

Thermal Degradation of Fluorotelomer Treated Articles and Related Materials

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Abstract

This study reports the first known studies to investigate the thermal degradation of a polyester/cellulose fabric substrate ("article") treated with a fluorotelomer-based acrylic polymer under laboratory conditions conservatively representing typical combustion conditions of time, temperature, and excess air level in a municipal incinerator, with an average temperature of 1000°C or greater over approximately 2 sec residence time. The results demonstrate that the polyester/cellulose fabric treated with a fluorotelomer-based acrylic polymer is destroyed and no detectable amount of perfluorooctanoic acid (PFOA) is formed under typical municipal

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incineration conditions. Therefore, textiles and paper treated with such a fluorotelomer-based acrylic polymer disposed of in municipal waste and incinerated are expected to be destroyed and not be a significant source of PFOA in the environment.

Keywords: Fluorotelomer, PFOA, Incineration, Thermal, Degradation

Introduction

Fluorotelomer-based acrylic polymers (Banks et al., 1994; Kissa, 2001) are applied to textiles and paper to impart oil and water repellency. Textile fabrics are made from natural (i.e. cotton, wool) and synthetic (i.e. poly-ester, -amide, -propylene) fibers and their blends. Paper is comprised mainly of cellulosic fiber, principally wood pulp. Some paper may also contain natural fibers such as cotton.

Perfluorinated sulfonic and carboxylic acids have been found in people and the environment (Hansen, 2001; Kannan, 2004; Hekster, 2003; Schultz, 2003; Dimitrov, 2004; Stock, 2004). They are persistent chemicals and efforts to determine their potential sources and precursors are of interest to regulators worldwide (USEPA, 2003). PFOA is a representative perfluorocarboxylic acid that may be a potential thermal degradation product. When textiles and paper treated with fluorotelomer-based polymers are disposed of in municipal waste, they are often incinerated. Incineration is therefore a principal route by which degradates of fluorotelomer-based polymers may enter the environment. As such, the fate of textile and paper treated with fluorotelomer-based polymers when they are incinerated is of significant interest. This paper reports the first known studies to investigate the thermal degradation of a fabric

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treated with a fluorotelomer-based acrylic polymer under laboratory conditions conservatively representing typical combustion conditions of time, temperature, and excess air level in a municipal incinerator. The principal focus of this work was to determine the environmental fate of the fluorotelomer-based polymer on the treated article when it is incinerated.

The test substrate was a fabric comprised of a blend of polyester (ethylene glycol, terephthalic acid) and cellulose fibers. Fabrics with and without a fluorotelomer-based acrylic polymer treatment were tested. The substrate was chosen to be representative of both synthetic and natural fibers that are used in textiles and cellulosic fibers (cotton, wood pulp) used in paper. Fluorotelomer-based acrylic polymers are most commonly used for treating textiles and paper. The fluorotelomer based polymer used was a proprietary formulation whose composition has been generally described (US Patent 4742140 and US Patent 5344903).

Experimental Approach

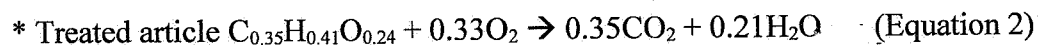
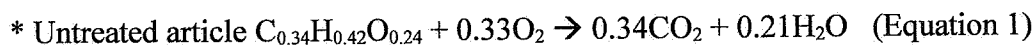
The advanced thermal reactor system (ATRS) was used for this study. The ATRS has been described and widely used for thermal degradation studies (Graham et al., 1986, Taylor et al., 1990; Graham et al., 1993; Taylor et al., 1995, 1996a-c). First, sample gasification behavior was determined using thermogravimetric analysis (TGA) to establish the sample gasification temperature. Second, sample materials were gasified and exposed to controlled thermal degradation in the ATRS. In-line gas chromatography/mass spectrometry (GC/MS) was used to generate the thermal decomposition profile of each sample and to identify major combustion byproducts under conditions conservatively representative of typical combustion conditions in a municipal incinerator. Quantitative CO, CO₂, and volatile organic carbon (VOC) analyses were

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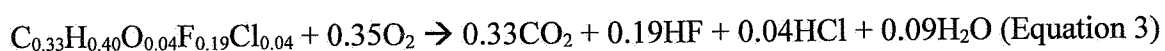
performed in separate experiments by collecting effluent from the exhaust line and using off-line GC with thermal conductivity detector and GC/MS analytical systems. PFOA, fluoride, and chloride were also sampled and determined in separate experiments. Third, quantitative transport of PFOA through the ATRS was verified.

Materials

Thermal testing was conducted on samples of articles and polymer. Tables 1 and 2 show the test sample weight and atomic compositions. Based on the atomic composition, the stoichiometric oxidation reaction for each test sample material can be written as follows.



* Fluorotelomer-based acrylic polymer



The amount of oxygen necessary for complete oxidation was established by using these stoichiometric equations (see Supplementary Materials for an example gasification calculation).

Thermogravimetric Analysis

A thermogravimetric analysis (TGA) study was conducted to establish the temperature for

complete gasification of each sample. TGA was performed in flowing air at a heating rate of 25°C/min from room temperature to the point where there was no further weight loss. Approximately 4 mg of sample was gasified with air and the weight % remaining was recorded as a function of temperature. Similar gasification behavior was observed for the treated and untreated articles. Gasification started at 380 and 350°C and ended at 600 and 550°C for untreated and treated articles, respectively. Weight remaining after gasification was 7 and 2.5% for untreated and treated articles, respectively. Gasification of the fluorotelomer-based acrylic polymer started at around 100°C. Continuous weight loss was observed until 600°C, where nearly 100% gasification was observed.

Instrumentation

Figure 1 presents a schematic of the ATRS, which consists of a sample inlet, reactor, cold trap, and in-line GC/MS system. The sample was placed into a sample cartridge (2 × 2.5 mm (i.d.×o.d.), 12.5 mm length quartz capillary tube, CDS Analytical Inc., Oxford, PA) which was inserted into a temperature-programmable pyroprobe (CDS-2000). The pyroprobe was placed into Inlet 1 and gasified with synthetic air (21% O₂ and 79% N₂, Airgas, Inc.) at 85% excess air. This excess air level very conservatively represents the level typically used for combustion in municipal incinerators (Giraud, 2004). All experiments were performed using synthetic air. The reactor dimensions were 4 × 6 mm (i.d.×o.d.) with an effective length of 15 cm. The mean, gas-phase residence time was 2.0 sec. Transfer lines were maintained at approximately 300°C for all experiments.

Thermal Degradation Conditions

The reactor volume ($\Pi r^2 h$) of 1.88 cm³ (0.4 cm i.d., 15 cm effective length) and residence time of 2.0 sec gives a fixed air flow rate of 0.94 mL/sec at 25°C. This flow rate was corrected with the reactor temperature as shown in Equation 4:

$$0.94 \text{ mL/sec} \times 298 / (T (^{\circ}\text{C}) + 273) \quad (\text{Equation 4})$$

Based on the TGA results, the initial and final gasification temperature of the untreated and treated articles were set at 350 and 650°C, respectively. Although the TGA results indicated the final gasification temperature for the untreated article to be 50°C higher than the treated article, the final gasification temperature for both was set to be the same for consistency and to facilitate comparison of results. The initial and final temperatures for the fluorotelomer-based acrylic polymer were set at 250 and 650°C, respectively. The temperature of Inlet 1 was set at 300°C for the untreated and treated articles and 250°C for the fluorotelomer-based acrylic polymer. The inlet temperature for the fluorotelomer-based acrylic polymer was reduced to prevent significant weight loss during system stabilization after sample insertion and before gasification. The sample heating rates were varied to adjust gasification time and obtain appropriate oxidative reaction conditions.

The reactor volume and gas-phase residence time are fixed parameters in this system. As a result, the flow rate cannot be changed to set the excess air level. Therefore, the gasification time and amount of sample were the only adjustable parameters for the ATRS to achieve the 85% excess air level. Since it was not possible to measure the desired sample mass with 10 µg precision, the sample gasification time was the experimental parameter adjusted to obtain the

desired sample to air ratio. Table 3 presents gasification times and heating rates. The supplementary material contains an example calculation illustrating how the gasification time for the fluorotelomer-based acrylic polymer was determined. The key assumptions in this calculation were: 1) the gasification starts when the pyroprobe temperature programming is initiated and ends at the final temperature (650°C), and 2) sample weight loss is linear with time.

To summarize, known sample amounts were subjected to controlled thermal degradation conditions. The mean gas-phase residence time in the reactor was maintained at 2 sec. The reactor temperature was maintained within $\pm 2^{\circ}\text{C}$ of the set temperature for all experiments. The flow rate was maintained within ± 0.2 mL/min of the target. 85% excess air was used for all experiments.

