Environmental Science & Technology

ARTICLE

pubs.acs.org/est

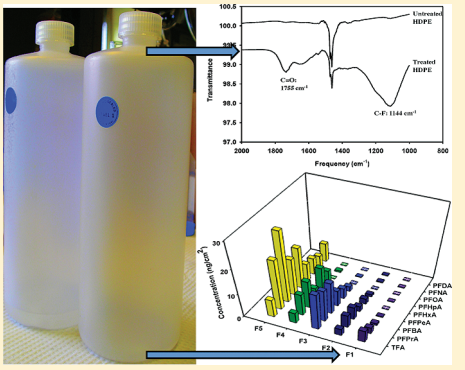
Perfluorinated Carboxylic Acids in Directly Fluorinated High-Density Polyethylene Material

Amy A. Rand and Scott A. Mabury*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada

Supporting Information

ABSTRACT: Perfluorinated carboxylic acids (PFCAs) are ubiquitous in the environment and have been detected in human blood worldwide. One potential route is direct exposure to PFCAs through contact with polymers that have been fluorinated through a process referred to as direct fluorination. PFCAs are hypothesized to be reaction byproducts of direct fluorination when trace amounts of oxygen are present. The objective of this research was to investigate whether PFCAs could be measured in directly fluorinated high-density polyethylene (HDPE) bottles. PFCAs were quantified using Soxhlet extraction with methanol, followed by LC-MS/MS analysis. Total concentrations of PFCAs ranged from 8.5 ± 0.53 to 113 ± 2.5 ng/bottle (1 L), with the short-chain PFCAs, perfluoropropanoic, perfluorobutanoic, perfluoropentanoic, and perfluorohexanoic acids, being the dominant congeners observed. Relative PFCA concentrations varied depending on fluorination level. Structural isomers were detected using ^{19}F NMR and are hypothesized to have formed during the fluorination process; NMR data revealed the linear isomer typically comprised 55% of the examined sample. Internally branched, isopropyl branched, and *t*-butyl PFCA isomers of varying chain length were also identified. Electrochemical fluorination was previously thought to be the only source of branched PFCA isomers. The observation here of branched isomers suggests direct fluorination may be an additional source of exposure to these chemicals. The purpose of this study was to measure PFCAs in directly fluorinated material, serving as a previously unidentified source contributing to the environmental load of PFCAs, with potential for human exposure.



INTRODUCTION

Perfluorocarboxylic acids (PFCA) are persistent contaminants that have been observed in surface waters, wildlife, and humans globally.[1−3] Although perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are the most prevalent compounds measured in human blood[2] followed by long-chain PFCAs (≥C8), PFCAs having a carbon chain length of C5 (perfluoropentanoate, PFPeA) and C6 (perfluorohexanoate, PFHxA) have been detected at low concentrations;[4−7] the literature is silent on shorter chain PFCAs. There have been no studies that have quantified short chain (C2−C4) above the detection limit. Attention has been focused on understanding the toxicity of PFCAs, especially for PFOA,[8−11] and long-chain (≥C8) PFCAs have been found to be bioaccumulative.[12] It is therefore necessary to understand sources of PFCAs to the environment.

Directly fluorinated polyolefins are utilized for industrial and consumer applications, including automotive fuel tanks and vessels for storage of organic liquids, drastically reducing the permeability of gases thereby increasing product preservation and increasing polymer adhesion.[13−15] Direct fluorination is a spontaneous surface treatment process whereby hydrogens on a polymeric backbone are replaced with fluorine, reportedly improving barrier properties, adhesion, and chemical resistance. For the majority of treated polymers, only the surface is modified (∼0.01−10 μm thickness) and the bulk properties of the polymer remain unchanged.[14] The process is advantageous as it obviates the challenging syntheses of fluorinated monomers, and also avoids their polymerization which can be inherently problematic due to the steric repulsion of fluorine, leading to low-weight molecular species.[16]

Direct fluorination has previously been challenging to control because of the amount of energy liberated during the reaction that must be either absorbed or carried away. The mechanism, indicated in reaction steps 1−5, involves a radical propagation step whereby elemental fluorine ($\Delta H_{298°K}$ F_2 = 29.7 kcal mol^{-1}) dissociates to atomic fluorine, which then reacts with R−H groups to form carbon radicals and R−F groups.[17,18] The reaction continues until two radicals collide, creating an overall reaction having a $\Delta G_{298°K}$ equal to −103.4 kcal mol^{-1}:[17]

$$\text{Initiation}: \quad F_2 \rightarrow F^{\cdot} + F^{\cdot} \qquad (1)$$

$$F_2 + RH \rightarrow R^{\cdot} + HF + F^{\cdot} \qquad (2)$$

Special Issue: Perfluoroalkyl Acid

Received: January 3, 2011
Accepted: June 1, 2011
Revised: May 16, 2011
Published: June 20, 2011

$$\text{Propagation}: \quad R{-}H + F^{\cdot} \rightarrow R^{\cdot} + H{-}F \tag{3}$$

