Insights into Oxidation Pathways, from Gaseous Products of Polypropylene with Selective Isotopic Labeling

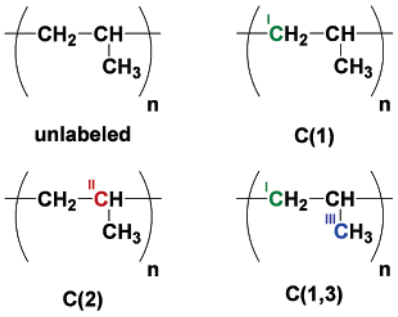
Steven M. Thornberg,[†] Robert Bernstein,[†] Daniel M. Mowery,[†] Sara B. Klamo,[‡,§] James M. Hochrein,[†] Jason R. Brown,[†] Dora K. Derzon,[†] and Roger L. Clough*,[†]

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

Received April 28, 2006
Revised Manuscript Received June 29, 2006

Polymer degradation mechanisms are exceedingly complex, but their understanding is fundamental to improving material durability. We have initiated selective isotopic labeling as a means of tracking oxidation chemistry, and chose polypropylene (PP) to test this approach, since it has a simple structure (three unique carbon sites along the chain), and is of commercial importance. There has in fact been much interest in the stability of PP, and many prior studies have contributed to the ongoing development of understanding its degradation processes.[1−19] In recent work,[20,21] we applied ^{13}C NMR to examine the solid-phase oxidation products of isotopically labeled PP; in this Communication, we begin identifying the volatile products.

PP samples which are selectively enriched with ^{13}C at each of the three sites in the repeating unit have been synthesized (see below).[20] The C(1) sample contained the ^{13}C label in the secondary position (∼97%), the C(2) sample had the ^{13}C in the tertiary position (∼99%), and the C(1,3) contained ^{13}C in both the secondary position (∼68%) and in the methyl group (∼31%) due to partial scrambling during polymerization. The mostly isotactic materials had M_w of ∼(1.6−2.6) × 10^5. For aging experiments, a 50 mg thin film of the additive-free PP, was held in oxygen in an enclosed vial at 130 °C for ∼60 h, after which GC-mass spectroscopy was performed, using the "SPME" (solid-phase microextraction) technique to sample the atmosphere in the vial.



Identification of PP Oxidation Products: Use of ^{18}O. ^{18}O-labeled oxygen gas was used in the atmosphere in one parallel set of thermal oxidation experiments, to ensure that each volatile product observed had originated from the aging exposure and not from oxygen-containing impurities already in the material (such as side products during polymerization). Additionally, a comparison of the ^{18}O and ^{16}O spectra gave the number of oxygen atoms in each mass spectral fragment, which is useful in structural assignments.

Acetic Acid. Figure 1. shows mass spectra of one volatile product originating from both unlabeled and ^{13}C-labeled PP samples following exposure in air at 130 °C. The product formed under ^{18}O oxygen was found to contain two ^{18}O oxygen atoms. High-resolution MS analysis with perfluorokerosene as internal marker confirmed an atomic composition of $C_2H_4O_2$, and the structure was further verified by matching with a library spectrum of acetic acid.

By comparison of the mass spectra, it can be concluded that acetic acid formed by thermal oxidation of PP is comprised of one carbon originating from the C(2) position and one carbon from the C(3) position. This is seen by comparing the parent peak for acetic acid (mass 60 in the unlabeled PP), with the mass of 61 in the C(2) spectrum. In the C(1,3) material, the parent peaks occur at 61 and 60, with the 61 peak accounting for ∼$^1/_3$ of the combined peak intensities, as expected for a sample having 31% of the molecules labeled in the C(3) position. Acetic acid does not incorporate C(1) carbon (insignificant amounts, if any), as illustrated by the C(1) parent peak at 60. The unlabeled PP shows a peak at 15, assigned to a methyl fragment (CH_3). In the C(1) and C(2) spectra, the methyl fragment is similarly found at mass 15, whereas in the C(1,3) sample, the methyl signal occurs at both 16 and 15, with the peak at 16 accounting for ∼$^1/_3$ of the combined intensity. These results indicate that the methyl group in the acetic acid originates from C(3) in PP. Other peaks in the unlabeled sample at 43 (assigned to C_2H_3O, from loss of an OH group), and at 45 (assigned to CO_2H, from loss of methyl), are both shifted to 1 higher mass unit in the C(2) sample, consistent with labeling on the carboxyl carbon. On the basis of this analysis, we assign the origin of acetic acid as shown below.

