were unchanged. A similar effect was observed when these films were exposed to the WeatherOmeter for 24 h.

DISCUSSION

Over 30 years ago, Tarte suggested that the IR spectra of the nitrite products from NO reactions can be used to discriminate primary, secondary and tertiary alcohols.¹¹ Similarly, the data of Shelton and Kopczewski indicated clear differences between the spectra of primary, secondary and tertiary nitrates formed from the corresponding hydroperoxides.⁹ These differences are evident from Table 1. However, the direct use of NO reactions to identify and quantify —OH species produced by polyolefin oxidation is complicated by the reported formation of equimolar mixtures of nitrates and nitrites from dilute solutions of hydroperoxides.⁹ Our data for NO with oxidized iPP (Figs 2 and 4) are consistent with destruction of all —OH groups (3400 cm^{-1} loss) and nitrate formation (1302, 1290, 1278 and 860 cm^{-1} absorption) yet little nitrite formation was observed (weak 760–780 cm^{-1} absorptions). This discrepancy between reaction of the dilute liquid model hydroperoxide and the polymer was resolved by a study of concentration effects on liquid phase reactions. At low concentrations of tert.-butyl hydroperoxide in hexane, equimolar nitrate and nitrite mixtures resulted as reported.⁹ When high concentrations of hydroperoxide (close to 100%) were used, only nitrate was detected by FTIR. In the polyolefins, oxidation is expected to occur in relatively small domains around initiation sites because of restricted motion of the free radicals.¹⁶ The formation of oxidized domains in a matrix of non-oxidized polymer is consistent with the detection of predominantly hydrogen bonded oxidation products. Consequently, NO reactions will occur in these regions of high local hydroperoxide concentration, and yield predominantly nitrate.

Shelton and Kopczewski have previously suggested a complex free-radical chain process to account for nitrate and nitrite formation, involving initially NO attack on the O—O bridge in the hydroperoxide.⁹ This is unlikely as di-tert.-butyl peroxide is not attacked, and our results at high hydroperoxide levels are consistent with the overall reaction (1). Reaction

(1b) has been observed to be favoured in condensed phases.¹⁷ Our detection of the pale yellow–green gas after NO reaction with oxidized polyolefins is consistent with the formation of HNO.¹⁸

Reaction (1b) was confirmed, and found to be extremely fast, by a combination of esr and FTIR spectroscopy. When iPP film is γ -oxidized at -78°C , only peroxy radicals ($\text{PPO}_2\cdot$) are detected by esr.¹⁹ At low temperatures ($\leq -40^{\circ}\text{C}$) these $\text{PPO}_2\cdot$ neither terminate nor propagate.¹⁹ However, when all O_2 was evacuated and NO introduced, a rapid decay of the $\text{PPO}_2\cdot$ population occurred at -58°C (50% loss in ~ 6 min for 400 torr of NO). After complete decay of the $\text{PPO}_2\cdot$ signal, examination of the film by FTIR showed only traces of carbonyl species, but clear secondary and tertiary nitrate absorptions (~ 1630 , 1294 and 1275 cm^{-1}). A reaction similar to that for hydroperoxides can be written for the slower attack of NO on alcohols (composite reaction (2)).

From Figs 1 and 3, the products of NO reaction with γ -oxidized LLDPE are exclusively secondary nitrate (1631 , 1276 , 870 cm^{-1} absorptions) and secondary nitrite (1645 and 778 cm^{-1}). Neither tertiary nor primary species were detected in appreciable quantities from γ -oxidation. This was confirmed by NO treatment of oxidized LLDPE film after hydroperoxide destruction by iodometry (hydroperoxide is converted to alcohol by this process). These samples showed the production of the strong secondary nitrite absorptions at 1645 and 778 cm^{-1} , with only low levels of primary nitrite at high oxidation levels (1657 and 780 cm^{-1} absorption). From the extinction coefficients in Table 1, alcohol and hydroperoxide levels in γ -oxidized LDPE can be quantified after conversion to nitrites and nitrates, respectively. After a 20 Mrad dose, NO reaction with LLDPE indicates 0.054 and $0.012\text{ mole kg}^{-1}$ of secondary —OOH and —OH. In comparison, iodometry on this sample indicated $0.050\text{ mole kg}^{-1}$ of —OOH and a total —OH yield (alcohol and hydroperoxide from the 3400 cm^{-1} absorption) of $0.073\text{ mole kg}^{-1}$, both values in good agreement with the NO values. Contrary to the expectation of equimolar yields of alcohol and ketone groups from the γ -oxidation of LLDPE, —OH yields were consistently only 1/7 of the ketone level.²⁰

The products from NO reactions with γ -oxidized iPP (Figs 2 and 4) indicate a more complex oxidation product mix than found in LLDPE. From Table 1, the groups of absorptions at 1629 , 1302 , 1290 and 865 cm^{-1} and at 1278 and 870 cm^{-1} are consistent with tertiary and secondary nitrates, respectively, produced from the corresponding hydroperoxides. The absence of a clear peak at $\sim 1642\text{ cm}^{-1}$ implies little primary products.