$$R^{\cdot} + F_2 \rightarrow R{-}F + F^{\cdot} \tag{4}$$

$$\text{Termination}: \quad R^{\cdot} + F^{\cdot} \rightarrow R{-}F \tag{5}$$

$$R^{\cdot} + R^{\cdot} \rightarrow R{-}R \tag{6}$$

The reaction is exothermic enough to fracture carbon−carbon bonds ($\Delta H_{298°K}$ C−C = 84−88 kcal mol^{-1}), so care must be taken to minimize the amount of energy localized on adjacent atoms in order to preserve the carbon skeleton and limit fragmentation. Lagow and Margrave[17] proposed using an inert gas or gas mixture such as nitrogen or helium to dilute the concentration of fluorine gas, to greatly decrease the probability of simultaneous fluorine collisions on adjacent carbon atoms. As the reaction continues and as more C−F bonds are formed, the reactant molecule is able to withstand more fluorine collisions because the sites are sterically protected by fluorine.[17] Diluting with oxygen has also been proposed as a means to reduce the rate of fluorination[19] as oxygen would react with radicals formed during the fluorination process, thereby creating nonradical species.[20] However, the presence of oxygen, either as part of the diluting gas mixture or as an intrinsic contaminant of fluorine gas results in polymer fragmentation[17,20] and oxidation of fluorinated surfaces.[21] Oxidation leads to the formation of acid fluoride groups, which may subsequently hydrolyze to carboxylic acids.[22] This discovery serves as the basis for the research presented herein; through the oxidation and chain scission of polyolefin material, PFCAs of varying chain lengths are proposed to form from direct fluorination. The purpose of the present work was to determine the quantity of PFCAs (C_2−C_{10}) in directly fluorinated high-density polyethylene (HDPE) material. This study serves as the first to detect PFCAs within directly fluorinated material, thus relating direct fluorination as a potential source of PFCAs in the environment.

EXPERIMENTAL SECTION

Chemicals. All chemicals were used as received without further purification. The perfluorinated acids: perfluorobutanoate (PFBA; purity >99%), perfluoropentanoate (PFPeA; purity >99%), perfluorohexanoate (PFHxA; purity >99%), perfluoroheptanoate (PFHpA; purity >99%), perfluorooctanoate (PFOA; purity >99%), perfluorononanoate (PFNA; purity >99%), perfluorodecanoate (PFDA; purity >99%), $^{13}C_4$ PFBA (purity >99%), $^{13}C_2$ PFHxA (purity >99%), $^{13}C_4$ PFOA (purity >99%), $^{13}C_5$ PFNA (purity >99%), and $^{13}C_2$ PFDA (purity >99%) were obtained from Wellington laboratories (Guelph, ON, Canada). Trifluoroacetic acid (TFA; purity 99%) and perfluoropropanoate (PFPrA; purity 97%) were purchased from Sigma-Aldrich (Oakville, ON, Canada). HPLC-grade methanol (purity >99.8%) and Omnisolv grade water were purchased from EMD Chemicals (Gibbstown, NJ).

Sample Collection. Directly fluorinated 1-L high-density polyethylene (HDPE) bottles were obtained from two companies: Fluoro-Seal International (Allentown, PA) and Air Products and Chemicals (Airopak, Allentown, PA). From here on, these companies will be referred to as manufacturer A and manufacturer B, respectively. Manufacturer A had varying levels of fluorination per bottle, specified by a label marked F1, F2, F3, F4, or F5, where F1 received the least fluorination and F5 received the most, while manufacturer B had only one fluorination level. Untreated HDPE bottles were also purchased from VWR International (Mississauga, ON, Canada) as procedural blanks for the extraction. Untreated and treated bottles from each level and company were stored in separate polyethylene plastic bags at room temperature until extraction.

Extraction of Perfluorinated Acids from Directly Fluorinated HDPE Bottles. Prior to each Soxhlet extraction, the total surface area of the bottles was measured (approximately 1200 cm^2). Twenty 1-L fluorinated bottles were cut into five or six subsamples which were accurately weighed (±0.0001 g) to approximately 6 g for extraction. All glassware was washed with detergent, followed by distilled water and methanol rinses to minimize laboratory contamination. Each subsample was placed in a separate Soxhlet apparatus and extracted with 120 mL of methanol at 65 °C; no internal standards were added at this point of the extraction. At approximately 2 h, 15-mL samples were taken from each apparatus; further details about the extraction procedure are presented in the Supporting Information. The 15-mL extracts were blown to dryness using N_2, followed by reconstitution in 0.6 mL of a 80:20 distilled water/methanol mixture, and addition of 10 ppb of internal standards.

Water migration tests were carried out using three 1-L F3 bottles and one 1-L untreated HDPE bottle. Omnisolv-grade water was added to each bottle (200 mL), shaken for 10 min, and left to stand at room temperature for approximately one year. To avoid loss of water, the bottles were tightly sealed; visual inspection of the bottles suggested no discernible loss of water over the course of the experiment. Sample aliquots (240 μL) were taken from each bottle and added to 45 μL of methanol and 15 μL of a 200 ppb internal standard solution preceding analysis using LC-MS/MS; expecting no degradative or sorption losses of PFCAs, and the general finding that recoveries from water held in plastic-ware are generally good, obviated the requirement for a spike and recovery experiment.

Instrumental Analysis. Sample analysis was performed by liquid chromatography with negative ion electrospray tandem mass spectrometry (LC-MS/MS). Chromatographic separations were achieved using a Waters XBridge C18 column (4.6 mm × 50 mm, 3.5 μm particle size, Milford, MA). All samples were analyzed using a Waters Acquity LC system, coupled to a Waters Quattro Micro mass spectrometer. Instrumental and chromatographic details are provided in the Supporting Information.

ATR-IR Spectroscopic Analysis. Infrared transmission spectra of the surface of treated and untreated HDPE bottles were determined using a PerkinElmer Spectrum BX FT-IR system (Waltham, MA), equipped with a single reflection attenuated total reflectance MIRacle ZnSe prism (PIKE Technologies, Madison, WI).