In-Line GC/MS Analysis Method and Calibrations

The gasified sample was subjected to controlled thermal degradation and the reactor effluent was condensed in a cold trap maintained at -125°C using liquid nitrogen. The condensed materials were released by heating the cold trap to 280°C (with a temperature ramping rate of approximately $45^{\circ}\text{C}/\text{min}$) and introduced to the GC/MS system for analysis. An HP 5890A/5970B series GC-MS with DB-5 GC capillary column (30 m length, 0.25 mm i.d., 0.25 μ film thickness, Agilent Technologies, Inc. **Palo Alto, CA**) with a 1 to 24 split ratio was used. The condensed materials released from the cold trap were cryogenically trapped at the head of the GC column at -60°C . Following cryogenic focusing, the oven temperature was held at -60°C for 1 min, then increased to 280°C ($20^{\circ}\text{C}/\text{min}$) and held for 10 min at 280°C . The mass scan range was 12 - 450 m/z to allow analysis of a wide range of compounds including water vapor.

Calibration curves were created for three aliphatic fluorocarbons spanning a range in molecular weight: CF_3H (98+%, Lot # 22912MI, Aldrich, Milwaukee, WI), C_4F_8 (98% minimum, Lot # 8B-110, SynQuest Labs., Inc., Alachua, FL), and C_8F_{18} (98%, Batch # 17024MA, Aldrich, Milwaukee, WI). Calibration and detection limit determinations were consistent with prior thermal decomposition studies conducted in this laboratory (Tirey et al., 1990; Taylor et al., 1995, 1996a-c; Wehrmeier et al., 1998).

Treated and Untreated Articles: Off-line GC/MS Analysis of Volatile Organic Compound (VOC) and Fixed Gas Analysis at 1000°C

Thermal degradation in the ATRS reactor was conducted at 1000°C to conservatively represent combustion at the average temperature across a 2 sec residence time typical of the high temperature zone of municipal waste incinerators in the U.S. (Giraud, 2004). The reactor effluent from treated and untreated article combustion at 1000°C was analyzed for volatile organic compounds using a gas sampling bag and off-line GC/MS analysis. The gas sample was taken from the exhaust line shown in Fig. 1 using a 0.5 L Tedlar® bag (SKC Inc., Eighty Four, PA). Silicone tubing (0.063 in. i.d., 0.125 in o.d., 30 cm. length, Cole Parmer Instrument Co., Vernon Hills, IL) was used for the transfer line. The collected gas sample was used for both VOC and fixed gas (CO , CO_2) analyses. The sample of each article was gasified and thermally degraded in the same manner as ATRS experiments with in-line GC/MS analysis. The entire system, including cold trap, was heated at 300°C for this analysis. A Supelco Q PLOT column (30 m $\times$ 0.53 mm ID, SUPELCO Inc., Bellefonte, PA) was used for analysis and the injection volume was 0.5 mL. The GC oven temperature was held at -60°C for 1 min, then increased to 280°C at a rate

of 20°C/min and held 5 min at 280°C. The mass scan range was 12 - 450 m/z to allow analysis of a wide range of compounds including water vapor.

CO and CO₂ were analyzed using a thermal conductivity detector coupled to a gas chromatograph (8610C gas chromatograph, SRI Instruments, Torrance, CA). CO and CO₂ were separated from other compounds using a 6 ft molecular sieve packed column and silica gel column, respectively, which were preinstalled by the manufacturer (SRI Instruments). A standard four-point calibration was conducted prior to the analyses. Carbon mass balance was calculated based on the sample gasified and the amounts of VOC, CO, and CO₂ measured.

Treated and Untreated Articles: PFOA, Fluoride, and Chloride Determination at 1000°C

The reactor effluent from the thermal degradation of the treated and untreated articles at 1000°C was sampled and PFOA, fluoride, and chloride were determined. The sample was gasified and thermally degraded in the same manner as the ATRS experiments with in-line GC/MS analysis. The effluent was taken from the exhaust vent and passed through an aqueous solution bubbler system. The bubbler system consisted of two bubblers (120 mL amber glass jar, I-CHEM, New Castle, DE) with 1 × 3 mm i.d. × o.d., 4 in length quartz stem filled with 60 mL HPLC grade water (HPLC Grade Ultrapure Water, Stock #22934, Lot #L10N39, Alfa Aesar, Ward Hill, MA). Silicone tubing (0.063 in i.d., 0.125 in o.d., 12 in length, Cole Parmer Instrument Co., Vernon Hills, IL) was used as a transport line between the exhaust vent and first bubbler. The same type of tubing, approximately 2 in. in length, was used to connect the two bubblers. Following each experiment, the silicone tube that connected the exhaust line and the

first bubbler was rinsed with 5 mL HPLC grade water (Alfa Aesar) and this extract was added to the first bubbler.

Fluoride and chloride ion determinations were made using ion chromatography. PFOA was sampled from the exhaust gas and determined using two independent methods: 1) aqueous sampling followed by HPLC/MS/MS analysis as described above, and 2) in-line gas-phase sampling with in-line GC/MS analysis. Quantitative transport of PFOA through the ATRS was determined for each of these two sampling methods.

PFOA Transport through ATRS

The significant polarity of PFOA necessitated transport tests through the ATRS to verify that its concentration in the ATRS exhaust could be accurately and reliably determined. Two independent experiments were conducted. First, ATRS effluent was sampled in an aqueous solution bubbler system for PFOA followed by HPLC/MS/MS analysis. Second, ATRS effluent was sampled and analyzed for PFOA using in-line GC/MS analysis. Solid PFOA samples for these studies were obtained from Oakwood Products, Inc. (West Columbia, SC, Lot No. 210002).

Aqueous Sampling

Transport tests were conducted at 170°C and 300°C reactor temperatures. All transfer lines, reactor, and cold trap were maintained at the same temperature to prevent sample condensation and decomposition. The injection ports were kept at 170°C. The sample was placed into a sample cartridge which was inserted into Inlet 1 using the pyroprobe and gasified at 170°C. The pyroprobe temperature was increased from 100°C to 170°C at the rate of 70°C/min and held at 170°C for 4 min. The ATRS effluent was passed through two aqueous solution

bubblers connected in series to collect PFOA. The transfer line (12 in silicone tubing (0.063 in i.d., 0.125 in o.d., Cole Parmer Co., Vernon Hills, IL)), was rinsed with 5 mL HPLC grade water (HPLC Grade Ultrapure Water, Stock #22934, Lot #L10N39, Alfa Aesar, Ward Hill, MA), and added to the first bubbler.

After the effluent was collected in the aqueous solutions, a steam extraction procedure was performed to extract any possible PFOA condensate remaining in the ATRS system. The steam was collected from the ATRS exhaust line and condensed into two glass vials (40 mL Vial, Amber, Wheaton, Millville, NJ) which were connected in series and immersed in an ice bath. Steam was injected at a flow rate of 200 mL/min at 300°C. Five mL of HPLC grade water (Alfa Aesar) was injected at a rate of 4 mL/hr, generating 174 mL/min of steam flow through the system. The extraction procedure was performed five times consecutively. Following each steam extraction, the silicone tubing connecting the ATRS exhaust line and the first vial was rinsed with 5 mL HPLC grade water (Alfa Aesar) and added to vial 1. A HPLC grade water (Alfa Aesar) blank and a second blank of HPLC water injected through the syringe were also conducted for background PFOA determination. The pyroprobe used to hold the sample cartridge for gasification was also rinsed using 100 mL HPLC grade water (Alfa Aesar). This water sample was placed in a separate glass jar. The aqueous samples were analyzed by LC/MS/MS for PFOA.

In-Line Gas-Phase Sampling

PFOA transport efficiency was determined by comparing (a) the total PFOA ion peak area obtained after PFOA introduction into Inlet 1 of the ATRS followed by in-line GC/MS analysis with (b) the total PFOA ion peak area obtained by direct PFOA injection into the

GC/MS. These two studies were conducted under identical GC/MS conditions.

For the ATRS test, the temperature (inlets, transport lines, reactor and the cold trap) were set at 235°C. Synthetic air was used as carrier gas. The total flow rate was set at 33 mL/min (22 mL/min to inlet 1 and 11 mL/min to inlet 2) to maintain the sample residence time in the reactor at 2.0 sec at 235°C. PFOA was placed into a sample cartridge which was placed in the pyroprobe. The pyroprobe temperature was increased from 100 to 300°C at 200°C/min and held at 300°C for 2 min. After gasification, the system was swept with Helium for 3 min and the GC temperature programming was started. The initial GC temperature was 40°C and held for 1 min then increased to 280°C at the rate of 20°C/min and held for 5 min at 280°C.

For the direct GC injection tests, helium was used as the carrier at a flow rate through the injector of 33 mL/min. The sample was introduced into the GC injection port using the sample cartridge while the injection port was kept at 40°C. The injection port temperature was then increased to 235°C at a rate of approximately 20°C/min and held for 1 min at 235°C. The PFOA total ion chromatogram peak areas for the two methods were integrated, and the ratio of the peak areas was used to determine the PFOA transport efficiency through the ATRS.

