*Macromolecules* **2005,** *38,* 5035−5046

# Solid-State $^{13}$C NMR Investigation of the Oxidative Degradation of Selectively Labeled Polypropylene by Thermal Aging and $\gamma$-Irradiation

**Daniel M. Mowery,[†] Roger A. Assink,*,[†] Dora K. Derzon,[†] Sara B. Klamo,[‡] Roger L. Clough,[†] and Robert Bernstein[†]**

*Organic Materials Department, Sandia National Laboratories, Albuquerque, New Mexico 87185, and Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125*

*Received December 20, 2004; Revised Manuscript Received March 13, 2005*

ABSTRACT: Unstabilized polypropylene (PP) films having selective $^{13}$C isotopic labeling were subjected to thermal aging at 50, 80, and 109 °C and to $\gamma$-irradiation at 24 and 80 °C. The oxidized films were examined using solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy. Dramatic differences were found in the type and distribution of oxidation products originating from the three carbon atom sites within the PP macromolecule (tertiary carbon, secondary carbon, and methyl side group). Most of the oxidation products that formed on the polymer chain originated through chemical reactions at the PP tertiary carbons. Under all of the aging conditions examined, tertiary peroxides (from the PP tertiary site) were the most abundant functional group produced. Also originating from the PP tertiary carbon were significant amounts of tertiary alcohols, together with several more minor products that included "chain-end" methyl ketones. No significant amount of peroxides or alcohols associated with the PP *secondary* carbon sites was detected. A substantial yield of carboxylate groups was identified (acids, esters, etc.). The majority of these originated from the PP secondary carbon site, from which other minor products also formed, including in-chain ketones. We found no measurable yield of oxidation products originating from reaction at the PP methyl group. Remarkably similar distributions of the major oxidation products were obtained for thermal aging at different temperatures, whereas the product distributions obtained for irradiation at the different temperatures exhibited significant differences. Time-dependent concentration plots have been obtained, which show the amounts of the various oxidation products originating at the different PP sites, as a function of the extent of material oxidation.

## 1. Introduction

Polypropylene is a widely used synthetic polymer that is susceptible to oxidative degradation initiated by heat, ultraviolet radiation, and $\gamma$ radiation. Many of the applications utilizing polypropylene involve long-term material aging with continuous or periodic exposure to one or more of these environmental stresses. For example, in the medical field, polypropylene devices are sterilized with high-energy radiation, such as $\gamma$ rays or electron beam.[1] Discerning the underlying mechanisms and detecting the chemical products of the oxidative degradation of synthetic polymers such as polypropylene are important in the optimization of their useful lifetimes and overall reliability.

Because of its commercial importance, much work has been published on the oxidation of polypropylene, including useful reviews.[2,3] Although many of the oxidation products in polypropylene have been identified, others remain in question or have yet to be recognized. Quantification of these products (or indeed of the reaction products of any chemical modification of macromolecular materials) is difficult due to their low concentrations.

In chemical reactions conducted on small organic molecules, each reaction product can be isolated by chromatography or similar means, and each product's structure can be precisely determined by various spectroscopic techniques. However, in the case of macromolecular materials, the various chromophores and structures resulting from chemical reactions are not readily separated.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool in the study of polymer chain structure and dynamics.[4,5] NMR has proven very useful in studying both oxidative degradation and radiation-induced changes in polyolefin thermoplastics such as polyethylene,[6−10] polypropylene,[11,12] and ethylene copolymers,[13,14] as well as other common industrial polymers.[15−20] Due to the relatively wide range of isotropic chemical shifts, $^{13}$C NMR offers good spectroscopic resolution and effective identification of resonance peaks originating from the different oxidation products. Typically, $^{13}$C NMR analyses of oxidation-induced functional groups in polymers have been conducted on samples in liquid solution at high temperatures (>100 °C). However, such measurement conditions can induce further chemical reactions that could significantly alter the structure and concentration of the oxidation products. Assink et al.[10] have recently employed solid-state $^{13}$C NMR to analyze oxidation products formed by $\gamma$-irradiation in polyethylene samples that were 99% $^{13}$C enriched. The use of $^{13}$C enriched polymer samples provides an increase in detection sensitivity of nearly 2 orders of magnitude. Used together with magic-angle spinning (MAS) NMR, isotopic enrichment eliminates the need for dissolving or swelling the material at high temperatures.

To provide more direct insight into the complex chemical reaction pathways by which polymers undergo oxidative degradation, we have introduced with this

---

* To whom correspondence should be addressed. E-mail: raassin@sandia.gov. Telephone: 505-844-6372. Fax: 505-844-9781.

[†] Sandia National Laboratories.

[‡] California Institute of Technology.

10.1021/ma047381b CCC: $30.25

**Table 1. Material Properties of Selectively $^{13}$C Labeled Polypropylenes**

| PP material | relative $^{13}$C abundance of main-chain carbons[a] CH | $CH_2$ | $CH_3$ | $M_w$[b] (g/mol) | $M_w/M_n$[b] | $\Delta H_f$[c] (J/g) |
|---|---|---|---|---|---|---|
| C(1) | 1.0 ± 0.2 | 96.7 ± 0.5 | 2.3 ± 0.3 | 159000 ± 27000 | 1.9 ± 0.6 | 81 ± 3 |
| C(1,3) | 0.9 ± 0.1 | 68.3 ± 0.7 | 30.8 ± 0.6 | 255000 ± 10200 | 3.2 ± 0.5 | 83 ± 7 |
| C(2) | 98.5 ± 0.3 | 0.8 ± 0.1 | 0.8 ± 0.1 | 207000 ± 4400 | 2.5 ± 0.2 | 91 ± 15 |

[a] Determined with high-temperature, solution $^{13}$C NMR spectroscopy. Samples of the PP powder were dissolved in 1,2,4-trichlorobenzene at 130 °C. [b] Molecular weight parameters determined with PP powder samples using high-temperature size exclusion chromatography calibrated with polystyrene standards. [c] Heats of fusion $\Delta H_f$ of the melt-pressed thin films were measured with differential scanning calorimetry (DSC) calibrated with indium and zinc, and using a heating rate of 10 °C/min.

paper the use of selective isotopic labeling of macromolecules, combined with solid-state NMR analysis of the materials following exposure to chosen environments. The thin-film samples examined in this study were prepared from unstabilized polypropylene powders that were enriched with selective $^{13}$C labeling of the three different chain sites. By selectively labeling polypropylene with the $^{13}$C nucleus, we are able to unambiguously identify the origin of the various oxidative products and their relative concentrations with consideration to mechanisms of their formation. Oxidation was carried out by thermal aging and by exposure to $\gamma$-radiation. $^{13}$C resonances were assigned to various oxidation-induced functional groups and the distribution and kinetic accumulation of these oxidation products were obtained. We were also able to show that resonances previously identified with unsaturated carbons should be attributed to ketal and/or acetal functional groups.

## 2. Experimental Section

**2.1. $^{13}$C Labeled Polypropylene Materials.** Three polypropylene samples with different $^{13}$C labeling schemes were employed in this study. They are referred to as C(1), C(1,3), and C(2) labeled samples. All of the polypropylene materials were predominantly isotactic based on high-temperature (130 °C) solution $^{13}$C NMR results, and the samples exhibited a semicrystalline morphology. Material properties for each of the labeled PP samples are summarized in Table 1. The C(1,3) and C(2) labeled samples were purchased (Isotec) in powder form. For these samples, the $^{13}$C labeled monomers were polymerized using triisobutylaluminum and $TiCl_4$ in an anhydrous xylene/toluene solution. In the C(2) labeled material, the tertiary (or methine) carbons were enriched with ~99% $^{13}$C. In C(1,3) labeled samples, the secondary (or methylene) and primary (or methyl) carbons were enriched with ~68% and ~31% $^{13}$C, respectively. The distribution of labeled carbons in the C(1,3) sample was the result of scrambling during the polymerization of 1-$^{13}$C-propylene.

The C(1) labeled polypropylene was prepared in our laboratory (Pasadena, CA). All air and/or moisture sensitive compounds were manipulated using standard high vacuum line or Schlenk techniques, or in a glovebox under a nitrogen atmosphere, as described previously.[21] Toluene (EM Science) was dried by the method of Grubbs[22] and stored under vacuum over sodium benzophenone ketyl. Prior to experiments, toluene was collected at −78 °C by vacuum transfer and stored in a glovebox under a nitrogen atmosphere. Aqueous hydrochloric acid (36.5−38%, EM Science), methanol (EM Science), and *rac*-ethylenebis(indenyl)zirconium dichloride (Strem) were purchased and used as received. Methylaluminoxane was purchased (Albemarle) and prepared by removing toluene and free trimethylaluminum in vacuo; the white MAO solid was dried at 25 °C for 48 h at high vacuum. 1-$^{13}$C-propylene (99.2 atom % $^{13}$C, 99% chemical purity) was purchased (CDN Isotopes), purified by passage through a column of MnO on vermiculite and activated molecular sieves, transferred into a thick walled glass vessel at −196 °C, and stored under vacuum at −78 °C. ***CAUTION!*** **Extreme care should be taken with the storage of propylene in a closed container as its vapor pressure at room temperature exceeds 12 atm.**