Qualitative NMR Analysis. ^{19}F NMR spectroscopy was used to probe for structural isomers that were unresolved in our LC-MS/MS methods. Combined water extracts from two F3 bottles (390 mL total volume) were evaporated on a Heidolph Laborota 4002 rotary evaporator (Asynt, Cambridgeshire, UK), and reconstituted in methanol. The methanol extract was blown to dryness under N_2, and reconstituted with 0.6 mL of d_4-methanol. A 16 mg/mL $Cr(acac)_3$ solution (250 μL) in methanol was added to the extract as a relaxation agent,[23] as well as 50 μL of a 1000 mg/L solution of 4-trifluoromethoxyaniline (4-TFMeAc) in methanol as an internal standard. Spectra were obtained on a Varian 400 NMR spectrometer with an ATB8123-400 autoswitchable probe tuned to ^{19}F (376.14 MHz) or a Varian Unity

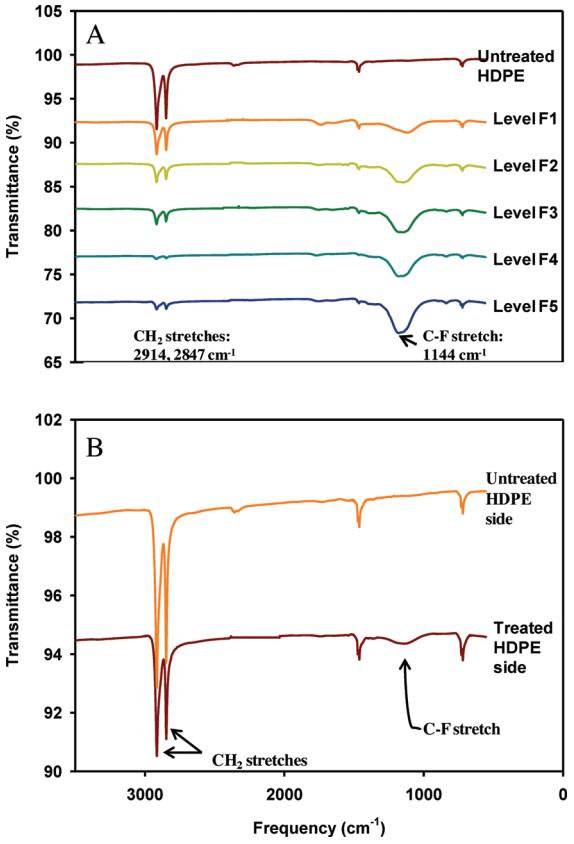


Figure 1. ATR-IR spectra of untreated and treated HDPE: (A) comparison of untreated HDPE with Manufacturer A's five-fluorination level treatment process, (B) comparison of two sides of a HDPE bottle fluorinated by Manufacturer B. Spectra have been shifted along the *y*-axis to minimize overlapping.

500 NMR spectrometer with a 5-mm NaloracHF decoupling probe tuned to ^{19}F (470.35 MHz). The acquisition time was 1 and 0.582 s, and relaxation delay time was 1 and 2.10 s for the Varian 400 and Unity 500 NMR, respectively. Chemical shifts were reported relative to 4-TFMeAc (−58.1 ppm).[24] The scanning width generally chosen was +50 ppm to −195 ppm on the Varian 400 NMR and −40 ppm to −160 ppm for the Unity 500; approximately 20 000 scans were acquired.

Quality Control. Data quality and assurance included procedural (method) blanks with untreated HDPE bottles, instrumental blanks, and at least triplicate ($n = 3-6$) analyses. Limits of detection (LODs) were defined as the concentration producing a signal-to-noise ratio of three, and limits of quantification (LOQs) were defined as the concentration producing a signal-to-noise ratio of ten.[25] LODs and LOQs were determined based on the standard deviation of the signals arising from the procedural blanks. Results indicated generally acceptable recovery: 110 ± 7% (TFA), 106 ± 11% (PFPrA), 97 ± 10% (PFBA), 119 ± 10% (PFPeA), 81 ± 8% (PFHxA), 75 ± 7% (PFHpA), 82 ± 6% (PFOA), 85 ± 9% (PFNA), and 85 ± 7% (PFDA). Reported sample concentrations were not corrected for recovery. Further quality control and assurance details are provided in the Supporting Information.

RESULTS AND DISCUSSION

Chemical Composition of Directly Fluorinated HDPE. To understand how the chemical composition of the HDPE bottle surface was influenced by the fluorination process for each fluorination level, relative to other levels, attenuated total reflectance infrared (ATR-IR) spectroscopy was used to elucidate the functional features on the surface of both the untreated and treated HDPE (Figure 1). The relative extent of fluorination between levels can be evaluated by the intensity of the C−F and CH_2 stretches (Figure 1A) in the IR spectra. The bands at 2914 cm^{-1} and 2847 cm^{-1} are attributed to the $-CH_2$ asymmetric and symmetric stretches, respectively. The broad band at 1144 cm^{-1} is due to the C−F stretching vibration.[26] As the fluorination level rises, the C−F stretch intensifies while the CH_2 stretches decrease. Therefore, as the level of fluorination increases, the hydrogens in HDPE CH_2 groups are being replaced to a greater extent with fluorine, giving rise to an increased number of total C−F groups on the polymer.