PFOA Calibration Curve and Detection Limits – In-Line Gas-Phase Sampling

This study was conducted to identify the actual retention time of PFOA in the GC/MS total ion chromatogram, quantify PFOA if it was formed, and determine the PFOA detection limit using the ATRS with same experimental procedure used for the combustion tests. The sample cartridge was loaded with 1, 5, 10, 50, and 100 µg PFOA. To load these amounts of PFOA, three PFOA solutions with different concentrations were prepared as shown in Table 4.

The ATRS inlets, transport lines, and reactor temperatures were set at 300°C. The total gas flow was set at 29.4 mL/min (19.6 mL/min to inlet 1 and 9.8 mL/min to inlet 2) to maintain a gas-phase residence time in the reactor at 2.0 sec at 300°C. The pyroprobe temperature was increased from 100 to 300°C at a rate of 200°C/min and held at 300°C for 2 min to gasify PFOA. The system was then swept with helium for 3 min. The gasified PFOA was condensed at the cold trap and released for in-line GC/MS by heating the cold trap to 280°C. The GC conditions were the same as during the combustion tests. In order to determine if any PFOA was lost during solvent evaporation (drying) following loading of PFOA solutions into the pyroprobe sample cartridges, similarly prepared 500 µg samples were weighed before and after drying. More than 90% of the PFOA remained following drying. More than 90% of the PFOA remained following drying. The mass equivalent to this ca. 10% difference is within the uncertainty of the analytical balance used for the weight measurements.

Results

GC/MS Determination of Major Ions: Thermal Decomposition Profile Construction

Preliminary tests identified the chemical species associated with the major GC peaks and determined the major ions used to construct the thermal decomposition profile. Thermal testing was initiated at 600°C. The total ion chromatogram obtained at this reactor temperature indicated the gasification products present under conditions of minimal oxidation. Benzoic acid was the largest constituent of the combustion effluent for the untreated and treated articles at 600°C. Figure 2 shows a total ion chromatogram of the effluent from untreated article

combustion at 600°C, and Figure 3 shows the mass spectrum of the largest signal at a retention time of 13.4 min. Mass spectral comparison with the library spectra indicated the peak was most likely benzoic acid. The 8 min. peak is water formed during combustion. The 16 min peak has strong mass 149 ion and is most likely a terephthalic acid derivative. Similar results were obtained for the treated article.

Benzoic acid and a terephthalic acid derivative are expected thermal decomposition products of polyester (Ohtani et al., 1995; Radlein et al., 1991). All peak areas were integrated within a mass range between 35 and 450 m/z to eliminate the peak associated with water from the analysis, and the ratio of these two peaks were calculated. The results showed that benzoic acid consists of 33 and 36% of total peak area for untreated and treated articles, respectively, and the terephthalic acid derivative consists of 13% of the total peak area for both samples. The total integrated peak area of these extracted ions was used for constructing the thermal decomposition profiles for the treated and untreated articles.

Figure 4 shows the total ion chromatogram resulting from fluorotelomer-based acrylic polymer combustion at 600°C. The baseline elevation at 8 min is due to formation of water. The larger, well-resolved peaks were identified as fluorinated hydrocarbons. Figure 4 also shows major extracted ions 69 and 77 for the largest GC peaks. The structures of these ions ($\bullet\text{CF}_3$: 69, $\bullet\text{CF}_2\text{CH}=\text{CH}_2$: 77) are plausible combustion byproducts the telomer chain. The total peak area of these extracted ions was used for constructing the polymer thermal decomposition profile.

In-line GC/MS analysis was conducted for Telomer B Alcohol ($\text{CF}_{2n+1}\text{CH}_2\text{CH}_2\text{OH}$) thermal decomposition at 200 and 600°C to confirm that ion 77 formation observed in the fluorotelomer-based acrylic polymer combustion tests was from decomposition of the "Telomer"

($\text{CF}_{2n+1}\text{CH}_2\text{CH}_2\text{-X}$) functionality. The results affirmed that compounds containing the $\bullet\text{CF}_2\text{CH=CH}_2$ fragment did form and in greater amounts with increasing temperature.

99.9% Destruction Temperature Determination

Consistent with prior thermal degradation studies in this laboratory, a thermal decomposition profile for each sample was generated from 600°C to $T_{99.9}$. Blank runs were performed using the same procedure as the sample runs, but without sample insertion. A blank analysis was performed before each test to examine any carryover from previous tests. If any carryover was observed, the reactor assembly, cold trap, and GC column would be cleaned at elevated temperature with air (for reactor assembly and trap) and helium (for GC column) and a second blank analysis would be performed. No such carryover was observed in these experiments.

Treated and Untreated Article

Ions 122 (benzoic acid) and 149 (terephthalic acid derivative) were used to determine the thermal decomposition profile of the untreated article. Table 5 shows the results. Ions 149 and 122 disappear at 700 and 725°C, respectively. The analysis was repeated at 750°C to ensure complete sample destruction. The total ion counts were also normalized by gasified sample mass and the relative degradation was calculated. $T_{99.9}$ was obtained at 725°C. Ions 122 and 149 were also extracted for combustion at 1000°C to ensure that these compounds were not reformed at higher temperature. At 1000°C only a background signal was observed indicating no reformation.

Ions 122 and 149 were also used to determine the thermal decomposition profile of the

treated article. Table 6 shows the results. The behavior of the major ions was similar to the results for the untreated article, with ions 149 and 122 disappearing at 700 and 725°C, respectively. The analysis was repeated at 750°C to ensure complete sample destruction. $T_{99.9}$ was obtained at 725°C. Ions for fluorinated species fragments (69 for $\bullet\text{CF}_3$, 119 for $\bullet\text{CF}_2\text{CF}_3$, and 131 for $\bullet\text{CF}_2\text{CF}=\text{CF}_2$) were extracted to evaluate the degradation of the fluorotelomer-based acrylic polymer. All three ions were observed in decreasing yields with increasing temperature. Ion 69 was observed at 725°C, but the amount was very small. Ions 119 and 131 were below background at 725°C. No other fluorinated species were observed at 725°C. Ions 122 and 149 were extracted for the combustion at 1000°C to ensure these compounds were not reformed at higher temperature. Only a background signal was observed.

Fluorotelomer-based Acrylic Polymer

Ion 69 and 77, the major ions from the gasification of the fluorotelomer-based acrylic polymer, were used to determine its thermal decomposition profile. Table 7 shows the results. Ion 69 and 77 still existed at 1000°C, but the relative amount remaining was $\leq 0.1\%$. The analysis was repeated at 1000°C to ensure 99.9% sample destruction. The total ion counts were also normalized by gasified sample mass and the relative degradation profile was calculated. $T_{99.9}$ was obtained at 1000°C. Figure 5 summarizes the degradation profiles of the treated and untreated article and the fluorotelomer-based acrylic polymer.

VOC and Fixed Gas Analysis at 1000°C

VOCs from untreated and treated article combustion at 1000°C were collected in a

Tedlar® bag and analyzed using off-line GC/MS analysis. Three major chromatogram peaks corresponding to air, carbon dioxide, and water vapor were observed. No other peaks were observed for both untreated and treated articles, indicating that volatile fluorocarbons were not detected.

Quantitative CO and CO₂ analyses from the combustion of the treated and untreated articles at 1000°C were conducted using off-line GC/TCD analysis. Table 8 shows the concentration of CO and CO₂, number of moles of CO and CO₂ collected, number of moles gasified, and the carbon recovery. The average CO₂ concentration is almost identical for untreated and treated article combustion. The average CO concentration differs somewhat between untreated and treated article combustion. Nearly 100% carbon recovery was obtained for both untreated and treated articles. The slight overestimation of the carbon recovery may result from the estimation of gas exhaust volume based on inlet flow rates before the sampling and collection time.

Fluoride and Chloride Determination at 1000°C

Aqueous bubbler samples of reactor effluent from 1000°C combustion tests of the treated and untreated articles were analyzed for fluoride and chloride ion, representative of the combustion byproducts HF and HCl. No fluoride or chloride was detected at a detection limit of 10 µg/L and 40 µg/L, respectively.

Silicon tetrafluoride (SiF₄) was observed in the fluorotelomer-based acrylic polymer combustion tests with integrated peak area increasing with temperature as shown in Figure 6. SiF₄ is not formed by sample combustion but by reaction of hydrogen fluoride (HF) and the fused

silica reactor surfaces. Therefore, these results clearly indicate that HF formed by combustion reacted with the fused silica reactor surfaces to form SiF_4 . SiF_4 was not observed in the total ion chromatograms from the combustion of the treated and untreated articles, consistent with the substantially lower fluorine levels in these samples versus the polymer.

PFOA Transport Study - Aqueous Sampling

Three transport efficiency tests with aqueous sampling and ATRS temperatures at 170°C showed poor recovery and repeatability (0.5 to 4.4%). The transport efficiency test at ATRS temperatures at 300°C showed recoveries of 14.8 to 20.6%. In an effort to determine the fate of the injected fluorine, two aqueous solution samples were analyzed for total fluorine using the Wickbold Torch method (Wickbold, 1954; Kissa, 1998). The fluorine recovery was determined to be 9.8% at 170°C and 45.9% at 300°C. These low recoveries and separately conducted absorption tests strongly suggest that PFOA condensation was occurring in the unheated silicone tube transport line to the aqueous bubblers.