3-Pentene-2-one. Figure 2. shows mass spectra obtained on another volatile PP product, for which the ^{18}O experiment indicated one oxygen atom incorporated. High-resolution analysis confirmed an atomic composition of C_5H_8O, and the structure was verified by matching a library spectrum.

By comparison of the parent peak (84) in the unlabeled sample to the parent peaks of the three labeled materials, it is concluded that this PP oxidation product is comprised of one carbon atom from the C(1) position, two carbons from the C(2) position, and two carbons from the C(3) position. The largest fragmentation peak in the unlabeled material is at 69, assigned to loss of a methyl group from the parent ion. This same fragmentation in the C(1) and C(2) spectra similarly corresponds to a loss of 15 mass units, consistent with no C(1) or C(2) labeling in the methyl group lost. In contrast, for the C(1,3) sample, the spectrum indicates that loss of methyl from the 86 parent ion can involve loss of 16 mass units [compare the ratio of the 86/85 peaks to the 71/70 peaks].

Peaks in unlabeled material at 43 and 41 can be assigned to the fragments from cleavage of the bond between the carbonyl group and the double bond (i.e., 43 is the methyl carbonyl fragment, C_2H_3O, while 41 is the methyl alkene fragment, C_3H_5). In the C(2) spectrum, both fragments are shifted to one higher mass unit, indicating one C(2) carbon atom in each

* To whom correspondence should be addressed.
[†] Sandia National Laboratories.
[‡] Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology.
[§] Current address: Dow Chemical Company, 1776 Building, Midland, MI 48674.

10.1021/ma060945m CCC: $33.50
Published on Web 07/20/2006

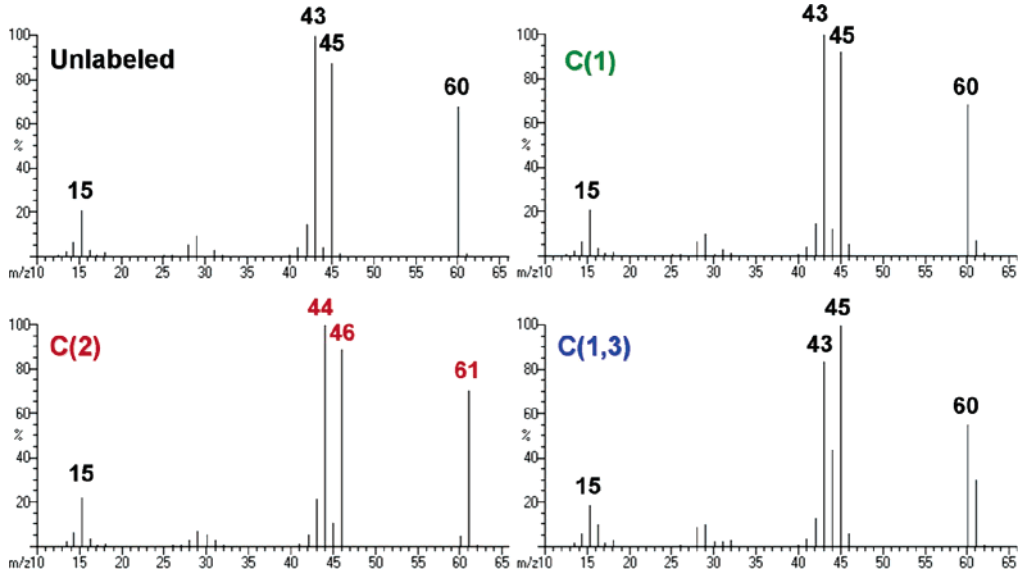


Figure 1. Mass spectra of acetic acid from the degradation of ^{13}C-labeled PP.