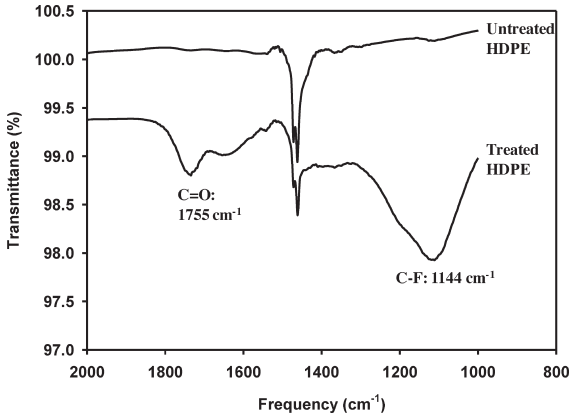


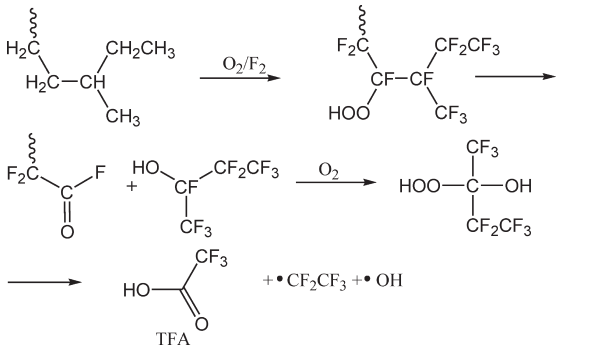
Figure 2. ATR-IR spectrum of a untreated and treated HDPE bottle fluorinated using Manufacturer A's F2-level treatment process. Spectra have been shifted along the *y*-axis to minimize overlapping.

Unlike manufacturer A's fluorination process, which fluorinates both sides of a HDPE bottle (not shown), manufacturer B presumably only fluorinates one side of their HDPE bottles (Figure 1B), as can be seen from the absence of the C−F stretch on the outer side of the bottle.

Any presence of oxygen within the fluorinating mixture may result in the formation of acid fluoride −COF groups[22] which, in the presence of water, undergo hydrolysis to form the corresponding carboxylic acid, −COOH. To evaluate whether the PFCAs were extracted from the directly fluorinated HDPE bottles or whether their acid fluoride precursors were extracted and transformed into their corresponding PFCAs due to hydrolysis in the LC-MS/MS negative ion electrospray source,[27] ATR-IR spectroscopy was used to examine the surface functional groups present on the fluorinated polymer. As evidenced from the IR spectrum (Figure 2), a C═O vibration at 1755 cm^{-1} exists due to the presence of −COOH groups and not the acid fluoride precursor; −COF groups have a carbonyl vibration between 1900 and 1870 cm^{-1}.[26]

During the fluorination process, acid fluorides are produced due to the presence of oxygen, either present as a diluting gas or as a contaminant of fluorine or nitrogen gas.[21,22] Historically, there has been uncertainty about the mechanism by which oxygen reacts with the polymer to form acid fluoride groups. Lagow et al. only observed functionalization to occur in polymers that had pendant methyl or other alkyl groups, whereas linear polymers such as HDPE failed to produce significant functionalization.[28] However, functionalization of HDPE was

Scheme 1. Proposed Mechanism of Directly Fluorinated HDPE Fragmentation Leading to the Production of PFCAs



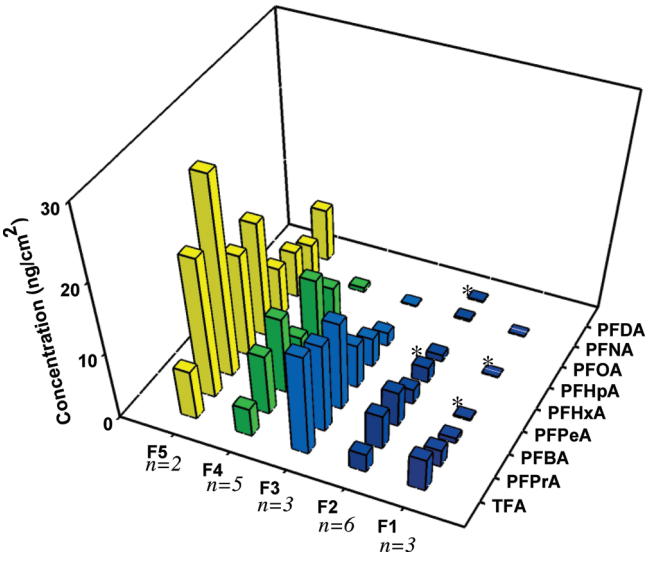


Figure 3. Comparative PFCA concentrations among fluorination levels F1−F5 obtained from manufacturer A. PFCA concentrations less than the LOD are reported as zero, and concentrations less than the LOQ are indicated with an asterisk (*).

noted by Sanderson et al.[20] who proposed that triplet oxygen reacts with carbon radicals to form peroxy radicals, later confirmed experimentally by Florin.[29] Partial fragmentation of the fluorinated polymer occurs through production of peroxy radicals which ultimately results in chain scission and the formation of PFCAs, as illustrated by Scheme 1 adapted from Chiellini et al.[30]

