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Investigation of Oxidative Degradation in Polymers Using ^{17}O NMR Spectroscopy

Todd M. Alam*, Mathew Celina, Roger A. Assink, , Roger L. Clough, Kenneth T. Gillen and David R. Wheeler

Sandia National Laboratories, Department of Aging and Reliability, Bulk Materials, Albuquerque, New Mexico 87185-1407

ABSTRACT: The thermal oxidation of pentacontane ($C_{50}H_{102}$), and of the homopolymer polyisoprene, has been investigated using ^{17}O NMR spectroscopy. By performing the oxidation using ^{17}O labeled O_2 gas, it is possible to easily identify degradation products, even at relatively low concentrations. It is demonstrated that details of the degradation mechanism can be obtained from analysis of the ^{17}O NMR spectra as a function of total oxidation. Pentacontane reveals the widest variety of reaction products, and exhibits changes in the relative product distributions with increasing O_2 consumption. At low levels of oxygen incorporation, peroxides are the major oxidation product, while at later stages of degradation these species are replaced by increasing concentrations of ketones, alcohols, carboxylic acids and esters. Analyzing the product distribution can help in identification of the different free-radical decomposition pathways of hydroperoxides, including recombination, proton abstraction and chain scission, as well as secondary reactions. The ^{17}O NMR spectra of thermally oxidized polyisoprene reveal fewer degradation functionalities, but exhibit an increased complexity in the type of observed degradation species due to structural features such as unsaturation and methyl branching. Alcohols and ethers formed from hydrogen abstraction and free radical termination

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* Author to whom correspondence should be addressed.

reactions are the dominant oxidation products. In polyisoprene, the formation of esters and carboxylic acids is relatively minor, distinctly different from the oxidation of pentacontane. An approximately linear increase in these degradation functionalities is observed with increasing oxidation levels. These results demonstrate the promise of ^{17}O NMR as a new technique for detailed investigation of oxidative polymer degradation.

Introduction

Understanding polymer aging and degradation is crucial for accurate prediction of polymer lifetime, durability and reliability. There continues to be extensive interest and research into the aging of polymer materials.[1] The elucidation of the chemical and physical mechanisms at the molecular level leading to material degradation is an important objective in achieving this goal. To probe the complex chemical changes that occur during polymer aging, a variety of analytical techniques have been used, including a number of spectroscopic studies such as ultraviolet (UV), infrared (IR), fluorescence, chemiluminescence, nuclear magnetic resonance (NMR) and mass spectrometry (MS).[1-3]

NMR spectroscopy has been used extensively to characterize polymer structure and morphology.[2-7] Molecular details about polymer aging have also been obtained using NMR spectroscopy, including ^{13}C NMR studies of thermal oxidation in polyethylene;[8] polypropylene[9] and poly(propylene oxide),[10] and irradiation damage in polyisobutylene,[11] polyethylene,[12,13] and polyisoprene.[14] ^{1}H studies of thermal degradation of polyisoprene[15] and polyethylene have also been reported.[16] One of the difficulties encountered in ^{13}C and ^{1}H NMR is the identification and quantification of the small signal arising from degradation species in the presence of native or unaged polymer signal. Recently we demonstrated that by using ^{17}O NMR and isotopic enrichment, the difficulty of distinguishing degradation species signal from the dominant unaged polymer signal can be eliminated, thus providing a powerful tool for the investigation of oxidative degradation in polymer systems.[17-19] In this paper, ^{17}O NMR spectroscopy is used to investigate the thermal oxidative aging of pentacontane ($C_{50}H_{102}$), a model long-chain alkane system, and the aging of the homopolymer polyisoprene.

Pentacontane was chosen for initial investigations into oxidative degradation using ^{17}O NMR because long chain alkanes have previously been used as a model of linear polymers such as polyethylene, and can provide insights into molecular structural changes accompanying polymer aging. The majority of previous investigations into the thermal oxidation and pyrolysis of alkanes have concentrated on the combustion of hydrocarbons at high temperatures (> 250 °C), or the formation of petrochemical intermediates by liquid phase oxidation. These reports have included detailed analysis of mechanisms and kinetic description that occur within the flame.[20-23] A series of investigations into the autoxidation of alkanes as models for lubricant degradation have also been reported, including investigations of *n*-octane (C_8H_{18}),[24] *n*-hexadecane ($C_{16}H_{34}$),[25-29] and squalene ($C_{30}H_{62}$).[30] ^{13}C NMR spectroscopy has been used to investigate thermal aging in *n*-hexadecane[28] and radiation damage in *n*-tetratetracontane ($C_{44}H_{90}$).[8]

The homopolymer polyisoprene also provides an excellent model polymer system for the investigation of thermooxidative aging because of its chemical simplicity and completely amorphous morphology. Due to the industrial importance and variety of different applications employing polyisoprene rubbers, there have been extensive investigations into the aging mechanisms of this material.[14,15,31-37]

Experimental Section

Oxidative Aging. The pentacontane ($C_{50}H_{102}$) and polyisoprene polymer samples were obtained from Aldrich (97 % cis 1,4-polymer, avg. $M_w = 800{,}000$), and used without further purification. The purity of the pentacontane sample was checked prior to aging studies using high resolution ^1H and ^{13}C NMR. Appropriate weights of the materials were placed in ampoules and filled with differing molar amounts of 82% enriched $^{17}O_2$ (Isotec). The samples were then aged at 125 °C for pentacontane and 95 °C for polyisoprene for varying amounts of time ranging from less than a day for pentacontane to 31 days for polyisoprene. The details of the oxidation are given in Table 1. During the experiment the O_2 pressure decreased from approximately 160 Torr to 100 Torr. This pressure drop per sample weight (~ 0.1 to 0.4 g) determined the extent of oxidation. The residual oxygen as well as CO and CO_2 formed during the degradation process were accurately determined with gas chromatography (GC) using a thermal conductivity detector (a technique commonly utilized for precise oxygen consumption measurements).[38] The concentration of O_2 in the sample (oxidation levels, see Table 1) was obtained by calculating the total amount of O_2 that reacted during the thermal exposure and correcting for the O_2 that was consumed in the formation of CO_2 and CO and partly in other O_2-containing volatiles (which is commonly on the order of ~ 10%). We did not correct for the formation of H_2O, which is difficult to quantify with any oxygen-uptake approach, but is also only a minor product representing a few percent of the total oxidation products as evident in Table 2. Under these assumptions the oxidation levels listed in Table 1 and 2 represent a maximum.

Considering the nature of the underlying free radical autooxidation reaction, the amount of O_2 incorporation is not a simple function of aging time, and is often dictated by trace impurities and catalyst. Due to this effect it proved difficult to produce samples with increasing O_2 incorporation levels by simply relying on variation of the oxidation time. Rather, the oxidation was terminated after varying times and then the conversion and oxidation products were determined (as shown in Table 1 and 2).

NMR Measurements. The ^1H and ^{13}C high resolution NMR spectra were obtained at resonant frequencies of 399.9 and 100.1 MHz, respectively on a Bruker DMX400 NMR spectrometer using a 5mm broadband probe and standard pulse sequences. To reduce the interference between ^1H decoupler modulation and the weak signals from degradation species in the ^{13}C NMR spectra, a combined bi-level adiabatic decoupling scheme[39] with a 48-step super-cycled WALTZ composite pulse decoupling sequence[40] was utilized.[41] Samples were referenced to residual signal of the deuterated solvent. Solid-state magic-angle spinning (MAS) ^{13}C NMR spectra were obtained at 100.1 MHz on a Bruker AMX 400 using a 4mm broadband MAS probe, referenced to the carbonyl signal of glycine ($\delta = 176.0$ ppm). Solid-state spectra were obtained using a single pulse with high-power proton decoupling and a spinning speed of 4 kHz.

^{17}O NMR Experimental Considerations. The oxygen isotope ^{17}O has a spin of $I = 5/2$ (therefore possessing a quadrupolar moment), and occurs at an extremely low natural abundance (0.037%). By using isotopically enriched (81%) O_2 gas as the oxidizer, the resulting degradation species are easily identified. The ^{17}O solution NMR spectra

reported here were obtained at a resonant frequency of 54.3 MHz on a Bruker DMX 400 spectrometer using a 5mm broadband probe. Spectra were obtained using 1K to 64K scans, a 10μs π/2 pulse and a 500 ms recycle delay. It was found that 500 ms was sufficient for complete spin-lattice relaxation in these samples. A standard single pulse sequence with Waltz-16 composite pulse ^{1}H decoupling was employed. Linear prediction of the first four to six points was utilized to reduce baseline roll resulting from acoustic ringing. ^{17}O NMR spectra were referenced to an external reference of natural abundance $H_2{}^{17}O$ ($\delta = 0.0$ ppm) at room temperature. For all experiments described, approximately 80 to 100 mg of thermally oxidized pentacontane was dissolved in 1 ml of toluene-d_8, while for aged polyisoprene 12 to 100 mg was dissolved in 1 ml of trichlorobenzene. Since the ^{17}O nucleus possesses a quadrupolar moment, the spin-spin relaxation (T_2) (which is inversely proportional to the line width) as well as the spin-lattice relaxation (T_1) are a direct function of the quadrupolar coupling constant $(e^2qQ/\hbar)$, asymmetry parameter η and the molecular correlation time τ_c

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{40}\frac{2I+3}{I^2(2I-1)}\left(1+\frac{\eta^2}{3}\right)\left(\frac{e^2qQ}{\hbar}\right)^2 \tau_c \qquad (1)$$

Since larger molecules exhibit slower correlation times, this proportionality to τ_c can produce dramatic increases of the observed line width. It has been shown that by increasing the temperature (and thereby reducing the molecular correlation time), the observed ^{17}O NMR line width in aged polymer samples can be greatly reduced.[19] The ^{17}O NMR spectra reported in this paper were all obtained at elevated temperatures to reduce the observed line width. All pentacontane spectra were recorded at 75°C, while the polyisoprene spectra were recorded at 125 °C.