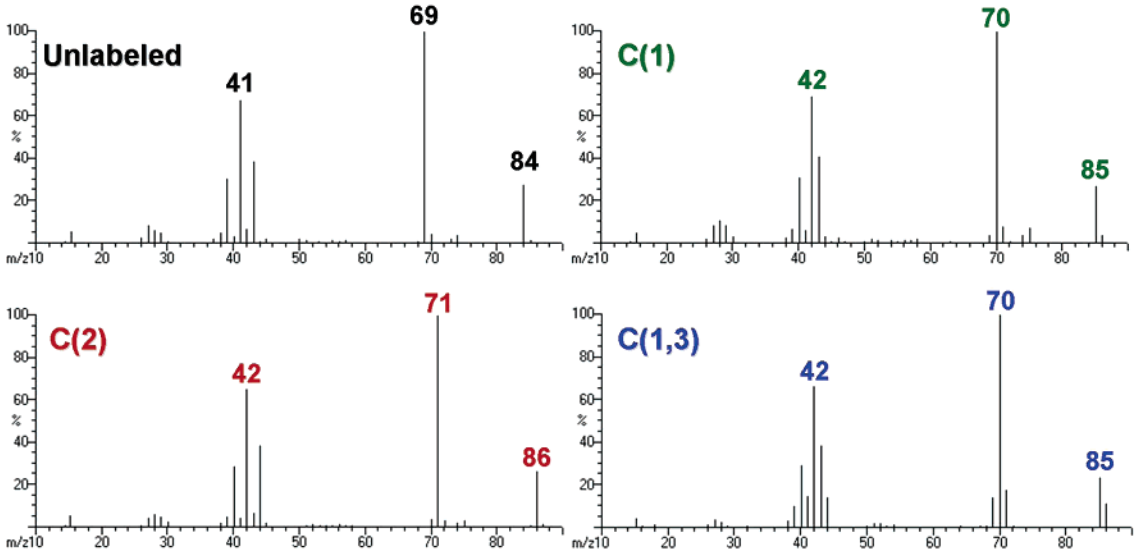


Figure 2. Mass spectra of 3-pentene-2-one from the degradation of ^{13}C-labeled PP.

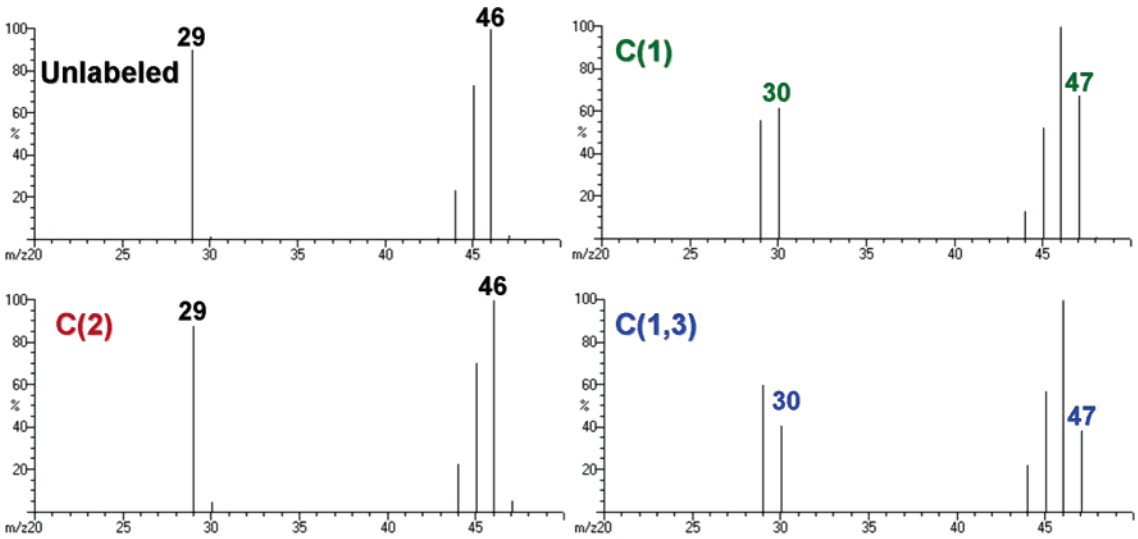
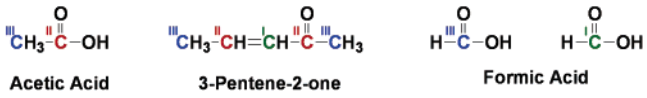