PFOA Transport Study – In-Line Gas Phase Sampling

Table 9 shows the results of gas-phase transport studies where PFOA was transported through the ATRS into the GC and directly injected into the GC injection port. Two system blank runs were performed through the ATRS to confirm no PFOA carryover from each previous experiment. The first blank runs indicated a small amount of carryover while carryover was negligible in the second blank runs. No carryover was observed after one system blank performed for the direct injection experiment. The peak areas obtained from the blank runs were

added to the peak area obtained from the first GC run as shown in Table 9. Each peak area was normalized by the gasified sample mass and the three determinations were averaged. Based on the average peak area, 74.3% transport efficiency through the ATRS was obtained.

PFOA Calibration Curve and Detection Limit Studies

PFOA appeared at 16 min retention time. The extracted ion 131, which is the most abundant of the major PFOA ions, was used to construct the calibration curve shown in Figure 7. Figure 8 shows the full scan PFOA peak spectra for the 100.40, 50.80, 10.16, 5.50, and 1.10 μg injections. The spectra contained ions 131 ($\bullet\text{CF}_2\text{CF}=\text{CF}_2$), 69 ($\bullet\text{CF}_3$), 31 ($\bullet\text{CF}$), and 93 ($\bullet\text{C}_3\text{F}_3$) in decreasing intensity. The relative ion intensities are consistent with the reference spectrum for PFOA obtained from the NIST129K library (G1701BA Version B03.00, Agilent Technologies). Ion 131 was used to establish a gas-phase PFOA detection limit of 0.35 ppmv. This was based on a S/N ratio at the limit of detection of 3:1.

PFOA Analysis Using In-line GC/MS Analysis

The ion chromatograms obtained from the treated and untreated article combustion tests were examined to identify the potential existence and quantity of PFOA in the exhaust. The elution time between 14 and 18 min was monitored because this is where PFOA was expected to elute under these gas chromatographic conditions. No PFOA peak was detected. Examination of the fluorotelomer-based acrylic polymer ion chromatograms indicated that peaks appeared at 16.35, 17.10, 17.70 and 17.95 min at temperatures of 600, 650, 700, and 750°C. However, none of these peaks were PFOA based upon evaluation of their mass spectra. The re-examination of the ion chromatograms for the combustion tests indicates the absence of PFOA formation at the

sub-ppm level for all three samples studied at temperatures between 600 to 1000°C with 85% excess air and a gas-phase residence time of 2.0 sec.

Discussion

The objective of this study was to investigate the thermal degradation of a polyester/cellulose fabric treated with a fluorotelomer-based acrylic polymer under laboratory conditions conservatively representing typical combustion conditions of time, temperature, and excess air level in a municipal waste incinerator (Giraud, 2004). The treated article is reasonably expected to be present in municipal waste as discarded textile or paper. The principal focus of this work was to determine the environmental fate of the fluorotelomer-based polymer on the treated article when it is incinerated. Supplementary studies examined an untreated article, the fluorotelomer-based acrylic polymer, and a Telomer B Alcohol raw material to assist in the interpretation of the experimental observations for the treated article.

The test protocols used were similar to those developed for recent testing of fluorotelomer-based materials (Yamada and Taylor, 2003). Thermogravimetric analysis was used to define the gasification conditions. Thermal experiments were then conducted at non-flame reactor temperatures from 600 to 1000°C for a mean, gas-phase residence time of 2.0 sec. 85% excess air was used for all ATRS experiments.

The temperature for 99.9% destruction of the treated and untreated articles was 725°C. This temperature regime (700-750°C) for 99.9% conversion is consistent with the results of prior tests of hydrocarbon-based materials using similar thermal instrumentation systems (Dellinger et al. 1984; Dellinger, 1989; Taylor, et al. 1990). The temperature for 99.9% destruction ($T_{99.9}$) of

the fluorotelomer-based acrylic polymer alone was 1000°C. The $T_{99.9}$ value for the fluorotelomer-based acrylic polymer was slightly higher than that measured for other fluorotelomer-based materials using the same experimental apparatus (Graham, 2002). The difference may be related to the levels of excess air present in the respective combustion tests. Combustion tests with the fluorotelomer-based acrylic polymer used 85% excess air, while previous tests with other fluorotelomer-based materials employed considerably higher excess air levels.

Excellent carbon mass balances were obtained from the combustion tests of the untreated and treated articles (101.9 and 103.6%, respectively) at 1000°C. The only product of incomplete combustion that was observed under these conditions was carbon monoxide. Fluorinated organic byproducts were not observed via GC/MS in the combustion tests of the treated and untreated articles. In-line GC/MS was employed to determine the presence of heavier, less volatile fluorinated by-products. None were detected. Additionally, off-line GC/MS was employed to determine the presence of volatile fluorinated by-products in the gas exhaust from the 1000°C tests of the treated and untreated articles. None were detected.

Combustion tests of the fluorotelomer-based acrylic polymer were conducted to facilitate interpretation of the treated article combustion results. At 1000°C, 99.9% destruction of the polymer was observed. Based upon this result, the fluorotelomer-based acrylic polymer would be destroyed under typical municipal incinerator conditions. Analysis of the reactor effluent from additional combustion tests of the fluorotelomer-based acrylic polymer indicated the formation of a variety of compounds at temperatures below 1000°C. Many of these compounds could not be identified using either the NIST mass spectral library or manual mass spectral interpretation. As a result, a limited number of combustion experiments were conducted on the Telomer B Alcohol

raw material to try to determine the origin of these unidentifiable peaks. The experiments confirmed that selected ions were the same for the polymer and alcohol indicating their origin was indeed from the telomer functionality. Potential volatile combustion byproducts from the combustion of the fluorotelomer-based acrylic polymer were not analyzed.

Of specific interest was to determine if incineration of treated articles may be a source of PFOA in the environment. Analysis for PFOA in combustion tests of the treated and untreated article at 1000°C using both off-line HPLC/MS/MS and in-line GC/MS showed no detectable level of PFOA. Transport tests using in-line GC/MS analysis validated the sampling approach. It can therefore be concluded that under typical municipal waste incineration conditions no significant quantity of PFOA would be formed from the incineration of a textile or paper substrate treated with a fluorotelomer-based acrylic polymer even without consideration of post-combustion pollution control equipment for acid gas scrubbing in place at municipal incinerators.

Based upon the combustion product analyses, it was clear that carbon-fluorine bonds were severed at 1000°C. While no detectable fluoride as HF was observed, significant etching of the reactor surface and silicon tetrafluoride (SiF_4) observed in the combustion of the fluorotelomer-based polymer indicated that HF formed rapidly reacts with the silica reactor. SiF_4 has been observed in previous combustion tests of highly fluorinated materials using high-temperature fused silica reactors (Yamada and Taylor, 2003; Graham, 2002).

Conclusions

The polyester/cellulose fabric treated with a fluorotelomer-based acrylic polymer is destroyed and no detectable amount of PFOA is formed under typical municipal incineration

conditions. Therefore, textiles and paper treated with such a fluorotelomer-based acrylic polymer disposed of in municipal waste and incinerated are expected to be destroyed and not be a significant source of PFOA in the environment.

Acknowledgements

This research was supported in part by a contract from E. I. du Pont de Nemours and Company. The authors acknowledge Richard C. Striebich for assistance with mass spectral interpretation and John L. Graham for performing the thermogravimetric analysis.

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Table 1. Sample Weight Composition (%)

Sample	C	H	F	O	Cl	N
Untreated article	49.1	5.1		45.8		
Treated article	49.7	4.9	0.2	45.2		
Fluorinated acrylic polymer	40.5	4.0	35.5	6.5	13.1	0.3

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Table 2. Sample Atomic Composition

Sample	C	H	F	O	Cl	N
Untreated article	0.340	0.422		0.238		
Treated article	0.350	0.410	0.001*	0.239		
Fluorinated acrylic polymer	0.334	0.401	0.185	0.040	0.037	0.002*

* Neglected for the stoichiometry calculation.