Model Compounds. Model long-chain ketone, alcohol and ester compounds were synthesized to provide precise ^{17}O chemical shift information under the solvent and temperature conditions used during the present investigation. The model ketone compound ^{17}O-labeled hexatricontan-18-one was synthesized from the reaction of octadecyl magnesium bromide (generated from 1-bromooctadecane (Aldrich) in THF/Toluene (1/1) with magnesium under reflux) with stearonitrile (Aldrich, recrystallized) followed by hydrolysis with $H_2{}^{17}O$ and acid. Alternatively, the labeled ketone was also synthesized using unlabeled water, then labeled via formation of n-butylimine (excess n-butylamine, catalytic acid, 4Å molecular sieves) and hydrolysis with $H_2{}^{17}O$ and a full equivalent of acid. The resulting material was purified by chromatography on a short pad of silica gel using hot toluene, followed by recrystallization from hot hexane/toluene (10/1). Products from the two syntheses proved identical and were both used for the NMR analysis as well as starting material for the synthesis of the model long chain alcohol. ^{1}H $\delta = 1.56$ (m, 1H, CHO), $\delta = 1.34$ (66H, CH_2), $\delta = 0.91$ (t, 6H, CH_3), ^{13}C (Tol-d_8, 75 °C) $\delta = 208.4$ (CO), $\delta = 43.2$ (CH_2), $\delta = 34.8$ (CH_2), $\delta = 30.6$ ($27CH_2$), $\delta = 30.2$ (CH_2), $\delta = 28.7$ (CH_2), $\delta = 24.8$ (CH_2), $\delta = 22.4$ (CH_2), $\delta = 14.6$ ($2CH_3$), ^{17}O (Tol-d_8, 75 °C) $\delta = 567$ ($\Delta\nu = 895$ Hz).

The model alcohol compound, ^{17}O-labeled hexatricontan-18-ol was synthesized by the reduction of the ^{17}O labeled ketone with excess $LiAlH_4$ in refluxing tetrahydrofuran. The product was purified after hydrolysis and extraction by recrystallization from hot hexane/toluene (10/1). ^{1}H (Tol-d_8, 75 °C) $\delta = 3.45$ (m, 1H, C*H*), $\delta = 1.35$ (66H, C*H*$_2$), $\delta = 0.91$ (t, 6H, C*H*$_3$), ^{13}C (Tol-d_8, 75 °C) $\delta = 72.2$ (*C*H), $\delta = 38.6$ (*C*H$_2$), $\delta = 32.7$ (*C*H$_2$), 30.5 (30 *C*H$_2$), $\delta = 30.1$ (*C*H$_2$), $\delta = 26.5$ (*C*H$_2$), $\delta = 23.4$ (*C*H$_2$), $\delta = 14.5$ (2*C*H$_3$), ^{17}O (Tol-d_8, 75 °C) $\delta = 29$ ($\Delta\nu = 376$ Hz), ^{17}O (trichlorobenzene, 75 °C) $\delta = 27$ ($\Delta\nu = 518$ Hz).

The model carbonyl ^{17}O-labeled ester was synthesized from the ^{17}O-labeled ketone using classic Baeyer-Villiger oxidation.[42] The ketone was allowed to react with a slight excess of *m*-chloroperoxybenzoic acid (Aldrich) in methylene chloride. The crude reaction product was purified by washing with dilute aqueous base followed by recrystallization from hexane/toluene. While the oxidation affords two different products, octadecyl octadecanoate and heptadecyl nonadecanate (depending on which primary alkyl group migrates), these compounds are virtually indistinguishable and proved to be inseparable. Because the only source of ^{17}O is the labeled ketone, the Baeyer-Villiger reaction will produce an ester with labeled carbonyl exclusively.[42] ^{1}H (Tol-d_8, 75 °C) $\delta = 4.04$ (t, 2H, OC*H*$_2$), $\delta = 2.17$ (t, 2H, C*H*$_2$CO), $\delta = 1.62$ (m, 2H, C*H*$_2$CH$_3$), $\delta = 1.55$ (m, 2H, C*H*$_2$CH$_3$), $\delta = 1.34$ (58H, C*H*$_2$), $\delta = 0.91$ (t, 6H, C*H*$_3$), ^{13}C (Tol-d_8, 75 °C) $\delta = 173.1$ (*C*O), $\delta = 64.6$ (OCH$_2$), $\delta = 43.2$ (*C*H$_2$), $\delta = 32.8$ (*C*H$_2$), $\delta = 30.2$ (26*C*H$_2$), $\delta = 29.8$ (*C*H$_2$), $\delta = 26.9$ (*C*H$_2$), $\delta = 24.7$ (*C*H$_2$), $\delta = 23.5$ (*C*H$_2$), $\delta = 14.6$ (2*C*H$_3$), ^{17}O (Tol-d_8, 75 °C) $\delta = 359$ (C=O*) ($\Delta\nu = 610$ Hz).

Results and Discussion

Representative ^{17}O NMR spectra for thermally oxidized pentacontane ($C_{50}H_{102}$) dissolved in toluene-d_8 are shown in Figure 1 for different weight percent levels of O_2 incorporation: a) 0.18 %, b) 0.57%, c) 1.96% and d) 3.36%. All observable ^{17}O NMR resonances are a direct result of the oxidation process, since the original alkane samples contain no oxygen, and the $^{17}O_2$ gas used for the oxidation is the only source of the NMR active oxygen nucleus. Figure 1 clearly shows that a variety of degradation species have been formed during the oxidation process, with chemical shifts ranging from approximately $\delta = +600$ to -20 ppm. The production of CO_2 and CO per consumed O_2 ($CO_2/\Delta O_2$ and $CO/\Delta O_2$) along with the total O_2 incorporated are presented in Table 1 for the six samples of oxidized pentacontane investigated. The amounts of CO_2 and CO produced during the oxidation process (as measured by GC) show some variation, but are relatively independent on oxidation levels. For pentacontane the $CO_2/\Delta O_2$ ratio is on average smaller than that observed during oxidation of polyisoprene, while the $CO/\Delta O_2$ observed in pentacontane is slightly larger than that observed in polyisoprene.

In Figure 2, the ^{17}O NMR spectra for thermally oxidized polyisoprene are shown for different levels of O_2 incorporation: a) 0.08%, b) 0.29% c) 0.68% and d) 1.38%. As in pentacontane, the ^{17}O NMR spectrum of polyisoprene reveals resonances for a variety of different degradation species. Figure 1 and Figure 2 reveal that the spectra share ^{17}O NMR signatures for many of the same chemical species, but the upfield region of the polyisoprene samples is highly overlapped and complex. The richness of the ^{17}O NMR spectra in this upfield region of polyisoprene results from oxidation reactions and intermediates involving additional structural features (double bonds and methyl substituents). The identification of the different degradation species observed in the ^{17}O NMR spectra is detailed below.

The benefit of utilizing ^{17}O NMR spectra for investigation of oxidative degradation can be appreciated by comparing the ^{17}O NMR spectra in Figure 1 to the ^{13}C NMR spectra obtained on the identical samples. Figure 3a and 3c show the ^{13}C NMR solution spectrum for unaged pentacontane, while Figure 3b and 3d show the spectrum for oxidatively aged pentacontane (3.36%). Figure 3b and 3d were obtained from the same sample used to obtain the ^{17}O NMR spectrum in Figure 1d. Figures 3c and 3d show an expansion (x150) such that the new signals arising from degradation species are easily observable. Even at these relatively high oxidation levels the ^{13}C NMR signals are dominated by native or unaged polymer signal, with the degradation species having very low signal intensities which in many cases may overlap with the signals from unaged material. The possibility of spectral overlap with unaged signal, plus the large dynamic range in intensities observed, can lead to errors making accurate identification and quantification of degradation species difficult. In addition the ^{17}O NMR spectrum (Figure 1) clearly reveals the presence of ketones, carboxylic acids and esters in the oxidized pentacontane, while the ^{13}C NMR spectrum (Figure 3b) reveals no new resonances between $\delta = +220$ and $+170$ ppm corresponding to these degradation species. It has been suggested that the 10 s recycle time used to obtain the ^{13}C NMR spectra may be insufficient for complete relaxation of these carbonyl functionalities, demonstrating one of the experimental difficulties encountered in accurate quantification of ^{13}C results. The detection limit using ^{17}O NMR is demonstrated in Figure 2a, which is the NMR spectrum for thermally oxidized polyisoprene at a very low O_2 incorporation level of only

0.08%. This spectrum clearly shows that signals from different degradation species can still be observed and identified. Comparison of Figures 1,2 and 3 demonstrates the power of ^{17}O NMR for probing oxidative degradation and identifying degradation species at low concentrations.