Figure 3. Mass spectra of formic acid from the degradation of ^{13}C-labeled PP.

fragment. In the C(1) spectrum, the 41 peak has shifted to one higher mass unit, whereas the 43 peak is unchanged, showing that the C(1) carbon atom is contained in the alkene fragment only. This leads to the obvious deduction that there must be one C(3) atom in each of these two fragments, and the splitting pattern in the C(1,3) spectrum is consistent with this conclusion. The overall interpretation of the labeling in 3-pentene-2-one is not completely unambiguous − for example, distinguishing between the two carbons of the double bond would be very difficult. However, based on the overall information, we assign the most likely labeling structure to this molecule as shown below.

Formic Acid. Figure 3 shows spectra for a volatile product found to incorporate two oxygen atoms in the ^{18}O experiment, which is confirmed as formic acid by high resolution analysis and by comparison with a library spectrum. From Figure 3, it is seen that none (or only an insignificant amount) of the formic acid comes from the C(2) carbon in PP, but must originate from two separate reaction pathways: one from C(1) carbon and one from C(3), in roughly similar amounts.



Concluding Remarks. This paper establishes an approach to identifying the origins of gaseous oxidation products from PP by specific isotopic labeling of the polymer, followed by GC-mass spec analysis. Structural assignments of three key volatile species have been made, in terms of their positions of origin from within the macromolecule, which are remarkably specific. Acetic acid has been seen before as an important oxidation product in unlabeled PP, under a variety of thermal and photochemical conditions.[22−26] That the carboxyl group in this compound originates solely from the C(2) position is consistent with a proposed mechanism, involving attack of hydroxyl radical on a C(2) methyl ketone, that has been under discussion for many years.[22,26] In the case of formic acid (also seen before from PP oxidation),[23−25] the fact that the carboxyl comes entirely from C(1) and C(3) provides an intriguing mechanistic contrast with acetic acid. In the case of the 3-pentene-2-one, the very specific labeling is consistent with an origination from the PP macromolecular framework, with chain scission events having occurred at two C(2) carbon atoms (both of which still have their C(3) methyl groups attached). The one chain cleavage event would have come from a C(2) alkoxy radical, giving a methyl ketone, while the other cleavage would have come through radical reactions that culminated in a disproportionation to form a double bond. We conclude that the isotopic labeling approach to identifying macromolecular reaction pathways is promising in terms of sorting out very complex transformations in bulk polymers, particularly when combined with the complementary information that can be obtained on solid-phase reaction products,[20] using the same labeled polymer systems (by NMR or other means). The evaluation of other volatiles from PP oxidation is in progress.

Acknowledgment. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. D.O.E. National Nuclear Security Administration under Contract DE-AC04-94AL8500. The authors thank Judith F. Banet, Rachael D. Boyd, Jessica D. Leong, and MacKenzie Naething for assistance in analyzing the GC/MS data.