To control the fluorination process, the amount of fragmentation must be limited within the initial stages of the reaction. To do so, Lagow and Margrave proposed the use of dilutent gases to reduce the concentration of fluorine, thereby decreasing the probability of fluorine collisions of adjacent sites which caused fragmentation.[17] They noted the necessary removal of oxygen from the fluorination chamber to avoid cross-linking and the formation of carbonyl groups, which greatly decreased the yield of the perfluorocarbon.[17] However, it was later noted that if the level of oxygen present in the fluorination process did not exceed 5% by volume, the fluorination of polyolefin material was reported to be successful.[19] The presence of oxygen may in part control the rate of fluorination, by reacting with radicals formed from the fluorination process[20] and by decreasing the fluorine permeability by more than 2 orders of magnitude through the formation of carbonyl groups.[31]

PFCAs in Directly Fluorinated HDPE Bottles. PFCAs were detected in all of the extracted bottles that were labeled as directly fluorinated by Manufacturer A. The average PFCA concentration per fluorination level is presented in Figure 3. Concentrations were calculated based on a mass/surface area unit, where the approximate surface area of the bottles was 1200 cm^2, accounting for fluorination treatment on the inner and outer sides of the bottle. All concentrations extracted from bottles produced from manufacturer A were in the ng/cm^2 range; the shorter chain acids, specifically TFA, PFPrA, PFBA, PFPeA, and PFHxA, dominated the concentration profile for fluorination levels 1−5. Concentrations generally increased with increasing fluorination level; the total PFCA concentration for fluorination level F1 was 8.5 ± 0.53 ng/cm^2; for F2, 19 ± 0.63 ng/cm^2; F3, 54 ± 1.0 ng/cm^2; F4, 47 ± 1.4 ng/cm^2; and F5, 113 ± 2.5 ng/cm^2. All PFCAs were found to be below the LOD for each analyte in a bottle obtained from manufacturer B. Based on these results, we hypothesize that manufacturer A likely uses oxygen as a dilutent of their fluorination gas mixture. In contrast, Manufacturer B may employ a fluorination process which is oxygen-free and instead uses a nitrogen-diluted fluorine mixture to fluorinate HDPE.[32,33] In addition to the total PFCAs present, the concentration profiles of the different PFCA congeners were also affected by the fluorination level produced by manufacturer A. The dominant congener from levels F1 and F3 was TFA, and from levels F2, F4, and F5 was PFBA. Although the process of direct fluorination for manufacturer A is unknown to us, it is presumed that differences in the fluorination process from level F1 to level F5 may change the relative PFCA concentrations. Evidence of the formation of longer chain PFCAs in higher fluorination levels is hypothesized to occur if the bottles are left in the reaction chamber for a greater amount of time, or subject to a greater concentration of fluorine. With an increased fluorine concentration, or longer reaction times, the process is expected to become increasingly exothermic and release more chains from the polymer backbone, resulting in a greater concentration of PFCAs at higher fluorination levels. Experiments are ongoing to determine whether incomplete fluorination may lead to the production of mixed hydro/fluoroalkyl acids.

To investigate the extent to which PFCAs may migrate into aqueous-based substances stored in directly fluorinated HDPE material, three level F3 bottles from manufacturer A and one untreated blank bottle were stored with water (approximately 1 year). Unlike the Soxhlet extractions, concentrations from this study were calculated based on a surface area of 600 cm^2 rather than 1200 cm^2 due to the detected PFCAs originating from the inside of the F3 bottles rather than both sides. The average total PFCA level observed within the F3 bottles was 314 ± 12 ng/cm^2, where TFA (186 ± 18 ng/cm^2) and PFPrA (66 ± 5.7 ng/cm^2) comprised 80% of the total PFCAs. PFOA, PFNA, and PFDA were not detected. The total PFCA level observed was significantly higher than that reported from the extraction with methanol. It is possible the fluorinated HDPE bottles, over the course of the year-long period, continued to undergo auto-oxidation and chain scission leading to further production of PFCAs. It would therefore be of interest to directly explore this potential to determine whether these conditions preferentially yield the shorter chain acids.

^{19}F NMR Results. ^{19}F NMR spectrometry was used to establish whether structural variations of the PFCAs existed with the samples. This approach was selected because NMR

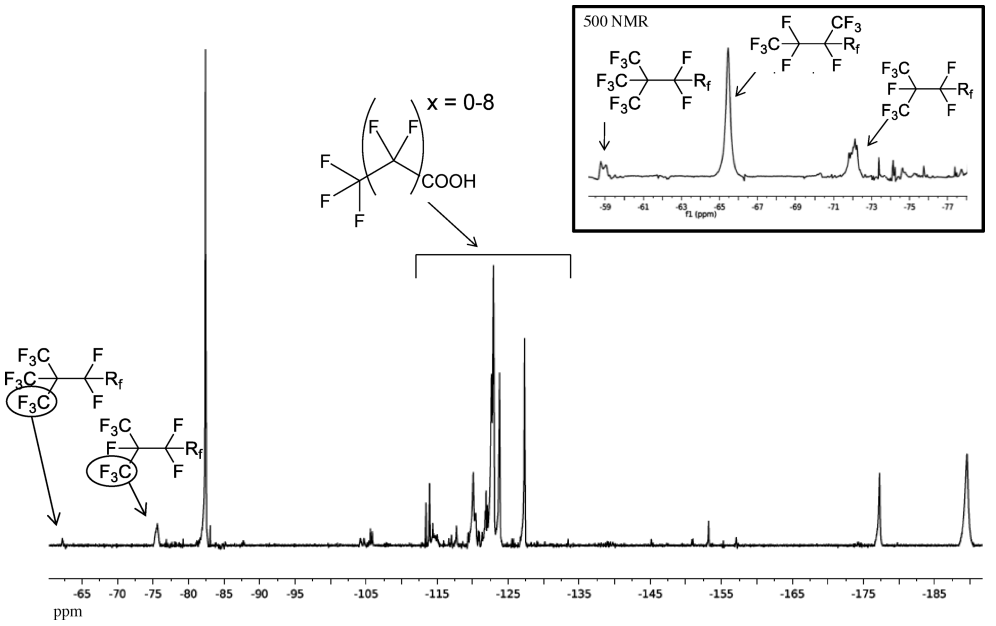


Figure 4. ^{19}F spectrum of PFCAs extracted with water from a level F3 bottle, acquired using a Varian 400 NMR spectrometer. An enhanced view of the region from −58 to −77 ppm is presented in the inset, and obtained using a Varian 500 NMR spectrometer.