Polymerizations of the 1-$^{13}$C-propylene yielding the C(1) labeled polypropylene were carried out in 1:1 (v/v) toluene/1-$^{13}$C-propylene at 0 °C in a thick-walled glass vessel (V ≈ 70 mL) sealed with an 8 mm Kontes needle valve. A ground glass joint was also present for connection to a vacuum line. The monomer was first distilled through a dry ice/acetone cooled trap into a calibrated cone for volume measurement, and then distilled into the liquid nitrogen cooled reaction vessel. Polymerization experiments were conducted using the following procedure. In an inert atmosphere glovebox, a polymerization vessel equipped with a stir bar was charged with MAO (80 mg, ≈ 2200 equiv), toluene (1 mL), and *rac*-ethylene-bis-indenylzirconium dichloride (0.26 mL of a 2.4 mM solution in toluene) to give a yellow-orange solution. The vessel was then cooled in liquid nitrogen and evacuated on a high vacuum line. 1-$^{13}$C-propylene (1 mL at −78 °C, ≈ 20 000 equiv) was added by vacuum transfer. In the fume hood behind a blast shield, the reaction was warmed to 0 °C in a sodium chloride/ice water bath. The polymerization was allowed to proceed for 10 min with rapid stirring. The vessel was then transferred to a dry ice/acetone bath and residual monomer was recovered via vacuum transfer on a high vacuum line. The polymerization was quenched with a 4:1 (v/v) mixture of methanol and dilute aqueous HCl (50 mL). The contents of the vessel were transferred to a flask with additional methanol (150 mL) and toluene (4 mL) and allowed to stir overnight. The polymer precipitated from this solution as a white solid; this powder was removed by filtration, washed with methanol, and dried in vacuo at 25 °C for 24 h. Approximately 300−400 mg of the C(1) labeled polymer was typically isolated.

**2.2. Film Samples.** Thin, melt-pressed films were prepared from the unstabilized powders in our laboratory (Albuquerque, NM). Before pressing, the C(1,3) labeled polypropylene was ground using a Spex 6700 freezer/mill for about 1.3 min resulting in particles that were ≤ 1 mm in size. The C(1) and C(2) labeled materials were pressed as received. Using a Carver laboratory press, 0.62 g of powder was pressed for 60 s between two polished aluminum plates at a temperature of 180 °C and a pressure of 1.4 MPa. The films were then quenched in room-temperature (24 °C) water. The average thickness of the films was 100−150 $\mu$m. Film samples were kept in a commercial refrigerator at −25 °C to inhibit oxidation.

**2.3. Thermal Aging.** The pressed films were cut into pieces about 1−3 mm in size and packed into 4 mm outer diameter zirconia rotors used for NMR MAS experiments. Approximately 60 mg of material was packed into each rotor. Leaving one end of each rotor open to the environment, the packed rotors were placed into air-circulating, commercial aging ovens under ambient atmospheric conditions (~630 mmHg in Albuquerque, NM). The temperatures of the ovens used were at 50, 80, and 109 °C, with a temperature control of ±2 °C. After a selected period of time in the aging ovens, the packed rotors were removed, allowed to cool to room temperature, and analyzed with $^{13}$C solid-state NMR. The packed rotors were then placed back into the oven for continued thermal aging.

**2.4. $\gamma$-Radiation Aging.** Larger pieces (about 2−3 cm in size) of the pressed films were employed in irradiation experiments. The film pieces were placed into open 20 mL glass vials for irradiation. Radiation aging was conducted at the Low Intensity Cobalt Array (LICA) facility (Albuquerque, NM), which has been previously described in detail.[23] Samples were subjected to $\gamma$-irradiation under flowing air at room temperature (24 °C) and at 80 °C. The $\gamma$-irradiation was generated with a $^{60}$Co source at a dose rate of 80−90 krad/h. Samples were irradiated for varying times up to 11 days maximum, which equates to irradiation doses up to 23 Mrad. Following irradiation, samples were kept in a commercial refrigerator until they were analyzed with $^{13}$C solid-state NMR.

**2.5. NMR Parameters.** Solid-state NMR experiments were conducted at room temperature (21 °C) in a Bruker Avance NMR spectrometer operating at a $^{13}$C resonance frequency of 100.6 MHz. Samples were analyzed under magic-angle spinning (MAS) conditions using 4 mm zirconia rotors with Kel-F caps at a spinning frequency of typically 10 kHz. This spinning speed is optimal for the detection and characterization of common oxidation-induced functional groups in polyolefins, as the resulting spinning sidebands do not overlap with any significant resonances attributed to these degradation products.[10] In this study, $^{13}$C direct polarization (DP) spectra were acquired with a 60-s recycle delay and a $^{13}$C excitation pulse length of 4 $\mu$s. The justification for employing a 60-s recycle delay time will be detailed later in the paper. High-power $^1$H decoupling at $\gamma B_1/2\pi = 63$ kHz utilizing the two-pulse phase modulation (TPPM) decoupling scheme[24] was applied. $^{13}$C isotropic chemical shifts were calibrated with an external glycine standard. Unless a specific reference is given, the isotropic chemical shifts of $^{13}$C resonances observed in this study were identified with distinct chemical moieties based on simulations carried out using the ACD/CNMR software package (Advanced Chemistry Development, Toronto, Canada).

## 3. Results and Discussion

### 3.1. $^{13}$C Resonance Identification.

The $^{13}$C DP/MAS spectra of thermooxidatively aged C(2), C(1,3), and C(1) labeled polypropylene samples are shown in Figure 1. The selective $^{13}$C isotopic labeling is clearly visible in the NMR spectra, based on the three main-chain resonances (peaks 1−3 in Figure 1). Solid-state $^{13}$C MAS NMR spectra of neat isotactic polypropylene exhibit three distinct resonances, each resonance corresponding to the three different carbon sites on the PP chain.[25,26] The dominant resonance in the C(2) spectrum at 25.9 ppm is attributed to the methine or tertiary (CH) carbon. The two main resonances in the C(1,3) spectrum at 43.5 and 21.4 ppm are identified with the methylene or secondary carbon ($CH_2$) and the methyl or primary carbon ($CH_3$), respectively. The dominant resonance in the C(1) spectrum at 43.5 ppm corresponds to the methylene carbon. First-order spinning sidebands of the labeled main-chain resonances due to MAS at 10 kHz are found at 125.4 ppm for the C(2) sample, 143.3 and 120.9 ppm for the C(1,3) sample, and 143.3 ppm for the C(1) sample. A very small, narrow peak near 0.9 ppm in the C(2) spectrum and a small, broad peak at ~161 ppm in the C(1) spectrum were present in the unaged PP material and did not increase or decrease with subsequent oxidation. The resonance near 0.9 ppm is consistent with a methyl carbon bonded to a siloxane group, present as an impurity. The small, broad peak at ~161 ppm could be associated with a formate ester end group −OCHO.

Both thermal and $\gamma$-initiated oxidation yielded functional groups on the polypropylene chains that showed distinct $^{13}$C resonances in all of the labeled sample NMR spectra. The resonances were subsequently identified with various functional groups based on their isotropic chemical shifts (peaks a−g in Figure 1). A summary of these observed resonances and their corresponding identifications are also listed in Table 2. The specific position of origin on the PP chain (i.e., the C(1), C(2), or C(3) carbon) and the aging conditions (aging temperature and exposure to $\gamma$-radiation) in which the functional group is experimentally observed are given as well. It is immediately apparent from the list of resonances in Table 2 that the majority of oxidation-induced functional group types formed on the PP chain originates from the tertiary carbon (the C(2) site on the unaged polymer chain). The tertiary carbon site is generally regarded as the most susceptible to hydrogen abstraction during oxidation.

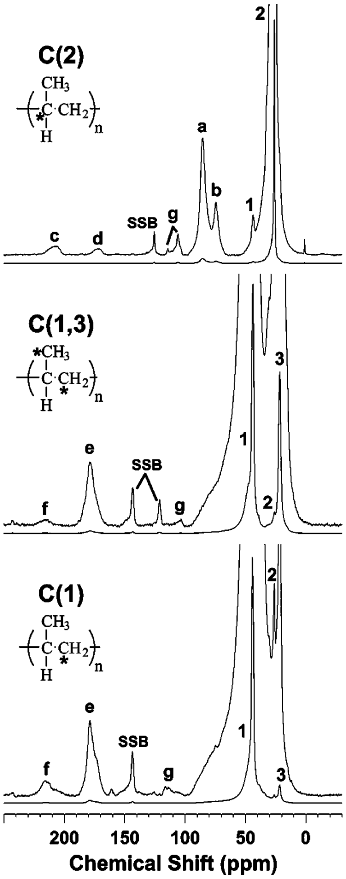


**Figure 1.** 60-s $^{13}$C DP/MAS spectra of C(2) and C(1,3) labeled polypropylene samples thermally aged at 50 °C for 211 days and of a C(1) labeled polypropylene sample thermally aged at 109 °C for 42 h. Spectra at maximum intensity and 25× are given for each sample. Major $^{13}$C resonances are identified. Main-chain resonances: (1) secondary or methylene ($CH_2$) carbon; (2) tertiary or methine (CH) carbon; (3) primary or methyl ($CH_3$) carbon. Functional group resonances: (a) tertiary hydroperoxides and/or dialkyl peroxides; (b) tertiary alcohols; (c) methyl ketones; (d) esters and/or peresters; (e) carboxylic acids and/or esters; (f) in-chain ketones; (g) ketals and/or acetals. Spinning sidebands of the main-chain resonances due to MAS at 10 kHz are designated with "SSB". Minor resonances near 0.9 ppm in the C(2) spectrum and ~161 ppm in the C(1) spectrum were present in the unaged polymer and did not increase or decrease with oxidative aging. Because of scaling, relative peak heights cannot be compared between the various samples in this figure.