References and Notes

(1) Chien, J. C. W.; Boss, C. R. *J. Polym. Sci.: Part A-1* **1967**, *5*, 3091−3101.
(2) Chien, J. C. W.; Boss, C. R. *J. Polym. Sci.: Part A-1* **1967**, *5*, 1683−1697.
(3) Chien, J. C. W.; Vandenberg, E. J.; Jabloner, H. *J. Polym. Sci.: Part A-1* **1968**, *6*, 381−392.
(4) Carlsson, D. J.; Wiles, D. M. *Macromolecules* **1969**, *2*, 587−597.
(5) Carlsson, D. J.; Wiles, D. M. *Macromolecules* **1969**, *2*, 597−606.
(6) Adams, J. H. *J. Polym. Sci.: Part A-1* **1970**, *8*, 1077−1090.
(7) Adams, J. H. *J. Polym. Sci.: Part A-1* **1970**, *8*, 1269−1277.
(8) Adams, J. H. *J. Polym. Sci.: Part A-1* **1970**, *8*, 1279−1288.
(9) Niki, E.; Decker, C.; Mayo, F. R. *J. Polym. Sci.: Polymer Chem.Edition* **1973**, *11*, 2813−2845.
(10) Decker, C.; Mayo, F. R. *J. Polym. Sci.: Polym. Chem. Ed.* **1973**, *11*, 2847−2877.
(11) Carlsson, D. J.; Wiles, D. M. *J. Macromol. Sci.—Rev. Macromol. Chem.* **1976**, *C14*, 65−106.
(12) Geuskens, G.; Kabamba, M. S. *Polym. Degrad. Stab.* **1982**, *4*, 69−76.
(13) Iring, M.; Tüdös, F. *Prog. Polym. Sci.* **1990**, *15*, 217−262.
(14) Lacoste, J.; Vaillant, D.; Carlsson, D. J. *J. Polym. Sci.: Part A: Polym. Chem.* **1993**, *31*, 715−722.
(15) Gijsman, P.; Hennekens, J.; Vincent, J. *Polym. Degrad. Stab.* **1993**, *42*, 95−105.
(16) Celina, M.; George, G. A.; Billingham, N. C. *Polym. Degrad. Stab.* **1993**, *42*, 335−344.
(17) Gijsman, P.; Kroon, M.; Oorschot, M. v. *Polym. Degrad. Stab.* **1996**, *51*, 3−13.
(18) Gugumus, F. *Polym. Degrad. Stab.* **1998**, *62*, 235−243.
(19) George, G. A.; Celina, M. In *Handbook of Polymer Degradation*, 2nd ed.; Hamid, S. H., Ed.; Marcel Dekker: New York, 2000; pp 277−313.
(20) Mowery, D. M.; Assink, R. A.; Derzon, D. K.; Klamo, S. B.; Clough, R. L.; Bernstein, R. *Macromolecules* **2005**, *38*, 5035−5046.
(21) Mowery, D. M.; Assink, R. A.; Derzon, D. K.; Klamo, S. B.; Bernstein, R.; Clough, R. L. *Radiat. Phys. Chem.*, in press.
(22) Barabás, K.; Iring, M.; Lazlo-Hedvig, S.; Kellen, T.; Tudos, F. *Eur. Polym. J.* **1978**, *14*, 405−407.
(23) Hoff, A.; Jacobsson, S. *J. Appl. Polym. Sci.* **1982**, *27*, 2539−2551.
(24) Hoff, A.; Jacobsson, S. *J. Appl. Polym. Sci.* **1984**, *29*, 465−480.
(25) Philippart, J. L.; Posada, F.; Gardette, J. L. *Polym. Degrad. Stab.* **1995**, *49*, 285−290.
(26) Commereuc, S.; Vaillant, D.; Philippart, J. L.; Lacoste, J.; Lemaire, J.; Carlsson, D. J. *Polym. Degrad. Stab.* **1997**, *57*, 175−182.

MA060945M