spectroscopy allows the investigation of samples without a prior knowledge of the structural identity of the analytes present within samples, unlike LC-MS or GC-MS methods. The energy produced from fluorination may lead to fragmentation, resulting in the production of linear PFCAs of varying chain length. By the same mechanism, structural isomers may also form, giving a mixture of linear and branched chain isomers, where the majority of the perfluoroalkyl chains are linear due to the linear arrangement of HDPE. The spectra in Figure 4 indicate structural isomers are present within F3 bottles, and the signals present within the spectra are similar to signals assigned based on previously reported chemical shifts.[34−36]

The following characteristic signals were identified, as shown in Figure 4: the terminal CF_3-groups of a linear CF_3-(CF_2)-chain at −82 ppm; the CF_2-groups within the linear chain PFCAs with multiple signals ranging from −113 to −127 ppm, due to the presence of multiple chain length PFCAs; the CF_3- and CF- groups of isopropyl groups having a $(CF_3)_2CFCF_2$-chain at −76 ppm and −177, respectively; the signals of CF_3- and CF-groups of internal monomethyl branched isomers, having the general structure CF_3CF-$(CF_3)CF_2$- at −67 and −187 ppm, respectively; and the CF_3-groups of a terminal *tert*-butyl branch, $(CF_3)_3C(CF_2)$- at −62 ppm. The signals corresponding to the linear, isopropyl, monomethyl, and *t*-butyl CF_3-groups were also integrated with respect to the linear CF_3-group at −82 ppm, to provide a comparison with the isomeric abundance found in electrochemically fluorinated (ECF) PFOA.[37] The relative isomer composition of PFCAs within the F3 samples contain approximately 55% of the linear, 11% of the isopropyl branched, 26% of the internally branched, and 7% of the *t*-butyl isomer. This composition contrasts from the published composition of ECF PFOA,[34] which has a typical composition of 78.0% of the linear, 12.5% of the internally branched, 9.0% of the isopropyl branched, and 0.2% of the *t*-butyl branched isomer. These results provide evidence for an additional source of branched isomers of PFCAs potentially released to the environment.

Implications. This is the first instance where PFCAs formed on directly fluorinated HDPE material have been extracted, positively identified, and quantified. The presence of carbonyl groups on the HDPE surface, giving an IR transmission frequency at 1755 cm^{-1}, is due to the presence of −COOH groups. From this, it can be suggested that the PFCAs may be formed from oxidation and fragmentation on directly fluorinated HDPE. The amount of PFCAs formed on directly fluorinated HDPE is proportional to the amount of fluorination the HDPE receives, and presumably the amount of oxygen within the fluorination chamber; the amount of PFCAs found on the bottle produced from manufacturer B were below the LOD for each analyte, and it is therefore hypothesized that manufacturer B either rinses their fluorinated products before use, or precludes oxygen from the fluorination process. In contrast, manufacturer A yields total PFCA concentrations ranging from 8.5 ± 0.53 ng/cm^2 (F1) to 113 ± 2.5 ng/cm^2 (F5). One explanation for this observation would include the presence of oxygen in manufacturer A's fluorination. In addition, the structural isomers, particularly the *t*-butyl, monomethyl branched, and isopropyl branched isomers, were detected and found to be significant. This finding marks an additional mechanism toward the formation of isomeric PFCAs, proceeding by the same mechanism described for the production of linear PFCAs.

This investigation has demonstrated the direct fluorination of polyolefin material may be a new source of PFCA contamination to the environment, especially the C2−C6 acids. The results from the present study demonstrate that PFCAs are produced as reaction byproducts during direct fluorination and are readily extractable with methanol and water. However, it is challenging to estimate the contribution of PFCAs on directly fluorinated material to the overall load of PFCAs to the environment. According to information provided by manufacturer A, over 300 million containers, articles, and plastic bottles are fluorinated each year.[38] Given the average total PFCA concentration from a level F3 HDPE bottle, it is estimated that 54 kgs of PFCAs may

be found on fluorinated material per year, offering potential for environmental exposure. This value also appears less than the human exposure to PFCAs from the biotransformation of polyalkylfluorinated phosphates (PAPs) found on food contact papers,[39] indicating that the potential for human exposure to PFCAs from directly fluorinated material is expected to be low. The improvement of barrier and adhesion properties, and cost effectiveness of the process allows for a variety of applications, including the fluorination of medical and dental parts, pipes, fuel tanks, tubing, assorted bottles, food, polypropylene toys, polyolefin aquiculture netting, squeeze tubes, films, and cosmetic containers. The overall production of PFCAs from direct fluorination may be significant due to the number of applications. To gain appreciable insight to environmental and potential human exposure, the specific applications and extent to which PFCAs migrate into consumer products must be determined.