**3.1.1. C(2) Sample Resonances.** The largest NMR peak attributed to oxidation was consistently observed near 85.3 ppm in the C(2) labeled sample spectra, regardless of the aging conditions. This resonance is identified with hydroperoxides and/or dialkyl peroxides (peak a in Figure 1). In their solid-state $^{13}$C NMR analysis of $\gamma$-irradiated, $^{13}$C enriched polyethylene films, Assink et al.[10] found a similar resonance at ~85 ppm which they attributed to secondary hydroperoxides.

Likewise, a resonance in the range 83−85 ppm was observed in high-temperature, solution-state $^{13}C$ NMR analyses of aged polyethylene[8] and polypropylene,[12] and these workers also identified the peak with hydroperoxide groups.

The important role of hydroperoxides in the autoxidation of polypropylene has been known for decades.[2,3,27−29] The formation of hydroperoxides results from the propagation sequences in the free radical oxidation mechanism of any organic polymer P (eq 1, parts a and b). Polymer alkyl radicals (P•) react with oxygen to form peroxy radicals (POO•), as shown in eq 1a. These alkyl peroxy radicals subsequently abstract a hydrogen atom to produce hydroperoxides (POOH) along with a new polymer alkyl radical, propagating the free radical oxidation process (eq 1b).

$$P^{\bullet} + O_2 \rightarrow POO^{\bullet} \tag{1a}$$

$$POO^{\bullet} + PH \rightarrow POOH + P^{\bullet} \tag{1b}$$

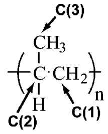
$$POO^{\bullet} + P^{\bullet} \rightarrow POOP \tag{1c}$$

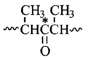
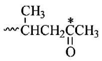
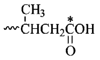
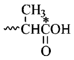
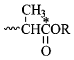
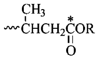
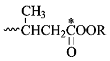
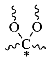
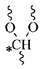
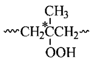
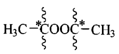
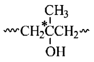
$$\begin{aligned} POO^{\bullet} + POO^{\bullet} &\rightarrow POOOOP \\ &\rightarrow POOP + O_2 \end{aligned} \tag{1d}$$

Intuitively, the tertiary hydrogen atom is considered the most labile in the course of polypropylene oxidation, thus leading to hydroperoxide structures that are predominantly tertiary. However, other hydroperoxide structures, particularly secondary hydroperoxides, were not discounted in polypropylene degradation. Carlsson and co-workers[30,31] derivatized PP hydroperoxides with nitric oxide to produce different nitrates (tertiary, secondary, etc.) that could be analyzed with IR spectroscopy and used to quantify the different hydroperoxide structures. Employing this method, it was reported[31] that 90% of the hydroperoxides in polypropylene oxidized by various means (thermal-, photo-, and $\gamma$-initiated) were tertiary, with the remaining 10% being secondary. However, the overlap of IR absorbance bands made this measurement difficult. In the PP samples examined in this work, the 85.3-ppm resonance is only detected in the C(2) labeled sample spectra, indicating the exclusive formation of tertiary hydroperoxides, with no primary or secondary hydroperoxides detected in either the C(1) or C(1,3) labeled sample spectra.

Dialkyl peroxides, which can act as chemical cross-links between adjacent PP chains, can form by termination reactions in the free radical oxidation process involving bimolecular recombinations (eq 1, parts c and d).[2,3] The carbons in dialkyl peroxide linkages will also resonate near 85 ppm and cannot be readily distinguished from the hydroperoxide carbons. However, it was suggested that the recombination of alkyl peroxy radicals in thermooxidatively aged isotactic PP (eq 1d) was minimal, based on a mass spectroscopic analysis of the volatile gases produced when the polymer was aged in a mixed $^{32}O_2/^{36}O_2$ labeled environment.[32] If present, the dialkyl peroxides would also form exclusively between tertiary carbons.

**Table 2. $^{13}C$ Resonances of Oxidation-Induced Functional Groups Observed in Solid-State NMR Spectra of Selectively Labeled Polypropylene Samples**



| $^{13}C$ chemical shift (ppm) | Functional group | | PP position of origin | Aging conditions observed[a] |
|---|---|---|---|---|
| ~215<br>(broad) |  $\sim CH(CH_3)\overset{*}{C}(=O)CH(CH_3)\sim$ | in-chain ketone | C(1) | Δ (50 °C, 80 °C, 109 °C)<br>γ (80 °C) |
| ~207<br>(broad) |  $\sim CH(CH_3)CH_2\overset{*}{C}(=O)CH_3$ | methyl (chain-end) ketone | C(2) | Δ (50 °C, 80 °C, 109 °C)<br>γ (24 °C, 80 °C) |
| ~185<br>(broad) |  $\sim CH(CH_3)CH_2\overset{*}{C}(=O)OH$ | carboxylic acid | C(2) | Δ (50 °C)<br>γ (24 °C) |
| ~179<br>(broad) |  $\sim CH(CH_3)\overset{*}{C}(=O)OH$ | carboxylic acid | C(1) | Δ (50 °C, 80 °C, 109 °C)<br>γ (24 °C, 80 °C) |
| |  $\sim CH(CH_3)\overset{*}{C}(=O)OR$ | ester | | |
| 170–175<br>(broad) |  $\sim CH(CH_3)CH_2\overset{*}{C}(=O)OR$ | ester | C(2) | Δ (50 °C, 80 °C, 109 °C)<br>γ (24 °C, 80 °C) |
| |  $\sim CH(CH_3)CH_2\overset{*}{C}(=O)OOR$ | perester | | |
| 100–117<br>(several peaks) |  $(\sim O)_2\overset{*}{C}(\sim)_2$ | ketal | C(1)<br>C(2) | Δ (50 °C, 80 °C, 109 °C)<br>γ (24 °C, 80 °C) |
| |  $(\sim O)_2\overset{*}{C}H\sim$ | acetal | | |
| 85.3 |  $\sim CH_2\overset{*}{C}(CH_3)(OOH)CH_2\sim$ | tertiary hydroperoxide | C(2) | Δ (50 °C, 80 °C, 109 °C)<br>γ (24 °C, 80 °C) |
| |  $H_3C-\overset{*}{C}(\sim)_2OO\overset{*}{C}(\sim)_2-CH_3$ | dialkyl peroxide | | |
| 74.2 |  $\sim CH_2\overset{*}{C}(CH_3)(OH)CH_2\sim$ | tertiary alcohol | C(2) | Δ (50 °C, 80 °C, 109 °C)<br>γ (24 °C, 80 °C) |

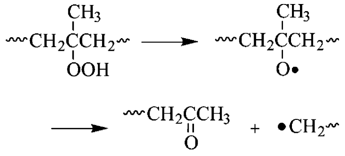
[a] Key: Δ = thermal aging only; $\gamma$ = exposure to $\gamma$-irradiation

Two other significant $^{13}C$ resonances attributed to oxidation-induced functional groups were observed in the C(2) labeled sample spectra near 74 and 207 ppm with all of the applied aging conditions. Like the resonance attributed to hydroperoxides and dialkyl peroxides, the $^{13}C$ resonance at 74.2 ppm due to alcohol groups (peak b in Figure 1) was only observed in the C(2) sample spectra. 3-Methyl-3-pentanol, a representative small-molecule tertiary alcohol, exhibited an alcohol resonance at 73.0 ppm in $^{13}C$ NMR spectra, when dissolved in chloroform.[33] Primary and secondary alcohol groups gave smaller isotropic chemical shifts. Thus, the observed chemical shift, along with its origin from the tertiary carbon, indicates the 74.2-ppm peak to be due to tertiary alcohol groups. Classic autoxidation schemes of polypropylene and other organic polymers show that alcohol groups are produced when alkoxy radicals formed from the degradation of hydroperoxides abstract hydrogen atoms from the same or a nearby polymer chain (eq 2, parts a and b).[2,3] Hence, the tertiary alcohols detected in the C(2) labeled samples most likely originated from the decomposition of tertiary hydroperoxides. It should be noted here that although secondary and primary peroxide and alcohol groups were not experimentally detected in this study, they still might be present during the course of PP oxidation.

$$POOH \rightarrow PO^\bullet + {}^\bullet OH \quad (2a)$$

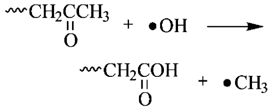
$$PH + PO^\bullet \rightarrow P^\bullet + POH \quad (2b)$$

The broad resonance at ~207 ppm is identified with methyl ketones (peak c in Figure 1), which would occur at the ends of PP chains, thus implying chain scission reactions. The IR absorbance peaks of methyl and in-chain ketones overlap, and these two ketonic species were first distinguished experimentally in oxidized polypropylene with high-temperature solution-state $^{13}C$ NMR.[12] Methyl ketones are formed by the $\beta$-scission of an alkoxy radical, which results in the formation of a primary alkyl radical and a corresponding reduction in molecular weight (eq 3).[34,35] Therefore, according to this mechanism, the carbonyl carbon in the methyl ketone group would originally have been a tertiary carbon (C(2) site) on the preoxidized chain backbone, as observed here.