Chemical Species Identification. Figures 1 and 2 show a wide variety of oxygen functionalities. The observed range of ^{17}O chemical shifts is relatively large at approximately 650 ppm. In general, there is a correlation between C-O π bond order and the observed chemical shift, with a downfield shift resulting from increased π bond order. The ^{17}O NMR resonances observed between $\delta = +650$ and +550 ppm can be assigned to ketones and aldehydes. The chemical shift for aldehydes ranges from approximately +600 to +500 ppm, while the range for acyclic and cyclic aliphatic ketones is slightly smaller ranging from +580 to +490 ppm.[43] Heterocyclic ketones and quinones have a considerably larger ^{17}O chemical shift extending from $\delta = +600$ to +350 ppm. Due to the large range of observed ketone chemical shifts there is partial overlap with resonances from the carbonyl oxygen of esters ($\delta = +400$ to +275 ppm), but the contributions of the overlapping ketone and ester resonances can be separated as detailed below in the ester species identification section. It should be noted that the cyclic and acyclic aliphatic ketones have a very distinct chemical shift range compared to that observed for the carbonyl resonance of esters, and these are the major type of ketone produced during the oxidation of pentacontane or polyisoprene. The ^{17}O labeled ketone model compound, hexatricontan-18-one, representing a carbonyl oxygen in the center of an aliphatic chain, gave a resonance at $\delta = 567$ ppm, which matches with the major resonance in this range for both the petancontane and polyisoprene sample. Distinguishing between aldehydes and ketones is not possible with ^{17}O NMR, but ^{1}H NMR provides a unique signature for aldehydes in the $\delta = 7 - 9$ ppm range. ^{1}H NMR spectra of the aged pentacontane and polyisoprene samples show that aldehydes have a relatively low concentration and represent less than < 1% of the total oxidized species. The two overlapping resonances in this region for the pentacontane spectra, and the multiple resonances in the oxidized polyisoprene spectra, suggest that variations in the carbonyl environments of the ketones/aldehydes are present. A variety of substituent-induced chemical shift effects (SCS) have been shown to play a distinctive role in the observed ^{17}O chemical shift. For aliphatic ketones and aldehydes the effects of α,β-unsaturation are known to be rather small. The SCS effects of α or β OH or C=O substitution have not been reported for ketones, but the β-OH SCS effect in alcohols was shown to be quite large[44] and may produce a similar change in the ^{17}O NMR chemical shifts for ketones. Because of these observations, the signals between $\delta = +650$ and + 550 ppm will be combined for analysis and are considered to result from predominantly ketone species. The resonances between $\delta = +400$ and 275 ppm involve both ketones and the carbonyl oxygen of esters, but are separated as described below. The ^{17}O NMR signal for the carbonyl oxygen in anhydrides would be observed between $\delta = +410$ and +370 ppm with the central anhydride oxygen being observed from $\delta = + 300$ to +260 ppm, with a 2:1 ratio between carbonyl and central oxygen signal. In oxidatively aged pentacontane and polyisoprene samples there are no resonances that are consistent with the presence of anhydrides, and therefore they are not indicated to be a significant oxidation product under the conditions investigated here.

The carbonyl in lactones and esters would be observed between δ = + 400 and +275 ppm with the ester C-O-C oxygen being observed between +200 and +150 ppm. The ^{17}O NMR spectra for both the aged pentacontane and polyisoprene have resonances in these regions. The 1:1 correspondence between the carbonyl oxygen and the C-O-C oxygen allows the ester contribution to the δ +400 to 275 ppm region to be separated out from the ketone contribution to the same region, while the remaining integrated intensity in this region (~ 0 to 4%) is assigned to heterocyclic ketones or quinines. The model ^{17}O labeled esters, octadecyl octadecanoate and heptadecyl nonadecanate (carbonyl oxygen only), representing a long chain ester species, showed a single ^{17}O NMR resonance at δ = + 359 ppm. This resonance corresponds to the downfield shoulder of the major ester/lactone resonance observed in pentacontane. Very little ester was observed in the oxidized polyisoprene samples. The concentration of esters/lactones will be combined in our subsequent data analysis, and will generically be referred to as ester functionalities.

Carboxylic acids, peroxides and hydroperoxides are all expected to have ^{17}O NMR signals that occur between δ = + 270 and + 200 ppm. In the oxidized pentacontane samples with high O_2 incorporation, only a single resonance at approximately δ = + 260 to +263 ppm was observed. At very low O_2 incorporation levels (0.57 % and 0.18 %) multiple resonances are observed at δ = + 263, +238 and + 212 ppm (See Figure 1a and Figure 4a). In oxidized pentacontane these resonances represent a major degradation species (Table 2), and therefore it is important to distinguish between carboxylic acid and peroxide oxygen functionalities. To accomplish this identification, a series of chemical modifications to the aged samples were performed. As an example, in Figure 4 the ^{17}O NMR spectra for (a) oxidized pentacontane (0.18%), (b) following treatment with dimethylsulfide $(CH_3)_2S$ and (c) followed by subsequent treatment with lithium aluminum hydride (LAH) are presented. The $(CH_3)_2S$ reacts preferentially with peroxides and hydroperoxides converting them to alcohols, while the LAH reaction is non-selective, converting all remaining carbonyl oxygens to alcohols. An expansion of the alcohol/ether region in the ^{17}O NMR spectra is also shown for the untreated oxidized pentacontane (Figure 4d), and following treatment with $(CH_3)_2S$ (Figure 4e). The difference spectra is shown in Figure 4f.

Figure 4a-c shows that the two major resonances at $\delta = +238$ and $+ 212$ ppm in oxidized pentacontane should be assigned as hydroperoxides/peroxides since these are effectively eliminated with the addition of $(CH_3)_2S$ (Figure 4b). Following reaction with $(CH_3)_2S$ three new alcohol resonances are observed at $\delta = +13, +25$ and $+33$ ppm, with a relative intensity ratio of 73:26:1 (Figure 4f). All of these shifts are consistent with secondary (2°) alcohols, clearly demonstrating that the hydroperoxides/peroxides were predominantly 2° species in this long chain alkane. The ^{17}O NMR resonance at $\delta = +25$ ppm is assigned to a simple aliphatic 2° alcohol,[43] and is consistent with the model alcohol compound hexatricontan-18-ol (see discussion of alcohol chemical shifts below). The minor species at $\delta = +33$ ppm is consistent with a 2° alcohol near a chain end.[43,45] The major resonance at $\delta = + 13$ ppm is upfield from the range typically expected for a simple 2° alcohols, but is consistent with a 2° alcohol experiencing oxygen-SCS effects such as upfield γ-SCS(OH) effect reported in diols.[44] The selective appearance of the $\delta = +13$ ppm resonance following the reaction with $(CH_3)_2S$ (Figure 4e), shows that the peroxides producing these alcohols are converted to other degradation functionalities under oxidative conditions. Note this alcohol species is not present in high concentrations in the untreated oxidized pentacontane sample (Figure 4d). Whether the differential reactivity is governed by nearest neighbor substituent effects, or has another explanation, was not determined.

The resonance at $\delta = +263$ ppm is assigned to a carboxylic acid, consistent with its disappearance upon addition of LAH (Figure 4c). The slight broadening of the carboxylic acid observed in Figure 4b may reflect exchange effects due to the alcohol and trace amounts of water produced by the reduction of the hydroperoxides. The small resonance observed at approximately $\delta = +198$ ppm was not affected by the addition of $(CH_3)_2S$ and was assigned to the C-O-C oxygen of an ester as noted above. For the oxidized polyisoprene samples, no significant ^{17}O NMR resonances corresponding to hydroperoxides ($\delta = +238$ to $+210$ ppm) were observed for the entire range of O_2 concentrations investigated.

Both the observation and the relative stability of the hydroperoxides or peroxides in the low-oxygen-concentration pentacontane samples were unexpected, since the peroxides should quickly decompose during the oxidation experiment as well as the NMR experiment. The ^{17}O NMR for the pentacontane sample (0.18%) dissolved in toluene-d_8 at 75 °C remained unchanged for up to 48 hours at these elevated temperatures. It has been argued that in solution, at these temperatures, the hydroperoxide/peroxide species would react to form secondary oxidation products since they are known to be thermally labile.[46-48] The disappearance of the peroxides with increasing values of O_2 incorporation and the lack of significant ^{17}O NMR peroxide signal in the polyisoprene samples may result from auto catalytic reactions at the 95 -125 °C temperatures used for aging. It has been suggested[48] that the high temperatures utilized in the ^{17}O NMR measurement (to reduce line width), may accelerate or induce the reaction of hydroperoxides species that may have existed in the sample immediately following the oxidation exposure. To address this concern, room temperature ^{13}C MAS experiments were performed on the solid oxidized pentacontane material (not shown). In addition, high-resolution ^{13}C experiments of pentacontane and polyisoprene dissolved in toluene-d_8 (at room temperature) were performed to investigate the presence of peroxide species (which should show a distinct resonance at $\delta(^{13}C) \sim 85$ ppm) prior to heating the sample. Both of these ^{13}C NMR experiments revealed no observable signal from peroxide species (except at the low oxygen concentrations of 0.18% and 0.57%), implying that significant concentrations of hydroperoxide species are not present in the thermally oxidized polyisoprene or pentacontane samples at high oxygen incorporation amounts.

We were also concerned that the use of high solution temperatures during the ^{17}O NMR experiments could produce or accelerate secondary reactions changing the distribution of products observed. The observation of invariant product distributions between initial, short time NMR experiments (~5 minutes), and the product distribution of longer overnight accumulations, supports the argument that these reactions are very rapid or that significant changes or additional reactions are not occurring in these samples due to elevated solution temperatures used during the ^{17}O NMR experiments.

The ^{17}O NMR signal for saturated and unsaturated ethers (and epoxides) would be observed between $\delta = +150$ to -50 ppm, while alcohols appear between $\delta = +80$ and -50 ppm. The ^{17}O NMR chemical shifts for saturated alcohols have been reported, ranging from $\delta = -3$ to $+10$ ppm for primary (1°) alcohols, $\delta = +25$ to $+40$ ppm for secondary (2°) alcohols, and from $\delta = +50$ to $+70$ ppm for tertiary alcohols (3°).[45,49,50] The SCS effect of β,γ-unsaturation in alcohols has been reported to be only + 3 to + 5 ppm, while γ,δ-unsaturation is smaller ranging from -0.2 to + 2 ppm.[45] Simple long chain unbranched saturated ethers would be observed between δ = 0 and -50 ppm. Due to the large SCS effect for alkoxy and methyl substituents, β-branched and β-alkoxy substituted aliphatic ethers will have ^{17}O NMR chemical shifts between δ + 60 and 0 ppm. SCS effects for unsaturation also result in the ^{17}O NMR chemical shifts of α,β-unsaturated ethers being observed between δ + 150 and + 100 ppm.