Table 3. Gasification Times (s) with 85% Excess Synthetic Air

Sample	Typical Amount (mg)	600°C	700°C	800°C	900°C
Untreated article	1.2	20.0	22.3	24.6	26.9
Treated article	1.2	20.2	22.5	24.8	27.2
Fluorinated acrylic polymer	1.6	24.3	27.0	29.8	32.6

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Table 4. Solution Concentration (PFOA in Methanol) and Volume Required to Produce 1, 5, 10, 50, and 100 μg PFOA Injection

Dried Sample Mass (μg)	Solution Used (Concentration) (mg PFOA / mL MeOH)	Solution Loaded (μl)	Drying Time (hr)
1	1	1	3
5	1	5	15
10	10	1	3
50	10	5	15
100	100	1	3

Table 5. Major Ion Counts - Untreated Article

Temp (°C)	Ion 122	Ion 149	Total	Mass (mg)	Normalized	
					By Mass	Relative %
600	2.31E+08	4.48E+07	2.76E+08	1.11	2.48E+08	100.00
650	1.82E+08	1.31E+06	1.83E+08	1.01	1.81E+08	72.95
700	4.53E+07	0.00E+00	4.53E+07	1.02	4.44E+07	17.86
725	0.00E+00	0.00E+00	0.00E+00	1.00	0.00E+00	0.00
750	0.00E+00	0.00E+00	0.00E+00	0.97	0.00E+00	0.00
750	0.00E+00	0.00E+00	0.00E+00	1.04	0.00E+00	0.00

Table 6. Major Ion Counts - Treated Article

Temp (C)	Ion 122	Ion 149	Total	Mass (mg)	Normalized by Mass	Relative %
600	2.80E+08	5.43E+07	3.34E+08	1.22	2.74E+08	100.00
650	2.38E+08	6.15E+06	2.44E+08	1.25	1.95E+08	71.27
700	1.49E+06	0.00E+00	1.49E+06	1.22	1.22E+06	0.45
725	0.00E+00	0.00E+00	0.00E+00	1.23	0.00E+00	0.00
750	0.00E+00	0.00E+00	0.00E+00	1.24	0.00E+00	0.00
750	0.00E+00	0.00E+00	0.00E+00	1.23	0.00E+00	0.00

Table 7. Major Ion Counts - Fluorinated Acrylic Polymer

Temp (C)	Ion 69	Ion 77	Total	Mass (mg)	Normalized by Mass	Relative %
600	1.44E+09	2.08E+09	3.51E+09	1.60	2.20E+09	100.00
650	1.21E+09	1.15E+09	2.36E+09	1.69	1.40E+09	63.58
700	1.02E+09	2.24E+08	1.25E+09	1.68	7.43E+08	33.81
750	8.13E+08	1.44E+07	8.27E+08	1.62	5.10E+08	23.24
800	6.80E+08	1.50E+07	6.95E+08	1.63	4.26E+08	19.41
850	3.29E+08	7.45E+06	3.36E+08	1.62	2.07E+08	9.45
900	1.14E+08	5.13E+06	1.19E+08	1.63	7.30E+07	3.32
950	4.79E+07	4.62E+06	5.25E+07	1.58	3.32E+07	1.51
1000	1.13E+06	1.54E+06	2.68E+06	1.61	1.66E+06	0.08
1000	4.43E+05	3.61E+06	4.06E+06	1.61	2.52E+06	0.11
1000	2.12E+06	1.08E+06	3.21E+06	1.58	2.03E+06	0.09

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Table 8. Carbon Recovery for Untreated and Treated Article Combustion at 1000°C

Sample	CO Conc. (ppm)	CO₂ Conc. (ppm)	Total Gas Volume (mL)	Moles of CO Collected	Moles of CO₂ Collected	Moles of C Collected	Moles of C Gasified	Carbon Recovery (%)
Untreated 1	826	9712	96.33	7.09E-06	8.34E-05	9.05E-05	8.92E-05	101.4
Untreated 2	635	10165	97.30	5.66E-06	9.06E-05	9.62E-05	9.16E-05	105.0
Untreated 3	468	9756	96.09	3.85E-06	8.01E-05	8.39E-05	8.55E-05	98.2
Average	643	9878		5.53E-06	8.47E-05	9.02E-05	8.88E-05	101.5
Treated 1	351	9737	102.70	4.08E-06	1.13E-04	1.17E-04	1.15E-04	102.2
Treated 2	448	9485	102.29	5.09E-06	1.08E-04	1.13E-04	1.13E-04	100.2
Treated 3	321	10326	101.74	3.38E-06	1.09E-04	1.12E-04	1.05E-04	106.8
Average	373	9849		4.18E-06	1.10E-04	1.14E-04	1.11E-04	103.1

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Table 9. PFOA Transport Results: Gas-phase Sampling and GC/MS Analysis

	Peak Area from First GC Run (1)	Peak Area from Blank Run (2)	Total Peak Area = (1) + (2)	Sample Mass (mg) (3)	Total Peak Area Normalized by Mass = [(1+2) ÷ 3]
ATRS Run #1	684994647	10510992	695505639	0.44	1580694634
ATRS Run #2	673277175	4069277	677346452	0.45	1505214338
ATRS Run #3	814730308	289003	815019311	0.45	1811154024
			Average	Peak Area 1	<u>1632354332</u>
Direct GC 1	966189956	0	966189956	0.45	2147088791
Direct GC 2	1030933423	0	1.031E+09	0.48	2147777965
Direct GC 3	1033245273	0	1.033E+09	0.45	2296100607
			Average	Peak Area 2	<u>2196989121</u>
			Transport Efficiency (%)		74.3
			(Peak Area 1) ÷ (Peak Area 2)		
			× 100		

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List of Figure Captions

Figure 1. General schematic of the advanced thermal reactor system (ATRS).

Figure 2. Total ion chromatogram of reactor effluent from untreated article combustion at 600°C.

Figure 3. Mass spectra at 13.4 min. Source: total ion chromatogram of reactor effluent from untreated article combustion at 600°C (see Figure 2).

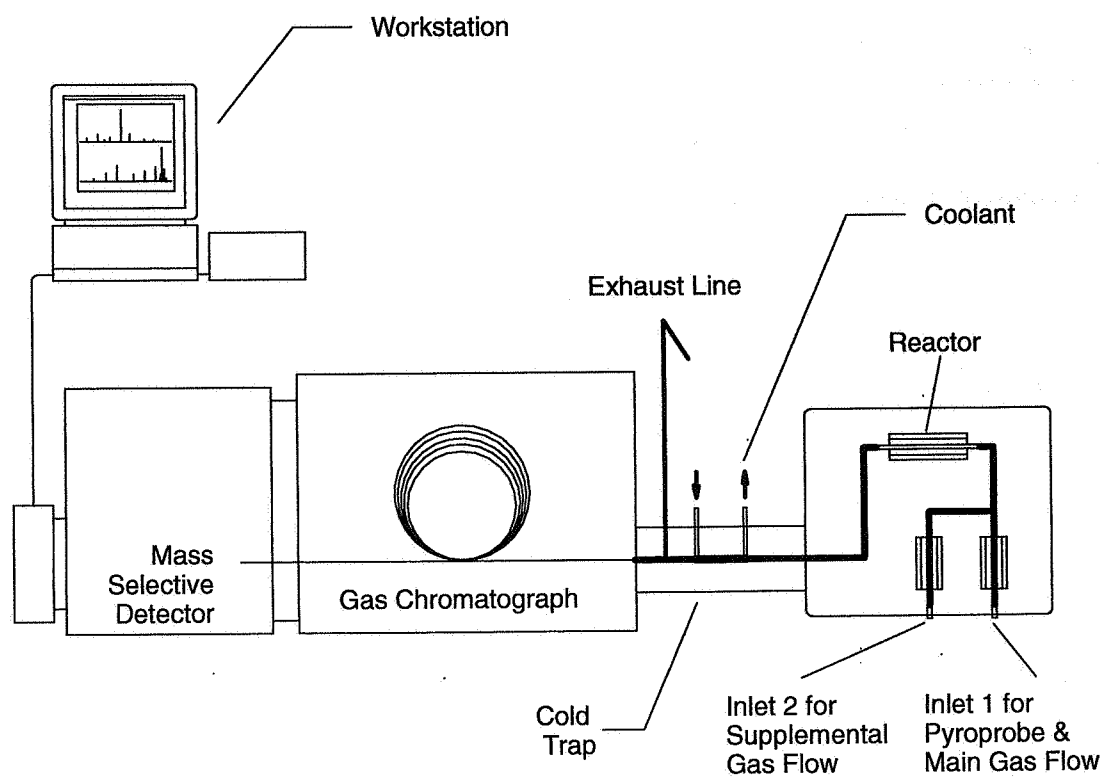
Figure 4. Total ion chromatogram (top) and extracted ions 69 (middle) and 77 (bottom) for reactor effluent from fluorinated acrylic polymer combustion at 600°C.

Figure 5. Thermal destruction profile of untreated article, treated article and fluorinated acrylic polymer normalized by sample mass.

Figure 6. Temperature vs. integrated normalized peak area of ion 85 (SiF_3) for effluent from combustion of fluorinated acrylic polymer.

Figure 7. PFOA calibration curve.

Figure 8. PFOA full scan mass spectra for 100.40, 50.80, 10.16, 5.50, and 1.10 μg injection.