In iPP, the quantification of the $\sim 1302\text{ cm}^{-1}$ peak is complicated by the underlying 1305 cm^{-1} band of iPP itself. From spectral subtraction this band does increase slightly during oxidation, consistent with increased helical content as a result of chain scission.²¹ However, the aPP samples also clearly showed a $\sim 1300\text{ cm}^{-1}$ shoulder after oxidation and NO treatment, yet aPP is completely free of the 1305 cm^{-1} (isotactic) absorption.

The similar photo and thermal sensitivity of the species absorbing at 1302 and 1290 cm^{-1} in iPP implies that they are both tert.-nitrates. The observation of these two tert.-nitrate peaks in model compounds and from oxidized samples is obviously important although not easy to interpret. The $\sim 1302\text{ cm}^{-1}$ absorption was found from tert.-butyl nitrate and from NO-treated, oxidized 1,3,5-trimethylcyclohexane, 2,4,6-trimethylheptane and 2,6,10,14-tetramethylpentadecane as well as iPP and aPP. The second peak occurs at $1294\text{--}1290\text{ cm}^{-1}$ in iPP and aPP (depending on the degree of oxidation) and at $\sim 1292\text{ cm}^{-1}$ in the NO-treated 1,1,3,3-tetramethyl-1-butyl hydroperoxide, oxidized 2,4,6-trimethylheptane, and 2,6,10,14-tetramethylpentadecane.

The two tert.-nitrate absorptions do not stem from differences between isolated and α , γ , ε ... runs of nitrate groups, as expected from PP oxidation.²² This was shown by the identical nitrate absorption envelope from oxidized, then NO-treated, 2,4,6-trimethylheptane and 2,6,10,14-tetramethylpentadecane. The former should oxidize largely to a trihydroperoxide whereas the latter should give predominantly isolated —OOH groups.²³ The $\sim 1290\text{ cm}^{-1}$ peak from iPP may come from normal tert.-nitrate groups with long alkyl substituents whereas the $\sim 1302\text{ cm}^{-1}$ peak results from nitrate groups with adjacent unbranched substituents (at chain ends or next to other oxidation products). This was supported by the FTIR spectrum of the product from $\text{PPO}_2\cdot$ reaction with NO. After NO reaction at -58°C , a clear doublet was found at 1293 and 1276 cm^{-1} , but no trace of the 1300 cm^{-1} species. In addition, the 1276 cm^{-1} absorption was significantly larger than the 1293 cm^{-1} , consistent with the product ratios now depending on selective reactions other than $\text{PPO}_2\cdot$ selectivity of C—H attack, which controls the ratios of products from chain oxidations.

The weak 778 cm^{-1} and 760 cm^{-1} absorptions in Fig. 2 are consistent with secondary and tert.-nitrite from traces of secondary and tert.-alcohols. After —OOH conversion to —OH by iodometry (together with some extraction of low molecular weight scission products), γ -oxidized iPP films reacted with NO to give a strong doublet at 778 cm^{-1} and 760 cm^{-1} , with complete absence of the $1302/1290/1278$ trio (Fig. 4). In both cases, only traces of primary nitrite may be present (very weak ~ 1653 shoulder). The NO products shown in Fig. 2 indicate concentrations for total tert. —OOH of 0.13 mole/kg and for sec. —OOH of 0.03 mole/kg . This is in fair

agreement with the value of total —OOH by iodometry (0.20 mole/kg). Only $\sim 1 \times 10^{-2}$ mole/kg of tert.-alcohol was found from the nitrite absorption. This gives a total yield of all —OH species of 0.17 mole/kg from NO products, close to the level found by direct FTIR from the 3400 cm^{-1} absorption (~ 0.22 mole/kg).

The use of NO reactions indicated a much richer mix of oxidation products from photo- or thermally oxidized iPP and LLDPE films as compared to γ -oxidized samples. For iPP, photo-oxidation (xenon arc WeatherOmeter) mainly resulted in a lower final yield of secondary and tertiary —OOH species (detected as their nitrates) and a much higher yield of primary, secondary and tertiary alcohol groups (detected as nitrites), in comparison with γ -oxidation products. Similarly, the photo-oxidation of LLDPE films (both low and high density) gave low yields of secondary hydroperoxide and high secondary alcohol yields. Exposure to NO of films from iodometry (when all —OOH groups are converted to —OH) gave clear 1657 cm^{-1} absorptions which indicated the presence of some primary —OH, and hence primary —OOH in the original photo-oxidized LLDPE.