Figure 1 shows that the ^{17}O NMR spectra for the thermally oxidized pentacontane samples are rather simple for this chemical shift region, dominated by a single resonance at δ = + 29 ppm. The dominant resonance is assigned to a long chain 2° alcohol, in agreement with the ^{17}O-labelled model compound, hexatricontan-18-ol, that exhibits a single resonance at δ = + 29.5 ppm in toluene-d_8 at 75 °C. Only a very small concentration of 3° alcohols is observed, consistent with oxidation of unbranched alkane chains. There is a small amount of 1° alcohol or methyl substituted or branched saturated ether produced (especially at higher O_2 incorporation levels) which may arise from abstraction reactions involving the terminal carbon of the hydrocarbon chain (reaction of an alkoxy radical) or from chain cleavage reactions (see below). No significant amounts of unbranched aliphatic ethers or α,β-unsaturated aliphatic ethers are produced during the degradation of pentacontane, since there is no signal intensity in these spectral regions. Because there is overlap between the ^{17}O chemical shifts of alcohols and saturated aliphatic ethers, the concentration of degradation species containing these oxygen functionalities will be combined and referred to collectively as alcohols/ethers.

The ^{17}O NMR spectra of aged polyisoprene samples in Figure 2 reveal multiple overlapping resonances in this upfield chemical shift region, making absolute assignments very difficult. In the spectra of oxidized polyisoprene the alcohol/saturated ether region can be deconvoluted into four major overlapping resonances at $\delta = +49$, $+38$, $+27$ and $+16$ ppm, with the downfield species increasing in concentration at higher O_2 incorporation levels. This large observed variation in the ^{17}O chemical shifts suggests that substituents and different degrees of unsaturation are present in the polyisoprene alcohol and ether degradation species produced, giving rise to multiple and overlapping signals. The resonance at $\delta = +27$ ppm is consistent with a long chain unsubstituted 2° alcohol (see model compound above) while the resonance at $\delta = +38$ ppm arises from 2° alcohols containing α-methyl substitutions[49] or β,γ-unsaturation.[45] The resonance at $\delta = +16$ ppm is consistent with an α-methyl substituted ether[49], while the $\delta = +49$ ppm resonance could result from either an α- or β-methyl substituted ether or a 3° alcohol.[49] The ^{17}O NMR spectra of oxidized polyisoprene also reveal a major resonance at $\delta = +118$ ppm, which indicates the formation of an α,β-unsaturated ether,[49] consistent with recombination of radicals that are in the β-position with respect to unsaturation. For the analysis below, the following assumptions and assignments will be made. The signal intensity between $\delta = +100$ ppm and -50 ppm will be attributed to alcohols and saturated ethers, while the resonances between $\delta = +150$ and $+100$ ppm result from α,β-unsaturated ethers.[49]

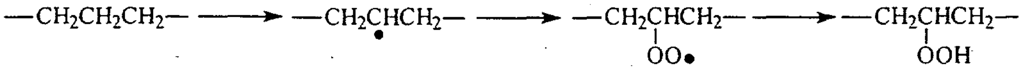
The ^{17}O chemical shift of undiluted or natural abundance water is observed at $\delta = 0.0$ ppm at room temperature, and is the external chemical shift standard for ^{17}O NMR.

Hydrogen bonding effects have been shown to produce major shifts in alcohol and ketone resonances, with the shift of the water resonance being documented to vary greatly in a variety of solvents.[19,51-53] The assignments of the water resonance, in both the thermally oxidized pentacontane and polyisoprene ^{17}O NMR spectra, were obtained by adding small amounts of labeled water to the aged samples and observing the corresponding increase in this signal intensity of the water resonance. These spiking experiments, in addition to independent investigations of solvent effects on the ^{17}O NMR shift of water in toluene-d_8 and trichlorobenzene, allowed the assignment of trace water to the resonance at $\delta = -13$ ppm in toluene-d_8 (75 °C) and $\delta = -16$ ppm in trichlorobenzene (125 °C). No appreciable amounts of water were observed in the ^{17}O NMR spectra of thermally oxidized pentacontane (Table 2), while spectra of aged polyisoprene revealed that water comprises up to 11 % of the oxygenated degradation products (Table 2). The variation in the water concentration observed for oxidized polyisoprene results from differences in the sample storage history.

Pentacontane Thermal Oxidation. Figure 5 displays the concentration of oxygen-containing functional groups for pentacontane as a function of oxidation. In Table 2 the relative percentage of the various oxygen functional groups as a function of total oxygen incorporation are presented. For thermally oxidized pentacontane only significant amounts of the following five major functional groups were observed and analyzed: ketones, esters, carboxylic acids, peroxides and alcohols/ethers (primarily 2° alcohol). The concentration of water and unsaturated ether functionalities in oxidized pentacontane are extremely small and were not considered further.

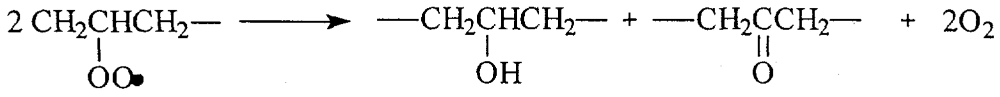
From inspection of Figure 5 there are several important observations that can be made. The first observation is that the total concentration of four of the five major functional groups increases with increasing oxygen consumption. The exception to this trend is the concentration of peroxides, which is the major product observed at an O_2 incorporation level of 0.18 %, and which decreases to undetectable levels with increasing O_2 incorporation. A very small amount of peroxides (~1%) is still observed at 0.57% O_2 incorporation (See Table 2). It is interesting to note that while the peroxides are by far the most important product for the 0.18% sample, there are also higher oxidation products present. These products include mainly ketones, acids and some alcohols, but also trace H_2O and CO_2 (which was detected as a volatile). Mechanistically this implies that higher oxidation products can be formed essentially from the onset of the oxidative aging, an important result that has often been difficult to demonstrate using less sensitive techniques on weakly oxidized samples. Ketones (and aldehydes) as well as alcohols and ethers are the dominant species formed during the thermal oxidation of pentacontane. They show a slightly non-linear concentration variation with increasing oxidation. The ester and carboxylic acid concentrations initially lag, then begin to increase at oxygen incorporation levels greater than ~ 1%. The ester and carboxylic acid functionalities contain two oxygens per functional group, and have been appropriately scaled to reflect the concentration of the functional group.

From previous oxidation investigations of long chain alkanes and polymers, the first step in the oxidation process is normally the formation of hydroperoxides (eqn 2).



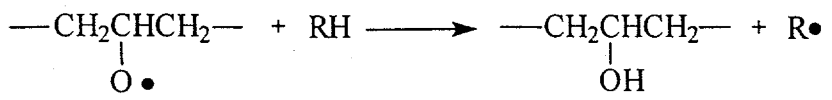
$$—CH_2CH_2CH_2— \longrightarrow —CH_2\underset{\bullet}{C}HCH_2— \longrightarrow —CH_2\underset{OO\bullet}{\underset{|}{C}}HCH_2— \longrightarrow —CH_2\underset{OOH}{\underset{|}{C}}HCH_2— \qquad (2)$$

From Figures 1d and 4a-c the formation of peroxides in pentacontane is confirmed; this is the dominant species at the very lowest O_2 incorporation level, 0.18 % (see Table 2). The disappearance of the alkyl hydroperoxides via free radical decomposition leading to new radical initiation will create the remainder of the secondary degradation species observed in this ^{17}O NMR investigation. It has been postulated that in simple alkanes, one mechanism for the formation of ketones and alcohols can be a bimolecular termination reaction of alkyl peroxyradicals[26,54] (eqn 3)



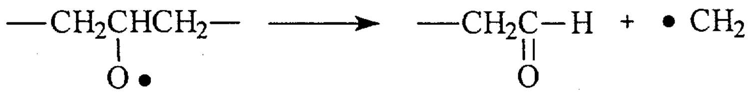
$$2\,CH_2\underset{OO\bullet}{\underset{|}{C}}HCH_2{-} \longrightarrow {-}CH_2\underset{OH}{\underset{|}{C}}HCH_2{-} + {-}CH_2\underset{O}{\underset{\|}{C}}CH_2{-} + 2O_2 \qquad (3)$$

Tertiary peroxide radicals cannot undergo bimolecular termination via this mechanism; alternative multi-step mechanisms have been proposed that still produce alcohols and ketones for tertiary radicals.[55] If the termination shown in eqn 3 were the only reaction, the concentration of ketones and alcohols would be equal. Chain scission via a cyclic peroxide intermediate has also been forwarded as a mechanism for the formation of ketones. Alkoxy radicals, formed from a homolysis reaction of the corresponding hydroperoxides,[8,24,26,29] may also yield secondary alcohols (eqn 4a) or aldehydes (eqn 4b).



$$-\mathrm{CH_2}\underset{\mathrm{O}\bullet}{\underset{|}{\mathrm{C}}}\mathrm{HCH_2}- + \mathrm{RH} \longrightarrow -\mathrm{CH_2}\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\mathrm{HCH_2}- + \mathrm{R}\bullet$$