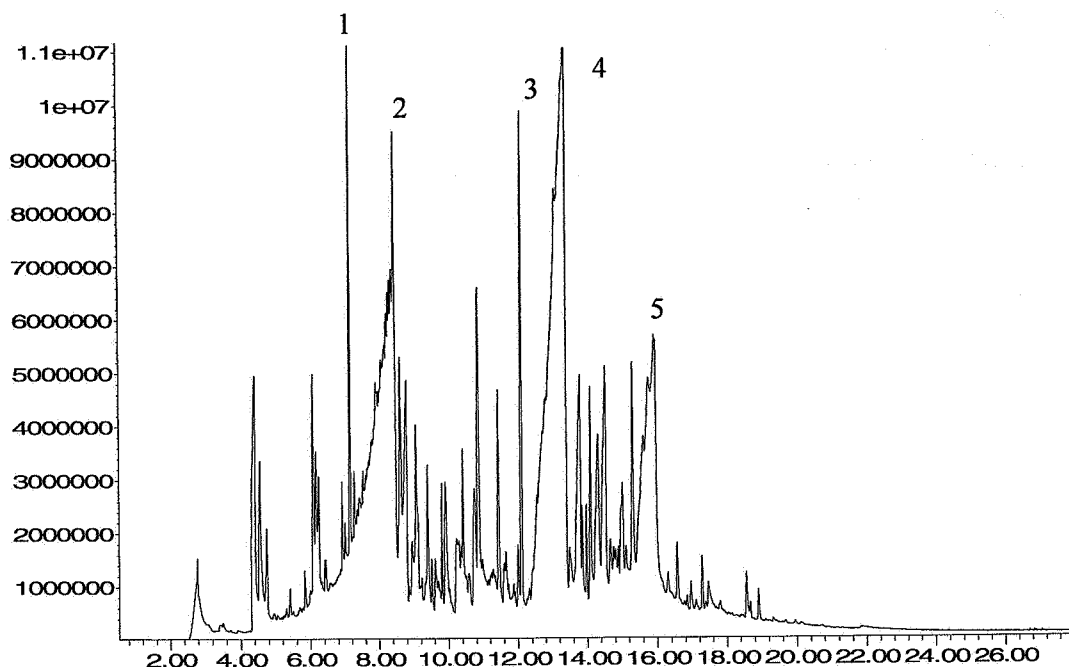
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Figure 1.

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Abundance



Time-->

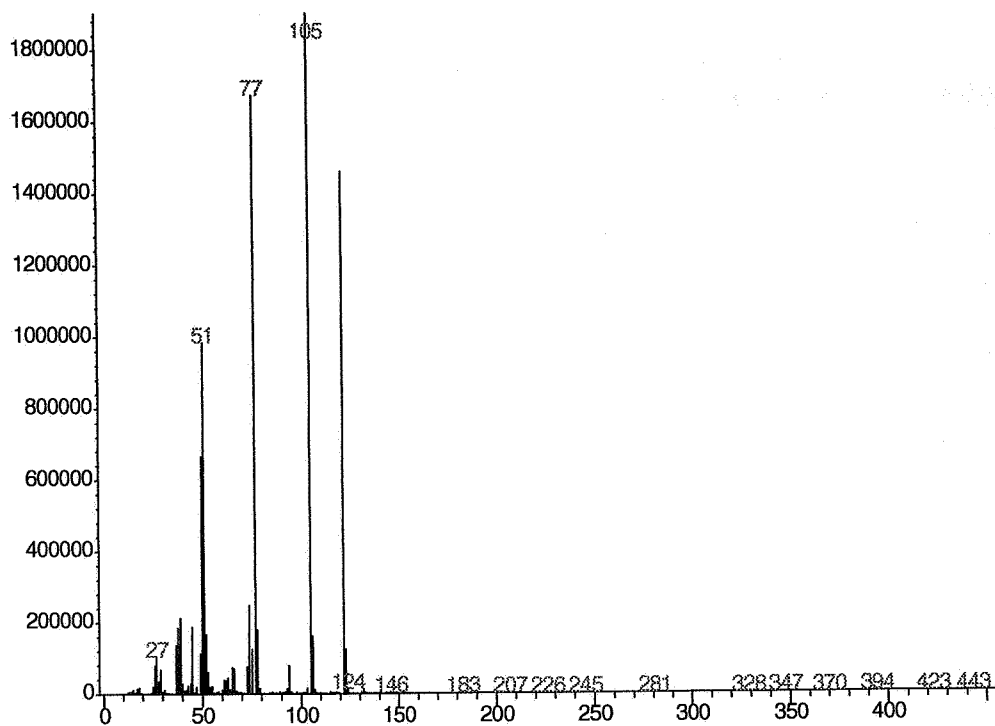
ID #	Compound Name
1	Benzene
2	Toluene ^a
3	1-Phenyl-1,2-propanedione
4	Benzoic acid
5	Terephthalic acid derivative ^b

^a Toluene is located on top of the large water peak. ^b This compound could not specifically be identified, but is most likely a terephthalic acid derivative based on manual mass spectral analysis.

Figure 2.

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Abundance



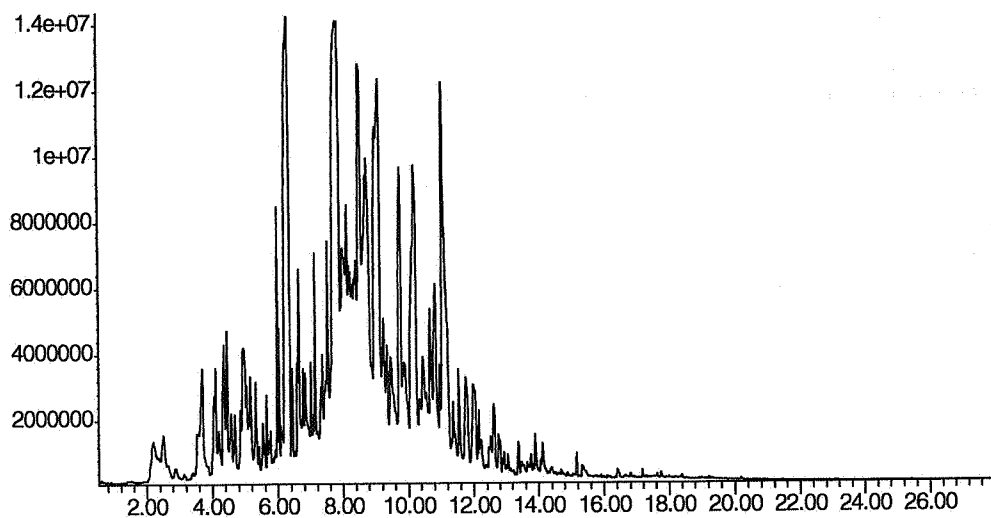
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Figure 3.

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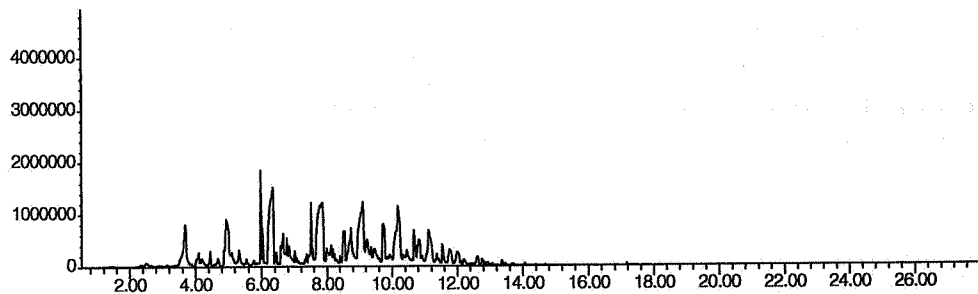
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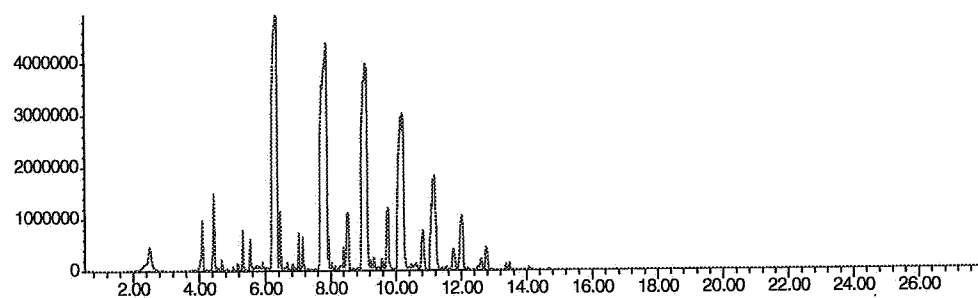
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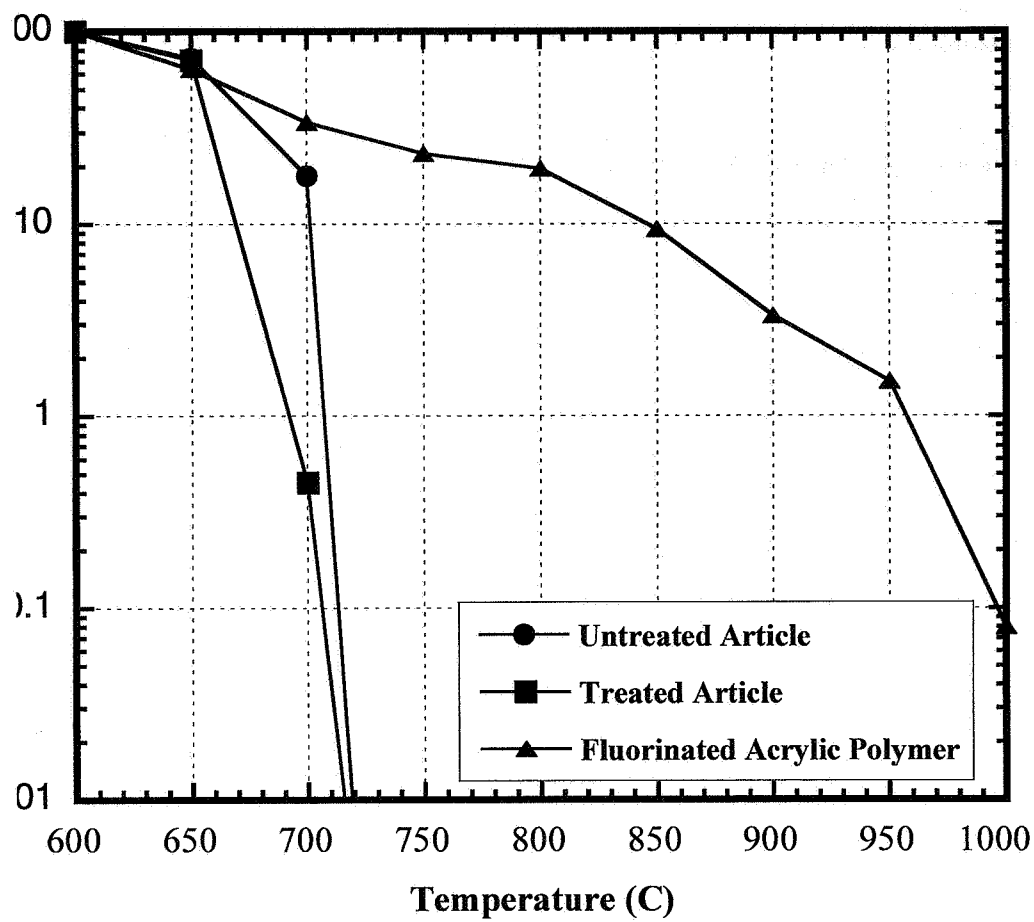