■ ASSOCIATED CONTENT

Supporting Information. Liquid chromatography details and determination of PFCA extraction times; internal standards, and MRM transitions; QA/QC details, and procedural LOD and LOQ values. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*Phone: (416) 978-1780; e-mail: smabury@chem.utoronto.ca.

■ ACKNOWLEDGMENT

Funding was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC). We thank Robert Di Lorenzo and Hanin Issa (University of Toronto, Toronto, ON, Canada) for their assistance with sample preparation and extraction, as well as Barbara Weiner (University of Toronto, Toronto, ON, Canada) for help with the Unity 500-^{19}F NMR experiment, and to Anthony Chibba and Mark Nitz for use of their Heidolph rotary evaporator. Thanks also to Wellington Laboratories for the donation of native and mass labeled internal standards. Funding to A.A.R. was provided by an Ontario graduate scholarship. S.A.M. acknowledges receipt of an NSERC Discovery award.

■ REFERENCES

(1) Yamashita, N.; Kannan, K.; Taniyasu, S.; Horii, Y.; Petrick, G.; Gamo, T. A global survey of perfluorinated acids in oceans. *Mar. Pollut. Bull.* **2005**, *56*, 658–668.

(2) Houde, M.; Martin, J. W.; Letcher, R. J.; Solomon, K. R.; Muir, D. C. G. Biological monitoring of polyfluoroalkyl substances: A review. *Environ. Sci. Technol.* **2006**, *40*, 3463–3473.

(3) Olsen, G. W.; Church, T. R.; Miller, J. P.; Burris, J. M.; Hansen, K. J.; Lundberg, J. K.; Armitage, J. B.; Herron, R. M.; Medhdizadehkashi, Z.; Nobiletti, J. B.; O'Neill, E. M.; Mandel, J. H.; Zobel, L. R. Perfluorooctanesulfonate and other fluorochemicals in the serum of American Red Cross adult blood donors. *Environ. Health Perspect.* **2003**, *111*, 1892–1901.

(4) Miyake, Y.; Yamashita, N.; Soa, M. K.; Rostkowski, P.; Yaniyasu, S.; Lamb, P. K. S.; Kannan, K. Trace analysis of total fluorine in human blood using combustion ion chromatography for fluorine: A mass balance approach for the determination of known and unknown organofluorine compounds. *J. Chromatogr. A* **2007**, *1154*, 214–221.

(5) Kärrman, A.; van Bavel, B.; Järnberg, U.; Hardell, L.; Lindström, G. Perfluorinated chemicals in relation to other persistent organic pollutants in human blood. *Chemosphere* **2006**, *64*, 1582–1591.

(6) Taniyasu, S.; Kannan, K.; So, M. K.; Gulkowskad, A.; Sinclair, E.; Okazawa, T.; Yamashita, N. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. *J. Chromatogr. A* **2005**, *1093*, 89–97.

(7) Yeung, L. W.; Chimiyake, Y.; Taniyasu, S.; Wang, Y.; Hongxia, Y.; So, M. K.; Jiang, G.; Wu, Y.; Li, J.; Giesy, J. P.; Yamashita, N.; Lam, P. K. S. Perfluorinated Compounds and Total and Extractable Organic Fluorine in Human Blood Samples from China. *Environ. Sci. Technol.* **2008**, *42* (8140), 8145.

(8) Lau, C.; Anitole, K.; Hodes, C.; Lai, D.; Pfahles-Hutchens, A.; Seed, J. Perfluoroalkyl Acids: A Review of Monitoring and Toxicological Findings. *Toxicol. Sci.* **2007**, *99*, 366–394.

(9) Das, K. P.; Grey, B. E.; Zehr, R. D.; Wood, C. R.; Butenhoff, J. L.; Chang, S.-C.; Ehresman, D. J.; Tan, Y.-M.; Lau, C. Effects of Perfluorobutyrate Exposure during Pregnancy in the Mouse. *Toxicol. Sci.* **2008**, *105*, 173–181.

(10) Chengelis, C. P.; Kirkpatrick, J. B.; Radovsky, A.; Shinohara, M. A 90-day repeated dose oral (gavage) toxicity study of perfluorohexanoic acid (PFHxA) in rats (with functional observational battery and motor activity determinations). *Reprod. Toxicol.* **2009**, *27*, 342–351.

(11) Andersen, M. E.; Butenhoff, J. L.; Chang, S.; Farrar, D. G.; Kennedy, G. L., Jr.; Lau, C.; Olsen, G. W.; Seed, J.; Wallace, K. B. Perfluoroalkyl acids and related chemistries — Toxicokinetics and modes of action. *Toxicol. Sci.* **2008**, *102*, 3–14.

(12) Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. G. Dietary accumulation of perfluorinated acids in juvenile rainbow trout (*Oncorhynchus mykiss*). *Environ. Toxicol. Chem.* **2003**, *22*, 189–195.

(13) Lagow, R. J.; Margrave, J. L. The controlled reaction of hydrocarbon polymers with elemental fluorine. *J. Polym. Sci: Polym. Lett.* **1974**, *12*, 177–184.

(14) Kharitonov, A. P.; Taege, R.; Ferrier, G.; Teplyakov, V. V.; Syrtsova, D. A.; Koops, G.-H. Direct fluorination — useful tool to enhance commercial properties of polymer articles. *J. Fluorine Chem.* **2005**, *126*, 251–263.