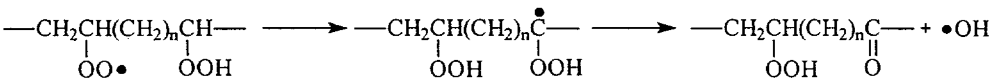
(4a)



$$-\mathrm{CH_2}\underset{\mathrm{O}\bullet}{\underset{|}{\mathrm{C}}}\mathrm{HCH_2}- \longrightarrow -\mathrm{CH_2}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{H} + \bullet\,\mathrm{CH_2}$$

(4b)

It has been argued that ketones can also be formed from intramolecular hydrogen abstraction by peroxy radicals to form intermediate hydroperoxyalkyl radicals (eqn 5).



$$-\mathrm{CH_2}\underset{\mathrm{OO}\bullet}{\underset{|}{\mathrm{C}}}\mathrm{H(CH_2)_n}\underset{\mathrm{OOH}}{\underset{|}{\mathrm{C}}}\mathrm{H}- \longrightarrow -\mathrm{CH_2}\underset{\mathrm{OOH}}{\underset{|}{\mathrm{C}}}\mathrm{H(CH_2)_n}\overset{\bullet}{\underset{\mathrm{OOH}}{\underset{|}{\mathrm{C}}}}- \longrightarrow -\mathrm{CH_2}\underset{\mathrm{OOH}}{\underset{|}{\mathrm{C}}}\mathrm{H(CH_2)_n}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}- + \bullet\mathrm{OH}$$

(5)

A variety of different mechanisms for the production of alcohols and ketones have been suggested for the oxidation of alkanes. Investigation of oxidation in *n*-hexadecane indicated that the bimolecular reaction (eqn 3) was the primary mechanism for the oxidative processes,[25,26] with the extra alcohol produced by simple intermolecular abstraction reactions (eqn 4a). For the thermal oxidation of pentacontane reported here, the almost equal concentrations of alcohol and ketone degradation species through ~ 1.0 % total O_2 incorporation is consistent with the bimolecular termination reaction (eqn 3) and is similar to that observed in *n*-hexadecane. At O_2 incorporation levels above ~ 1.0 % the change in the relative concentration ratio of ketone to alcohol degradation species (see Fig. 5) suggests that there are additional ketone-forming reactions and/or that the alcohol is being consumed by secondary reactions. It is possible that a combination of various secondary reactions (as discussed below) may account for the observed concentration profiles.

The delayed appearance or slower production of esters and carboxylic acids may suggest that these species were not derived directly from alkyl hydroperoxides, but rather result from subsequent secondary oxidation reactions. Similar arguments have been made for oxidative production of esters and acids in *n*-hexadecane.[25-29] One possible mechanism involves the formation of carboxylic acids from the direct oxidation of aldehydes. The aldehydes may be produced from the β-scission of alkoxy radicals (eqn 4b), or through α,γ-cleavage of hydroperoxy ketones.[25,26,29]

As noted in the chemical identification section, there are no appreciable concentrations of aldehydes observed in the thermally oxidized pentacontane sample. This could be explained by the rapid oxidation of aldehydes to carboxylic acids at high oxygen concentrations as suggested by Jensen et al. for the oxidation of hexadecane.[25] While this explanation seems quite pausible, the two major carbonyl resonances in the ketone/aldehyde chemical shift range for oxidized pentacontane ($\delta \sim 574$ and 562 ppm) have relative concentration ratios that remain unchanged with increasing oxygen incorporation. This observation, in addition to the delayed appearance of a carboxylic acid resonance that increases with oxygen incorporation levels, suggests that either aldehydes do not play a significant role in the oxidation of pentacontane or that the aldehydes possess a very short life time before they are converted to carboxylic acids. Garcia-Ochoa et al. [24] have also modeled the oxidation of octane using a direct ketone oxidation to form carboxylic acids. If a similar mechanism were present in the thermal oxidation of pentacontane, the ketone concentration would be expected to diminish due to the formation of carboxylic acids.

In the thermal oxidation of pentacontane the concentration of esters is approximately equal to the concentration of carboxylic acids produced. The mechanisms leading to the formation of esters are poorly understood. In general they are thought to result from the reaction of carboxylic acids and 2° alcohols,[8,27,29] but they may also involve fragment migration in peroxide radicals.[56] Early investigations of oxidation of *n*-dodecane noted the formation of esters very early in the oxidation process prior to formation of significant amounts of carboxylic acids, [57] while the thermal degradation of polyethylene[8] revealed the formation of only minor amounts of esters. Different possible mechanisms have been proposed including rearrangement of an α-hydroxyketone, the reaction of a peracid with a ketone, and the reaction of an alkoxy free radical with a gem-hydroperoxyalkyl free radical.[57] While the ^{17}O NMR data presented here reveal the production of significant concentrations of esters, details into the mechanism were not obtained.

The formation of O-heterocycle ethers during the oxidative degradation can also be addressed by analysis of the ^{17}O NMR spectra. A variety of different O-heteorcycles may result from the radical isomerization of the alkylperoxides.[20] The small resonance observed at $\delta = +6$ ppm in the 1.96 and 3.36 % O_2 pentacontane sample could result from a 6 membered O-heterocycle or could be assigned to a simple 1° alcohol (a conclusive assignment was not obtained). Signals corresponding to 3,4 and 5 membered O-heterocycles in oxidized pentacontane were not observed experimentally. Because this ^{17}O NMR signal represents a very small contribution of approximately 0.8% of the total oxygen signal, it is clear that the formation of the O-heterocycles is not a dominant product in the oxidation of pentacontane.

Polyisoprene Thermal Oxidation. The variation of concentrations for oxygen-containing functional groups produced in thermally oxidized polyisoprene for different amounts of total oxygen incorporation is shown in Figure 6 and in Table 2. For polyisoprene the dominant functional groups observed were alcohols/ethers, α,β-unsaturated ethers, and ketones, along with smaller concentrations of water. This distribution of degradation species is significantly different from that observed in the oxidation of pentacontane, given that the dominant pathway in polyisoprene is the formation of alcohols and ethers. In polyisoprene the formation of carboxylic acids and esters during degradation is not an important degradation mechanism, in contrast to the results for oxidized pentacontane. In thermally oxidized polyisoprene (Figure 6), the concentration of alcohol/ethers, ketones, and α,β-unsaturated ethers shows a steady, approximately linear increase with oxidation level. Even under oxidative conditions where there is complete O_2 consumption by the polyisoprene sample (see the 5.31% entries in Table 2) the relative concentrations of the different oxidation products remains very similar.

Similar to the discussion of thermal oxidation of pentacontane, the degradation species of thermally oxidized polyisoprene observed in the ^{17}O NMR experiments are expected to result from the reactions of the initially formed peroxide species (eqn 2). The high concentration of alcohols would suggest that hydrogen abstraction by alkoxy radicals is a primary mechanism (eqn. 4a). In addition, the postulated bimolecular termination reaction of peroxy radicals (eqn 3) is not consistent with the high alcohol concentration and the lower ketone concentration. The formation of significant concentrations of both saturated and unsaturated ethers, is consistent with alkoxy radical reactions involving both addition to double bonds, and recombination with allylic radicals.

The degradation product distributions observed in this ^{17}O NMR investigation of polyisoprene differ from those reported in high temperature degradation studies. Investigation of the oxidative pyrolysis of polyisoprene at 268 to 340 °C by Chien and Kiang[31] identified 14 different degradation products, with ketones and aldehydes being the dominant species. Morand[32] investigated the oxidation of polyisoprene in air at 100 °C and reported the identification of 26 different volatile species, with vinyl ketones and aldehydes being the primary products. They postulated that these species were produced by the scission of the main polyisoprene chain.[33-35] An explanation for the observed differences between the present study and the Morand study is that ^{17}O NMR provides a measure of the non-volatile degradation species remaining in the polymer sample, whereas Morand measured out-gassing products. The latter represent only one segment of the oxidation chemistry, primarily scission fragments of chain-end radical intermediates. In the case of the Chien and Kiang study,[31] it is likely that oxidation mechanisms at such high temperatures differ from the reaction pathways operative under conditions of long-term aging utilized here.

Conclusions

The use of ^{17}O NMR to investigate thermal oxidation in pentacontane and polyisoprene has been presented. These experiments show a variety of different oxidation products in both polymers. Using ^{17}O NMR, the concentration of different oxygen-containing species produced as a function of total oxygen incorporation was determined for these two materials. These ^{17}O NMR results illustrate that the preferred degradation pathway is significantly different for pentacontane and polyisoprene under similar oxidative degradation exposure conditions. In the case of the long chain alkane pentacontane, the degradation is dominated by the formation of ketones and 2^{o} alcohols, following initial production of hydroperoxides and peroxide species. In contrast the thermal oxidative degradation of the homopolymer polyisoprene predominantly produces a mixture of alcohols and ethers likely resulting from reactions of alkoxy and alkyl radicals.

These investigations demonstrate the potential of using ^{17}O NMR to probe oxidative degradation in polymer systems. The ^{17}O NMR spectra in these isotopically-labeled degradation experiments allow identification of oxidation products unencumbered by background signals from the starting (unaged) polymer. Differences in the degradation mechanisms can be obtained from simple analysis of the ^{17}O NMR spectra. Further structural elucidation can be achieved by ^{17}O NMR analysis subsequent to chemical modification of the oxidized sample. Unlike IR spectroscopy, ^{17}O NMR also allows direct quantification of the relative amounts of all the oxidation products formed, since the signal response of the different oxidation species is the same. The examples presented here regard thermal oxidation, but it should be noted that there are many additional possibilities for future ^{17}O NMR investigations including degradation via hydrolysis, or reactions involving other oxygen containing chemical species. The use of ^{17}O NMR to probe degradation of polymer systems under a variety of different environmental conditions is presently being pursued.