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Figure 4.

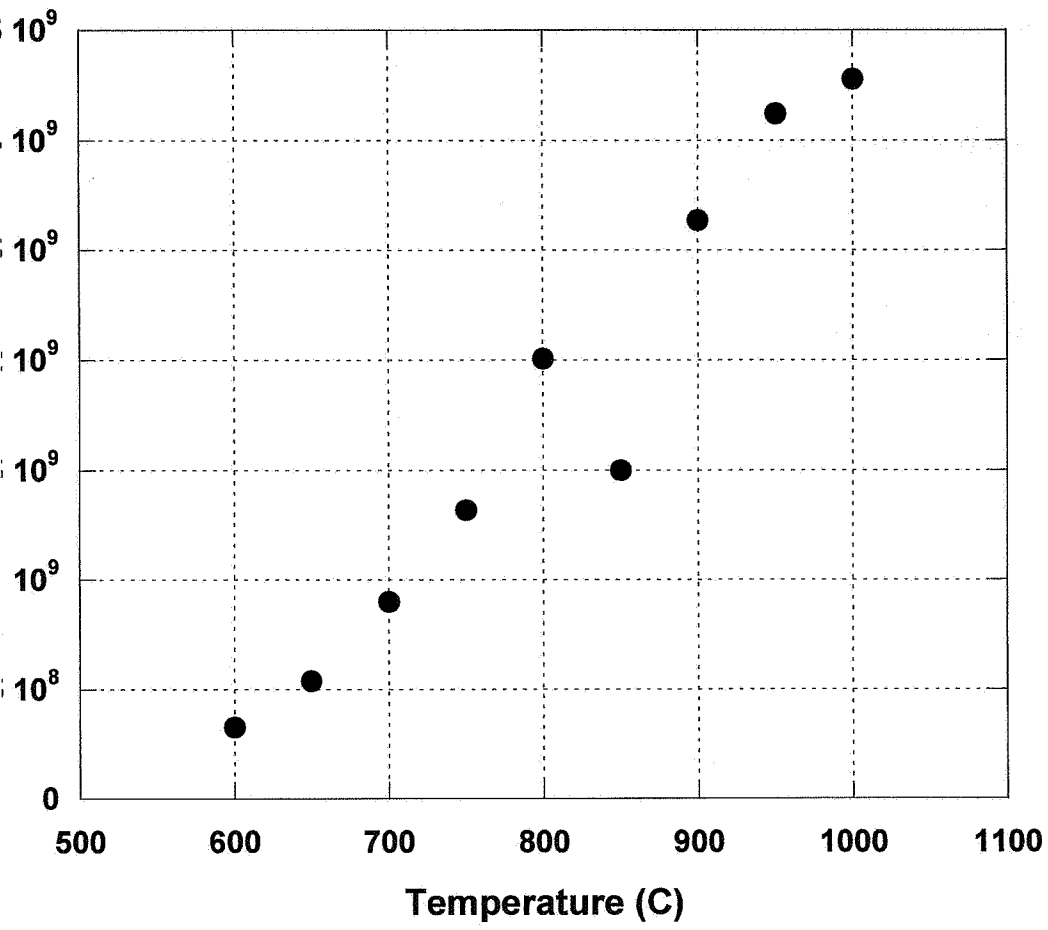
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Figure 5.

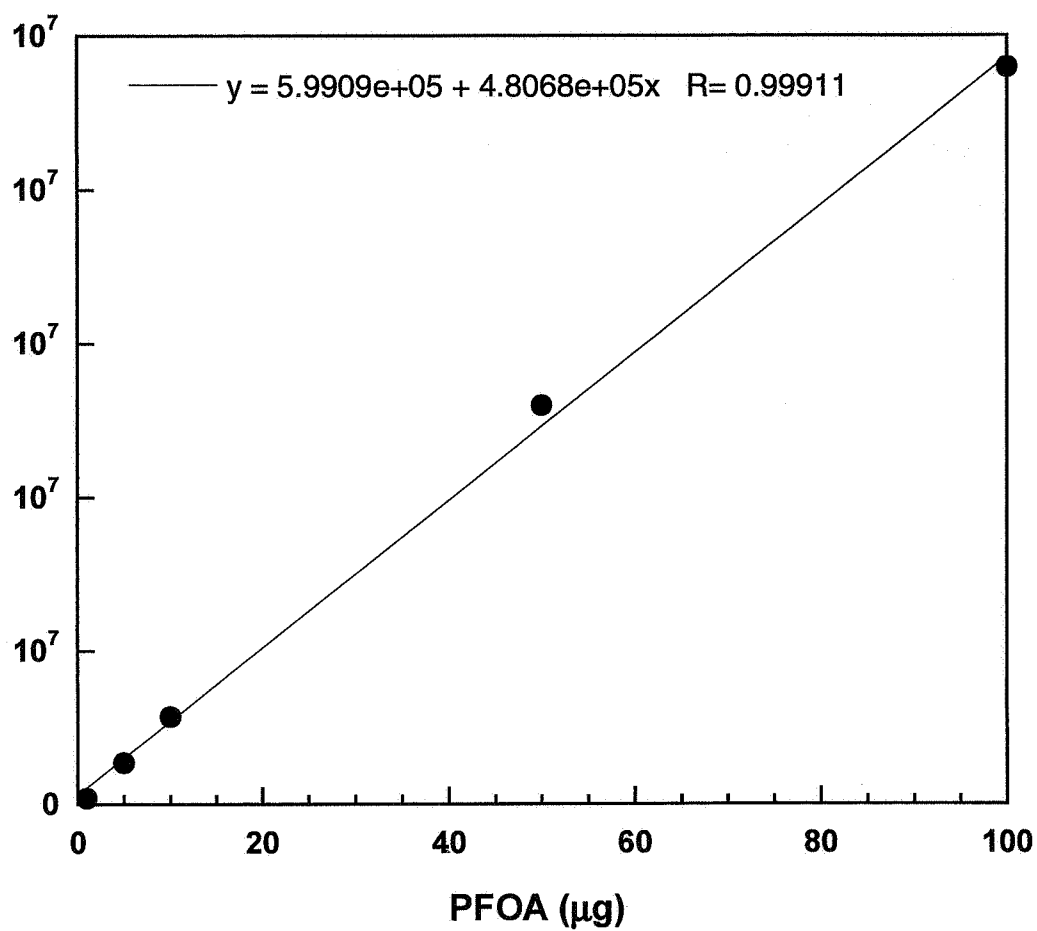
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Figure 6.