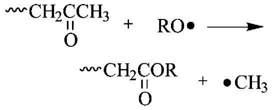


$$\sim CH_2\underset{OOH}{\overset{CH_3}{C}}CH_2\sim \longrightarrow \sim CH_2\underset{O\bullet}{\overset{CH_3}{C}}CH_2\sim \longrightarrow \sim CH_2\underset{O}{\overset{}{\underset{\|}{C}}}CH_3 + \bullet CH_2\sim \quad (3)$$

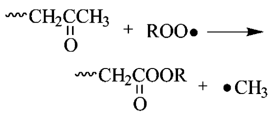
Resonances identified with carboxylic acids and esters have $^{13}C$ chemical shifts ranging from 170 to 185 ppm. In solid-state NMR spectra of the C(2) labeled material, two small, broad resonances were observed in this spectral range, the most prominent at either 170−174 ppm or ~175 ppm, and the other at ~185 ppm. The former resonance was seen for all of the applied aging conditions, with slightly differing chemical shift. The latter resonance, at ~185 ppm, was detected only with $\gamma$-irradiation at 24 °C and thermal aging at 50 °C. The 185-ppm peak is identified with the carbonyl carbon of a carboxylic acid group. Geuskens and Kabamba[36] suggested a mechanism in which carboxylic acids are produced when a ketone is attacked by a hydroxyl radical (eq 4a). Hence, the carboxylic acid groups detected in the C(2) labeled material could have formed from further oxidation of the chain-end ketones.



$$\sim CH_2\underset{O}{\underset{\|}{C}}CH_3 + \bullet OH \longrightarrow \sim CH_2\underset{O}{\underset{\|}{C}}OH + \bullet CH_3 \quad (4a)$$



$$\sim CH_2\underset{O}{\underset{\|}{C}}CH_3 + RO\bullet \longrightarrow \sim CH_2\underset{O}{\underset{\|}{C}}OR + \bullet CH_3 \quad (4b)$$



$$\sim CH_2\underset{O}{\underset{\|}{C}}CH_3 + ROO\bullet \longrightarrow \sim CH_2\underset{O}{\underset{\|}{C}}OOR + \bullet CH_3 \quad (4c)$$

The broad resonance with a $^{13}C$ chemical shift of either 170−174 ppm or ~175 ppm is identified with the carbonyl carbon of ester and/or perester groups (peak d in Figure 1). The 175-ppm peak was only observed for C(2) labeled samples $\gamma$-irradiated at 24 °C. With the C(2) labeled samples $\gamma$-irradiated at 80 °C or thermally aged at 50, 80, and 109 °C, the resonance is shifted slightly upfield from ~175 to 170−174 ppm. A recent study[19] of thermooxidatively degraded poly(ethylene oxide) by solution-state $^{13}C$ NMR revealed a similar distribution of resonances from 170 to 174 ppm attributed to in-chain esters. The NMR peaks at 172−174 ppm in the aged PEO spectra showed slightly higher mobility than the corresponding peaks at 170−171 ppm, which the authors stated was a result of the enhanced mobility of end groups relative to in-chain groups.

Similar to the oxidation of ketones to carboxylic acids, esters might be produced when a ketone is attacked by an alkoxy radical (eq 4b).[36] Likewise, a perester can form when an alkyl peroxy radical attacks the ketone group,[36] as shown in eq 4c. Lacoste et al.[31] noted that the total concentration of peroxidic species in PP samples as measured by iodometry was slightly greater than the hydroperoxide concentration measured by derivatization with nitric oxide. They attributed this difference to the presence of peresters. The carbonyl carbon of a peracid would also resonate from 170 to 175 ppm. The detection of peracids has been reported with the infrared spectroscopic analysis of oxidatively aged polypropylenes treated with dimethyl sulfide,[37−39] although these findings have been disputed.[40]

Two small, reasonably narrow resonances were observed at 105.7 and 114.1 ppm in the C(2) labeled sample spectra (peaks labeled "g" in the C(2) spectrum of Figure 1). The peak at 114.1 ppm was not detected in the sample $\gamma$-irradiated at 24 °C. A distribution of relatively smaller intensity was generally found between the two peaks. In previous high-temperature solution-state $^{13}C$ NMR studies of oxidatively degraded polypropylene,[11,12] a resonance at 111.5 ppm was observed and identified with the vinylidene carbon. However, the corresponding resonance of the second unsaturated carbon in the double bond, which should appear in the range 135−155 ppm, was not seen in the solution-state NMR spectra. Overlap with the strong solvent peaks in the same spectral region was cited as the reason for the lack of detection of this second peak.

In the current work, no resonance in the range of 135−155 ppm was observed in the C(2), C(1,3), or C(1) labeled sample spectra. The spinning frequency was adjusted to 5 kHz and 7 kHz, and spectra of the C(2) and C(1,3) samples were recorded at each of these spinning speeds so that the spectral region of interest was free of spinning sidebands. No additional peaks in the 135−155 ppm region were found, ruling out vinylidene and other unsaturated structures. We attribute the resonances observed from 100 to 110 ppm in the C(2) labeled sample spectra to carbons in alkyl O−C−O (unprotonated ketal and protonated acetal) groups. Acetals have been detected in thermooxidized poly(ethylene oxide) using solution-state $^{13}C$ NMR.[19,20] We have employed a solid-state NMR technique utilizing $^{13}C$ CSA dephasing[41] in the characterization of the selectively labeled PP samples in this study, confirming these resonances at 100−110 ppm to be associated with alkyl sp$^3$-hybridized carbon sites. This work will be reported in detail elsewhere.[42]

**3.1.2. C(1) and C(1,3) Sample Resonances.** Three significant $^{13}C$ resonances attributed to oxidation-induced functional groups were observed in the C(1) and C(1,3) labeled sample spectra. A large, broad resonance at ~179 ppm was seen for all aging conditions (peak e in Figure 1). This peak can be identified with the carbonyl carbon of a carboxylic acid or an ester. It may also be identified with the carbonyl carbon of a $\gamma$-lactone structure, which incorporates an ester group. $\gamma$-lactones were detected by infrared spectroscopy in thermo-oxidized PP samples subjected to selected chemical treatments[43] and were also implied in FT-IR emission studies[44] of thermally degraded polypropylenes as the absorbance at 1780 $cm^{-1}$. The C(1) carbon of the $\gamma$-lactone structure would have a corresponding C(2) carbon that would resonate near 85.5 ppm. This C(2) resonance would be masked by the strong peroxide peak in same region of the C(2) sample spectra. Adams[43] proposed a polypropylene oxidation scheme in which primary carboxylic acids, esters, and $\gamma$-lactones were derived from the degradation of secondary hydroperoxides, resulting in chain scission. Iring and Tüdös[45] suggested that $\gamma$-lactone formation was the result of an intramolecular dehydration reaction between a tertiary hydroperoxide and a nonadjacent primary hydroperoxide. However, no distinct resonances attributed to secondary or primary hydroperoxides were detected in the C(1) or C(1,3) spectra.

The second $^{13}C$ resonance observed in the C(1) and C(1,3) labeled sample spectra was found at ~215 ppm (peak f in Figure 1) and occurred in all of the aging conditions examined except for $\gamma$-irradiation at 24 °C. This chemical shift is identified with in-chain (or internal) ketones.[12] These ketones are most likely to form on the methylene carbons (C(1) site). Along with acids, esters, and $\gamma$-lactones, the polypropylene oxidation scheme proposed by Adams[43] shows that in-chain ketones could also arise from the decomposition of secondary hydroperoxides by hydrogen abstraction from a secondary alkoxy radical. If secondary hydroperoxides did exist during the oxidative degradation of the polypropylene samples in this current study, they were unstable and rapidly degraded into other products, probably derivatives of in-chain ketones via $\beta$-scissions.

As with the C(2) spectra, resonances in the range of 100−117 ppm were detected in the C(1) and C(1,3) spectra (resonance labeled “g” in the C(1,3) and C(1) sample spectra of Figure 1). The resonances were broad, showing poorly defined peaks at either ~103 ppm or 113−116 ppm. The resonances were more intense in the C(1) spectra compared to the C(1,3) spectra, which indicates they predominantly originate from the methylene C(1) carbons on the polymer chain. As with the C(2) labeled sample spectra, these resonances are identified with ketal and/or acetal groups. Ketal and acetal groups could be present in some type of cyclic peroxidic structure, such as an ozonide. Mechanisms yielding such structures have been proposed.[46]

Besides $^{13}C$ resonances directly attributed to oxidation-induced functional groups, several minor resonances in the alkyl region appeared with oxidative aging in the C(1) and C(1,3) sample NMR spectra. In the aged C(1,3) sample spectra, two very small peaks were seen near 30 ppm (Figure 2). As shown in Figure 2, these resonances appeared with aging due to $\gamma$-irradiation at 80 °C. The peaks also were present in thermally aged C(1,3) sample spectra. However, the peaks were not detected in any C(1) spectra, indicating that they originate from the methyl C(3) carbon. These two small resonances are attributed to methyl groups in the methyl ketone structure and the tertiary alcohol structure, which form through oxidation at the C(2) carbon site. The isotropic chemical shifts of methyl groups in PP methyl ketones and tertiary alcohols were calculated to be 28.3 and 29.1 ppm, respectively, based on simulations. Indeed, representative small-molecule compounds showed similar $^{13}C$ chemical shifts for these specific methyl groups.[33] The methyl group in the methyl ketone structure of 4-methyl-2-pentanone and in the tertiary alcohol structure of 3-methyl-3-pentanol (both dissolved in chloroform) was found to resonate at 30.3 and 33.7 ppm, respectively.