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Table 1. Oxidative Aging Conditions for Pentacontane and Polyisoprene Samples

Sample	Time (hours)	$CO_2/\Delta O_2$[a]	$CO/\Delta O_2$[b]	$\%O_2$[c]	$\%\ ^{17}O_2$[d]
Pentacontane [Aged at 125 °C]	21.5	0.14	0.00	0.18	0.15
	14.5	0.05	0.05	0.57	0.46
	18.5	0.05	0.05	0.83	0.67
	14.5	0.05	0.04	1.22	0.99
	20.7	0.12	0.05	1.96	1.59
	23.5	0.11	0.05	3.36	2.72
	Avg.	0.09	0.04		
	Time (days)				
Polyisoprene [Aged at 95 °C]	5	0.25	0.00	0.08	0.06
	10	0.19	0.00	0.22	0.18
	15	0.12	0.04	0.29	0.24
	15	0.11	0.02	0.32	0.26
	15	0.17	0.00	0.61	0.49
	21	0.11	0.02	0.68	0.55
	20	0.14	0.02	0.91	0.74
	22	0.12	0.02	1.38	1.11
	31[e]	0.13[e]	0.03[e]	5.31[e]	4.30[e]
	Avg.	0.15	0.02		

[a] $CO_2/\Delta O_2$ = moles CO_2 produced per mole O_2 consumed. [b] $CO/\Delta O_2$ = moles CO produced per mole O_2 consumed. [c] Weight percent O_2 incorporated into polymer sample. [d] Weight percent $^{17}O_2$ incorporated into polymer sample, based on 81% isotopic enrichment of $^{17}O_2$ gas. [e] Total O_2 consumption was observed for this polyisoprene sample and is only presented as a limiting example, and was not used for analysis in Fig. 5 or 6.

Table 2. Relative Percent Distribution of Oxygen Functionalities in Oxidatively Aged Pentacontane and Polyisorpene.[a]

Sample	% O_2 Consumption[b]	Ketones[c]	Esters[d]	Carboxylic Acids[e]	Hydroperoxides[f]	Unsaturated Ethers[g]	Alcohols/ Ethers[h]	Water[i]
Pentacontane	0.18	16.1	1.6	12.2	53.1	0.0	16.1	0.9
[Aged at 125 °C]	0.57	33.0	7.2	18.0	1.0	0.0	40.0	0.8
	0.83	38.6	12.4	6.5	0.0	0.0	35.0	0.1
	1.22	37.8	10.8	21.8	0.0	0.0	29.0	0.6
	1.96	32.8	19.4	23.4	0.0	0.0	23.8	0.6
	3.36	27.6	23.7	26.2	0.0	0.0	21.7	0.8
Polyisoprene	0.08	24.4	0.0	0.0	0.0	14.3	53.6	7.7
[Aged at 95 °C]	0.22	19.1	0.0	0.0	0.0	19.1	60.4	1.5
	0.29	20.4	0.0	0.0	0.0	14.7	53.9	11.0
	0.32	23.4	3.5	0.5	0.0	20.5	42.6	9.5
	0.61	10.0	1.5	0.0	0.0	14.2	73.2	1.1
	0.68	11.7	2.8	2.9	0.0	14.3	62.1	6.2
	0.91	11.0	1.5	0.5	0.0	17.4	65.3	4.3
	1.38	14.3	1.6	1.2	0.0	14.9	64.2	3.8
	5.31[j]	6.9	2.1	1.3	0.0	17.8	70.8	1.1

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[a] Relative intensities obtained directly from line shape integration of ^{17}O NMR spectra. [b] Percent oxygen incorporated into aged sample. Oxidative exposure conditions detailed in Table 1. [c] Relative percent of all carbonyl oxygen functionalities resonating between $\delta = +650$ and 275 ppm, minus the contribution of the carbonyl of esters. [d] Relative percent of oxygen functionalities between $\delta = +400$ and $+275$ ppm, plus all resonances between $\delta = +220$ and $+150$ ppm. The integration includes both the carbonyl and ether oxygen functionalities within the ester group, minus the contributions from ketone carbonyls. [e] Relative percentage of oxygen functionalites between $\delta = +270$ and 240 ppm. This includes both rapidly exchanging oxygens of the carboxylic acid functionality. [f] Relative percentage of oxygen functionalities between $\delta = +240$ and $+200$ ppm that are reactive to dimethylsulfide. [g] Relative percentage of oxygen functionalities between $\delta = +150$ and $+100$ ppm. [h] Relative percent of oxygen functionalities between $\delta = +100$ and -50 ppm, excluding the water resonance. [i] Relative percentage of the water resonance at $\delta = -13$ ppm in toluene-d_8 (75 °C) and $\delta = -16$ in tricholorbenzene (125 °C). [j]Total O_2 consumption was observed for this polyisoprene sample and is only presented as a limiting example, and was not used for analysis in Fig. 5 or 6.

Figures

Figure 1. Solution ^{17}O NMR spectra of thermally oxidized pentacontane ($C_{50}H_{102}$) at different levels of oxidative degradation: a) 0.18%, b) 0.57%, c) 1.96% and d) 3.36% by weight O_2 incorporation. Oxidative exposure conditions are detailed in Table 1. A variety of degradation species and oxygen functionalities as a result of thermal oxidative degradation are evident including hydroperoxides, alcohols, carboxylic acids, esters and ketones.

Figure 2. Solution ^{17}O NMR spectra of thermally oxidized polyisoprene at different levels of oxidative degradation: a) 0.08%, b) 0.29% c) 0.68% and d) 1.38% by weight O_2 incorporation. Oxidative exposure conditions are detailed in Table 1. Polyisoprene reveals a wider variety of alcohol and ether degradation species compared to pentacontane (Figure 1).

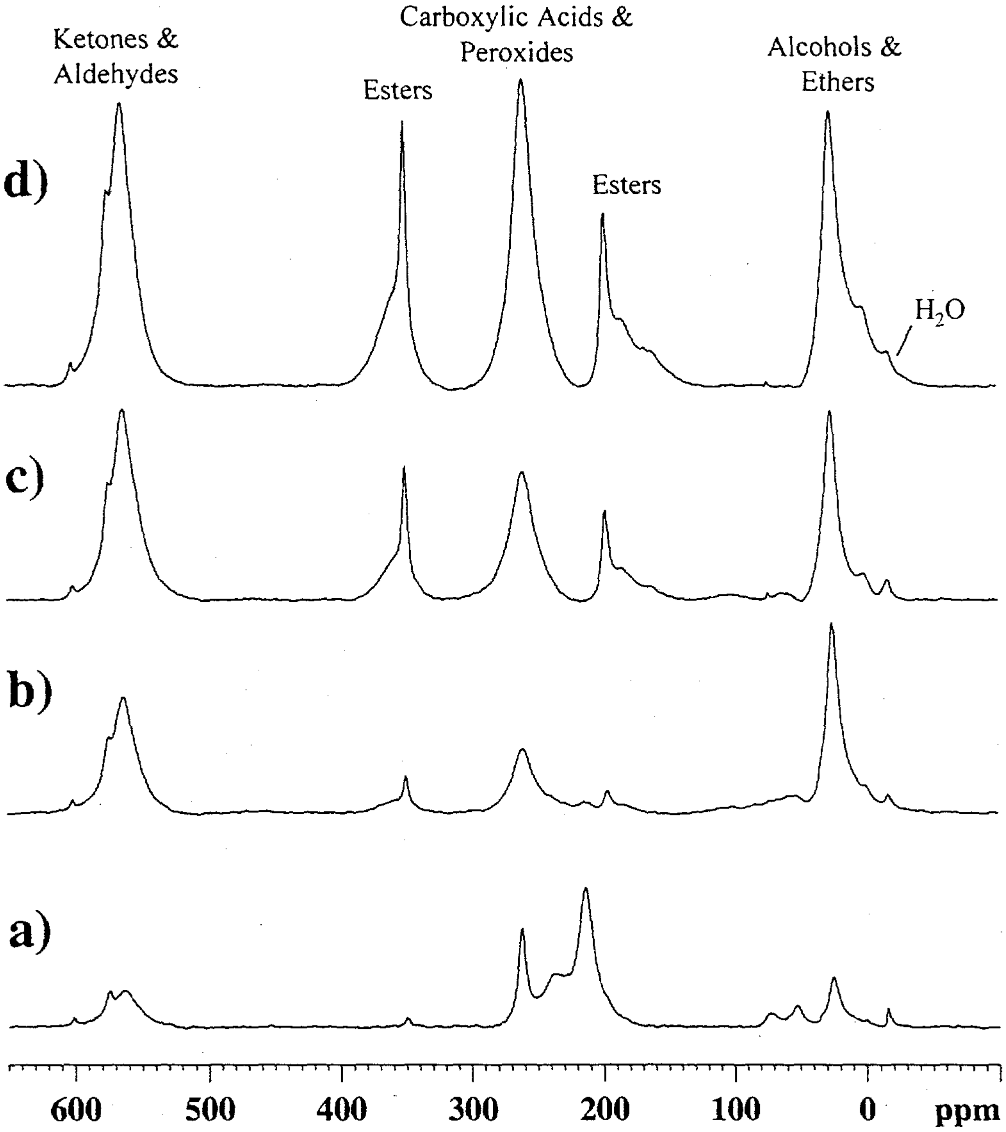
Figure 3. Solution ^{13}C NMR spectra of a) unaged and b) thermally oxidized pentacontane (3.36 % O_2 incorporation). An x150 expansion of the methylene region for the c) unaged and d) thermally oxidized pentacontane is also presented allowing the new resonances for the degradation species to be apparent.