In both NO-treated, oxidized iPP and LLDPE, small but reproducible IR peaks were found at 1560 cm^{-1} , although long NO contact times (≥ 100 h) were required to reach a plateau level. In fact, this peak appeared even when non-oxidized films were NO treated. The 1560 cm^{-1} absorption was particularly evident after NO treatment of photo-oxidized LLDPE, and was accompanied by the loss of the 910 cm^{-1} absorption (vinyl unsaturation) produced during irradiation. Similar changes were found when model olefins were NO treated. The 1560 cm^{-1} absorption is attributed to the

formation of nitro-olefins ($\text{>C}=\text{C}-\text{NO}_2$), as reported by Brown for NO reaction with isobutylene.²⁴

It is important to compare the potential of the NO-reaction method for characterizing —OH and —OOH species with the previously used methods of liquid phase nmr, direct IR and other derivatization methods. High resolution nmr on hot solutions has allowed the identification and

quantification of secondary —COOH and —COH groups in oxidized

polyethylene.^{3,4} However, long scan times were required and also the instability of the hydroperoxide group(s) at the solution temperature (110°C for up to 20 h) is likely to be a major problem. Although high resolution nmr is claimed to be capable of detecting oxidation products down to ~ 0.03 mole/kg, this level is easily attained by FTIR with instrument times which are several orders of magnitude shorter. In addition, the reported identification of —OOH groups in PE oxidized at 160°C yet not in 60°C

oxidized samples is surprising.⁴ This again points to the possibility of decomposition reactions during the hot solution stage, distorting the results. No report has appeared on the application of the nmr technique to oxidized, isotactic PP where much higher solution temperatures are required as compared to PE and where a more complex mix of products is to be expected.

Lemaire *et al.* have proposed that —OOH groups at differing backbone sites in oxidized polyurethanes may be discriminated by IR, based upon small ($\pm 25\text{ cm}^{-1}$) changes in vague maxima on the broad, hydrogen-bonded —OH absorption at $\sim 3400\text{ cm}^{-1}$.²⁵ Similarly, Jelinski *et al.* have used the sharp (non-bonded) —OH absorption at 3550 cm^{-1} as well as the weak, broad $\sim 3400\text{ cm}^{-1}$ absorption to identify hydroperoxides in oxidized polyethylenes, but also (erroneously) attributed part of this latter absorption to carboxylic acid.⁴ However, we feel that these absorptions are unreliable for the precise identification and quantification of alcohols and hydroperoxides.

Some of the most thorough attempts at the identification of oxidation products in polyethylene by derivatization have been made by Rasmusen *et al.*² In their work, the IR peaks from the fluoro-ester formed by reaction with trifluoroacetic anhydride was used to identify alcohol groups in corona treated film. However, we have found that hydroperoxide groups also yield the same esters as do alcohols when oxidized polymer is treated with the fluoro-anhydride. The reaction of SO_2 has been suggested to offer a sensitive method for the estimation of —OOH groups.²⁶ We have recently reported on the unpredictable stoichiometry of this reaction.²⁷ Chemical derivatization is now being exploited to overcome the inherent low resolution of ESCA. It is interesting to note that gas-polymer reactions are also being promoted as the most reliable way to 'tag' functional groups and so avoid extraction or restructuring problems caused by liquid phase reactions.²⁸

CONCLUSIONS

The products from the reaction of NO with oxidized polyolefins provide an informative method for the identification and quantification of the complex mix of alcohol and hydroperoxide species. The method gives results comparable to iodometry for total —OOH, but discriminates tertiary from secondary and primary groups. Similarly, primary, secondary and tertiary alcohol groups may be quantified from a comparison of the IR bands after NO reactions. The sensitivity of the NO method is appreciably higher than that of direct IR analysis both because of the higher extinction coefficients for nitrates and nitrites (Table 1, *cf.* an extinction coefficient of ~ 90 litre

mole⁻¹ cm⁻¹ for all —OH groups) and because of the sharpness of these peaks as compared with the hydrogen bonded —OH and —OOH absorptions. Quantifications of the different nitrate products from iPP will require deconvolution of the overlapped peaks at 1305–1270 cm⁻¹ (Fig. 4). This may be possible by mathematical curve analysis procedures or by the use of the spectral subtraction procedure using the absorptions of pure model compounds or, for example, secondary nitrate absorption from LLDPE.

The most important immediate discoveries from the application of the NO method are the detection of appreciable secondary —OOH products in oxidized iPP and the low yields of alcohols, as compared with ketonic groups, in polyethylenes. The extent and significance of these facts are under active investigation.

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