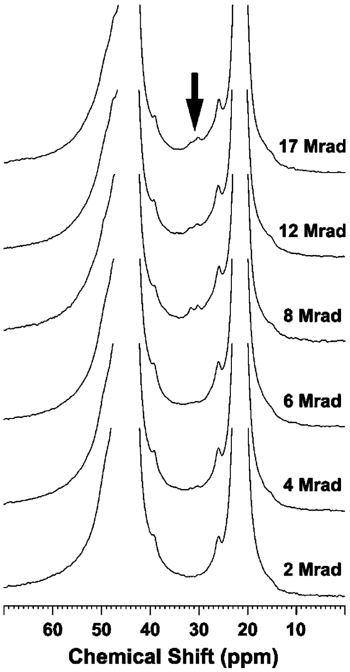


**Figure 2.** 60-s $^{13}C$ DP/MAS spectra of C(1,3) labeled polypropylene samples exposed to $\gamma$-radiation at 80 °C, with radiation dose given. Spectra are presented at 5× the maximum intensity. The two small resonances near 30 ppm (identified with an arrow) are attributed to methyl groups in the methyl ketone structure and the tertiary alcohol structure.

The broad shoulder on the downfield side of the methylene resonance (peak 1 in Figure 1) was observed to grow in intensity in both C(1) and C(1,3) labeled sample spectra with oxidation. A high-temperature (130 °C), solution-state $^{13}C$ NMR spectrum of a C(1,3) sample thermally aged at 50 °C for 250 days revealed a small peak near 51 ppm induced by oxidative aging. This peak in the solution-state NMR spectrum could explain the increased shoulder on the C(1) resonance in solid-state NMR spectra. The methylene ($CH_2$) unit α to the methyl ketone group would resonate near 51 ppm.

**3.2. Distribution and Kinetic Accumulation of Oxidation Products.** Solid-state NMR can provide a direct, quantitative measurement of all the oxidation products formed in the polypropylene materials, provided that a suitable recycle delay is chosen so that the magnetization of all $^{13}C$ sites is sufficiently relaxed. Using a C(2) labeled PP sample subjected to ~1 day of thermal aging at 109 °C, $^{13}C$ DP/MAS spectra were acquired with an extremely wide range of recycle delays from 2 to 2000 s. The integrals of the various $^{13}C$ resonances described in the previous section were measured at each recycle delay (Figure 3). From the $^{13}C$ $T_1$ relaxation curves shown in Figure 3, it is seen that a 60-s recycle delay allows for sufficient relaxation of the $^{13}C$ magnetization in all the detected resonances. A relaxation experiment on the C(1,3) labeled material led to the same conclusion.

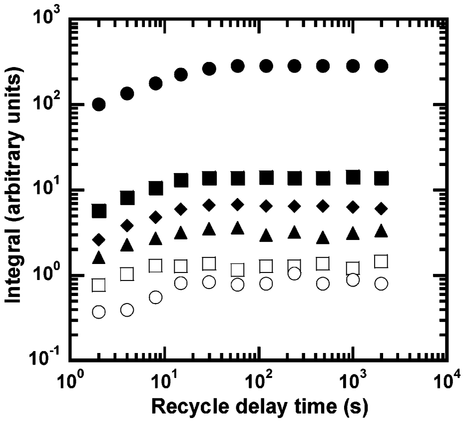


**Figure 3.** Resonance integrals vs recycle delay time for $^{13}$C DP/MAS spectra of a solid C(2) labeled polypropylene sample thermally aged at 109 °C for ~1 day. $^{13}$C resonances: (●) +60 to −10 ppm (main-chain carbons); (■) 85.3 ppm (tertiary hydroperoxides and/or dialkyl peroxides); (◆) 74.2 ppm (tertiary alcohols); (▲) ~207 ppm (methyl ketones); (□) 170−175 ppm (esters and/or peresters); (○) 100−110 ppm (ketals and/or acetals).

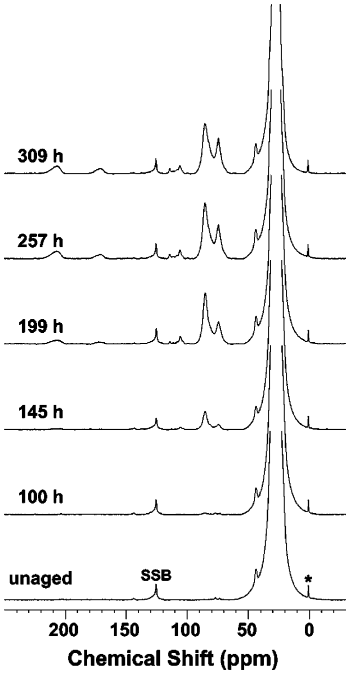


**Figure 4.** 60-s $^{13}$C DP/MAS spectra of a C(2) labeled polypropylene sample thermally aged at 80 °C for varying times, as indicated in the figure. Spectra are presented at 25× the maximum intensity. The spinning sideband is denoted with "SSB" in the unaged spectrum, and the impurity peak is marked with an asterisk (∗).

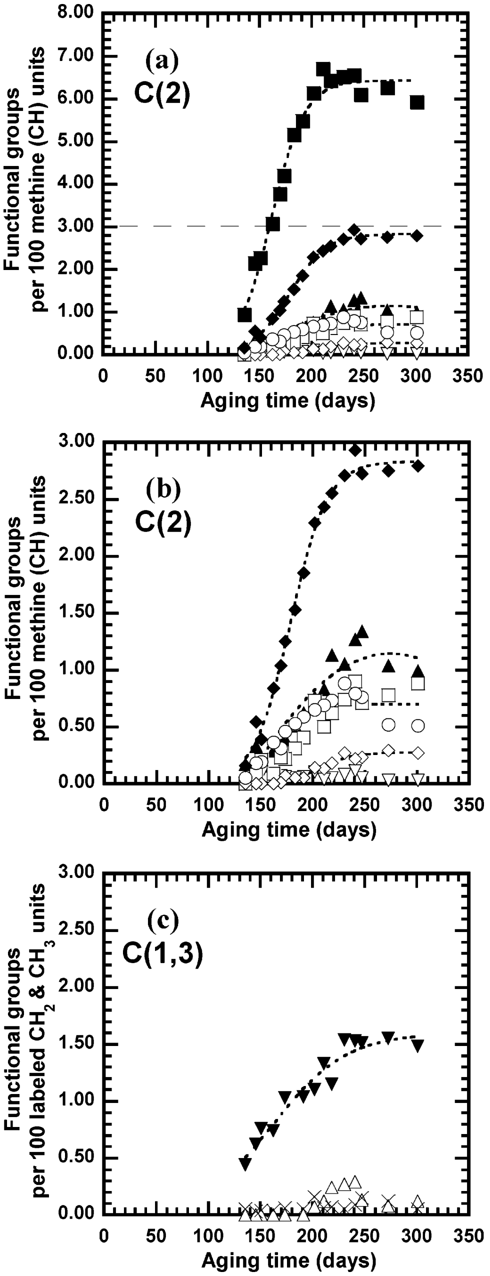


**Figure 5.** Kinetic accumulation of oxidation products in solid polypropylene samples thermally aged at 50 °C. Key: (a) C(2) labeled sample, all products; (b) C(2) labeled sample, low concentration products; (c) C(1,3) labeled sample. Functional groups: (■) tertiary hydroperoxides and/or dialkyl peroxides; (◆) tertiary alcohols; (▲) methyl ketones; (△) in-chain ketones; (▽) carboxylic acids on C(2) carbon; (□) esters and/or peresters on C(2) carbon; (▼) carboxylic acids and/or esters on C(1) carbon; (◇) ketals and/or acetals on C(2) carbon (114.1 ppm); (○) ketals and/or acetals on C(2) carbon (105.7 ppm); (×) ketals and/or acetals on C(1) carbon (100−117 ppm). Dotted lines are guides to the eye.

Solid-state $^{13}$C DP/MAS spectra of the C(2), C(1,3), and C(1) labeled polypropylene samples were acquired at different thermal aging times and γ-radiation doses for the specific aging conditions examined in this study (as listed in Table 2). An example is given in Figure 4, in which 60-s spectra of a C(2) labeled PP sample thermally aged at 80 °C were obtained at various aging times. The accumulation of oxidation products is clearly seen as the $^{13}$C resonances attributed to oxidation-induced functional groups increase in intensity with aging. Using the resonance identifications detailed in the previous section (Table 2), the distribution and kinetic accumulation of these functional groups were analyzed for each specific aging condition. The effects of aging temperature and γ-radiation on the distribution and buildup of oxidation products can thus be investigated. Similar studies have been previously conducted and reported in the literature for thermally aged[31,43,47] and γ-irradiated[31,48,49] polypropylenes using infrared spectroscopy.