Figure 4. Solution ^{17}O NMR spectra of chemically derivatized oxidatively aged pentacontane. The carbonyl and peroxide ^{17}O chemical shift region is shown for: a) untreated, aged (0.18 % O_2 incorporated), b) treated with 3 equivalents of methyldisulfide

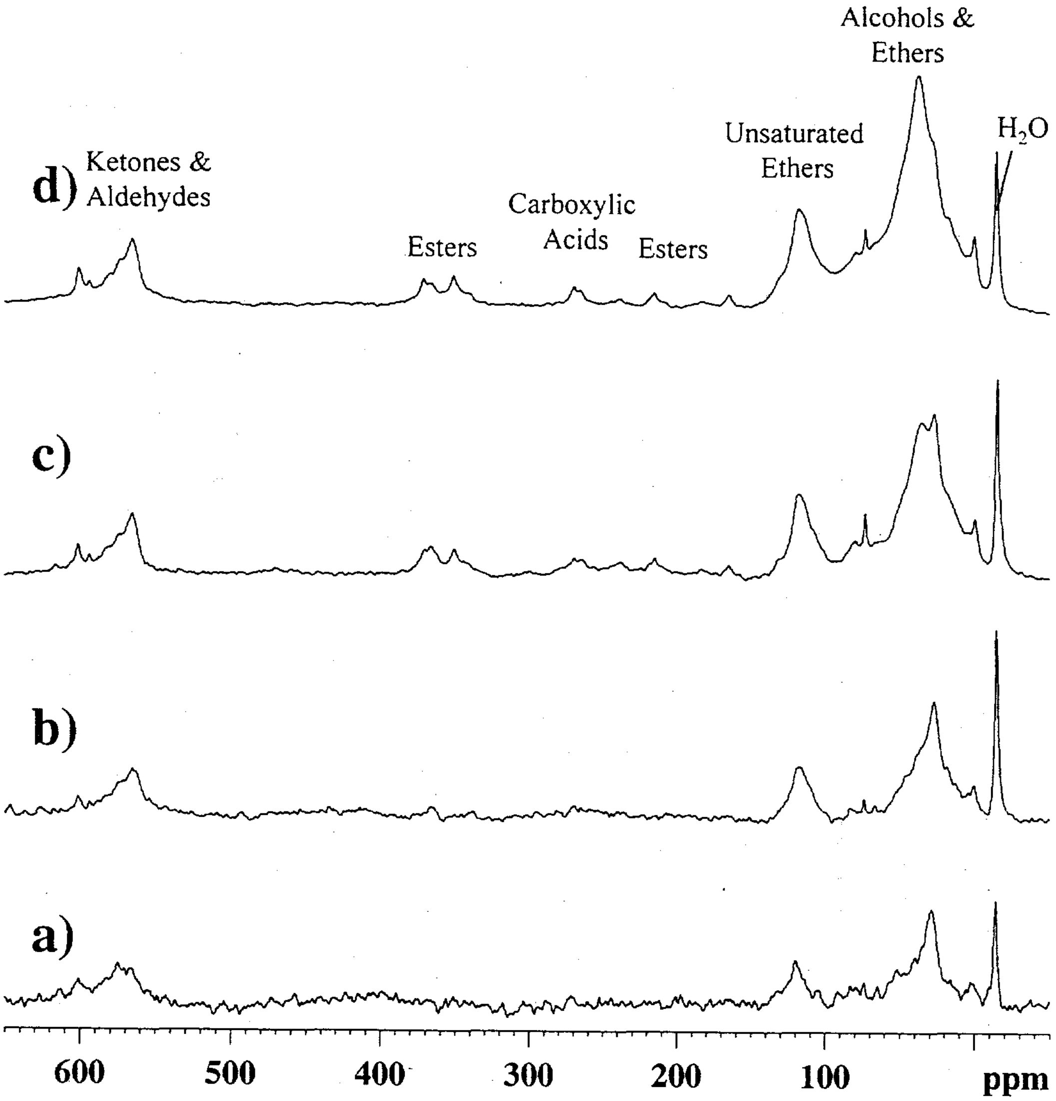
and c) followed by 3 equivalents of lithium aluminum hydride. These spectra confirm the assignment of the $\delta = +263$ ppm resonance as a carboxylic acid, the resonances at $\delta = +198$ and $+350$ ppm as esters oxygens, and the resonances at $\delta = +212$ and $+238$ ppm as hydroperoxide and peroxide species. The alcohol and ether ^{17}O chemical shift region is also shown for: d) untreated, aged (0.18 % O_2 incorporated) pentacontane and e) following treatment with methyldisulfide. The difference spectrum is shown in e) where the formation of secondary alcohols following treatment demonstrates the peroxides were predominantly secondary peroxides.

Figure 5. Distribution of oxygen containing degradation species in thermally oxidized aged pentacontane as a function of total O_2 incorporation: (▲) peroxides, (❑) alcohol/ethers, (❍) carboxylic acids, (■) esters and (●) ketones. For clarity the water and unsaturated ethers concentrations are not shown, since the concentration of these species is extremely small. The polynomial lines are included for visual aid only and do not represent theoretical fits or predictions.

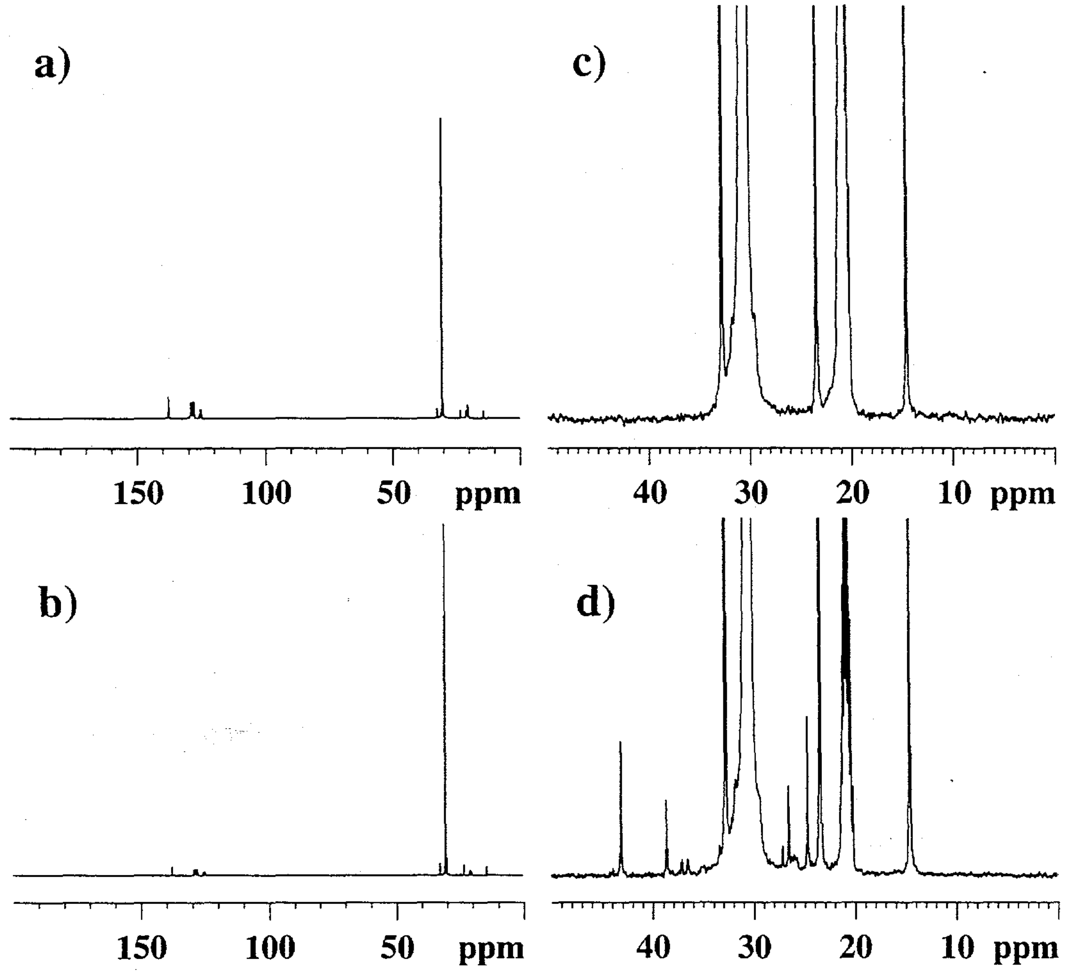
Figure 6. Distribution of oxygen containing degradation species in thermally oxidized polyisoprene as a function of total O_2 incorporation: (❑) alcohols/ethers, (◆) α,β-unsaturated ethers, (●) ketones, and (Δ) water. Carboxylic acids and esters are not shown, since the concentrations of these species are small. Lines are included for visual aid only and do not represent theoretical fits or predictions.