(15) Tressaud, A.; Durand, E.; Labrugère, C.; Kharitonov, A. P.; Kharitonova, L. N. Modification of surface properties of carbon-based and polymeric materials through fluorination routes: From fundamental research to industrial applications. *J. Fluorine Chem.* **2007**, *128*, 138–391.

(16) Lagow, R. J.; Wei, H.-C. Direct fluorination of polymers. In *Fluoropolymers 1: Synthesis*; Houghmam, G., Cassidy, P. E., Johns, K., Davidson, T., Eds.; Kluwer Academic/Plenum Publishers: New York, 1999; p 209.

(17) Lagow, R. J.; Margrave, J. L. Direct fluorination: A "new" approach to fluorine chemistry. *Prog. Inorg. Chem.* **1979**, *26*, 162–210.

(18) Miller, W. T.; Koch, S. D.; McLafferty, F. W. The mechanism of fluorination. II. Free radical initiation reactions. Fluorine sensitized chlorination and oxidation. *J. Am. Chem. Soc.* **1956**, *78*, 4992.

(19) Dixon, D. D.; Hayes, L. J. Fluorination of polyolefin and polyacrylonitrile fibers. U.S. Patent 4,020,223, 1977.

(20) Sanderson, R. D.; du Toit, F. J.; Carstens, P. A. B.; Wagener, J. B. Fluorination rates of polyolefins as a function of structure and gas atmosphere. *J. Therm. Anal.* **1994**, *41*, 563–581.

(21) Hayes, L. J. Surface energy of fluorinated surfaces. *J. Fluorine Chem.* **1976**, *8*, 69–88.

(22) Shinohara, H.; Iwasaki, M.; Tsujimura, S. Fluorination of polyhydrofluoroethylenes. I. Direct fluorination of poly(vinyl fluoride) film. *J. Polym. Sci.* **1972**, *10*, 2129–2137.

(23) Ellis, D. A.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. Development of an 19F NMR method for the analysis of fluorinated acids in environmental water samples. *Anal. Chem.* **2000**, *72*, 726–731.

(24) Tugnait, M.; Lenz, E. M.; Phillips, P.; Hofmann, M.; Spraul, M.; Lindon, J. C.; Nicholson, J. K.; Wilson, I. D. The metabolism of 4-trifluoromethoxyaniline and [^{13}C]-4-trifluoromethoxyacetanilide in the rat: Detection and identification of metabolites excreted in the urine by NMR and HPLC-NMR. *J. Pharma. Biomed. Anal.* **2002**, *28*, 875–885.

(25) Keith, L. H.; Libby, R. A.; Crummett, W.; Taylor, J. K.; Deegan, J., Jr.; Wentler, G. Principles of environmental analysis. *Anal. Chem.* **1983**, *55*, 2210–2218.

(26) Socrates, G. *Infrared Characteristic Group Frequencies*; John Wiley & Sons: Bath, U.K., 1980.

(27) Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J. Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol.* **2004**, *38*, 3316–3321.

(28) Adcock, J. L.; Inoue, S.; Lagow, R. J. Simultaneous fluorination and functionalization of hydrocarbon polymers. *J. Am. Chem. Soc.* **1978**, *100*, 1948–1950.

(29) Florin, R. E. Electron spin resonance spectra of polymers during fluorination. *J. Fluorine Chem.* **1979**, *14*, 253–262.

(30) Chiellini, E.; Corti, A.; D'Antone, S.; Baciu, R. Oxo-biodegradable carbon backbone polymers − oxidative degradation of polyethylene under accelerated test conditions. *Polym. Degrad. Stab.* **2006**, *91*, 2739–2749.

(31) Kharitonov, A. P.; Moskvin, Y. L. Direct fluorination of polystyrene films. *J. Fluorine Chem.* **1998**, *91*, 87–93.

(32) Dixon, D. D.; Manly, D. G.; Recktenwald, G. W. Process for producing blow molded thermoplastic articles having improved barrier properties. U.S. Patent 3,862,284, 1975.

(33) Hobbs, J. P.; et al. Fluorinated high-density polyethylene barrier containers: Performance characteristics. In *Barrier Properties and Structures*; Koros, W. J.; American Chemical Society: Washington, DC, 1990; p 280.

(34) Weigert, F. J.; Karel, J. K. A fluorine NMR database. *J. Fluorine Chem.* **1987**, *37*, 125–139.

(35) Vyas, S. M.; Kania-Korwel, I.; Lehmler, H.-J. Differences in the isomer composition of perfluoroctanesulfonyl (PFOS) derivatives. *J. Environ. Sci. Health Part A.* **2007**, *42*, 249–255.

(36) Arsenault, G.; Chittim, B.; Gu, J.; McAlees, A.; McCrindle, R.; Robertson, V. Separation and fluorine nuclear magnetic resonance spectroscopic (19F NMR) analysis of individual branched isomers present in technical perfluorooctanesulfonic acid (PFOS). *Chemosphere* **2008**, *73*, S53–S59.

(37) Stevenson, L. U.S. Environmental Protection Agency Public Docket, AR226-1150, 2002.

(38) Fluoro-Seal Customer Support; http://www.fluoroseal.com/Overview.pdf.

(39) D'eon, J. C.; Mabury, S. A. Exploring indirect sources of human exposure to perfluoroalkyl carboxylates (PFCAs): Evaluating uptake, elimination, and biotransformation of polyfluoroalkyl phosphate esters (PAPs) in the rat. *Environ. Health Perspect.* **2011**, *119*, 344–350.