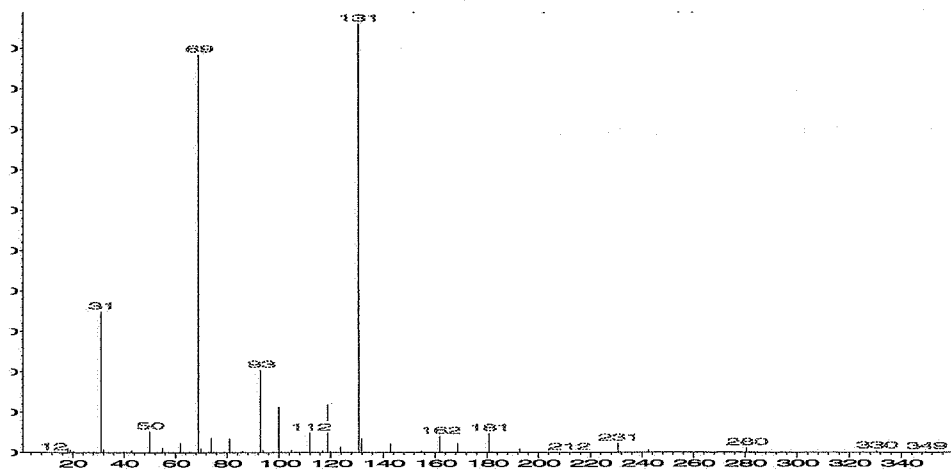
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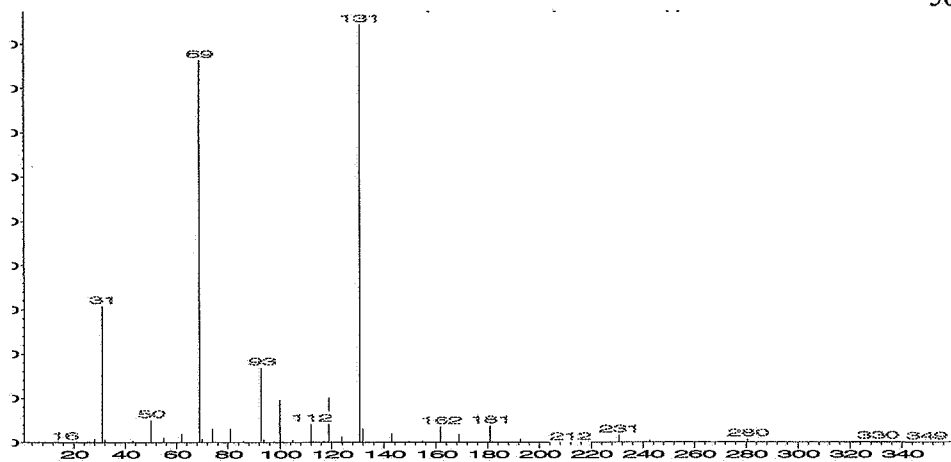
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Figure 7.

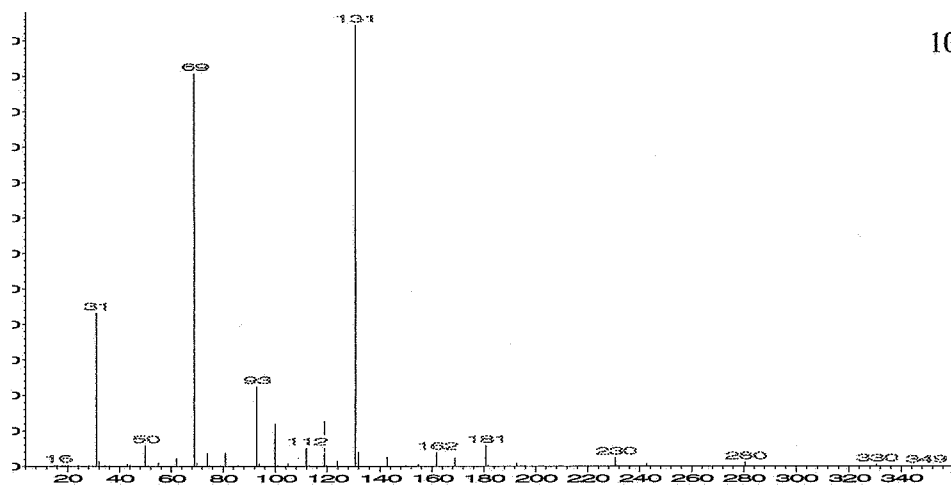
100.40 μg



50.80 μg



10.16 μg

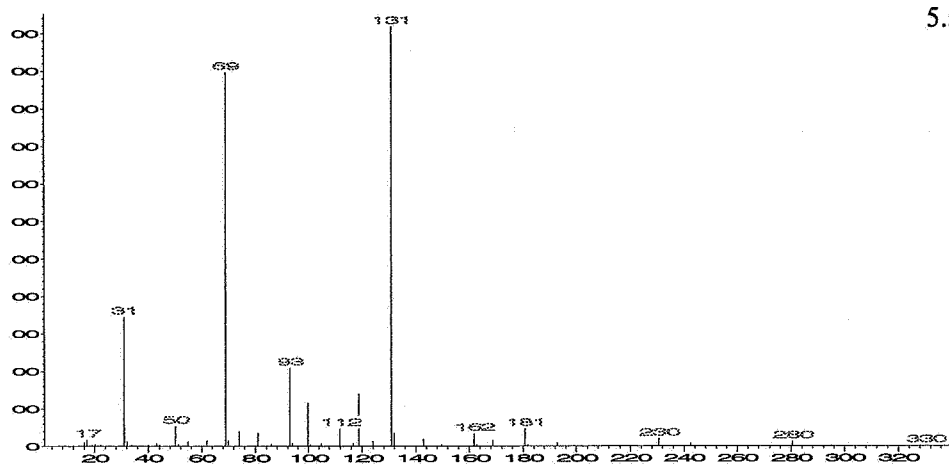


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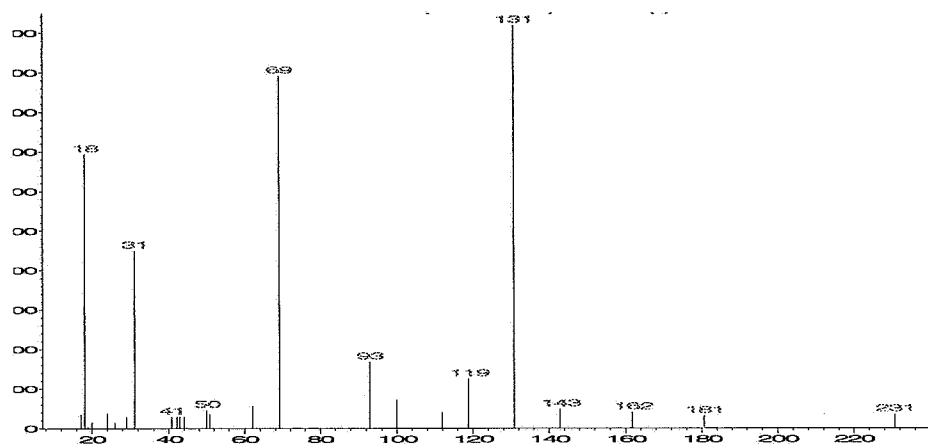
Figure 8.

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5.5 μg



1.1 μg



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Figure 8 (continued).

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Supplementary Materials (Quantity of Air Supplied and Gasification Time Calculation)

Suppose the weight of the fluorinated acrylic polymer used for combustion at 600°C is

2.25 mg. The molecular weight of the hypothetical polymer shown in Equation 3 is 9.88.

The molar amount of polymer in this sample is $2.25/1000(\text{g})/9.88(\text{g/mol}) = 2.28 \times 10^{-4}$ moles.

From the stoichiometric reaction for the polymer (Equation 3), the oxygen required can be calculated as:

$$2.28 \times 10^{-4} \text{ mol} \times 0.35$$

The volume of air (21% oxygen and 79% nitrogen) in units of mL with 85% excess air (85% $\times 0.21 = 17.85\%$ excess oxygen) at 1 atm and 25°C can be calculated as:

$$[2.28 \times 10^{-4}(\text{mol}) \times 0.35 \times 1.1785 \times 0.0821(\text{atm/mol-K}) \times 298(\text{K}) / 1(\text{atm})] / 0.21 \times 1000(\text{mL/l}) = 11.0 \text{ mL}$$

The flow rate at 600°C is

$$0.94(\text{mL/sec}) \times 298 (\text{K}) / (600 + 273) (\text{K}) = 0.32 \text{ mL/sec.}$$

The gasification time can then be calculated as follows:

$$11.0 \text{ mL}/0.32(\text{mL/sec}) = 34.4 \text{ sec}$$

Since the initial and final gasification temperatures for the polymer are 250 and 650°C, respectively, as discussed in Experimental Approach section, the pyroprobe temperature was

linearly increased from 250 to 650°C at a heating rate of:

$$(650-250)^{\circ}\text{C}/34.4 \text{ sec} \times 60 \text{ sec/min} = 698^{\circ}\text{C/min}$$

The key assumptions are that gasification starts when the pyroprobe temperature programming for the polymer starts (250°C) and ends at the final temperature (650°C), and sample weight loss is linear with time. The same calculation method was applied for treated and untreated article to calculate the amount of air supplied and gasification time.