**3.2.1. Thermal Aging.** The kinetic accumulation of functional groups due to oxidation in solid polypropylene samples thermally aged at 50, 80, and 109 °C are presented in Figures 5, 6, and 7, respectively. $^{13}$C resonance integrals were normalized by the total inte-

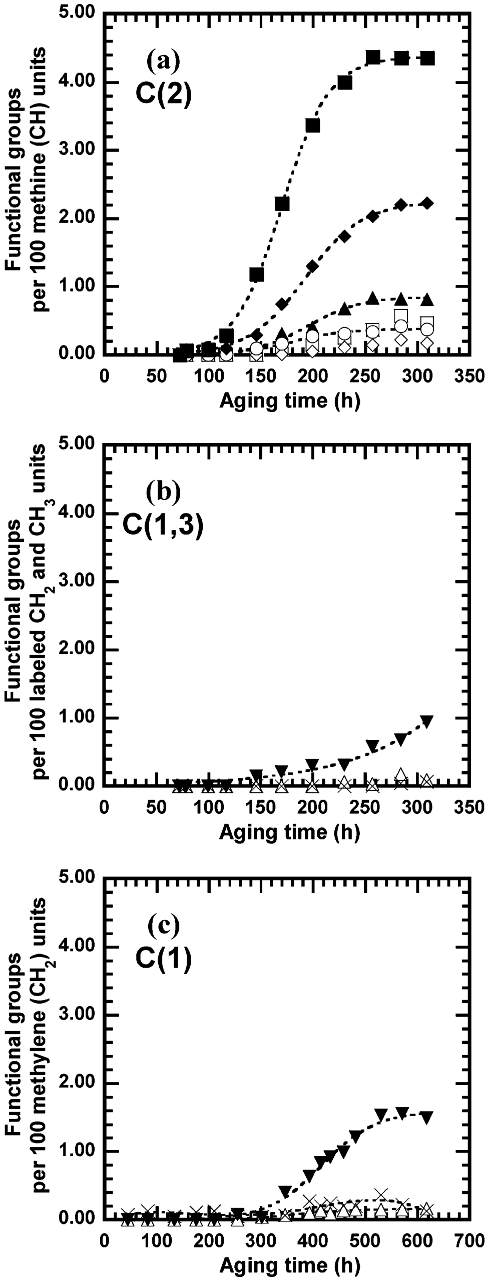


**Figure 6.** Kinetic accumulation of oxidation products in solid polypropylene samples thermally aged at 80 °C. Key: (a) C(2) labeled sample; (b) C(1,3) labeled sample; (c) C(1) labeled sample. Symbols for functional groups as in Figure 5. Dotted lines are guides to the eye.

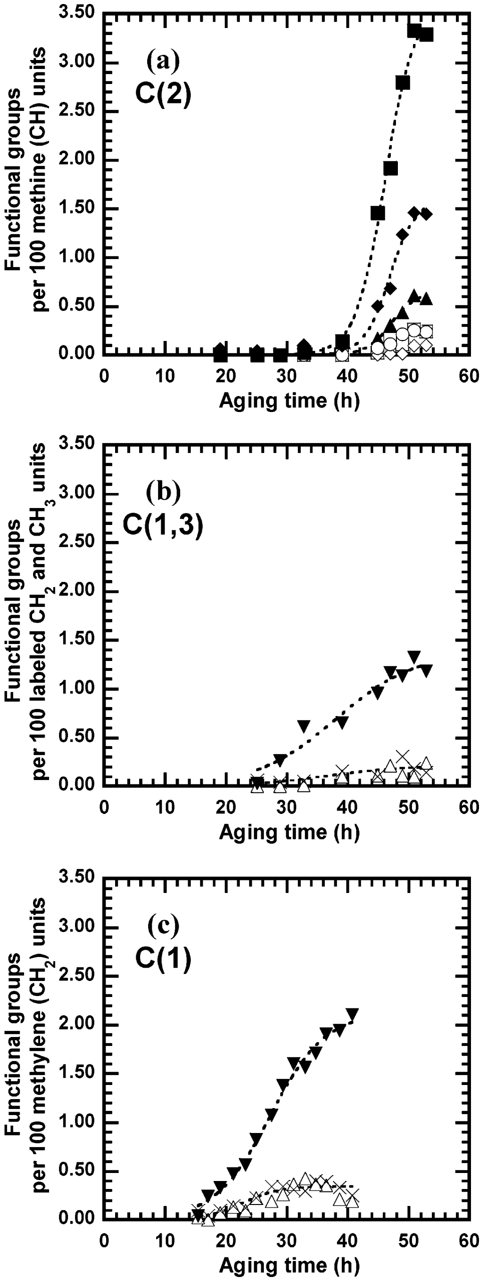


**Figure 7.** Kinetic accumulation of oxidation products in solid polypropylene samples thermally aged at 109 °C. Key: (a) C(2) labeled sample; (b) C(1,3) labeled sample; (c) C(1) labeled sample. Symbols for functional groups as in Figure 5. Dotted lines are guides to the eye.

gral of the spectrum. These normalized integrals can thus be equated to functional group concentrations (no. of functional groups per 100 PP main-chain units). In the case of the C(1,3) samples, for every 100 labeled $CH_2$ and $CH_3$ units there are approximately 69 methylene ($CH_2$) units and 31 methyl ($CH_3$) units (Table 1). Characteristic sigmoidal build-up curves with definite induction periods are observed, typical of homogeneous autoxidation. The sigmoidal shape of the build-up curves arises from exhaustion of the most reactive sites.

Peroxides (tertiary hydroperoxides and/or dialkyl peroxides) clearly comprise the largest fraction of thermal oxidation products on the tertiary C(2) carbon at all of the aging temperatures examined (Figures 5−7, part a). The significantly large hydroperoxide concentration resulting from thermal oxidation was also seen by Lacoste et al.[31] Tertiary alcohols and methyl ketones are the next most abundant oxidation products associated with the tertiary carbons. This observation agrees with accepted mechanisms that show their direct formation from alkoxy radicals produced by the degradation of tertiary hydroperoxides (eqs 2 and 3). Ketals and/or acetals on the C(2) carbon, which resonate at 105.7 and 114.1 ppm, make up only a small portion of the detected oxidation products on the C(2) carbon. Overall, the C(2) thermal oxidation product concentrations in the plateau region of the accumulation curves (Figures 5−7, part a) appear to be largest at 50 °C, smaller at 80 °C, and smaller still at 109 °C. Carboxylic acids and/or esters resonating at ∼179 ppm (peak e in Figure 1) comprised the vast majority of oxidation products observed in the C(1) and C(1,3) labeled sample spectra, as seen in Figure 5, part c, and Figures 6 and 7, parts b and c.

**Table 3. Distribution[a] of Oxidation-Induced Functional Groups Observed in Thermally Aged Polypropylene Samples**

| | aging temp and time after induction period | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 50 °C, ~100 days | | 80 °C, ~175 h | | | | 109 °C, ~14 h | | | |
| functional group | C(2)[b] | C(1,3)[c] | C(2)[b] | C(1,3)[c] | C(2)[b] | C(1) | C(2)[b] | C(1,3)[c] | C(2)[b] | C(1) |
| tertiary hydroperoxides/dialkyl peroxides | 45.3 | | 42.7 | | 42.9 | | 45.7 | | 44.0 | |
| tertiary alcohols | 18.8 | | 21.6 | | 21.7 | | 20.0 | | 19.3 | |
| methyl ketones | 7.3 | | 8.0 | | 8.1 | | 8.1 | | 7.8 | |
| carboxylic acids on C(2) carbon | 0.6 | | | | | | | | | |
| esters/peresters on C(2) carbon | 5.1 | | 5.6 | | 5.6 | | 3.3 | | 3.2 | |
| carboxylic acids/esters on C(1) carbon | | 11.7 | | 13.8 | | 11.9 | | 13.3 | | 14.3 |
| in-chain ketones | | 2.5 | | 1.3 | | 1.5 | | 2.0 | | 2.5 |
| ketals/acetals on C(2) carbon (114.1 ppm) | 1.9 | | 2.2 | | 2.2 | | 1.4 | | 1.3 | |
| ketals/acetals on C(2) carbon (105.7 ppm) | 6.1 | | 4.1 | | 4.1 | | 3.2 | | 3.1 | |
| ketals/acetals on C(1) carbon | | 0.7 | | 0.7 | | 2.0 | | 3.1 | | 4.5 |

[a] Values presented are the mole percents of the total oxidation products on the PP chain with each aging temperature. [b] Values derived from the C(2) labeled sample NMR spectra are relative to values from *either* the C(1,3) *or* C(1) labeled sample spectra. [c] Integral fractions from the C(1,3) NMR spectra were normalized by 0.68, based on the assumption these products originate exclusively from the C(1) carbon.

The overall distribution of oxidation-induced functional groups in aged isotactic polypropylene, taking into account contributions from the C(1), C(2), and C(3) main-chain carbons, can be estimated from the selectively labeled isotactic PP films in this study. We have shown that the PP samples have relatively similar crystallinity (based on the measured heats of fusion) and molecular weight parameters (Table 1). It has been shown experimentally that a heterogeneous polypropylene material can show a range of induction periods.[50] If a specific aging time *after* the induction period is chosen for a given aging temperature, then the different selectively labeled samples may be assumed to have similar degrees of aging.

One further assumption was made concerning the functional groups observed in the C(1) and C(1,3) labeled samples. Note that in Figures 6 and 7 the product concentrations in the C(1) samples are consistently higher than in the C(1,3) samples. If the product concentration values in the C(1,3) samples are normalized by 0.68 (factor obtained from the $^{13}CH_2$ abundance in Table 1), assuming all of the functional groups originate exclusively from the secondary C(1) carbon with no functional groups forming on the methyl C(3) carbon site, the concentration values of the two samples would be visibly similar. This assumption is incorporated into the estimation of the oxidation product distributions given in Table 3 for thermally aged PP samples. At 80 and 109 °C aging, the C(2) product quantities are determined relative to both the C(1,3) and C(1) product quantities. Note that the product quantities for the C(1) and C(1,3) samples are comparable, accounting for experimental error, giving further support to the assumption that functional groups originating from the methyl carbon are negligible.

Upon evaluation of the data in Table 3, it can be seen that the tertiary hydroperoxides and/or dialkyl peroxides constitute the largest fraction of oxidation-induced functional groups at all three aging temperatures. Tertiary alcohols are the next most abundant functional group, followed by carboxylic acids/esters on the C(1) carbon and methyl ketones on the C(2) carbon. Ketals/acetals on the C(2) carbon resonating at 105.7 ppm and esters/peresters on the C(2) carbon have similar product fractions at each temperature. Note that with increasing aging temperature, the product fractions of the C(2) esters/peresters and C(2) ketals/acetals at 105.7 ppm decrease while the corresponding fraction of ketals/acetals on the C(1) carbon increase.