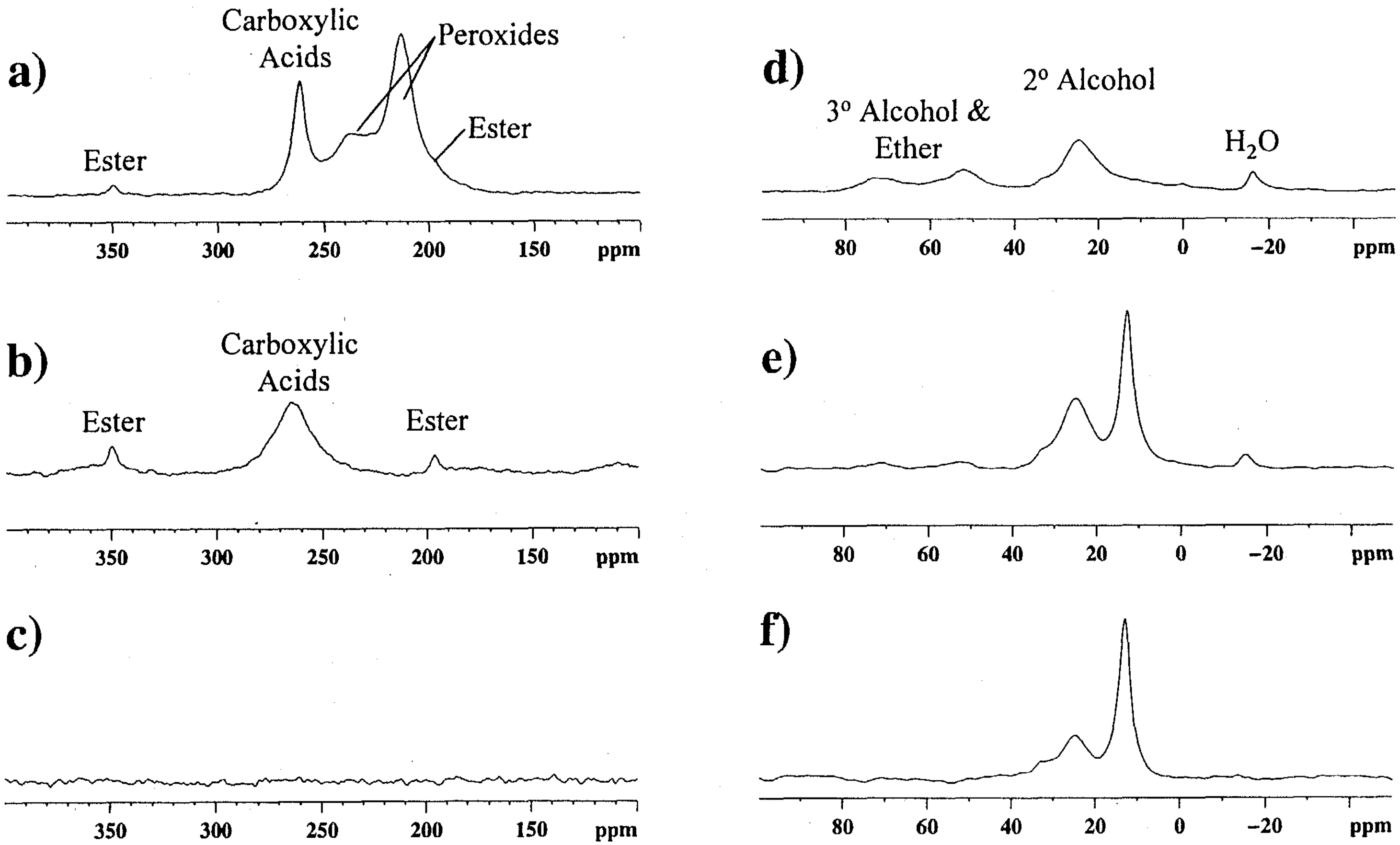
Alam et al. Fig. 1



Alam et al. Fig. 2



Alam et al Fig 3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Ester
Carboxylic Acids
Peroxides
Ester
350
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ppm
b)
Ester
Carboxylic Acids
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250
200
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c)
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150
ppm
d)
3° Alcohol & Ether
2° Alcohol
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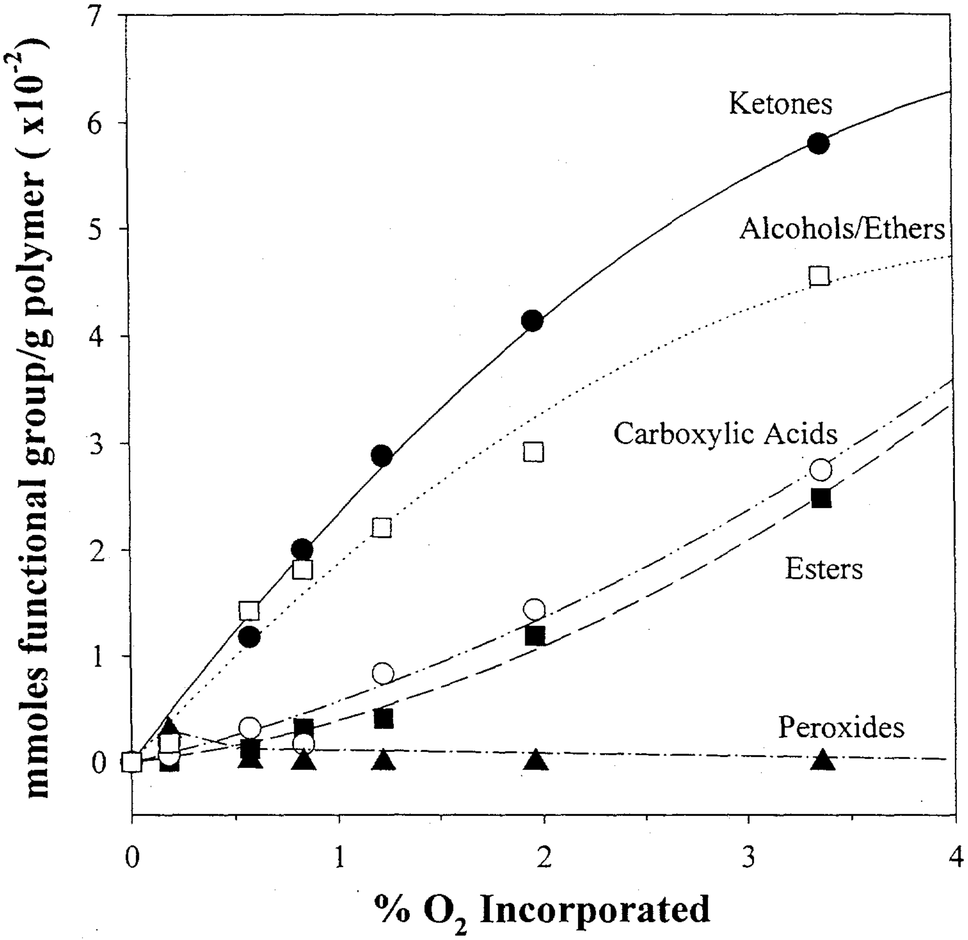
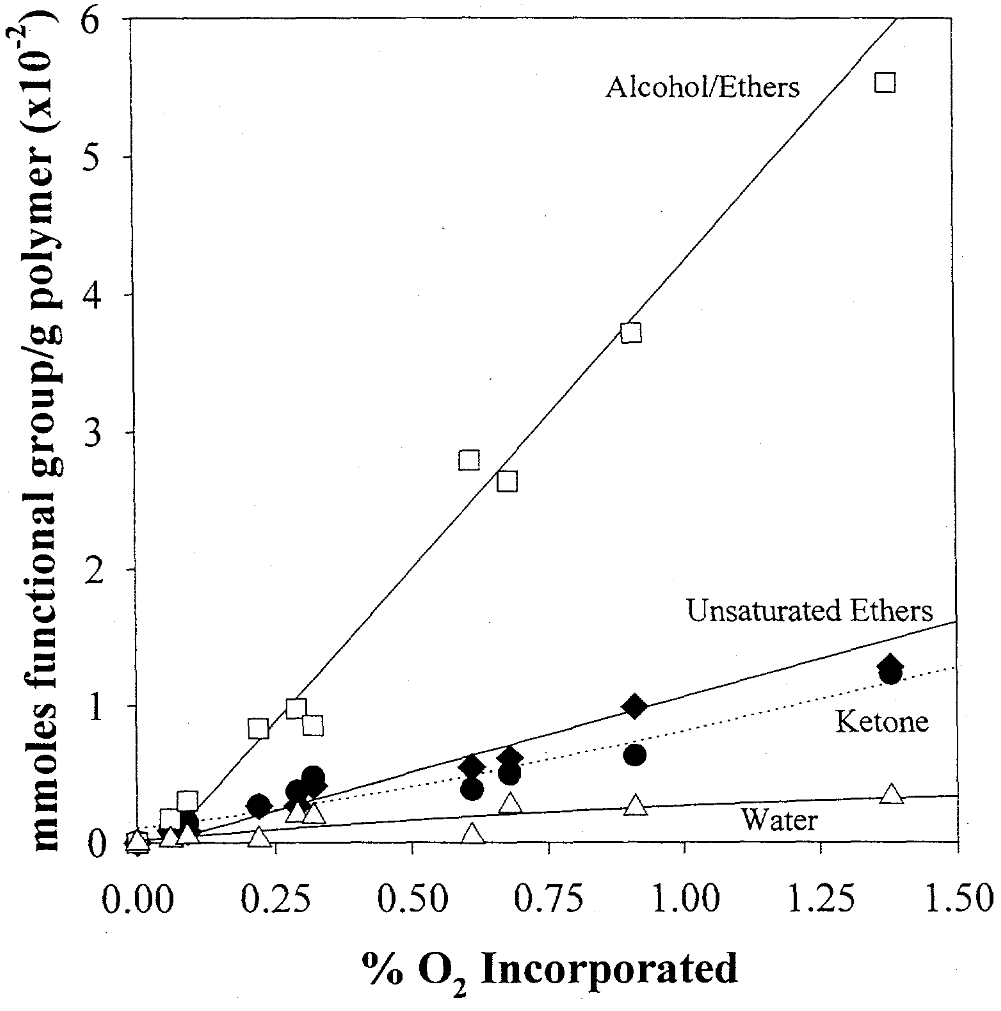


Alam et al Fig 5



Alam et al. Fig. 6