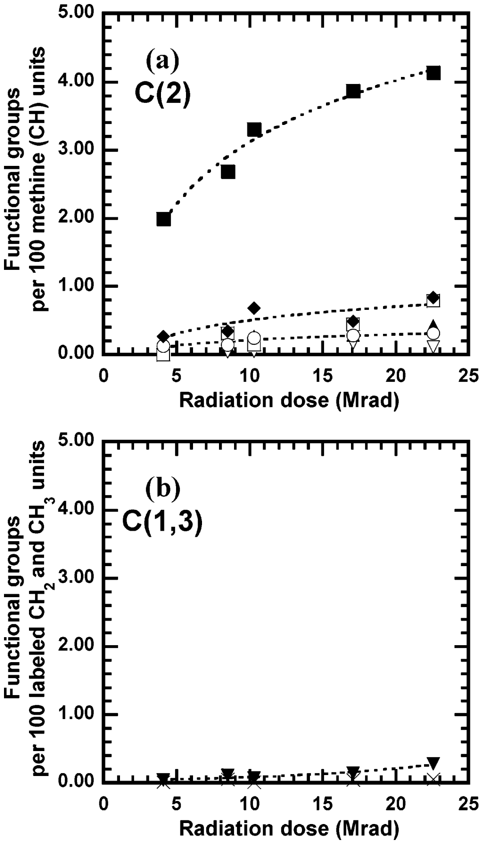


**Figure 8.** Kinetic accumulation of oxidation products in solid polypropylene samples exposed to $\gamma$-radiation at 24 °C. Key: (a) C(2) labeled sample; (b) C(1,3) labeled sample. Symbols for functional groups as in Figure 5. Dotted lines are guides to the eye.

The most noteworthy observation concerning Table 3, however, can be seen in the nearly equivalent product fractions of the four major functional groups at the three aging temperatures. Tertiary peroxides are consistently 44 ± 2% of the total oxidation products. Tertiary alcohols are 20 ± 2%, C(1) carboxylic acids/esters 13 ± 2%, and methyl ketones 8 ± 1%. Hence, the product fractions of the large majority of oxidation products are independent of the aging temperatures examined. These data are consistent with the micro heterogeneous oxidation-spreading model of Celina and George.[3,50−52] Indeed, it was further observed from thermal aging experiments that on ostensibly identical small (~60 mg) PP samples aged side by side, the induction time to the

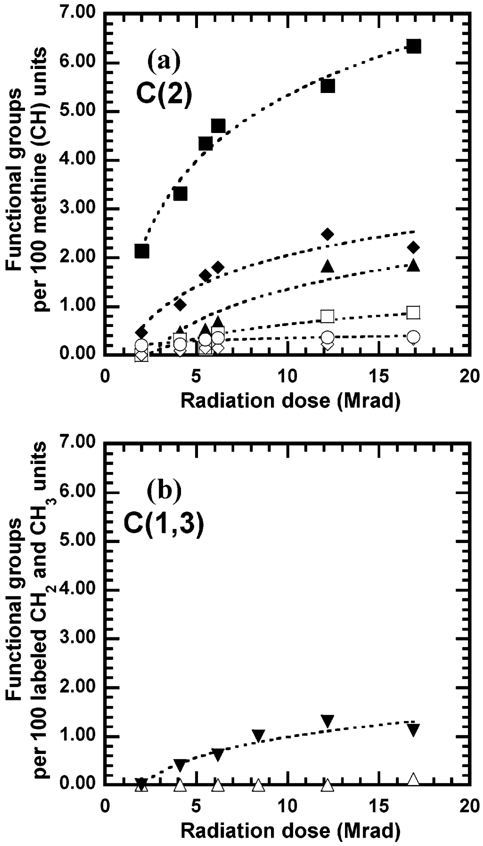


**Figure 9.** Kinetic accumulation of oxidation products in solid polypropylene samples exposed to $\gamma$-radiation at 80 °C. Key: (a) C(2) labeled sample; (b) C(1,3) labeled sample. Symbols for functional groups as in Figure 5. Dotted lines are guides to the eye.

onset of oxidation varied between samples. However, once oxidation began, the oxidation rates were similar. This behavior was first observed by Celina and George[50] and seen later with PP films.[47,53]

**3.2.2. $\gamma$-Radiation Aging.** The kinetic accumulation of functional groups in solid polypropylene samples due to oxidation by $\gamma$-irradiation at 24 °C and 80 °C are shown in Figures 8 and 9, respectively. The PP samples were exposed to $\gamma$-radiation at a dose rate of 80−90 krad/h. Unlike thermal aging, no apparent induction period is detected with the $\gamma$-irradiated PP samples. The radiation exposure has a much stronger initiation potential than thermal aging alone. Overall product distributions were estimated for the $\gamma$-irradiated polypropylenes (Table 4) as in the last section for the thermally aged materials. Again, the peroxides (tertiary hydroperoxides and/or dialkyl peroxides) are the most abundant oxidation product, which agrees with the results of previous studies[31,48,49] at dose rates ranging from 28 to 700 krad/h.

Radiation-oxidation products show some overall similarities to the thermal oxidation results, but also exhibit some differences. Increasing the irradiation temperature from 24 to 80 °C accelerates the rate of oxidation and increases the total product formation (Figures 8 and 9), which was also observed by Decker and Mayo[48] using IR analysis. Unlike thermal aging, product distributions are not independent of aging temperature when PP is $\gamma$-irradiated (Table 4). For irradiation at 24 °C, the tertiary peroxides (58.4%) and the esters/peresters (11.1%) are significantly higher than for the corresponding products obtained by thermal aging at any of the temperatures studied. These values are also higher compared with material irradiated at 80 °C. The samples irradiated at 24 °C also exhibited lower yields of several major secondary oxidation products compared with the thermal aging results, including tertiary alcohols, methyl ketones, and carboxylic acids/esters. The samples irradiated at 80 °C showed increased concentrations of alcohols, methyl ketones and carboxylic acids/esters, compared with the lower temperature irradiation, whereas the concentrations of peroxides and esters/peresters were substantially lower. This is consistent with enhanced decomposition of peroxides to form secondary oxidation products at the higher irradiation temperature. The large decrease in the ester/perester resonance (peak d in Figure 1) at higher temperatures is consistent with a significant component of peroxidic species in this peak in the case of the 24 °C irradiation.

The occurrence of a greatly enhanced methyl ketone signal in the 80 °C irradiated C(2) labeled sample spectra, compared with the 24 °C irradiated C(2) spectra, is significant. Interestingly, the methyl ketone signal in the 80 °C irradiated material is in fact much larger than that found in any of the thermal aging experiments, while the tertiary alcohol signal is smaller compared with the thermal experiments. When a tertiary peroxide decomposes, the two main reaction paths lead either: 1) to a methyl ketone, which also results in cleavage of the macromolecular chain (eq 3), or else 2) to a tertiary alcohol, which does not involve chain cleavage (eq 2). These facts can be considered in light

**Table 4. Distribution[a] of Oxidation-Induced Functional Groups Observed in Polypropylene Samples Exposed to $\gamma$-Radiation**

| | aging temp and radiation dose | | | |
|---|---|---|---|---|
| | 24 °C, 23 Mrad | | 80 °C, 17 Mrad | |
| functional group | C(2)[b] | C(1,3)[c] | C(2)[b] | C(1,3)[c] |
| tertiary hydroperoxides/dialkyl peroxides | 58.4 | | 46.1 | |
| tertiary alcohols | 11.7 | | 16.0 | |
| methyl ketones | 5.9 | | 13.5 | |
| carboxylic acids on C(2) carbon | 1.6 | | | |
| esters/peresters on C(2) carbon | 11.1 | | 6.3 | |
| carboxylic acids/esters on C(1) carbon | | 5.8 | | 11.9 |
| in-chain ketones | | | | 1.3 |
| ketals/acetals on C(2) carbon (114.1 ppm) | | | 2.3 | |
| ketals/acetals on C(2) carbon (105.7 ppm) | 4.4 | | 2.7 | |
| ketals/acetals on C(1) carbon | | 1.0 | | |

[a] Values presented are the mole percents of the total oxidation products on the PP chain with each aging temperature. [b] Values derived from the C(2) labeled sample NMR spectra are relative to values from the C(1,3) labeled sample spectra. [c] Integral fractions from the C(1,3) NMR spectra were normalized by 0.68, based on the assumption these products originate exclusively from the C(1) carbon.

of the long-standing observation by Clough and Gillen,[54] as well as others, that for many common polymers, the simultaneous application of radiation and elevated temperature often leads to a much stronger decrease in mechanical properties, compared with radiation exposure at room temperature. This observation has been described previously in terms of a "synergism" between the environmental effects of radiation and temperature.

## 4. Conclusions

Polypropylene samples were prepared, in which chains were isotopically labeled at specific positions with $^{13}$C. Unstabilized films of these materials were subjected to thermal aging and $\gamma$-irradiation and were analyzed with solid-state $^{13}$C NMR. It was found that the vast majority of oxidation-induced functional groups formed on the tertiary (CH) carbons of the polypropylene. Of these products, tertiary hydroperoxides and/or dialkyl peroxides, which share the same $^{13}$C resonance, were the most abundant, with tertiary alcohols as the second most abundant product. We detected no peroxides or alcohols originating from the *secondary* or the methyl positions of the PP; indeed we found no evidence of any macromolecular oxidation products originating from reaction at the methyl carbon. Substantial amounts of carboxylate products were observed (likely a mixture of acids, esters, and very likely peresters). The majority of the carboxylates originated from the secondary PP carbon atom. Other oxidation products included methyl ketones (from the tertiary PP carbon), in-chain ketones (from the secondary PP carbon), and ketal/acetal products (from both the tertiary and secondary PP carbons).

Time-dependent plots of thermal oxidation products were sigmoidal, typical of homogeneous autoxidation. Remarkably similar distributions of the major thermal oxidation products were found, independent of aging temperature, over the range of temperatures studied (50, 80, and 109 °C). In contrast, oxidation product distributions for irradiated materials were substantially different for room temperature vs elevated temperature exposure. Samples irradiated at 24 °C exhibited exceptionally high concentrations of peroxidic species. By comparison, irradiation at 80 °C gave rise to higher yields of secondary oxidation products, such as tertiary alcohols and carboxylic acids, and particularly large amounts of methyl ketones, indicative of a high yield of chain scission for a combined environment of radiation and temperature.

This paper indicates the utility of isotopic labeling to help sort complex degradation mechanisms in polymers. We expect this technique will also be useful for detailed analyses of macromolecular changes induced by other means, such as polymer processing (for example, studies of cross-linking, grafting or other chemical derivatization).

**Acknowledgment.** Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL8500. The authors are grateful to Mat Celina for offering valuable comments, to Prof. John Bercaw for cooperation in providing the C(1) labeled PP sample, to Michelle Shedd for DSC measurements, and to Sean Winters and Don Berry for assistance in preparing samples. Impact Analytical (Midland, MI) is acknowledged for acquiring the molecular weight data.

## References and Notes

(1) Clough, R. L. *Nucl. Instrum. Methods Phys. Res. B* **2001**, *185*, 8–33.
(2) Carlsson, D. J.; Wiles, D. M. *J. Macromol. Sci.—Rev. Macromol. Chem.* **1976**, *C14*, 65–106.
(3) George, G. A.; Celina, M. In *Handbook of Polymer Degradation*, 2nd ed.; Hamid, S. H., Ed.; Marcel Dekker: New York, 2000; pp 277–313.
(4) Bovey, F. A.; Jelinski, L.; Mirau, P. A. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Academic Press: San Diego, CA, 1988.
(5) Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers*; Academic Press: San Diego, CA, 1994.
(6) Cheng, H. N.; Schilling, F. C.; Bovey, F. A. *Macromolecules* **1976**, *9*, 363–365.
(7) Randall, J. C.; Zoepfl, F. J.; Silverman, J. *Radiat. Phys. Chem.* **1983**, *22*, 183–192.
(8) Jelinski, L. W.; Dumais, J. J.; Luongo, J. P.; Cholli, A. L. *Macromolecules* **1984**, *17*, 1650–1655.
(9) Horii, F.; Zhu, Q.; Kitamaru, R.; Yamaoka, H. *Macromolecules* **1990**, *23*, 3.
(10) Assink, R. A.; Celina, M.; Dunbar, T. D.; Alam, T. M.; Clough, R. L.; Gillen, K. T. *Macromolecules* **2000**, *33*, 4023–4029.
(11) Busfield, W. K.; Hanna, J. V. *Polym. J.* **1991**, *23*, 1253–1263.
(12) Vaillant, D.; Lacoste, J.; Dauphin, G. *Polym. Degrad. Stab.* **1994**, *45*, 355–360.
(13) O'Donnell, J. H.; Whittaker, A. K. *Polymer* **1992**, *33*, 62–67.
(14) O'Donnell, J. H.; Whittaker, A. K. *Radiat. Phys. Chem.* **1992**, *39*, 209–214.
(15) Hill, D. J. T.; O'Donnell, J. H.; Perera, M. C. S.; Pomery, P. J. In *Irradiation of Polymers: Fundamentals and Technological Applications*; Clough, R. L., Shalaby, S. W., Eds.; ACS Symposium Series 620; American Chemical Society: Washington, DC, 1996, pp 139–150.
(16) Yang, L.; Heatley, F.; Blease, T. G.; Thompson, R. I. G. *Eur. Polym. J.* **1996**, *32*, 535–547.
(17) Alam, T. M.; Celina, M.; Assink, R. A.; Clough, R. L.; Gillen, K. T.; Wheeler, D. R. *Macromolecules* **2000**, *33*, 1181–1190.
(18) Alam, T. M.; Celina, M.; Assink, R. A.; Clough, R. L.; Gillen, K. T. *Radiat. Phys. Chem.* **2001**, *60*, 121–127.
(19) Mkhatresh, O. A.; Heatley, F. *Macromol. Chem. Phys.* **2002**, *203*, 2273–2280.
(20) Mkhatresh, O. A.; Heatley, F. *Polym. Int.* **2004**, *53*, 1336–1342.
(21) Burger, B. J.; Bercaw, J. E. *New Developments in the Synthesis, Manipulation, and Characterization of Organometallic Compounds*; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.
(22) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
(23) Gillen, K. T.; Clough, R. L.; Jones, L. H. *Sandia Labs Rep. SAND81-2613* **1982.**
(24) Bennett, A. E.; Rienstra, C. M.; Auger, M.; Lakshmi, K. V.; Griffin, R. G. *J. Chem. Phys.* **1995**, *103*, 6951–6958.
(25) Bunn, A.; Cudby, M. E. A.; Harris, R. K.; Packer, K. J.; Say, B. J. *Polymer* **1982**, *23*, 694–698.
(26) Gomez, M. A.; Tanaka, H.; Tonelli, A. E. *Polymer* **1987**, *28*, 2227–2232.
(27) Chien, J. C. W.; Boss, C. R. *J. Polym. Sci.: Part A-1* **1967**, *5*, 3091–3101.
(28) Chien, J. C. W.; Vandenberg, E. J.; Jabloner, H. *J. Polym. Sci.: Part A-1* **1968**, *6*, 381–392.
(29) Carlsson, D. J.; Wiles, D. M. *Macromolecules* **1969**, *2*, 597–606.
(30) Carlsson, D. J.; Lacoste, J. *Polym. Degrad. Stab.* **1991**, *32*, 377–386.
(31) Lacoste, J.; Vaillant, D.; Carlsson, D. J. *J. Polym. Sci.: Part A: Polym. Chem.* **1993**, *31*, 715–722.
(32) Philippart, J. L.; Gardette, J. L. *Polym. Degrad. Stab.* **2001**, *73*, 185–187.
(33) Pouchert, C. J.; Behnke, J., Eds. *The Aldrich Library of $^{13}$C and $^{1}$H FT NMR Spectra*, 1st ed.; Aldrich Chemical Co.: Milwaukee, WI, 1993; Vol. 1.
(34) Carlsson, D. J.; Wiles, D. M. *Macromolecules* **1969**, *2*, 587–597.
(35) Mill, T.; Richardson, H.; Mayo, F. R. *J. Polym. Sci.: Polym. Chem. Ed.* **1973**, *11*, 2899–2907.
(36) Geuskens, G.; Kabamba, M. S. *Polym. Degrad. Stab.* **1982**, *4*, 69–76.

(37) Zahradnícková, A.; Sedlár, J.; Dastych, D. *Polym. Degrad. Stab.* **1991**, *32*, 155−176.
(38) Gijsman, P.; Hennekens, J.; Vincent, J. *Polym. Degrad. Stab.* **1993**, *42*, 95−105.
(39) Gijsman, P.; Kroon, M.; Oorschot, M. v. *Polym. Degrad. Stab.* **1996**, *51*, 3−13.
(40) Falicki, S.; Carlsson, D. J.; Gosciniak, D. J.; Cooke, J. M. *Polym. Degrad. Stab.* **1993**, *41*, 205−210.
(41) Mao, J.-D.; Schmidt-Rohr, K. *Solid State Nucl. Magn. Reson.* **2004**, *26*, 36−45.
(42) Mowery, D. M.; Assink, R. A.; Clough, R. L.; Bernstein, R. To be submitted for publication.
(43) Adams, J. H. *J. Polym. Sci.: Part A-1* **1970**, *8*, 1077−1090.
(44) George, G. A.; Celina, M.; Vassallo, A. M.; Cole-Clarke, P. A. *Polym. Degrad. Stab.* **1995**, *48*, 199−210.
(45) Iring, M.; Tüdös, F. *Prog. Polym. Sci.* **1990**, *15*, 217−262.
(46) Gugumus, F. *Polym. Degrad. Stab.* **2001**, *74*, 327−339.
(47) Gugumus, F. *Polym. Degrad. Stab.* **1998**, *62*, 235−243.
(48) Decker, C.; Mayo, F. R. *J. Polym. Sci.: Polym. Chem. Ed.* **1973**, *11*, 2847−2877.
(49) Tidjani, A.; Watanabe, Y. *J. Appl. Polym. Sci.* **1996**, *60*, 1839−1845.
(50) Celina, M.; George, G. A.; Billingham, N. C. *Polym. Degrad. Stab.* **1993**, *42*, 335−344.
(51) Celina, M.; George, G. A. *Polym. Degrad. Stab.* **1993**, *40*, 323−335.
(52) Celina, M.; George, G. A. *Polym. Degrad. Stab.* **1995**, *50*, 89−99.
(53) Gugumus, F. *Polym. Degrad. Stab.* **1998**, *62*, 245−257.
(54) Clough, R. L.; Gillen, K. T. *J. Polym. Sci.: Polym. Chem. Ed.* **1981**, *19*, 2041−2051.

MA047381B